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Nutrient Removal

Water Environment Federation® (WEF®)

WEF MANUAL OF PRACTICE No. 34

NUTRIENT REMOVAL

Prepared by the **Nutrient Removal Task Force** of the **Water Environment Federation®**

Robert Andryszak, P.E.
James Barnard, Ph.D., D.Ing. h.c., BCEE
Britt Bassett, P.E., BCEE
Somnath Basu, Ph.D., P.E.
James S. Bays, P.W.S.
Evangelina Belia, Ph.D.
Mario Benisch
Joshua P. Boltz, Ph.D., P.E.
Marie S. Burbano, Ph.D., P.E.
Kartik Chandran, Ph.D.
Chein-Chi Chang, Ph.D., P.E.
Stuart Kirkham Cole, Ph.D., P.E.
Yves Comeau, Ph.D., P.E.
Rhodes R. Copithorn, P.E.
Christine DeBarbadillo
Peter Dold
Paul Dombrowski, P.E., BCEE
Tom Dupuis, P.E.
Alex Ekster, Ph.D., P.E.
Ufuk Erdal, Ph.D., P.E.
Zeynep Erdal
Richard Finger
Ramesh Goel
Mikel Goldblatt, P.E.
Matthew Gray, P.E.
April Z. Gu, Ph.D.
Stephen R. Harper, Ph.D., P.E.
Guy Jamesson, P.E., BCEE
Samuel Jeyanayagam, Ph.D., P.E., BCEE
Richard Jones, Ph.D., P.Eng.
Jim Jordahl, Ph.D.
Dimitri Katehis
Ishin Kaya, P.Eng.
Edmund Kobylinski
John Koch, P.E.
Sock-Hoon Koh, P.E.
Andrew Kruzic, Ph.D., P.E.
Timothey L. LaPara, Ph.D.
Jian Li, Ph.D., P.Eng., P.E.
Pio Lombardo, P.E., DEE
Nancy Love, Ph.D.
Benjamin Magbanua, Ph.D., P.E.
Venkatram Mahendraker, Ph.D., P.Eng.
Jon Meyer
Indra Mitra, Ph.D., P.E., MBA, BCEE
Eberhard Morgenroth, Ph.D.
Sudhir Murthy, Ph.D., P.E.
JB Neethling, Ph.D., P.E., BCEE
Robert Nerenberg, Ph.D., P.E.
Vikram M. Pattarkine, Ph.D.
Marie-Laure Pellegrin, Ph.D.
Douglas L. Ralston, P.E.
Clifford W. Randall, Ph.D.
Dana Rippon, P.E.
Oliver Schraa
Dipankar Sen, Ph.D., P.E.
Andrew Shaw, P.E.
Mark Steichen
Peter F. Strom, Ph.D.
Imre Takacs
Jason Tincu
R. Rhodes Trussell, Ph.D., P.E.
K. C. "Kumar" Upendrakumar, P.E., BCEE
Cindy Wallis-Lage
Thomas E. Wilson, Ph.D., P.E., DEE
Kenneth N. Wood, P.E.

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Water Environment Federation®
601 Wythe Street
Alexandria, VA 22314–1994 USA
http://www.wef.org

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For information on membership, publications, and conferences, contact:

Water Environment Federation®
601 Wythe Street
Alexandria, VA 22314–1994 USA
(703) 684–2400
http://www.wef.org

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The WEF Technical Practice Committee (formerly the Committee on Sewage and Industrial Wastes Practice of the Federation of Sewage and Industrial Wastes Associations) was created by the Federation Board of Control on October 11, 1941. The primary function of the Committee is to originate and produce, through appropriate subcommittees, special publications dealing with technical aspects of the broad interests of the Federation. These publications are intended to provide background information through a review of technical practices and detailed procedures that research and experience have shown to be functional and practical.

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Preface

The purpose of this Manual of Practice (MOP) is to provide the user with a level of detailed nitrogen- and phosphorus-related information. Nutrient removal (and recovery) is fast becoming the standard in wastewater treatment. This MOP is focused on providing practitioners a deep understanding of the principles and issues related to nutrients.

This MOP has a more scientific (versus design) approach to nutrient removal in wastewater treatment systems.

Chapters 1 and 2 set the background in which nutrient removal affects the environment and the subsequent regulatory constraints put upon treatment facilities. Chapter 3 integrates together the treatment issues of combined nitrogen and phosphorus removal. Chapters 4, 5, and 6 address ammonia and total nitrogen removal. Chapters 7 and 8 address chemical and biological phosphorus removal, respectively. Chapter 9 addresses the special considerations of nitrogen and phosphorus removal in dewatering liquors treatment. Chapter 10 provides the basis on which the current generation of nutrient removal simulation tools are derived from. Chapter 11 provides an approach to troubleshooting nutrient removal facilities, and Chapter 12 deals with nutrient removal from a natural treatment systems perspective.

This MOP was produced under the direction of Bruce R. Johnson, P.E., BCEE, *Chair*. The principal authors of this MOP are as follows:

Chapter 1	Nancy Love, Ph.D.
	Deborah A. Bronk, Ph.D.
	Margaret R. Mulholland, Ph.D.
Chapter 2	Tom Dupuis, P.E.
	Guy Jamesson, P.E., BCEE
Chapter 3	JB Neethling, Ph.D., P.E., BCEE
	April Z. Gu, Ph.D.
	Vikram M. Pattarkine, Ph.D.
Chapter 4	Venkatram Mahendraker, Ph.D., P.Eng.
	Kartik Chandran, Ph.D.
	Christine DeBarbadillo

	Vikram M. Pattarkine, Ph.D.
	Cindy Wallis-Lage
Chapter 5	Kartik Chandran, Ph.D.
	Venkatram Mahendraker, Ph.D., P.Eng.
	Vikram M. Pattarkine, Ph.D.
Chapter 6	Dipankar Sen, Ph.D., P.E.
	Rhodes R. Copithorn, P.E.
Chapter 7	Zeynep Erdal
	Sudhir Murthy, Ph.D., P.E.
	Scott Smith, Ph.D.
Chapter 8	Samuel Jeyanayagam, Ph.D., P.E., BCEE
Chapter 9	Dimitri Katehis
Chapter 10	Imre Takacs
	Evangeliina Belia, Ph.D.
	Joshua P. Boltz, Ph.D., P.E.
	Yves Comeau, Ph.D., P.E.
	Peter Dold
	Richard Jones, Ph.D., P.Eng.
	Eberhard Morgenroth, Ph.D.
	Oliver Schraa
	Andrew Shaw, P.E.
	Bernhard Wett, Ph.D.
Chapter 11	Mark Steichen
	James Barnard, Ph.D., D.Ing. h.c., BCEE
	Christine DeBarbadillo
	Edmund Kobylinski
	Sock-Hoon Koh, P.E.
	Andrew Shaw, P.E.
Chapter 12	Andrew Kruzic, Ph.D., P.E.
	James S. Bays, P.W.S.
	Jim Jordahl, Ph.D.

In addition to the WEF Task Force and Technical Practice Committee Control Group members, reviewers include Ni-Bin Chang, Lee Potts, and Hua Xu, Ph.D.

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University of Michigan, Ann Arbor, Michigan
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University of Texas at Arlington, Arlington, Texas
University of Utah, Salt Lake City, Utah
Veolia Water North America, Indianapolis, Indiana
Virginia Polytechnic Institute and State University, Blacksburg, Virginia
Wilfrid Laurier University, Waterloo, Ontario, Canada
Woodard & Curran, Cheshire, Connecticut; Dedham Massachusetts

NUTRIENT REMOVAL

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Chapter 1

Nutrients and Their Effects on the Environment

1.0 OVERVIEW

The objectives of this chapter are to

(1) Review nitrogen (N) and phosphorus (P) biogeochemical cycles with a focus on aquatic systems.
(2) Describe known environmental transformations (biotic and abiotic) of nitrogen and phosphorus.
(3) Describe known effects of nitrogen and phosphorus on the aquatic environment.
(4) Describe the characteristics of nitrogen and phosphorus forms that exist in domestic wastewater treatment systems.

The complete cycles of nitrogen and phosphorus are complex. The focus of this chapter is on those aspects of nitrogen and phosphorus cycling that pertain most to wastewater treatment systems that are designed to remove nutrients. First, however, this chapter will introduce biological and abiotic transformation processes before discussing the fate of nitrogen and phosphorus and their effects in natural environments and engineered treatment systems. Nitrogen and phosphorus concentrations in industrial wastewaters can be significant and are sometimes more refractory than what is observed in domestic wastewater. It is beyond the scope of this book to review the nitrogen and phosphorus and industrial wastewaters; the reader is, therefore, referred to the Water Environment Federation's (WEF's) *Industrial Wastewater Management, Treatment, and Disposal* for more information (WEF, 2008).

2.0 BIOGEOCHEMICAL CYCLES OF NITROGEN AND PHOSPHORUS

The two most prominent macronutrients in aquatic systems are nitrogen and phosphorus, which can act as limiting nutrients or result in phytoplankton production. Excessive phytoplankton production can result in eutrophication, a condition that causes decreased dissolved oxygen concentrations and a severe reduction in aquatic life diversity. The limiting nutrient is the nutrient that exists in the lowest concentration relative to what organisms need. Many estuarine and freshwater systems, such as rivers, streams, and lakes, tend toward phosphorus limitation, while marine water systems tend toward nitrogen limitation (Doering et al., 1995; Fisher et al., 1999). The limiting nutrient is the one that should be targeted for removal by wastewater treatment systems to control eutrophication.

2.1 Nitrogen

2.1.1 Nitrogen Forms and Oxidation States

Nitrogen exists in marine and freshwater aquatic systems at oxidation states from –3 to +5 (Figure 1.1). There are four stable forms of inorganic nitrogen: ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), and $N_{2(g)}$. The first three forms are highly soluble, although ammonium can also lose a proton as pH increases above neutral to become ammonia (NH_3), which exists primarily as an insoluble gas. The fourth form is gaseous (g), which is the most abundant form of nitrogen on earth. Although N_2 can be biologically fixed to ammonia, the rate of fixation is slow. Because of this delay, N_2 is considered relatively inert in many environments, including conventional wastewater treatment plants (WWTPs). Nitrate is the most oxidized form of nitrogen (+5). It is often near the limit of detection in the surface water of ocean gyres (<0.5 µg N/L). Mean surface ocean concentrations are 98 µg N/L primarily because of high concentrations of nitrate in upwelling coastal systems and from coastal eutrophication (Paerl and Piehler, 2008; Wilkerson and Dugdale, 2008). Concentrations increase in the deep ocean, with a mean of 434 µg N/L (Gruber, 2008).

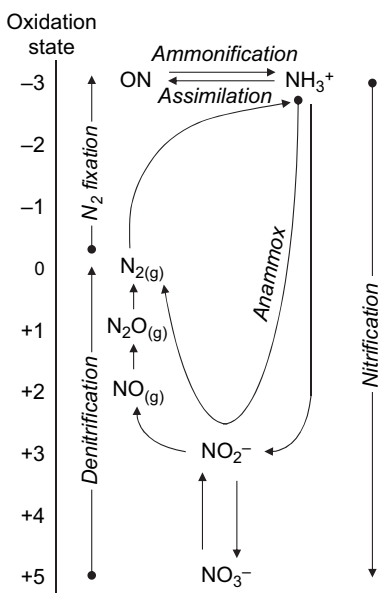

Figure 1.1 Simplified version of the nitrogen cycle in the aquatic system. Nitrogen species are aligned with their oxidation state and are soluble or gaseous (designated with (g)). Metabolic processes are italicized.

Rivers and estuaries can have elevated nitrate concentrations because of anthropogenic and groundwater inputs (Boynton and Kemp, 2008; Howarth et al., 1996). By far, however, the highest nitrate values are seen in urban or agriculturally influenced streams, where concentrations can increase to 21 000 µg N/L (Mulholland et al., 2008). Nitrite (+3) typically occurs at relatively low concentrations because it is an intermediate in the processes of nitrification and denitrification. In the environment, NH_4^+ (–3) exists as the acid-base pair NH_4^+-NH_3; the pK_a (acid dissociation constant) of the pair is 9.3. As a result, NH_4^+ is the dominant species in natural waters, which typically have a pH at or below 8.2. Concentrations of NH_4^+ are highly variable but tend to be near the limit of detection in marine surface waters, with higher concentrations inshore or in estuarine and freshwater environments. In this chapter, total ammonia nitrogen (TAN) will be used when both NH_3 and NH_4^+ contribute to the application being discussed; otherwise, the specific chemicals will be listed when only one form is known to be correct.

The largest pool of fixed nitrogen in estuarine, coastal, and marine surface waters is typically dissolved organic nitrogen (DON). The DON pool is composed of a suite of compounds, many of which are highly labile, or reactive. These compounds include urea; dissolved amino acids, both free and combined; nucleic acids; amino sugars; aromatic compounds; and humic substances. Humic substances are a broad class of organic substances that are abundant in freshwater and estuarine systems. There are three types of humic substances: humic acids, which are insoluble at a pH less than 2; fulvic acids, which are hydrophilic acids soluble under all pH conditions (isolated using XAD-4 resin); and humin, which is insoluble at any pH. Although many organic nitrogen compounds have been identified in natural waters, the bulk of the DON pool in any system typically is uncharacterizable with routine methods and probably changes on small temporal and spatial scales (Bronk, 2002).

Nitrogen in freshwater systems was thought to be primarily inorganic, but more recent studies have shown that the nitrogen transported in rivers is largely organic DON (Scott et al., 2007). Rivers can also carry substantial amounts of nitrogen from fertilizers. Over the last 30 to 40 years, there has been a transition from NH_4^{+-} and NO_3^--based fertilizers to urea-based fertilizers (Glibert et al., 2006). Urea is a highly labile organic nitrogen form. As a result, the DON delivered to water bodies via rivers and streams probably is much more bioavailable than it was a few decades ago. This change affects the overall load of nitrogen to receiving streams and the receiving capacity available for wastewater effluents.

2.1.2 *Nitrogen Global Cycle*

In the global nitrogen cycle, nitrogen moves between oceans and freshwater systems, the atmosphere, and terrestrial systems. Nitrogen can enter the aquatic or terrestrial portion of this cycle through atmospheric deposition or N_2 fixation (the conversion of N_2 to organic nitrogen and ammonia). This process occurs naturally by a specialized group of microorganisms (i.e., nitrogen fixers) that live in surface waters and sediments and symbiotically with the nodulated root zones of selected plants. In marine systems, the primary nitrogen fixer is the cyanobacteria *Trichodesmium*, although recent studies suggest that single-cell nitrogen fixers may be more important than previously believed (Montoya et al., 2004). Importantly, nitrogen fixation also occurs in industrial processes. Currently the amount of nitrogen fixed by industrial processes equals or exceeds that fixed by natural nitrogen fixation (Galloway et al., 2004). Nitrogen fixation within the water column or in sediments of water bodies results in the input of dissolved or particular organic nitrogen and NH_4^+ to aquatic systems.

Nitrogen is removed from the aqueous cycle through deep sediment burial or through $N_{2(g)}$ loss to the atmosphere via denitrification or the recently discovered anaerobic ammonium oxidation (anammox) metabolism, which is the conversion of $NH_4^+ + NO_2^-$ to $N_{2(g)}$, NO_3^-, and water (discussed in more detail in Section 3.1.1). Indeed, the involvement of anammox in nitrogen loss from ocean environments to atmospheric N_2 has recently been found to be much more significant than previously thought (Dalsgaard et al., 2003; Kuypers et al., 2003; Thamdrup and Dalsgaard, 2002).

Groundwater flow through shallow aquifers can also transport nitrogen through watersheds to coastal and estuarine systems (Paerl, 1997). The magnitude of nitrogen delivered via this mechanism is not well studied in most systems. Finally, atmospheric deposition can deliver nitrogen compounds to surface waters in the form of both wet and dry deposition (Kemp et al., 2005). The deposition of inorganic forms of nitrogen has been the focus of much research on atmospheric deposition. There is increasing recognition, however, of the importance of organic nitrogen, which is estimated to compose 11–41% of total dissolved nitrogen deposition, depending on the region (Cornell et al., 2003).

2.2 Phosphorus

2.2.1 *Phosphorus Forms and Oxidation States*

In the environment, phosphorus is bound up in particles or present as dissolved inorganic and organic phosphorus (DIP and DOP). Inorganic phosphorus exists in various

orthophosphate forms (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) (Sawyer et al., 1994). The relative abundance of these species varies with pH in aquatic systems although the oxidation state of all of these phosphoric acids is +5. Because seawater is well buffered, pH is fairly constant (approximately 8.2), and HPO_4^{2-} is the dominant form of DIP in seawater (Bianchi, 2007). The pH in freshwater systems is more variable but lower than seawater on average; therefore, $H_2PO_4^-$ is the dominant species.

The dominant phosphorus groups found in the DOP pool in aquatic systems are phosphonates (associated with phosphoproteins and phospholipids), phosphate monoesters, orthophosphate, phosphate diesters, pyrophosphates, and tri- and tetrapolyphosphates (Bianchi, 2007). In microbes and other organisms, phosphorus compounds are found as phosphorylated sugars such as nucleic acids (ribonucleic acid [RNA] and deoxyribonucleic acid [DNA]) and energy storage molecules (such as adenosine triphosphate [ATP] or polyphosphate granules). These compounds are also found in aquatic systems after being excreted or expressed from lysed cells but are highly labile and short-lived.

2.2.2 *Phosphorus Global Cycle*

The global phosphorus cycle is much simpler than the global nitrogen cycle. Unlike the global nitrogen cycle, phosphorus moves primarily between the earth's crust and the aquatic dissolved, particulate (including biota), and the sedimentary cycle. Although gaseous forms of phosphorus, such as the highly toxic gas phosphine, exist, and its prevalence as a component of the global phosphorus cycle is thought to be small, it is most often present in reduced environments and may be either produced or released through wastewater treatment processes (Dévai et al., 1988, 1999; Glindemann et al., 2005). Mineral phosphorus enters the hydrological cycle primarily through rivers, although some can be delivered through windblown dust. The significant source of phosphorus to rivers is from weathering of rocks or mineral material. Phosphorus is the tenth most abundant element on earth, and apatite is the most abundant phosphate mineral in the earth's crust. Consequently, the delivery of phosphorus to rivers depends largely on the geology of the watershed and the type of rocks being weathered in the vicinity.

During transport, phosphorus undergoes a variety of chemical and biological transformations. For example, phosphorus is taken up by biota to meet their cellular demands. Phosphorus is a plant macronutrient and is present in cells as genetic material (RNA and DNA), components of cell membranes (phospholipids), and as energy molecules (nucleotides) and is essential for cell viability. The amount of phosphorus necessary to meet the demand by biotic processes per year is greater

than the amount delivered by rivers from weathering. Consequently, biotic processes depend on phosphorus recycling in natural systems. Phosphorus is recycled when organisms decay or can be regenerated from sediments through microbial activity and redox reactions. Organic phosphorus compounds can be hydrolyzed extracellularly by organisms that have alkaline phosphatases, and the inorganic phosphates produced can be readily used by phytoplankton and bacteria. In this and other ways, phosphorus is rapidly regenerated in the water column and the sediments where regeneration rates are sensitive to temperature, salinity, and dissolved oxygen. Release of phosphorus from sediments is dependent on temperature, microbial activity, salinity, and redox conditions. Upwelling of deep ocean water also can return bioavailable phosphorus to the surface where it can fuel primary (phytoplankton) production.

3.0 NITROGEN AND PHOSPHORUS TRANSFORMATIONS IN THE ENVIRONMENT

3.1 Biotic Transformation Processes

Bacteria and algae are key contributors to the cycling of nitrogen and phosphorus in natural and engineered treatment environments. Recent advancements in molecular biology tools have shown that different groups of microorganisms are involved as discussed below.

3.1.1 Ammonia and Nitrite Oxidation

Bacterial ammonia oxidation typically is an autotrophic (inorganic electron donor, or energy source), aerobic process that occurs through a two-step metabolism known as nitrification. In the first step, ammonia oxidizing bacteria (AOB) oxidize NH_4^+ to NO_2^- in a process that consumes oxygen both for respiration (as a terminal electron acceptor) and to support enzymatic ammonia monooxygenase reactions (as a substrate in the oxidation of ammonia to the intermediate hydroxylamine). The second step involves the continued oxidation of NO_2^- to NO_3^- via nitrite oxidizing bacteria (NOB) with oxygen serving as the electron acceptor. Recent technological advances in process configurations that allow NH_4^+ oxidation but prevent NO_2^- oxidation (to be discussed further below and elsewhere in this book), require use of the term "nitritation." Nitritation has been popularly used to refer to ammonia oxidation without further oxidation of NO_2^- to NO_3^- (Van der Star et al., 2007).

The stoichiometry of ammonium oxidation/nitritation is well established. Assuming a biomass yield of 0.2 mg formed (as chemical oxygen demand [COD]) per milligram of ammonium-N oxidized, the molar stoichiometry of this reaction is (Ahn et al., 2008)

$$\begin{aligned} &NH_4^+ + 1.9O_2 + 0.069\,CO_2 + 0.017\,HCO_3^- \\ &\quad \rightarrow 0.017\,C_5H_7O_2N + 0.98\,NO_2^- + 0.97\,H_2O + 1.8\,H^+ \end{aligned} \tag{1.1}$$

Note that a substantial amount of acid is formed by nitritation, but that biomass yield is relatively low. The other important feature of nitritation is that the oxygen demand per mole of ammonium oxidized is high. Therefore, although nitrifying bacteria constitute a small percentage of the overall bacterial community in a natural or bioreactor environment, they must exert significant oxygen demand to function. These stoichiometric features are important to understand when considering the design factors presented elsewhere in this book.

In conventional nitrification processes, nitrite formed by AOB is consumed by NOB, which tend to exist in close proximity. Assuming a biomass yield of 0.1 mg formed (as COD) per milligram of nitrite-N oxidized and ammonia as a nitrogen source for growth, the molar stoichiometry of this reaction is (Ahn et al., 2008)

$$\begin{aligned} &NO_2^- + 0.0088\,NH_4^+ + 0.035\,CO_2 + 0.0088\,HCO_3^- + 0.46\,O_2 + 0.0088\,H_2O \\ &\quad \rightarrow 0.0088\,C_5H_7O_2N + 1.0\,NO_3^- \end{aligned} \tag{1.2}$$

The pH of environments containing ammonium is important because it determines if free ammonia (NH_3, the deprotonated form) is present and at what concentration. Free ammonia is known to inhibit nitritation. Neufeld et al. (1980) determined that free ammonia inhibits AOB according to substrate inhibition models. Anthonisen et al. (1976) determined that free ammonia inhibited AOB at concentrations as low as 10 mg/L N and NOB at concentrations as low as 0.1 mg/L N. The relationship between free ammonia and pH is

$$\left[NH_3\,(aq)\right] = \frac{K_a \times \left[NH_4^+\,(aq)\right]}{10^{-pH}} \tag{1.3}$$

Where K_a is the $10^{-9.3}$ at conditions encountered at most WWTPs.

Free ammonia typically is not present in sufficient quantities to cause nitritation inhibition in domestic WWTPs. It can, however, be present in wastes containing high TAN concentrations, such as in industrial applications or in dewatered reject

water where operation at pH values that typically avoid free ammonia inhibition in the mainstream process could be inhibitory in sidestream processes. Therefore, the theoretical free ammonia concentration in high TAN wastes must be considered if nitrification is desired.

As noted previously, some treatment processes rely upon achieving nitritation while preventing subsequent nitrite oxidation. The success of nitritation requires the growth of NOB to be limited so that NO_2^- is not oxidized to NO_3^-. Several methods have been used to limit the growth of NOB, including controlling dissolved oxygen concentrations and pH (to enhance free ammonia inhibition of NOB while preventing it in AOB), controlling reactor temperature, adding chemical inhibitors, or controlling sludge age. Of these, dissolved oxygen control is among the easiest and most cost-effective to achieve. The AOB have been shown to have a higher affinity for dissolved oxygen than NOB (Guisasola et al., 2005; Wyffels et al., 2004). Therefore, operating at low dissolved oxygen concentrations can help to reduce NOB growth and allow for nitritation, where desired, while reducing the cost of aeration.

Over the last decade, AOB have been reclassified based on phylogenetic methods. The AOB that are found in freshwater or low salinity systems include those strains in the *Nitrosomonas* (including *Nitrosococcus mobilis*) and *Nitrosospira* (including *Nitrosolobus* and *Nitrosovibrio*) lineages and are members of the β subclass of the proteobacteria (Purkhold et al., 2003). Different strains of ammonia oxidizers are found in natural and bioreactor environments depending upon their affinity for ammonium. Natural waters and drinking water environments tend to select for AOB that predominate under low-ammonium conditions because of their high affinity for the compound (e.g., *Nitrosomonas oligotropha* and *Nitrosospira briensis*) (Bollmann et al., 2002, 2005; Eichler et al., 2006; Regan et al., 2003). In contrast, domestic WWTPs, which are relatively rich in ammonium, tend to select for AOB that have a lower affinity for ammonia, such as *Nitrosomonas europaea* (Koops and Pommerening-Roser, 2001).

Similar to the case of AOB, the type of NOB typically present in different environments have been elucidated more carefully with the assistance of culture independent, molecular biology tools. There are two nonmarine genera of NOB: (1) the *Nitrobacter* genus, which belongs to the α-proteobacteria and was historically identified as the predominant NOB in many natural and engineered environments (Painter, 1977); and (2) the phylogenetically distinct *Nitrospira*, which commonly are found in nitrifying wastewater bioreactors, freshwater aquaria, and drinking water distribution systems (Burrell et al., 1998; Hovanec et al., 1998; Juretschko et al., 2002; Regan et al., 2002, 2003).

Recently, researchers have show that *Nitrospira* can be segregated into sublineages that have different affinities for high versus low concentrations of nitrite (Daims et al., 2006; Maixner et al., 2006). Therefore, the manner in which a bioreactor is operated and whether it is a flocculant or attached growth system will dictate the type of NOB found.

Ammonium oxidation extends beyond the commonly studied nitrifiers discussed above. Anaerobic ammonia oxidizers (anammox) were mentioned earlier and have been highlighted in marine environments because of their role in producing N_2 while oxidizing NH_4^+. In addition to the studies conducted in marine environments, these organisms have also been enriched for and used beneficially in wastewater treatment systems, especially in processes designed to treat waste streams with high concentrations of ammonia (e.g., reject water streams from dewatering processes). The stoichiometry of the metabolism performed by these unique microorganisms was proposed by Strous et al. (1998) (eqs 1.1–1.4) and was found to be consistent with observed performance during the startup of a single sludge NH_4^+ oxidation-anammox sequencing batch reactor system (Van der Star et al., 2007).

$$\begin{aligned} &NH_4^+ + 1.32\,NO_2^- + 0.066\,HCO_3^- + 0.13\,H^+ \\ &\quad \rightarrow 1.02\,N_2 + 0.26\,NO_3^- + 0.066\,CH_2O_{0.5}N_{0.15} + 2.03\,H_2O \end{aligned} \tag{1.4}$$

Several acronyms and patented processes have been coined that involve the anammox metabolism. As parallel research efforts ensued, confusion over the differences between these processes occurred. In this book, anammox (lowercase letters) will be used to describe the metabolism (defined in eqs 1.1 to 1.4), which is not patentable. Process configurations that incorporate this metabolism, some of which are patented, will be explicitly described as such. There are three distinguishing features of reactor configurations that incorporate anammox as a primary metabolic process: (1) whether the nitritation and anammox metabolisms are in the same reactor or separate reactors; (2) whether the process incorporates flocculant biomass or attached growth; and (3) whether granulation is a key feature. Van der Star et al. (2007) suggested universal terminology that should be incorporated to more clearly identify reactor system differences. This terminology will be incorporated to this book when anammox-focused treatment technologies are discussed.

More recently, archaeal (prokaryotic microorganisms that are of the domain Archaea, not the domain Bacteria) nitrifiers that belong to the prolific marine Crenarchaeota have been found in significant numbers in marine environments. They are believed to be prolific and are probably important in ocean nitrogen metabolism (Francis et al., 2007). The nitrifying Crenarchaeota also have been found to be a

significant fraction of the total Crenarchaeota in nitrifying activated sludge bioreactors, although their relative contribution to NH_4^+ oxidation in these reactors has not yet been elucidated (Park et al., 2006). Using a recent isolate with a proposed name of *Nitrosopumilus maritimus*, it was shown that the nitrifying marine Crenarchaeota are chemolithoautotrophs that use inorganic electron donors (e.g., ammonium) and an inorganic carbon source (e.g., CO_2) and perform near complete NH_4^+ oxidation to NO_2^- (Könneke et al., 2005). These organisms are significant contributors to nitrogen cycling in mesophilic marine and terrestrial environments, but their contribution to wastewater treatment nitrification has yet to be determined (Horner-Devine and Martiny, 2008; Nicol and Schleper, 2006).

3.1.2 Denitrification

Denitrification is a common process in natural environments and engineered bioreactors. Although denitrification was assumed to be the primary means of nitrogen loss as N_2 in marine systems for years, the recent discovery that anammox is a prevalent metabolism in marine nitrogen metabolism has resulted in a view that reduces (but does not eliminate) the relative role of denitrification in these environments. In freshwater headwater streams, denitrification is an important process in transforming dissolved inorganic nitrogen (DIN) into gaseous products, thereby reducing the transport of nitrogen downstream to rivers, lakes, and estuaries (Mulholland et al., 2008; Peterson et al., 2001). At the same time, Mulholland et al. (2008) have shown that anthropogenic inputs of nitrate to freshwater streams are disproportionately passed downstream because most streams do not have the capacity to denitrify this additional load. This emphasizes the importance of removing nitrogen from effluents that discharge into freshwater systems upstream of estuaries.

Bacterial denitrification is performed by a diverse collection of microorganisms fueled by reduced inorganic or organic compounds. As such, it is difficult to review the genera responsible given the scope of this book. Because inorganically fueled (e.g., H_2 gas) denitrification typically is not employed in domestic wastewater treatment applications, the focus in this book will be with heterotrophic denitrification.

The stoichiometry of heterotrophic denitrification, assuming methanol as the electron donor and a cell yield of 0.6 g cell biomass formed as COD per gram methanol consumed as COD, is given in eq 1.5:

$$\begin{aligned} &CH_3OH + 0.48\,NO_3^- + 0.18\,HCO_3^- + 0.18\,NH_4^+ + 0.48\,H^+ \\ &\rightarrow 2.05\,H_2O + 0.28\,CO_2 + 0.24\,N_2 + 0.18\,C_5H_7O_2N \end{aligned} \tag{1.5}$$

The stoichiometry shows that there is a net generation of alkalinity and consumption of acid (increase in pH) at the near-neutral pH of treatment systems. This is in contrast to the loss in alkalinity and decreases in pH observed with nitritation. Conveniently, nitrification and denitrification often are coupled to achieve nitrogen removal, and, as a consequence, the net loss in alkalinity is moderate. It is also possible to couple nitritation (NH_4^+ to NO_2^-) and denitritation (NO_2^- to N_2 gas) as a way to reduce the amount of dissolved oxygen and exogenous carbon source needed to fuel the reaction (Jetten et al., 1997). Heterotrophic denitrification typically has a significant biomass yield that must be managed during solids handling when applied in wastewater treatment. The enhanced interest in anammox-focused processes that convert reduced nitrogen to gaseous products is motivated in part by the substantial decrease in residual sludge, and competes directly with sludge-intensive heterotrophic denitrification processes. Although anammox-focused technologies are growing in popularity as an alternative to denitrification for concentrated ammonia wastewaters, it has not been applied to diluted wastewater typical of what is received at centralized wastewater treatment systems.

3.1.3 Ammonification

Bacteria are involved in the regeneration of ammonium from soluble or particulate organic nitrogen in a process called ammonification. This occurs when amino groups are released from organic nitrogen compounds, either because of intracellular or extracellular enzymatic activity. Ammonification is important in wastewater treatment because it makes organic nitrogen bioavailable for nitrification (Grady et al., in press).

3.1.4 Phosphorus Accumulating Organisms

Phosphorus accumulating organisms (PAOs) are bacteria that have the capacity to store phosphorus as inorganic polyphosphate granules intracellularly. In enhanced biological phosphorus removal (EBPR) wastewater treatment systems, the conditions that enable this storage to occur allow for phosphorus to be moved from the diluted liquid waste stream to the concentrated biosolids through solids separation processes. In this way, phosphorus can be managed through biosolids management methods.

Polyphosphate granule storage is an energy management feature of PAOs that allow them to compete with non-PAO heterotrophs in appropriately configured reactor systems. Under anaerobic conditions, PAOs expend energy by cleaving high

energy phosphate bonds in the polyphosphate granules to fuel the storage of volatile fatty acids (VFAs) into polyhydroxyalkanoate (PHA) granules. Reducing power is also needed to support PHA formation and is provided in part by glycogen; however, the amount of glycogen present in PAOs is not sufficient to provide all the reducing power needed for PHA formation, and other sources must be available (Martin et al., 2006). The ability that PAOs have to sequester VFAs into PHA is thought to be a competitive benefit that leads to the proliferation of PAOs in EBPR systems. During the anaerobic process, soluble COD concentrations decrease and phosphate concentrations increase. Under subsequent aerobic treatment, the PAOs metabolize the PHA aerobically and direct the energy captured from that metabolism to growth, reestablishing the polyphosphate granules and restoring glycogen pools. Phosphorus removal from wastewater effluent occurs when sludge is wasted after the aerobic phase, resulting in phosphorus accumulating in the biosolids.

Historically, *Acinetobacter* was thought to be the predominant microorganism responsible for EBPR (Fuhs and Chen, 1975). Culture-independent methods did not corroborate these early studies, however, leading researchers to look more carefully at the microbial diversity of EBPR systems (Wagner et al., 1994). Recent ecological studies of PAOs indicate that a predominant PAO believed to be important in EBPR systems is *Candidatus Accumulibacter phosphatis* of the *Rhodocyclus* group (Martin et al., 2006). Follow-up studies performed in full-scale EBPR treatment plants showed that although accumulibacter-related bacteria were prominent, they accounted for only 40% to 70% of the total PAO concentration. This indicated that other non-accumulibacter PAOs also were important in the EBPR processes (He et al., 2008). Furthermore, He et al. (2008) showed that accumulibacter-related PAOs appear to be more prevalent in systems that have larger anaerobic zone volumes and do not incorporate pre-fermentation. They hypothesized that this related to the apparent preference of accumulibacter-related PAOs for low VFA concentrations that would use the high-affinity phosphate uptake systems found in these organisms (Martin et al., 2006). Advances in knowledge of the microbial ecology of EBPR systems show how molecular biology can be coupled with whole-cell and full-scale performance data to enhance understanding of complex biological treatment processes. This understanding shows how design and operational decisions can affect microbial ecology, which influences performance.

3.1.5 Algal Transformations

Algae can use a variety of nitrogen and phosphorus compounds available in nature to support growth. Typically, nitrogen is taken up by cells, reduced intracellularly

to NH_4^+ and then assimilated into amino acids. A significant fraction of the nitrogen taken up during even short-term (hours) incubations can be released as NH_4^+ and amino acids. It is unclear why cells would release metabolites either before or after their assimilation into organic matter; nitrogen release is highly variable among systems. In addition to this passive release, nitrogen is released from phytoplankton during cell death and lysis, viral infection and lysis, and sloppy feeding (i.e., when a cell is damaged during grazing, resulting in the release of dissolved intracellular pools). Nitrogen compounds often are produced as rapidly as they are consumed, making it difficult to measure these processes separately.

Nitrogen uptake and assimilation by algae are stepwise processes that can result in a distinctly regulated uncoupling between uptake and growth (Wheeler et al., 1983). Furthermore, most of the enzymes involved in the uptake and assimilation of nitrogen are tied to factors associated with energy management (light, oxygen, metabolic cofactors). For example, uptake and metabolism of NO_3^-, NO_2^-, and urea have been linked to the light supply in phytoplankton and is thought to proceed at maximum rates only under light and in nutrient replete conditions. When nitrogen is depleted, active uptake of these compounds occurs in the dark and at 10% to 100% of the uptake rate measured in the light (Antia et al., 1991). There are significant diurnal variations in nitrogen cycling in waterways that support algae growth. Therefore, it is important to consider the influence of light-influenced diurnal cycles to get an accurate picture of the water quality of receiving streams.

Traditionally, DIN was thought to be the primary source of nitrogen supporting algal growth, and DON was thought to support bacterial growth. Recent research, however, has shown that organic nitrogen, particularly urea, is an important source of nitrogen for phytoplankton and that bacteria are strong competitors with phytoplankton for inorganic nitrogen, particularly NH_4^+ (Bronk et al., 2007; Kirchman, 2000; Mulholland and Lomas, 2008). DON can be rendered more or less available through extracellular enzymatic reactions that degrade DON into usable components (Berges and Mulholland, 2008; Bushaw-Newton and Moran, 1999; Chrost, 1991; Hoppe, 1983; Hoppe et al., 2002; Mulholland et al., 1998; Palenik and Morel, 1990a, 1990b; Pantoja and Lee, 1999; Pantoja et al., 1997) and through photochemical reactions. Although poorly characterized, the aquatic DON pool that has been described consists of highly reactive and relatively recalcitrant fractions (Bronk, 2002). The relative contribution and characteristics of effluent-derived organic nitrogen is not well described relative to background organic nitrogen compounds in natural waters. Fate of organic nitrogen in effluent is an important issue for effective removal by wastewater treatment

systems. Effluent-derived organic nitrogen has been shown to be assimilated by laboratory-cultured freshwater algae grown in the presence of bacteria that can presumably hydrolyze the organic nitrogen and make it bioavailable (Pehlivanoglu and Sedlak, 2004). The bioavailability of this material by algae indigenous to both freshwater and estuarine receiving waters, however, has not been demonstrated (Urgun-Demirtas et al., 2008). Finally, low DIN and high DON have been shown to selectively favor the growth of harmful algal species (Anderson et al., 2002). In particular, DON has been implicated as a nutrient source that may preferentially stimulate harmful algal blooms (Anderson et al., 2002; Graneli et al., 1999). The contribution of wastewater effluents to this phenomenon has not been established.

3.2 Abiotic Transformations

Several abiotic processes influence the fate of nitrogen and phosphorus in aquatic systems, including photochemical release and salinity.

3.2.1 Photochemical

Recent findings in freshwater and marine systems indicate that photochemical processes can result in the release of low molecular forms of nitrogen and phosphorus from dissolved organic matter (DOM), particularly those fractions that are aromatic in character, such as humic substances (Mopper and Kieber, 2002). Exposure to wavelengths in the ultraviolet region (280–400 nm) results in the most efficient photoproduction. For nitrogen, NH_4^+ and dissolved free amino acids are the most common products (Buffam and McGlathery, 2003; Bushaw et al., 1996; Wang et al., 2000). The global contributions of this phenomenon to nitrogen biogeochemical cycling is not entirely known. It has been found, however, that photoproduction makes a small but significant contribution in aquatic photic zones (Kitidis et al., 2006; Wang et al., 2000). Studies also have shown the photoproduction of phosphate (Kieber, 2000). Rates of photoproduction of both nitrogen and phosphorus can be highly variable and relatively little is known about the mechanisms responsible.

3.2.2 Salinity Effects

Salinity increases along the length of an estuary. Salt significantly influences the behavior, conformation, and reactivity of DOM as it moves through estuaries. Changes in salinity are known to alter the reactivity and bioavailability of DON and to affect photochemical reactions (Minor et al., 2006; See and Bronk, 2005). Salinity can also result in conformational changes, which can influence both the abiotic and

biotic reactivity of DOM, such as humic substances (Baalousha et al., 2006). Salinity also may affect the transport of labile nitrogen on organic compounds. Recent studies have shown that humic substances are capable of adsorbing NH_4^+ from surrounding waters to cation binding sites (See and Bronk, 2005). This adsorption makes humic substances a potentially important mode of transport for nitrogen that is produced upriver to the estuary and coastal ocean. As the humic materials move downriver and encounter higher salinities, the salt ions can displace the loosely bound amino groups on the humic structure, releasing them into the environment. The relevance of this phenomenon to wastewater effluent–derived organic nitrogen is not well understood and is discussed further in Section 4.3.2.

4.0 EFFECTS OF NITROGEN AND PHOSPHORUS IN THE AQUATIC ENVIRONMENT

4.1 Eutrophication and Water Quality

Water quality in coastal areas is deteriorating as a result of population pressure and consequent cultural eutrophication (Howarth et al., 2002; Nixon, 1995; Paerl, 1997; Smetacek et al., 1991; Vitousek et al., 1997; Vollenweider et al., 1992). As previously noted, productivity in most marine and estuarine ecosystems is thought to be limited by nitrogen. Over the past century, however, humans have significantly increased nitrogen (and phosphorus) inputs through the use of synthetic fertilizers in agriculture, expansion of fossil fuel combustion, and coastal urbanization (Beman et al., 2005; Paerl and Piehler, 2008). A national survey of estuarine health across the United States reported that high nitrogen loads into estuaries could be attributed to the effects of coastal urbanization, and that the extent of eutrophication in estuarine systems was not decreasing compared to older studies (Bricker et al., 2007). Total loads of phosphorus decreased following their ban from detergents in the mid-1980s; total loads of nitrogen, however, have increased since World War II as a result of increased use of nitrogen fertilizers (Howarth et al., 2002). For example, in the Chesapeake Bay region, human activity has resulted in substantial increases in nitrogen loading that are intermediate relative to other heavily urbanized estuaries worldwide (Boynton et al., 1995; Kemp et al., 2005).

In addition to the absolute amount of nitrogen input into coastal watersheds, there has been a change in forms of nitrogen being released into coastal systems. In the past few decades, inorganic nutrient loading has shifted to organic nutrient loading, largely because of the increase in organic urea-based fertilizers (Glibert et al.,

2005; Paerl and Piehler, 2008). Higher levels of DON selectively favor the growth of harmful and nuisance algal species (Anderson et al., 2002).

There are substantial differences in the cycling of nitrogen and phosphorus along the length of an estuary. Because freshwaters are often phosphorus-limited, phosphorus introduced at the head of an estuary may be rapidly removed by phytoplankton resulting in a proportional decrease of nitrogen and increase in algal growth in freshwater receiving waters. Phosphorus moves down-estuary either in dissolved or particulate form and can be recycled en route or buried in the sediments. Nitrogen, however, has a more complex cycle (see above). Nitrogen delivered at the head of an estuary may be taken up by algal cells or, if in excess, can be nitrified in the lower salinity reaches and then subsequently denitrified at mid-salinities as it moves through an estuary. Because more saline waters tend toward nitrogen limitation, nitrogen delivered to the mouth of an estuary can result in excess algal production in more saline waters.

Impairments to freshwaters because of high phosphorus loading resulted in phosphate detergent bans in the 1980s. As a result of phosphorus reductions, there has been an increase in nitrogen delivery downstream (it was no longer taken up with the phosphorus), away from proximate receiving waters. An excellent example of the unforeseen consequences of reducing phosphorus loading is the Neuse River Estuary in North Carolina. As a result of the reduction in phosphorus, the chlorophyll maximum moved down-estuary from the phosphorus-limited freshwater end to the more nitrogen-limited saline end—a region where nuisance phytoplankton blooms are now regular (Paerl et al., 2004). In short, the spatial and temporal extent of downstream nitrogen limitation is dependent on upstream nutrient management.

4.2 Gaseous Nitrogen Emissions and Atmospheric Quality

The primary form of nitrogen on earth is N_2 gas, which constitutes 78% of our atmosphere. A predominant byproduct of microbiological metabolism, N_2 is largely inert and stable. In contrast, partially oxidized gaseous nitrogen compounds are significant contributors to global warming (nitrous oxide, N_2O) and ozone depletion (nitric oxide, NO, and nitric oxide chemically generated by stratospheric N_2O). Of particular concern to global climate change is N_2O, which has an atmospheric lifetime of 114 years and a global warming potential (100-year basis) nearly 300 times greater than carbon dioxide (CO_2) (Forster et al., 2007). Both N_2O and NO are produced biologically under conditions generated by many biological nitrogen removal wastewater treatment configurations including liquid treatment streams, biosolids treatment, and incineration. Current estimates of the contributions of WWTP-generated N_2O

emissions to total global anthropogenic greenhouse gas emission are less than 0.5% (Bogner et al., 2008). Similarly, the effect of gaseous emissions from constructed wetland treatment systems was found to be negligible (Mander et al., 2005). The estimated global warming potential for wastewater treatment systems was based, however, on N_2O emissions data from a WWTP that used conventional activated sludge treatment without intentional nitrogen removal. The N_2O estimate for nitrogen removal treatment processes is expected to be higher. As worldwide interest in implementing nitrogen removal technologies grows, reduced nitrogen loads into the aquatic environment will be offset by increased release of partially oxidized nitrogen gaseous products if current biological treatment technologies are used.

Nitrous oxide is produced as a gaseous intermediate during both heterotrophic and autotrophic (AOB) denitrification. It has been known for quite some time that AOB produce N_2O when performing denitrification. This typically has been observed under low dissolved oxygen conditions (Beaumont et al., 2004; Lipschultz et al., 1981). Chandran (2009) reports the metabolic condition controlling AOB gaseous emissions. Varying dissolved oxygen conditions conducive to N_2O production can form in WWTPs because of aerobic/anoxic interfaces that exist within activated sludge flocs. Production also can occur in wastewater treatment processes that achieve nitrogen removal using single sludge approaches that put the biomass through sequential aerobic and anoxic conditions. Full- and laboratory-scale nitrogen removal systems have shown detectable N_2O gaseous emissions ranging from 0.1% to 1.4% of influent oxidizable nitrogen load (Kampschreur et al., 2008; Tallec et al., 2006). One exception to this showed that 30% of influent oxidizable nitrogen was converted to N_2O when the influent COD:N ratio fell below 3.5 (Itokawa et al., 2001). Studies suggest several conditions contribute to the relative emissions of N_2O generated by denitrifying AOB: (1) mixed liquor dissolved oxygen concentrations; (2) the presence of nitrite (which serves as the electron acceptor during AOB-based autotrophic denitrification); (3) pH (which defines the partitioning between nitrite and nitrous acid); and (4) the AOB microbial ecology (Bock et al., 1995; Jiang and Bakken, 1999; Shiskowski and Mavinic, 2006; Tallec et al., 2006). Generation of NO by AOB also has been observed in WWTPs, although it appears to be a smaller percentage of the final oxidized gaseous emissions (Kampschreur et al., 2008).

Heterotrophic denitrifying bacteria produce N_2O as an intermediate during routine metabolic process of reducing nitrogen to $N_2(g)$. It is unclear if AOB-based autotrophic denitrification is the predominant source in WWTPs as reported by Tallec et al. (2006) or if heterotrophic denitrification is the predominant source as reported by

Itokawa et al. (2001). Accordingly, the relative contribution between these two distinct groups may be a function of the reactor configuration and other operating conditions.

4.3 Domestic Wastewater Treatment

4.3.1 Influent Characteristics

The most prevalent forms of nitrogen in domestic wastewater are organic nitrogen and ammonium. The organic fraction exists both in soluble and in particulate forms. It is uncommon for oxidized forms of soluble nitrogen (e.g., nitrate or nitrite) to exist in domestic wastewater. These forms only occur if there is an upstream industry that discharges wastewater containing these compounds. Phosphorus in domestic wastewater typically exists as organic phosphorus or inorganic phosphorus (primarily orthophosphate). The inorganic phosphorus fraction is the primary form (typically at least 75%) of total phosphorus in wastewater. Typical concentrations for nitrogen and phosphorus constituents in domestic wastewater not under the influence of upstream industries are given in Table 1.1.

Recently, attention has been directed toward the potential for decentralized wastewater treatment. This would involve treating more concentrated wastewaters that are not diluted by infiltration or inflow or that are comprised of source-separated wastes where the urine and feces are collected separately (Etnier, 2007; Otterpohl et al., 1997;

TABLE 1.1 Nitrogen and phosphorus in domestic wastewater ranging from weak to strong (Tchobanoglous et al., 2003; WEF, 2009).

	Concentration (mg/L as N or P)	
	Soluble	**Particulate**
Nitrogen		
Organic N	1–2	7–23
Ammonia/ammonium	12–45	N/A[a]
Phosphorus		
Organic P	[b]	1–5
Inorganic P	3–10	N/A

[a] N/A = not applicable.

[b] Soluble organic phosphorus is a minor constituent in most domestic wastewaters.

Wilderer and Schreff, 2000; Zeeman and Lettinga, 1999). Source separation could make treatment of nitrogen and phosphorus from wastewater more efficient and could possibly enable opportunities for nutrient recovery (Maurer et al., 2006). Urine contains roughly 50% of the phosphorus and more than 80% of the organic nitrogen (urea, which hydrolyzes into ammonia) in municipal wastewater, but represents less than 1% of most wastewater flows (Larsen and Gujer, 1996). As more sustainable water management practices are implemented, shifting practices could influence how nitrogen and phosphorus are controlled in wastewaters.

4.3.2 Effluent Characteristics

The concentration of nitrogen in liquid effluent from WWTPs is a function of the treatment process configuration used, the disinfection process employed, and the composition of the wastewater received at the plant. Typically, treatment processes that use nitrification have effluents that contain oxidized nitrogen (nitrate). Processes that do not routinely achieve total nitrification but, instead, produce variable amounts of nitrite will have significant problems using chlorination for disinfection because of the preferred reactivity between free chlorine and nitrite. Treatment processes that use biological or enhanced nitrogen removal will have effluent concentrations of total nitrogen that vary from low (less than 3 mg/L as N) to moderate (8 mg/L as N). In all cases, NH_4^+-N concentrations typically will be low (well below 1 mg/L) if the treatment plant is fully nitrifying. Nitrogen removal plant effluents typically will contain a combination of oxidized nitrogen, NH_4^+, and organic nitrogen.

A recent survey of the effluents from nitrogen removal plants was conducted to characterize the organic nitrogen concentrations (effluent organic nitrogen). The average concentration was approximately 1 mg/L as nitrogen (Pagilla et al., 2006). The bioavailability of effluent organic nitrogen is unknown, although regulators assume it is bioavailable because it is included in the total nitrogen limit imposed upon treatment plants located in nutrient-sensitive regions. Research using a bioassay and freshwater algae has shown that up to 61% of the organic nitrogen contained in effluents is bioavailable (Pehlivanoglu and Sedlak, 2004; Urgun-Demirtas et al., 2008). The bioavailability of effluent organic nitrogen released from WWTPs that discharge into nitrogen-limited estuarine or marine environments is unclear (Mulholland et al., 2007).

Phosphorus concentrations in wastewater effluents that do not practice enhanced phosphorus removal are typically 3 to 5 mg/L and primarily in the form of inorganic P. Enhanced phosphorus removal processes are capable of achieving very low total (< 0.1 mg/L as P) phosphorus levels in effluents when chemical precipitation is used, either alone or in combination with EBPR.

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Chapter 2

Regulation of Nutrients in the Effluents of Wastewater Treatment Plants

1.0 INTRODUCTION

This chapter reviews the various laws and regulations applicable to discharge of nutrients in treated effluents from wastewater treatment facilities. This manual of practice (MOP) does not, however, provide a comprehensive summary of regulations—many of which may be expected to change during the useful life of this publication. It is the responsibility of the wastewater treatment plant (WWTP) owner/operator and its design engineer to understand the basis of regulatory requirements and the specific requirements for each facility. WWTP professionals should be proactive to ensure that applicable laws and regulations are appropriately applied to their facility. Similarly, they should be aware of the changing nature of laws and regulations and should anticipate, to the extent possible, the potential for future requirements that may be different (typically more stringent) from existing conditions.

This chapter does not attempt to provide all the details of all regulations that control nutrients in effluent discharges from WWTPs. The most current information can be found on the Web sites of the respective regulatory agencies. The U.S. Environmental Protection Agency (U.S. EPA) has good information on its various Web sites that explain the basis and history of relevant laws and regulations and provide both details and links to federal and state laws and regulations. For specific information for an individual WWTP, the regulatory agency that has jurisdiction must be consulted. Links to several of the Web sites that may provide helpful information relevant to regulation of nutrients are presented in the references at the end of this chapter.

2.0 SUMMARY OF WATER QUALITY AND NUTRIENT REGULATION IN THE UNITED STATES

2.1 Clean Water Act

Protection of surface water quality and regulation of pollutant discharges into U.S. waters is governed by the Clean Water Act (CWA). The law in its current form started with the Water Pollution Control Act Amendments of 1972. When amended in 1977, this law became known as the CWA. Various additional amendments have been enacted subsequently by the U.S. Congress to modify specific provisions. The act as currently amended remains the cornerstone of surface water quality protection in the United States.

Section 101(a) of the act states that the primary objective is "to restore and maintain the chemical, physical, and biological integrity of the Nation's waters." Accordingly, the act established national goals to achieve fishable and swimmable waters (wherever attainable) and a long-range goal to eliminate discharge of pollutants into U.S. waters. To achieve these goals, the CWA established a program to define water quality standards (WQS) and to regulate and permit discharges into U.S. waters.

Designated uses, water quality criteria to protect the uses, and antidegradation policies constitute the three major components of the WQS program established under the CWA. Designated beneficial uses such as recreation, human health (drinking water supply), and protection of aquatic life are determined for each water body. Appropriate water quality criteria are established under the act consistent with each use. Antidegradation policy establishes rules to address proposed activities that would lower the quality of waters that have attained or are better than the criteria for designated uses in a water body. In addition to these three major elements, the CWA regulations also allow general policies to address implementation issues, such as mixing zones, variances, and low-flow policies. These components and policies of WQS, when implemented and attained in a specific water body, are intended to assure viability of each designated use.

The CWA prohibits discharge of pollutants into U.S. waters unless a permit has been issued to the discharger. The National Pollutant Discharge Elimination System (NPDES) permit program provides the framework for issuance of these permits. Dischargers without permits or that exceed their permit limits are violating the law and may be subject to civil, administrative, or criminal penalties.

Authority to implement the CWA rests with the U.S. EPA. The U.S. EPA is also allowed to delegate this authority to the various states (through the respective environmental agency or department within each state government) if the state demonstrates that it has a program at least as stringent as U.S. EPA's regulations. Implementation of the CWA includes development of WQS and administration of the NPDES program (which includes permit issuance, monitoring and inspection, and enforcement).

2.2 National Pollutant Discharge Elimination System Permit Program

The NPDES permit program regulates point sources of pollution discharging to surface water bodies. Permit discharge limitations (limits) under the CWA are based on two types of standards: (1) treatment technology-based and (2) water-quality-based.

Technology-based limitations set a nationally uniform level of allowable discharge for certain pollutants, regardless of receiving water quality. Both municipal and industrial wastewater discharges must meet specified treatment performance standards—that is, the discharge must not exceed specific levels of pollutant discharge based on appropriate treatment technology. In accordance with the CWA, U.S. EPA establishes the treatment technology basis for various categories of wastewater.

All treated effluent from a municipal WWTP must achieve the degree of reduction attainable through application of secondary treatment technology, as defined by U.S. EPA. Secondary treatment performance is specified in terms of five-day biochemical oxygen demand (BOD_5), total suspended solids (TSS) removal, and pH, but does not include nutrient removal. Alternatively, it may be specified in terms of carbonaceous biochemical oxygen demand ($CBOD_5$), which includes only oxygen demand from degradation of organic carbon compounds, and excludes oxygen demand from nitrification; nitrification is biochemical conversion of ammonia to nitrate.

Industrial wastewater discharges to receiving waters must achieve technology-based effluent limits developed by U.S. EPA for various specific industrial categories. Called "effluent guidelines," these limits are derived from studies to determine the effluent levels for various pollutants that are achievable using various levels of available or cost-effective treatment technology appropriate for each specific industrial source category. Typically, industrial effluent guidelines do not include nutrient limits.

If the U.S. EPA or the states determine that the technology-based effluent limits for municipal or industrial category wastewater discharges are insufficient to meet WQSs of specific receiving waters, then water-quality-based effluent limits (WQBELs) are developed and applied in the respective NPDES permit(s). The WQBELs are derived from the receiving water body WQS, setting allowable pollutant levels in the effluent using a calculation that accounts for other point and nonpoint sources to meet the instream water quality criteria for the local water body (refer to Section 4.1 for further discussion of WQBEL derivation). If a total maximum daily load (TMDL) has been established for pollutant(s) in any receiving water, the WQBEL(s) must be consistent with the wasteload allocation (WLA) assigned to each source by the TMDL.

The NPDES permits must be reissued at least every five years. Although the regulatory agency can reevaluate permit effluent limitations at any time, it is typically done only at the time of permit renewal. Accordingly, permittees should be aware of changes to water quality criteria or regulations that may result in changes for future

effluent limitations. Permittees should anticipate potential changes and their effects on their wastewater treatment facility.

2.3 Water Quality Criteria

Under section 304(a) of the CWA, water quality criteria are based solely on scientific data and judgments about the relationship of pollutant concentrations to environmental and human health effects. Water quality criteria do not consider economic or social impacts. Social and economic factors, however, can be taken into account in establishing refined or subcategorized designated uses, which can occur via implementation of a "use attainability analysis." Numeric water quality criteria were established soon after enactment of the CWA related to the effects of "conventional pollutants" (e.g., BOD and TSS). These early criteria of most importance included dissolved oxygen, temperature, pH, and bacteria. The 1987 amendments focused on the control of toxic pollutants (e.g., toxic metals or toxic organic pollutants). Subsequently, criteria for many pollutants have been revised, and new criteria have been added for many other pollutants.

At the time of publication of this MOP, however, numeric criteria typically have not been established for nutrients, although efforts are under way to do so. The delayed development of numeric nutrient criteria is primarily because the adverse effects of excessive nutrients do not lend themselves to criteria development with the traditional approach used for toxic pollutants. The adverse effects of nutrients are influenced strongly by regional and local conditions, such as species diversity, hydrology, soil conditions, and climate, which make one-size-fits-all criteria inappropriate. For most other (nonnutrient) pollutants, U.S. EPA is able to evaluate how a particular chemical or compound affects aquatic life or human health, and the "safe" level typically applies to waters nationwide. States do have authority to develop criteria specific to conditions in their states or for individual water bodies. A defensible scientific basis is needed for such site-specific criteria, but their use has been fairly widespread and well accepted. However, in the case of nutrient pollutants, water and soil chemistry and physical habitat and configuration of the water body affect how nutrients may contribute to overenrichment. Because of this, the process of developing numeric criteria for nutrients is significantly more complex than for other types of pollutants.

In the absence of numeric criteria, narrative criteria have been used as the primary WQS for nutrients. Narrative criteria are WQS that specify a clean water goal, but essentially leave it up to the permit writer or TMDL developer to

establish appropriate nutrient permit limits on a site-by-site basis. The following are examples of typical narrative criteria established by two different states in their WQS:

- Idaho's regulations state that "Excess Nutrients. Surface waters of the state shall be free from excess nutrients that can cause visible slime growth or other nuisance aquatic growths impairing designated beneficial uses," and
- Ohio's regulations state that "[W]aters shall be … free from nutrients entering the waters as a result of human activity in concentrations that create nuisance growths of aquatic weeds and algae."

The respective narrative criteria also may be incorporated into each NPDES permit issued by some states as a general effluent limitation or prohibition, either directly or by reference to the narrative criteria section of the WQS, in addition to whatever specific numeric effluent limits each permit may have. Narrative criteria may result in subjectivity as well as uncertainty in their implementation, compliance, and enforcement.

Although narrative criteria for nutrients have served as an interim regulatory approach to control and reduce adverse effects on water bodies, development of numeric criteria for nutrients has been determined by U.S. EPA to be a necessary action and is ongoing in most states (see Section 3.1).

2.4 Total Maximum Daily Load Regulation of Nutrients

In the absence of numeric criteria for nutrients, many watersheds have had nutrient discharge loads regulated by the TMDL program. When monitoring and assessment indicate that a specific water body does not attain one or more of its WQS, it is placed on that state's "303(d) list," named after the section of the CWA that requires creation of such lists of impaired waters. The U.S. EPA or the state is required to develop a TMDL, which is a strategy that is expected to result in attainment of WQS.

TMDLs are essentially pollutant budgets, which determine the total load of a pollutant that a water body can receive and still meet WQS, and which allocate allowable portions of this total pollutant load to each significant source. Sources include both point and nonpoint sources and uncontrollable background sources. One impediment to successful implementation of TMDLs is that the CWA does not provide any legal authority for requiring nonpoint sources to reduce their loadings of pollutants.

Review of causes of impairment across the nation indicates that nutrients (phosphorus and nitrogen) have been identified as one of the most common causes of WQS nonattainment, especially for lakes, rivers, and streams. As a result, many TMDLs that have been developed to include TMDLs for nutrients. A majority of these is for phosphorus, because phosphorus has been more commonly associated with overenrichment in fresh water bodies. Nitrogen is a nutrient of concern for salt water systems, however. As a result, nitrogen and phosphorus TMDLs have been developed for estuaries and coastal waters. Notable examples of coastal waters for which TMDLs have been developed for nutrients include the Chesapeake Bay, the Northern Gulf of Mexico, and Long Island Sound (see Section 3.2).

As noted, TMDLs are water basin or water body specific, and the specific nutrient effluent limitations for WWTP sources within different TMDL watersheds can vary considerably. Total phosphorus effluent limits have been established by TMDLs as low as 0.01 mg/L, although many other TMDLs have established limits in the range of 0.5 to 1.0 mg/L. Total nitrogen effluent limits have been established by TMDLs as low as 3.0 mg/L, although many other TMDLs have established limits of 8.0 mg/L or higher.

An important programmatic aspect of TMDL implementation that has occurred fairly recently is the concept of water quality credit trading. Trading is one tool to achieve watershed goals more economically. For nutrients in particular, it may be more cost-effective to install nonpoint-source best management practices than to treat point sources to increasingly stringent limits, or it may be more cost-effective for larger point sources to remove nutrients than smaller point sources because of economy of scale considerations. More detailed descriptions of concepts and benefits of trading can be found in recent guidance from the U.S. EPA (2003). Credit trading programs have been established for several water bodies affected by nutrients, including the Chesapeake Bay, Tar-Pamlico Estuary, Neuse River Estuary, Long Island Sound, Lower Boise River, Cherry Creek Reservoir (Colorado), and others.

2.5 Development of Water-Quality-Based Effluent Limits

The actual numeric permit limits are established by the state regulatory agency (or U.S. EPA for states that have not been delegated NPDES program authority). The process starts with the establishment of WQS. The regulatory agency subsequently collects relevant information about the receiving water body, including data from

monitoring and assessment to determine whether it is attaining the established standards. Based on the water body data and information collected about the discharge, the state determines what pollutant discharge controls or strategies are needed. The state performs an analysis to determine whether the discharge has a "reasonable potential" to cause nonattainment of any water quality criteria in the receiving water. If effluent limits based on WQS are necessary, then the state determines WLAs for each pollutant and each discharger and then determines pollutant effluent limits based on WLAs. If a TMDL has been developed for the water body, then the effluent limits need to reflect the WLAs included in the TMDL (for further information, see Section 4.0).

If the WQS are in attainment, then the state's antidegradation policy may be applied. Antidegradation prohibits discharge of any new or increased pollutant load unless a required review and assessment is performed and approved by the state, which would authorize an additional discharge load because of significant social or economic benefits. When no increase in discharge load is allowed, the previously existing effluent concentration limits in the permit are reduced in proportion to the increased flow so that the previously permitted discharge load is not exceeded.

The development of effluent limits in NPDES permits for WWTPs discharges under the CWA is shown in a summary diagram in Figure 2.1.

Section 4.1 in this chapter provides further discussion of the development of WQBELs in NPDES permits. Although the regulatory agency determines the WQBELs for specific pollutants, the individual discharger does have an opportunity to review and comment on the NPDES permit conditions—including effluent limits—before final issuance of the permit. The regulatory agency is required to publish the proposed permit for public comment before it is finalized and must prepare a formal response to all comments received, including any from the treatment facility owner or operator. In addition, the regulatory agency typically provides a preliminary version of the draft permit to the permittee for informal review before the official public comment period.

The WWTP owner or operator should avail themselves of the opportunity to review any proposed effluent limits before they become final. Although the procedures to calculate WLAs and WQBELs must be followed in accordance with applicable state or federal regulations, it is possible that specific assumptions or use of data may be inappropriate or incorrect, and the permittee has the opportunity to address any such defect with the agency.

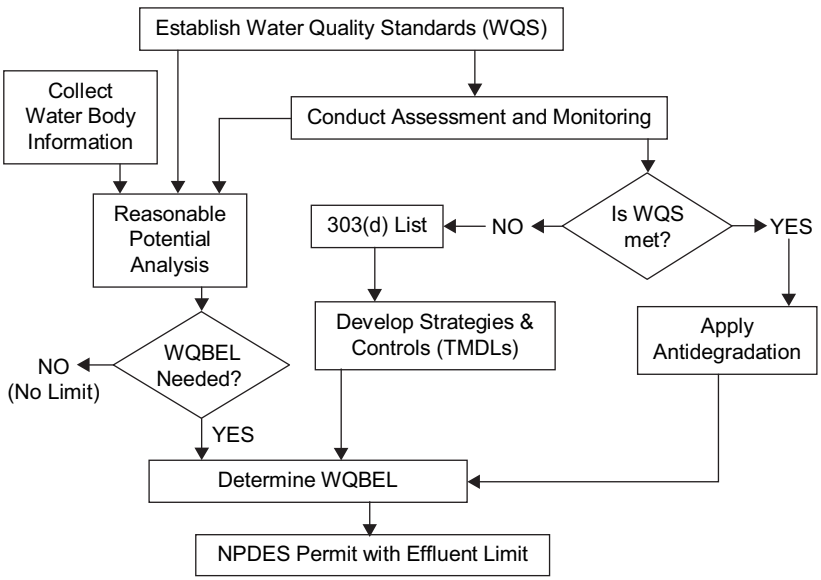

FIGURE 2.1 Development of WQBELs for CWA NPDES permits.

3.0 CURRENT SURFACE WATER QUALITY AND GROUNDWATER STANDARDS FOR NITROGEN AND PHOSPHORUS

Nitrogen and phosphorus are regulated via standards (criteria) in various forms and at varying concentrations depending on the surface water and groundwater uses that are being protected. In addition, they may be regulated using different permitting vehicles depending on whether surface water or groundwater is being protected and what the protected uses are. Table 2.1 summarizes these differences, and the remainder of this chapter is organized according to these broad categories of standards.

3.1 Surface Water Quality Standards Related to Eutrophication and Dissolved Oxygen

The U.S. EPA published a *National Strategy for Development of Regional Nutrient Criteria* in 1998, followed by a national action plan, *Development and Adoption of Nutrient*

TABLE 2.1 Summary of water quality and groundwater standards for nitrogen and phosphorus.

		Type of criterion				
Water type and use	**Purpose for protection**	**Causal variables**	**Response variables**	**Nitrogen forms regulated**	**Phosphorus forms regulated**	**Wastewater permitting vehicle(s)**
Surface water, aquatic life	Eutrophication	Nitrogen and/or phosphorus	Dissolved oxygen, pH, chlorophyll *a*, submerged aquatic vegetation, turbidity, secchi depth, narrative nuisance responses, algal toxins	TN or TIN	TP and/or soluble P	NPDES
Surface water, aquatic life	Toxicity	Ammonia	Whole effluent toxicity	Ammonia	NA	NPDES
Surface water, aquatic life	Low dissolved oxygen	Nitrogenous oxygen demand	Dissolved oxygen	TKN, ammonia, organic N	NA	NPDES
Surface water, drinking water	Human health	Nitrite and nitrate	NA	Nitrate and nitrate, sometimes TN or TIN	NA	NPDES

Surface water, drinking water	Human health	See eutrophication	Taste and odor, chlorinated organics, algal toxins	See eutrophication	See eutrophication	NPDES
Groundwater, drinking water	Human health	Nitrite and nitrate	NA	Nitrite and nitrate	NA	NPDES, effluent reuse (land application) permit, subsurface disposal permit, and/or SDWA source water protection
Groundwater, with connection to surface water	Potentially all of the above	Potentially all of the above	Potentially all of the above	Potentially all of the above	Potentially all of the above	Potentially all of the above

NPDES = National Pollutant Discharge Elimination Sywstem; TP = total phosphorus; TN = total nitrogen; TIN = total inorganic nitrogen; TKN = total Kjeldahl nitrogen; SDWA = Safe Drinking Water Act; and NA = not applicable.

Criteria into Water Quality Standards (2001). The U.S. EPA issued a series of technical guidance documents for developing criteria for various water body types (lakes, reservoirs, rivers, streams, estuaries, and coastal waters), as well as recommended nutrient criteria for most ecoregional areas (the country was divided into 14 nutrient ecoregions) (U.S.EPA, 2002). The objective of the nutrient policy is to have the states develop and implement numeric nutrient criteria.

There are two different approaches for the development of numeric nutrient criteria. One approach is referred to as "effects-based," wherein a process-based (deterministic) relationship between nutrient concentrations in water bodies and adverse effects is used to determine an acceptable nutrient level for a water body type. This typically is accomplished with a receiving water quality model. Another procedure is to establish empirical or statistical relationships between nutrient concentrations and effects. The effects of pollution may be indicated by levels of algae growth (measured by chlorophyll *a*), turbidity or water clarity, aquatic species diversity (relative abundance of desirable/sensitive species versus tolerant species), dissolved oxygen levels, and magnitude of dissolved oxygen swings. Determination of criteria using this approach requires a significant amount of field monitoring or modeling. The physical attributes of the water bodies, such as shade/solar input, and stream/river bottom conditions, also affect potential nutrient effects further complicating this approach. In fact, in states that have established biological water quality criteria, the water body will not attain its required WQS unless the physical habitat is adequate. Ideally, a cause-and-response relationship would be determined with sufficient statistical confidence that numeric nutrient criteria could be developed using this approach. In practice, however, this may be difficult. In 2009, U.S. EPA developed a draft guidance document for empirical approaches to determine stressor–response relationships to derive numeric nutrient criteria. U.S. EPA's Science Advisory Board reviewed the draft guidance and concluded that the draft document needed significant revision before release to appropriately use a weight-of-evidence approach to establish causal relationships between nutrients and their effects for criteria derivation (U.S. EPA SAB, 2010). Development of appropriate guidance for derivation of numeric nutrient criteria remains a work in progress as of the publication date for this publication.

The U.S. EPA earlier recommended another approach for development of numeric criteria that can be referred to as "reference-based." In this approach, a survey of nutrient concentrations in water bodies unaffected by humanmade nutrient inputs is used to determine nutrient levels at which no overenrichment or eutrophic conditions exist (U.S. EPA, 2002). Although this approach requires substantially

less data collection and evaluation—at least in states or ecoregions for which extensive data already exist to define reference concentrations with robust statistical certainty—it ignores the question of what levels of nutrients cause adverse effects in specific receiving water bodies. The U.S. EPA–recommended reference-based nutrient criteria published in its technical guidance documents for each ecoregion are low concentrations, which would in many cases result in effluent limits approaching or even beyond a reasonable treatment technology capability.

As of the writing of this MOP, few if any of the states have adopted U.S. EPA's reference-based criteria recommendations. Most states are in the process of collecting data, and a few states are developing criteria based on recent data collection using the effects-based approach. Within a few years it can be expected that most states will have developed effects-based numeric criteria for nutrients with a means of applying them to specific watersheds or ecoregions. Nonetheless, it is expected that many of the criteria values will be very stringent and in some cases may be below the capability of available and reasonably affordable treatment technologies. Hence, implementation of future nutrient criteria may be challenging for the states to accomplish, and may be especially difficult for small communities to afford.

The U.S. EPA has also recommended that development of nutrient criteria should include both "causal" pollutants (nitrogen and phosphorus) and "response" pollutants (chlorophyll *a* and transparency).

As described in Chapter 1, organic nitrogen and ammonia are nitrified (oxidized) in aquatic environments. If concentrations of these forms of nitrogen are high enough, then naturally occurring nitrification in water bodies may result in dissolved oxygen sags below the numeric criteria for dissolved oxygen. This nitrogenous oxygen demand typically is predicted with water quality models, and WQBELs are established in permits such that the dissolved oxygen criteria will be protected.

3.2 Regional Regulation of Nutrients

Nutrient regulations have been developed in some major regional areas with significant nutrient-related water quality impairments. Four examples of such regional regulations are outlined below.

3.2.1 Great Lakes Watershed

The United States and Canada signed the Great Lakes Water Quality Agreement of 1978 and subsequently agreed to the Phosphorus Load Reduction Supplement in

1983 (U.S. EPA, 2008). One significant provision of this agreement includes the establishment of a total phosphorus effluent limit of 1.0 mg/L for all municipal WWTPs discharging more than 3.8 ML/d (1 mgd). The agreement also calls for additional measures as necessary to meet further phosphorus loading reduction goals.

Monitoring and assessment of Great Lakes water quality is ongoing. Depending on future water quality and nutrient loadings, it is possible that there could be more stringent effluent limits for WWTPs discharging into the Great Lakes watershed in the future.

3.2.2 Chesapeake Bay Watershed

Maryland, Pennsylvania, Virginia, the District of Columbia, and U.S. EPA created a regional partnership, the Chesapeake Bay Program (2010), by signing the Chesapeake Bay Agreement of 1983. The original partner states were joined in 2000 by Delaware, New York, and West Virginia—states that include upstream tributaries to the watershed. In 1987, the partner states agreed to reduce total annual nitrogen and phosphorus loads into the watershed from all sources (point and nonpoint) by 40% from 1985 levels. Subsequently, under the 2000 Chesapeake Bay Agreement, the partner states agreed to further reduce nutrient loads from all sources, including WWTPs.

Under the current strategy, incorporated by the partner states to their respective regulations, dischargers to the Chesapeake Bay watershed receive total nitrogen and total phosphorus technology-based effluent limits according to their installed or required level of treatment technology. Permits typically have annual average load limits, with discharge concentration and flow reporting requirements. Regulations are similar for the various watershed partner states. Nutrient load goals have been established for each of the sub-watersheds by state within the overall Chesapeake Bay watershed. The states have established individual strategies to achieve overall goals by reducing point and nonpoint source loads.

Maryland, Pennsylvania, and Virginia, with a combined contribution of more than 90% of total nitrogen and phosphorus loads to the Chesapeake Bay, have established somewhat different implementation strategies for WWTP effluent load limits. Maryland requires that the "significant dischargers" implement enhanced nutrient removal (ENR) treatment technology to achieve effluent loads based on effluent limits of 3.0 mg/L total nitrogen and 0.3 mg/L total phosphorus. Pennsylvania has established annual load caps based on effluent limits of 6.0 mg/L total nitrogen and 0.8 mg/L total phosphorus at existing design flow for all

significant dischargers. Virginia has established slightly different load allocations for its five tributary basins, varying from effluent loads based on 3.0 to 4.0 mg/L total nitrogen, and 0.3 mg/L total phosphorus. Some flexibility is provided for specific treatment facilities within different tributary basins. In some instances, WWTPs are required to enhance existing biological nutrient removal treatment to ENR technology; in others, the ENR technology requirement may be applied only to new or expanded facilities. The Chesapeake Bay Program includes ongoing monitoring and assessment, and depending upon future water quality and nutrient loadings, it is possible that there could be more stringent future effluent nutrient limits for Chesapeake Bay watershed WWTPs.

3.2.3 Mississippi River/Gulf of Mexico Watershed

The Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (2010), consisting of members from federal and state agencies, was established in 1997 as part of a plan to address hypoxia in the Gulf of Mexico. Following scientific assessment of the causes and consequences of Gulf hypoxia, the task force developed an action plan (Mississippi River Task Force, 2001). The plan proposed long-term goals and strategies to reduce, mitigate, and control Gulf hypoxia. A second assessment report was produced by the U.S. EPA SAB in 2007, which updated understanding of causes and consequences and evaluated options for reducing the size of the hypoxia zone. The 2007 SAB report concluded that WWTPs represent a more significant source of nitrogen and phosphorus than previously identified. The report concluded that making point-source effluent nutrient limitations more stringent may offer the most certain short-term and cost-effective opportunities for nutrient reductions. It recommended, however, further cost analysis for nonpoint source reduction. The SAB panel report recommended that: "Tighter limits on N and P effluent discharge concentrations for major sewage treatment plants, together with concomitant reductions in nutrient discharges from non-domestic sewer users, should be considered, following an analysis of the cost and technical feasibility for a particular basin" (U.S. EPA SAB, 2007).

The Nutrient Task Force also prepared an updated action plan in 2008 (Mississippi River Task Force, 2008). Neither the 2001 nor 2008 plans proposed new regulations or laws for the various actions recommended. The plan proposes that regulatory agencies use existing laws and consider revision of existing regulations within the authority of current laws. Hence, new regulatory controls or other requirements for WWTPs have not been proposed.

3.2.4 Long Island Sound

Long Island Sound, situated between the states of Connecticut and New York, has experienced significant hypoxia caused by excess nitrogen loading, primarily from point sources. A nitrogen TMDL developed by the two states and U.S. EPA was approved in 2001, with a goal to reduce overall nitrogen loading to Long Island Sound 58.5% by 2014 (relative to 1990 baseline). Both states are implementing strategies to achieve their respective loading reductions allocated by the TMDL.

Connecticut's control strategy includes a point-source to point-source trading program to reduce nitrogen loadings from the 79 publicly owned WWTPs that discharge to Long Island Sound (2010). All treatment plants are required to comply with their permitted annual mass loading, or they must purchase equivalent nitrogen credits equal to the amount by which the facility's discharge exceeds their allowable load limit. An initial level of permit load limits was set for 2009, and more stringent limits were set for 2014. The state established a nitrogen credit exchange as a mechanism to implement this trading program and attain the TMDL goal. The exchange sets the price of an equivalent nitrogen credit each year, based on total treatment costs (capital plus operational) for all nitrogen removal facilities in the watershed. Each treatment plant either generates credits to sell based on their nitrogen removal to a level below their permit load limit, or must purchase credits equal to their discharge in excess of their allowable limit. The cost of credits has increased as the cost of nitrogen removal facilities has increased, and will continue to increase both with rising operational costs and as more WWTPs construct additional facilities to attain the more stringent 2014 load limitations.

3.3 Surface Water Quality Criteria Related to Ammonia

Ammonia can be toxic to most aquatic organisms. Accordingly, ammonia water quality criteria were developed by U.S. EPA in 1984, and subsequently updated in 1992 and 1999 as new toxicological information became available. Ammonia criteria are a function of both pH and temperature. Unionized ammonia (NH_3), and not the ammonium ion (NH_4^+), is the principal toxic form of ammonia. Aqueous ammonia equilibrium is affected by pH, causing the fraction of unionized ammonia in solution to increase as pH increases. Hence ammonia toxicity increases as pH increases. Ammonia toxicity also has been shown to increase as temperature increases. Current nationally recommended water quality criteria for ammonia are published on the U.S. EPA Web site (U.S. EPA, 2009b).

Nearly all states have adopted U.S. EPA criteria for ammonia toxicity, although some still are using the 1984 or 1992 criteria, and have not yet adopted the 1999 version. There are some significant differences between these versions of the criteria, as illustrated in Table 2.2.

In 2004, U.S. EPA published in the Federal Register (2004) a Notice of Intent to Re-Evaluate the Aquatic Life Ambient Water Quality Criteria for Ammonia. The U.S. EPA sought submittal of additional scientific data on the toxicity of ammonia to a certain family of freshwater mussels (known as "unionids"). This family has an early parasitic larval life stage (glochidium) that floats in the water for a few seconds or days until it attaches to gills or fins of fish. This short-duration glochidium stage has been shown in recent studies to be most sensitive to ammonia. Based on these studies, U.S. EPA proposed updated draft national recommended criteria for ammonia (U.S. EPA, 2009a) that include different values applicable when freshwater mussels are either present or absent. These draft values have not been finalized as of the publication date of this MOP. However, if these criteria are approved, they will likely have a significant effect on some dischargers because chronic criteria applicable when mussels are present are substantially more stringent than existing recommended criteria. Refer to the values shown in Table 2.2.

Table 2.2 Comparison of U.S. EPA recommended ammonia toxicity criteria.*

				Draft 2009	
Temperature, °C	**1984**	**1992**	**1999**	**Freshwater mussels present**	**Freshwater mussels absent**
	Acute criteria, mg/L as N				
15	12.2	—	13.3	15.6	23.6
20	12.0	—	13.3	10.3	17.8
	Chronic criteria, mg/L as N				
15	1.7	2.1	4.2	0.88	6.3
20	1.2	1.5	3.1	0.63	4.6

*All values shown are at a pH of 7.5; 1999 values shown assume salmonids and early life stages present.

3.4 Drinking Water Criteria

Federal standards for drinking water quality are set by U.S. EPA under the authority of the Safe Drinking Water Act (SDWA) and must be adopted and enforced by all states. These standards apply at the tap. In addition, under the CWA, states promulgate ambient surface water criteria to protect water bodies for drinking water quality where that is a designated use. These criteria apply in the water body, not at the tap. As a result, drinking water criteria under the CWA are not necessarily the same as SDWA standards.

For nitrogen, the primary concern historically has been with nitrite and nitrate in relation to their potential to cause methemoglobinemia in infants up to six months in age (also referred to as cyanosis or "blue baby syndrome"). The U.S. EPA's recommended nitrate criterion for drinking water supplies under the SDWA and CWA is 10 mg/L (as N). Nitrate, when ingested, is converted within the body to nitrite. Nitrite reduces the amount of oxygen in the baby's hemoglobin, which can cause shortness of breath and blueness of the skin. Because approximately 10% of ingested nitrate is converted to nitrite by infants, U.S. EPA has set the drinking water standard for nitrite at 1.0 mg/L (as N).

All states have adopted these nitrate and nitrite criteria for surface waters designated for drinking water and for groundwater aquifers that are used for drinking water. As indicated in Table 2.1, surface waters that are not directly used for drinking water but that influence groundwater supplies and are used for that purpose may be regulated accordingly. To date, this has occurred in several arid states in the western United States.

For phosphorus, the primary concern historically has been related to the adverse effects of eutrophication, including the taste and odor effects of algae, the formation of chlorinated organics, and more recently the potential for algal-produced toxins. Thus, the control of these effects on drinking water supplies is addressed by control of eutrophication, as discussed elsewhere in this chapter.

4.0 NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM PERMITS

In all but a few states, the NPDES program has been delegated to the respective state water quality agency. The CWA defines the overall framework for each state program, resulting in similarities between the various state processes and permits. A

good overall reference for the basic components and procedures used for NPDES permits is contained in the U.S. EPA's *Permit Writers Manual* (U.S. EPA, 1996). But it is important to recognize that there can be substantive differences between states, particularly in procedures for evaluating the need for and calculation of WQBELs. Thus, the user of this MOP is cautioned to research and understand the permitting methods specific to the applicable state in which the discharge is or will be occurring.

4.1 Water-Quality-Based Permit Limits

It is important to understand that WQBELs are not automatically included in all NPDES permits for all promulgated numeric criteria. Rather, the permitting agency first evaluates the need for such limits in each individual permit. For nitrogen and phosphorus parameters related to eutrophication and dissolved oxygen, this historically has been accomplished by receiving water quality modeling, either as part of permit-specific WQBELs evaluation or via a TMDL process. If the model shows that criteria would not be met at existing or proposed effluent quality, then WQBELs will be needed and are established.

For potentially toxic pollutants, including ammonia, this evaluation includes what is referred to as a "reasonable potential to exceed analysis." This analysis typically includes a statistical projection of the maximum probable effluent concentration, and if that concentration exceeds the WLA, then a WQBEL is needed. In most states, this analysis typically uses statistical methods contained in U.S. EPA's (1991) *Technical Support Document for Water Quality-Based Toxics Control*, often referred to as the TSD, or similar procedures. This TSD methodology estimates the maximum probable effluent concentration based on the coefficient of variation and number of effluent samples in the database.

If the RPA demonstrates that WQBELs are needed, then the next step in determining the limits is to calculate the WLA to meet acute and chronic aquatic life and/or human health criteria in the water body. The WLA is the pollutant concentration in the effluent that could be discharged while still meeting the criteria. This is done using mass balance equations. The general mass balance, steady-state equation used for calculating the WLA of a conservative substance discharged to a river, stream, or unidirectional reservoir is as follows:

$$\mathrm{WLA} = \frac{(\mathrm{WQC} \times (Q_e + (Q_r * M)) - (C_r \times Q_r \times M))}{Q_e} \tag{2.1}$$

Where,

WLA = wasteload allocation for a point-source discharge; calculated separately for each type of WQC (i.e., acute, chronic, human health, etc.), concentration;
WQC = water quality criterion, concentration;
Q_e = effluent design flow;
Q_r = receiving water design flow;
C_r = background concentration in the receiving water; and
M = fraction of receiving water flow allowed for mixing, as described in the mixing zone policy within the state WQS.

Types of WLAs include

WLA_a = WLA for aquatic life acute WQC;
WLA_c = WLA for aquatic life chronic WQC; and
WLA_h = WLA for human health WQC.

For discharges to oceans, estuaries, lakes and multidirectional reservoirs, the equation is:

$$WLA = (D + 1)(WQC) - D \times C_r \quad (2.2)$$

Where,

D = dilution factor at mixing zone boundary, as described in the mixing zone policy within the state WQS;
WQC = water quality criterion, concentration; and
C_r = background concentration in the receiving water.

Derivation of WQBELs for ammonia toxicity typically follows U.S. EPA's TSD, or similar procedures. This TSD methodology translates the WLAs calculated as shown above into monthly, weekly, or daily average permit limits using statistical procedures based on effluent variability and number of samples collected per month.

As noted above, the evaluation of the need for WQBELs for eutrophication and dissolved oxygen are typically from TMDLs or modeling exercises. The WQBELs themselves also are derived from this exercise. The averaging periods for these types of WQBELs are typically seasonal, monthly, or weekly, depending on the timeframe associated with the water quality criterion to be protected. One important recent development that has arisen as a result of litigation (U.S. Court of Appeals for the D.C. Circuit in *Friends of the Earth, Inc. v. EPA*, et al., No. 05–5015.) is that TMDLs must include

an expression of allocations in daily units even if the TMDL is based on a seasonal or annual average target, as is typically the case with nutrient TMDLs. The U.S. EPA (2006) has made it clear, however, that NPDES permit limits derived from such TMDLs do not have to be maximum daily limits, and thus annual, seasonal, monthly, or weekly limits may be more appropriate. Statistical procedures described in the TSD can be used to translate receiving water targets into permit limits of different averaging periods.

Whether permit limit averaging periods are established for one day or for longer periods is significant because treatment process performance will vary significantly in response to several factors, particularly seasonal temperature differences. Hence a daily average load limit based on a specific concentration value would be significantly more difficult to consistently achieve throughout the year than an annual average load limit based on the same concentration value. Typically, regulatory agencies have recognized this with respect to nutrients that total annual or seasonal loads are of greater significance to receiving water body quality than a single daily load.

4.2 Monitoring, Reporting, Compliance, and Enforcement Requirements

Routine monitoring is required for all parameters for which the permit contains effluent limits, whether water-quality- or technology-based. For nitrogen and phosphorus, the frequency of monitoring is highly variable depending on the policies and procedures of the responsible permitting agency. Monitoring may be daily, weekly, monthly, seasonal, or annual, depending on the averaging periods of the WQBELs and other circumstances.

The NPDES permit reporting includes, at a minimum, monthly discharge monitoring reports. These reports include results of all sampling and analyses that occurred during that particular calendar month. In addition, some permits may include other specific reporting requirements or milestones such as an annual report summarizing annual nutrient loading, seasonal, or annual water quality credit trading activity, or progress toward meeting a schedule of compliance.

The U.S. EPA and every state have extensive CWA-related compliance and enforcement programs. State authorities, penalties, and fines vary but may be assessed in addition to federal penalties and fines. Thus, the cost of noncompliance given the combination of federal and state enforcement authorities can be substantial.

In addition, the CWA authorizes third-party citizen suits that can be brought against any entity that is violation of the CWA or its NPDES permit. This substantially escalates the potential liability associated with noncompliance.

5.0 WASTEWATER REUSE AND SUBSURFACE DISPOSAL PERMITS

Municipal wastewater reuse via land application is a common practice today, particularly in the arid western United States. This practice is likely to become even more prevalent as water becomes scarcer and landscape irrigation becomes an increasingly attractive use of treated wastewater. In addition, subsurface disposal already is prevalent for smaller onsite community wastewater systems. This approach may become even more prevalent as an alternative to costly surface storage during the nonirrigation season in the arid West or as a way to provide hyporheic discharge opportunities in areas like the Pacific Northwest to mitigate the effects of warm effluents on coldwater streams and rivers. The hyporheic zone is a subsurface region beneath and adjacent to a stream or river bed where groundwater and surface water mix. Land application and subsurface disposal permits are issued by the state water quality agencies, sometimes via NPDES or state-enabled permitting authority.

To protect groundwater supplies from excessive inputs of nitrogen (in large part to prevent nitrate accumulation to levels greater than 10 mg/L), most states require that wastewater be applied at or near agronomic rates associated with the crops and soils at the application site. The agronomic rate is the application rate designed to provide the amount of nutrients needed by the crop or vegetation grown on the land. This practice minimizes the amount of nutrients that pass below the root zone of the crop or vegetation and into the groundwater. The agronomic application of phosphorus has become more of an issue in some states and watersheds because of the interconnection between some groundwaters and surface waters and the effects of phosphorus on surface waters. In many cases, the size of the application site can be adjusted to account for the nitrate concentration in the effluent, thus not necessarily requiring low concentrations of nitrate in the effluent. Other land application sites are size-constrained, however, or will be as population growth occurs.

Subsurface disposal practices typically are regulated such that nitrite/nitrate standards in groundwater supplies and aquifers will not be exceeded. This may be demonstrated by technical analyses showing that standards will be met at the property boundary or that dilution or attenuation will occur before effluent reaching an aquifer.

Wastewater reuse and subsurface disposal permits have many similarities to NPDES permits in relation to monitoring, reporting, compliance, and enforcement. The primary difference is that the groundwater resource is being protected, which means that groundwater and soils monitoring typically is part of the permit, and hydraulic and nutrient application rates and cropping practices also must be reported.

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Chapter 3

Overview of Nutrient Removal Processes

(continued)

1.0 NITROGEN REMOVAL

This chapter presents an overview of various nutrient removal processes. The reader is referred to other chapters for a more detailed description of the theory and specific applications of the various processes. The processes described in this chapter are grouped as follows:

- Target nutrient removed—nitrogen and phosphorus.
- Mechanism of removal—physical, chemical, and biological.
- Performance and selection of nutrient removal processes to achieve various treatment levels.

Table 3.1 summarizes various options for removing or converting nitrogen from one species to another. Five processes are available to remove nitrogen completely:

(1) Conversion of nitrogen to mostly nitrogen gas, $N_2(g)$, but also a small amount of nitrous oxide, $N_2O(g)$, and nitric oxide, NO(g), which escapes into the atmosphere. This is achieved in biological treatment systems (nitrification followed by denitrification or simultaneous nitrification/denitrification) or chemically (using breakpoint chlorination).
(2) Biological uptake of nitrogen for the growth of biomass followed by efficient solids removal.
(3) Removal of ammonia from the water through $NH_3(g)$ stripping at a high pH.

Table 3.1 Nitrogen removal and conversion processes (courtesy of HDR Engineering Inc.).

Initial species	Process	Ultimate species
Organic–N	Ammonification—biological conversion of organic nitrogen to ammonia	Ammonia, NH_4^+–N
Ammonia, NH_4^+–N	Biological nitrification	Nitrate, NO_3^-–N
	Biological nitrition	Nitrate, NO_2^-–N
	Stripping at high pH	Ammonia gas, $NH_3(g)$
	Biological uptake during bacterial growth	Organic nitrogen (biomass)
	Breakpoint chlorination	Nitrogen gas, $N_2(g)$
	Ion exchange will exchange ammonia for another cation	Chemically bound
Nitrite, NO_2^-–N	Denitritation	Nitrogen gas, $N_2(g)$
Ammonia, NH_4^+–N and Nitrite, NO_2^-–N	Anammox	Nitrogen gas, $N_2(g)$
Nitrate, NO_3^-–N	Biological denitrification	Nitrogen gas, $N_2(g)$
	Ion exchange will exchange nitrate for another anion	Chemically bound
rDON	Reverse osmosis	Phase separation of rDON
	Chemical coagulation/filtration	Adsorb/filter
	Oxidize rDON	Convert to biodegradable nitrogen

rDON = refractory dissolved organic nitrogen.

(4) Ion exchange to chemically exchange nitrogen ions as NH_4^+ or as NO_3^- using a cation or an ion-exchange resin, respectively. For example, the naturally occurring zeolite clinoptilolite has a greater selectively toward ammonium over competing cations.

(5) Membrane separation processes such as nanofiltration or reverse-osmosis membranes to remove particulate and dissolved nitrogen species. Efficiency varies with the type of membrane and nitrogen species. Ion separation

membrane processes such as reverse osmosis will remove all particulate and many soluble nitrogen species from water. Particulate nitrogen such as organic particles, including bacteria, is removed with all solids separation processes. Note that reject streams from membrane processes still contain the nitrogen and needs to be treated or disposed.

1.1 Biological Nitrogen Removal

Nitrogen in raw wastewater consists mostly of organic nitrogen and ammonia. Biological nitrogen removal (BNR) is achieved through a series of biochemical reactions that transform nitrogen from one form to another. Figure 3.1 summarizes the various processes that can be used to remove nitrogen from wastewater.

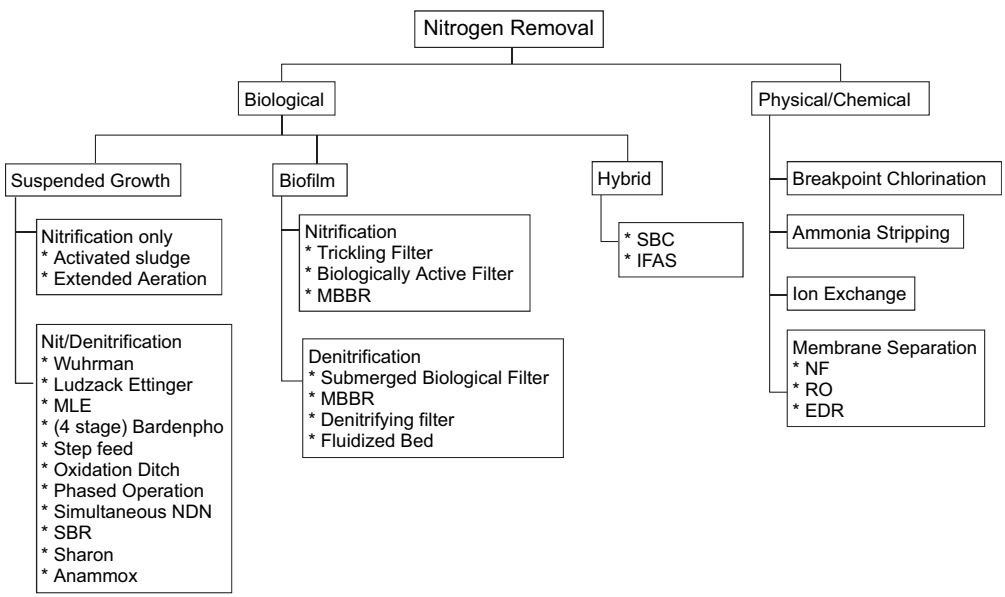


Figure 3.1 Typical processes used for nitrogen removal (EDR = electrodialysis reversal; IFAS = integrated fixed-film activated sludge; MBBR = moving bed biofilm reactor; NDN = nitrification-denitrification; NF = nanofiltration; RO = reverse osmosis; SBC = sequencing batch reactor; and SBR = sequencing batch reactor) (courtesy of HDR Engineering Inc.).

1.1.1 Biological Nitrogen Transformations

Biological processes can be described in terms of the nitrogen species consumed or produced in the process. The key nitrogen species and transformations are shown in Table 3.2. Oxidation and reduction of the nitrogen species often change the alkalinity in the water. Nitrification consumes alkalinity (7.14 mg alkalinity/mg NH_4-N oxidized) and denitrification returns alkalinity (3.57 mg alkalinity/mg NO_3-N reduced). The consumption of alkalinity during nitrification can lead to a reduction in pH in the liquid, which, in turn, could affect the biological nitrification rate.

1.1.1.1 Organic Nitrogen

Organic nitrogen is present in wastewater in particulate or dissolved form. Particulate organic nitrogen includes biomass grown in the process and other

TABLE 3.2 Biological nitrogen removal and conversion processes (courtesy of HDR Engineering Inc.).

Initial species	Process	Ultimate species
Organic–N	Ammonification—biological conversion of organic nitrogen to ammonia decay products from biological treatment	Ammonia, NH_4^+–N
	A fraction of the DON is not biodegradable in the process and appears in the effluent as rDON	Dissolved organic nitrogen, both bDON and rDON
Ammonia, NH_4^+–N	Biological ammonia oxidation, first step in nitrification using AOB	Nitrate, NO_2^-–N
	Biological nitrification—in reality the sum of ammonia and nitrite oxidation	Nitrate, NO_3^-–N
	Biological uptake during bacterial growth	Organic nitrogen (biomass)
	Anammox—direct oxidation of ammonia to nitrogen gas using nitrate	Nitrogen gas, $N_{2(g)}$
Nitrate, NO_2^-–N	Nitrite oxidation using NOBs	Nitrate, NO_3^-–N
	Denitrification of nitrite	Nitrogen gas, $N_{2(g)}$
Nitrate, NO_3^-–N	Biological denitrification	Nitrogen gas, $N_2(g)$
	Biological uptake during bacterial growth	Organic nitrogen (biomass)

AOB = ammonia oxidizing bacteria; bDON = biodegradable dissolved organic nitrogen; rDON = refractory dissolved organic nitrogen; and NOB = nitrite oxidizing organism.

particulate organic nitrogen in the influent. Dissolved organic nitrogen (DON) is present in the influent and can also be produced as a byproduct of biological treatment.

DON is often more challenging. A portion of soluble organic nitrogen is typically degradable in biological treatment systems and is considered "biodegradable DON" or bDON. Nevertheless, the remaining portion of the DON is not readily removed through biological processes and remains in the effluent following biological treatment. This remaining DON fraction is sometimes referred to as "refractory dissolved organic nitrogen" (rDON) or "non-biodegradable DON" (non-bDON). Both rDON and non-bDON species often are present in the influent to the WWTP but also can be formed as a byproduct of the biological process (Pehlivanoglu-Mantas and Sedlak, 2006). The "biodegradability" referred to above refers to microbial communities in the biological wastewater treatment processes. Another important aspect related to rDON is its bioavailability to receiving aquatic ecosystems. Although some earlier studies have indicated that wastewater-derived rDON can potentially be utilized by phytoplankton (e.g., algae), its impact on stimulated algal growth, species selection, and succession is still largely unknown (Bronk, 2002; Koopmans and Bronk, 2002; Minor et al., 2006; Pehlivanoglu-Mantas and Sedlak, 2006) (see also discussion in Chapter 1).

Organic nitrogen poses a significant challenge to achieving low total nitrogen concentrations. Particulate organic nitrogen can be removed through solids separation processes such as clarifiers, filters, and membrane processes. Biodegradable organic nitrogen (both particulate and dissolved) can be removed through biological treatment by hydrolyzing the organic nitrogen to ammonia. A portion of the organic nitrogen is resistant to biological treatment and cannot be removed in a typical biological wastewater treatment process and will appear in the effluent. Chemical coagulation with subsequent solids separation can remove some colloidal organic nitrogen that appears to be part of the rDON fraction.

1.1.1.2 Ammonia

Ammonia is readily oxidized to nitrate in a biological nitrification—the conversion of ammonium, NH_4^+, to nitrite, NO_2^-, and finally to nitrate, NO_3^-. Nitrition, the conversion of ammonia to nitrite, is performed by ammonia oxidizing bacteria (AOB). The main AOB grown in activated sludge are represented by *Nitrosomonas* sp. Further oxidation of nitrite to nitrate is carried out by nitrite oxidizing organism (NOB), typically *Nitrobacter* sp. (converting nitrite to nitrate). Modern molecular-based

technology allowed identification of diverse groups of AOB and NOB: AOB include the beta and gamma subclasses of proteobacteria (β- and γ-AOB, respectively), and NOB of the genera *Nitrobacter*, *Nitrococcus*, *Nitrospira*, and *Nitrospina*. Only three major groups, however, are expected to be found in wastewater treatment—AOB within betaproteobacteria and NOB of the genera *Nitrospira* and *Nitrobacter* (Koops et al., 2003; Purkhold et al., 2000; Schramm, 2003). Typically, autotrophic nitrifying bacteria are more sensitive to environmental conditions such as temperature, pH, and toxins than heterotrophic bacteria. In typical nitrification systems, the kinetics of the overall process are limited by the ammonia oxidation step, and nitrite is rapidly converted to nitrate by NOB. As a result, minimal nitrite (<0.2 mg/L) typically is found in full-scale facilities when nitrification is stable.

1.1.1.3 Nitrite

Nitrite is not typically found in raw wastewater but is produced by oxidation of ammonia by AOB and during incomplete nitrate denitrification. Typically, nitrite is rapidly oxidized to nitrate by NOB. These organisms are sensitive to environmental changes (pH and dissolved oxygen in particular), and nitrite oxidation can be limited under adverse environmental conditions. Nitrite is an undesirable product because it interferes with chlorine disinfection (Neethling et al., 1997).

Nitrite can be reduced to nitrogen gas through denitrition. BNR via the nitrite pathway is desirable because the elimination of nitrite oxidation reduces the oxygen requirement by approximately 25% and decreases the external carbon source demand (for subsequent denitrification) by approximately 40%. In addition, it has been reported that denitrition rates with nitrite are 1.5 to 2 times greater than with nitrate (Abeling and Seyfried, 1992). Furthermore, less sludge is produced (0.8 to 0.9 versus 1 to 1.2 kg dry weight/kg-N, according to Mulder, 2003). The realization of stable nitrite formation by selecting AOB is based on differences in growth rate, oxygen affinity, or inhibition characteristics between AOB and NOB. Among these approaches is the single reactor high activity ammonia removal over nitrite (SHARON) process (Hellinga et al., 1998). This approach is designed to achieve stable nitrification/denitrition over nitrite and is in operation at several full-scale reactors. Partial nitrification and denitrition over nitrite has gained attention lately. The SHARON reactor is operated at a high temperature (30–40°C), a neutral pH (approximately 7.0), and a short solids retention time (SRT) of less than 1 to 2 days. Under these conditions, NOB grow slower than AOB, so that they are washed out from the reactor (Mulder et al., 2006).

1.1.1.4 Nitrate

Nitrate is the stable product of complete nitrification. In the absence of dissolved oxygen, bacteria will use nitrate as a terminal electron acceptor and convert nitrate to nitrogen gas through a process commonly called denitrification. Denitrification requires nitrate, a carbon source, the right bacteria, and absence of dissolved oxygen. The denitrification rate depends primarily on the availability of an electron donor (carbon source) to drive the biological reaction.

Denitrification occurs under two distinct conditions:

(1) Rapid denitrification is achieved when an external substrate (such as biochemical oxygen demand [BOD] in wastewater or methanol) is available for bacterial growth. Substrate level denitrification is relatively rapid and proceeds typically at 0.03 to 0.11 kg NO_3^--N/kg VSS·d (Soap and Detergent Association, 1989). The concentration of available substrate (food-to-microorganism ratio) and the type of substrate will affect the denitrification rate. The chemical oxygen demand (COD) requirement to remove each unit amount of NO_3-N (COD/NO_3) depends on the yield and the SRT.

(2) Slow denitrification occurs when bacteria use nitrate under conditions when the external substrate is low; commonly referred to as "endogenous-level denitrification." Microbial decay and lysis provide an external carbon source for denitrification under endogenous-dominated conditions. Endogenous-level denitrification is slow and proceeds typically at rates between 0.01 and 0.03 kg NO_3^--N/kg VSS-d (Stensel, 1981). Endogenous-level denitrification rates are related to mean cell residence time (MCRT), or the active mass fraction.

Nitrate can also be used as a nutrient to support biological growth when ammonia is not present in significant amounts.

1.1.2 Nitrogen Removal in Nonbiological Nutrient Removal Processes

Nitrogen is an essential nutrient for biological growth. Ammonia and nitrate often are used by bacteria (and other organisms) for growth. Biological treatment processes that are not designed for nutrient removal will, therefore, remove nitrogen as part of the normal biological growth. Biomass typically contains 7% to 10% nitrogen (on volatile solids basis) (Water Environment Research Foundation [WERF], 2003).

1.1.3 Suspended-Growth Processes

The activated-sludge process is a typical suspended-growth system, where bacteria are kept in suspension under appropriate conditions to allow them to grow and consume pollutants from the water. Nitrification can be separated from carbon oxidation (BOD removal) in activated-sludge plants in a two-stage process by using a high-rate, first-stage activated-sludge process for BOD removal followed by a low-rate nitrification stage. Denitrification was added as a tertiary biological treatment stage, typically with addition of an external carbon source such as methanol.

Many current suspended growth processes rely on simultaneous BOD removal, nitrification, and denitrification integrated into one process. Suspended growth systems are designed to provide the appropriate environment and nutrients by adjusting aeration intensity and recycling nutrients. Aeration intensity is used to create aerobic conditions for nitrification and BOD oxidation; anoxic conditions (no aeration) for denitrification; micro-aerobic conditions (very low dissolved oxygen) for simultaneous BOD and ammonia oxidation and denitrification; or phased operation (turning aeration on and off sequentially) to nitrify and denitrify in separate phases (Neethling, et al., 2007; WERF, 2004).

For a suspended-growth system, it is important to maintain a sufficiently high MCRT to allow the slow-growing nitrifiers to reproduce in the aeration basin and prevent them from being wasted out of the system. The minimum required MCRT for nitrification is determined by temperature, pH, and other operating conditions. When estimating the MCRT of nitrifier sludge mass, the total MCRT must be reduced by considering only the sludge mass that is kept under aerobic conditions. This is because nitrifiers are obligate aerobes and do not grow under anoxic or anaerobic conditions. Those zones used for denitrification or anaerobic zones should, therefore, not be included when calculating the nitrifier MCRT.

After nitrification is established, most activated sludge processes can achieve effluent ammonia concentrations of less than 0.2 mg NH_4^+-N/L. The design and operation of a nitrification activated-sludge system is similar to a "normal" activated-sludge system operated for BOD removal only. Oxygen demand is significantly higher, however, and the operator must consider the effects of decreases in alkalinity and a possible drop in pH. Because the nitrifier growth is affected by pH, alkalinity supplementation may be required. Suspended-growth plants readily can achieve gentrification through creation of oxygen-depleted zones by replacing aeration with mixing in some areas. If these zones, without dissolved oxygen, are created at the

feed end of the aeration basin, then the presence of BOD in the feedwater provides substrate for denitrification and substrate level denitrification will occur. If the zone is created toward the end of the basin where the substrate level is low, then endogenous level denitrification can occur. An external substrate, such as methanol, also can be added to the denitrification basin to increase the denitrification rate.

Denitrification in activated-sludge secondary clarifiers potentially can lead to the flotation of solids because the gaseous $N_2(g)$ produced in the process becomes entrapped in the activated-sludge flocs and floats to the tank surface. Most full-scale facilities do not experience this problem because of the low nitrate concentration in the effluent and the low denitrification rate in the clarifier. Several methods can be used to control rising solids: reducing NO_3 before the clarifier by denitrifying in the reactor, producing a stable sludge with a long SRT, increasing the mixed-liquor dissolved oxygen before the water enters the clarifier, and removing solids more rapidly from the clarifier to reduce SRT (Siegrist et al., 1995).

1.1.4 Biofilm Processes

Biofilm (or fixed-film) processes—such as trickling filters, biological active filters (BAFs), moving bed bioreactors (MBBRs), and rotating biological contactors—have been used effectively for BOD removal, nitrification, and denitrification. By operating these processes in sequence, the desired biological transformation can be achieved in the appropriate environment.

Achieving simultaneous BOD removal, nitrification, and denitrification in a biofilm system is more complex than in suspended growth systems because bacteria are in direct competition for oxygen with heterotrophic bacteria and limited by their attachment on the fixed media (Okey and Albertson, 1989a, 1989b). Because the heterotrophic bacteria typically outgrow the nitrifiers, heterotrophic activity tends to dominate in areas where the BOD is high. If the BOD loading is reduced, however, then oxygen becomes more available for nitrifiers and nitrification starts.

Trickling filter effluent ammonia concentrations of 1 mg/L are achievable under favorable conditions. To achieve less than this concentration, however, the confidence level of the process decreases and additional facilities may be required to ensure that effluent limits are met consistently. Pilot testing for specific applications should be considered to determine process performance under site-specific conditions. At the Reno-Sparks, Nevada, WWTP, effluent ammonia levels below 1 mg NH_4^+-N/L were consistently achieved, even when the temperature of the water fell to 2°C (Parlin and Peel, 1990). Snails scavenging the biomass remain an operational problem with nitrifying trickling filters.

Nitrification in BAFs and MBBRs occurs in a more controlled environment with aeration providing oxygen and scouring the biofilm to maintain an active layer. These processes will produce less than 2 mg/L effluent ammonia and consistently have demonstrated effluent below 0.5 mg/L (WERF, 2000).

Because denitrification requires the absence of oxygen, denitrification can be achieved in biofilm reactors in a deep film or by operating in a submerged mode. Biofilm model calculations show that the denitrification is slow in the biofilm (Sen and Randall, 2008). Both upflow and downflow modes of operation can be used. An external carbon source, such as methanol, is often added to increase the denitrification rate and reduce the reactor size.

Denitrification can be achieved in filters and fluidized-bed reactors following any nitrification process. An external substrate such as methanol typically is added to increase denitrification rates. Koopman et al. (1990) found that complete denitrification (effluent nitrate plus nitrite <1 mg/L) can be achieved with addition of 3.3 to 3.5 g methanol/g N. Madireddi et al. (1994) achieved nitrate concentrations below 1 mg/L in an upflow fluidized-bed reactor receiving nitrified trickling filter effluent and adding methanol as a carbon source.

1.1.5 Hybrid Processes

Integrated fixed-film activated sludge (IFAS) processes can be used for nitrification and denitrification (WERF, 2000). The main advantages of an IFAS system include (1) higher capacity with a smaller footprint because of higher biomass inventory and the decoupling of SRT and growth rates of slow growers such as nitrifiers that accumulate on fixed film; (2) inherently more stable performance and resistant to loading changes; and (3) increased capacity without increasing solids loading to the secondary clarifiers. Many IFAS systems use a medium-bubble aeration system that requires less maintenance than fine bubble systems. This process can be used to upgrade plants because approximately 20% to 60% additional treatment capacity can be gained by adding fixed-media material to existing aeration tanks. Onnis-Hayden et al. (2007) studied a full-scale IFAS process with two stages of nitrification in series and showed that the majority of the nitrification occurs in biofilm on the media, which allows for retention of the slow-growing nitrifiers. Sustaining nitrification in the system depends on both the attached and suspended mixed liquor. Incorporation of media in the suspended mixed liquor increased nitrification capacity by 155% in stage 1 and by 25% in stage 2. Benisch et al. (2009) showed that the suspended SRT is a key parameter to sustain reliable nitrification in an IFAS system, specifically during variable loading.

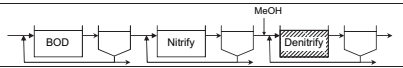
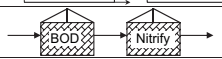
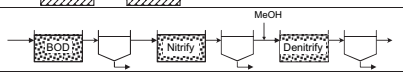
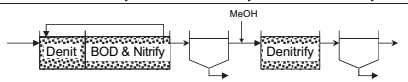
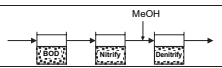
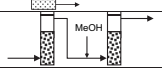
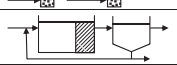
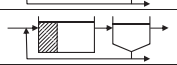
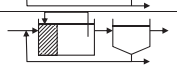
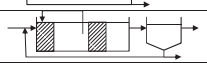
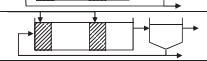
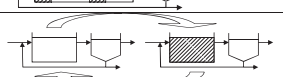
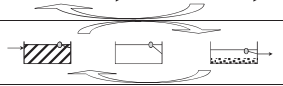
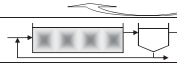
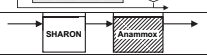
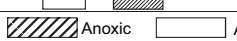
1.1.6 High-Purity Oxygen Systems

High-purity oxygen (HPO) activated sludge processes typically are used to treat high strength wastewater or to provide compact treatment plants for BOD removal. When used for nitrogen removal, HPO processes struggle because of the suppressed pH and low SRT of the systems. Low pH is typically the result of CO_2 entrainment associated with HPO systems and can be partially alleviated by stripping the CO_2 from the water. For wastewaters with high pH, using HPO systems may provide an advantage resulting from acid reduction for pH correction. The nitrifier population in the HPO system can be increased by increasing MCRT. This, however, requires additional basins and negates the benefit of compact treatment associated with using pure oxygen. Nitrification can be achieved in a HPO system by seeding it from a fully nitrifying system or operating a separately grown seed as used in the In-Nitri® process (Kos et al., 2000; Neethling et al., 1998).

1.1.7 Biological Nitrogen Removal Schemes

Figure 3.2 shows several BNR schemes used to take advantage of the biological nitrogen transformations. This is by no means a complete listing of all possible process schemes, but it demonstrates the variety of possible ways to achieve nitrogen removal. The columns to the right of the diagrams indicate the way by which various schemes achieve nitrogen removal:

- Separate processes—schemes 1 to 5 show processes that can be designed to remove a particular nitrogen species. Some modification to these basic processes can achieve multiple objectives (e.g, some nitrification and denitrification (NDN) in a BAF). These processes can also be added to existing facilities to achieve nitrogen removal.
- Staged processes—schemes 7, 8, 9, 10, and 11 show staged, sequential processes using separate basins to create aerobic and anoxic conditions for nitrification and denitrification. Denitrification is through substrate level or endogenous level.
- Integrated nitrification/denitrification processes—schemes 12 and 13 illustrate processes where nitrification and denitrification occur within the same reactor by manipulating the environmental conditions.
- Emerging processes—scheme 14 showing the Sharon/anammox process; typically used for return stream treatment.

		Process	Substrate level denitrification	Endogenous denitrification	Integrated nit/ denitrification	Separate nitrification	Separate denitrification
1		Activated sludge[a]				X	X
2		Trickling filter[a]				X	
3		Moving bed bioreactor (MBBR)[a]				X	X
4		MBBR[a]	X	X	X	X	X
5		Biologically activated filters[a]				X	X
6		Effluent filter[a]					X
7		Fluidized bed				X	X
8		Wuhrman		X			
9		Ludzack–Ettinger	X				
10		Modified Ludzack–Ettinger	X				
11		Bardenpho (four-stage Bardenpho)	X	X			
12		Step feed	X	X			
13		Phased operation[b]			X		
14		Sequencing batch reactor (SBR)	X	X	X		
15		Simultaneous NDN			X		
16		SHARON-anammox			X		
							

Notes:

FIGURE 3.2 Typical biological nitrogen removal schemes (NDN = nitrification–dentrification; separate processes indicate those that can be added to another unit process: [a]As a standalone process without zones or other process schemes. Can be added for single objective (i.e., nitrification). [b]Phased operation to generate sequential nitrification and denitrification in the same reactor (i.e., biodenitro, SBR) (courtesy of HDR Engineering Inc.).

1.2 Physical/Chemical Nitrogen Removal Processes

Nitrogen can be removed chemically by converting it to nitrogen gas, $N_2(g)$ using breakpoint chlorination, by stripping $NH_3(g)$, by an ion-exchange process; or by using membrane separation. Physical/chemical nitrogen removal processes typically are not used, and many of the earlier full-scale systems have been decommissioned. Biological processes have replaced physical/chemical nitrogen removal systems. A brief overview of these processes is included in the following sections.

1.2.1 Breakpoint Chlorination

In breakpoint chlorination, ammonium is oxidized to nitrogen gas. The process is efficient and follows a series of complex reactions where ammonia reacts with chlorine to form monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and ammonium trichloride (NCl_3). In addition to nitrogen gas, other nitrogen oxidation species also form, primarily nitrate, NO_3^-. Although the actual mechanisms for these reactions are quite complex, the stoichiometry of the breakpoint reaction is simply

$$2NH_4^+ + 3Cl_2 \rightarrow N_2(g) + 6Cl^- + 8H^+ \tag{3.1}$$

According to eq 3.1, 7.6 mg Cl_2/mg NH_4^+-N is required to oxidize ammonium to nitrogen gas. Because some ammonia is converted to nitrate and other oxidized nitrogen species, the actual practical chlorine dose is often approximately 10 mg Cl_2/mg NH_4^+-N. The breakpoint process produces a significant amount of acid (hydrochloric acid [HCl]), however, which will consume alkalinity at a ratio of 10.7 mg as $CaCO_3$/mg NH_4^--N. For a typical WWTP, oxidizing a 20-mg NH_4^+-N/L stream by breakpoint chlorination will therefore require 152 mg Cl_2/L and consume 214 mg/L as calcium carbonate of alkalinity.

Chlorine is a highly reactive oxidant and produces other byproducts of concern. Ammonium trichloride typically is produced during breakpoint, resulting in the release of noxious ammonium trichloride gas. Reactions with organic compounds in the water lead to formation of many halogenated organics, primarily trihalomethanes such as chloroform, $CHC1_3$. Chlorinated organic compounds are recognized as potential human carcinogens. Although monochloramine has been implicated in some health effect and is known to cause fish toxicity, it has been used for potable water disinfection.

Safety aspects of storage and dispensing of chlorine gas are major health and safety concerns, making the use of large quantities of chlorine gas unacceptable for

many public utilities. Fire and safety code requirements have placed severe restrictions on its use. Sodium hypochlorite is used to alleviate most safety concerns.

Full-scale applications of breakpoint chlorination as the primary means of nitrogen removal have largely been discontinued. Some utilities maintain the ability to breakpoint chlorinate as an emergency backup process.

1.2.2 Air Stripping

Ammonia nitrogen can occur in water as ammonium ion, which is in equilibrium with its conjugate base, ammonia. The equilibrium has a pK_a value of approximately 9.5, as follows:

$$NH_4^+ = NH_{3(eq)} + H^+ \quad pK_a = 9.5 \tag{3.2}$$

Aqueous ammonia exists in equilibrium with its gaseous counterpart in accordance to Henry's law:

$$[NH_{3(aq)}] = K_H \cdot [NH_{3(g)}] \tag{3.3}$$

The equilibrium in eq 3.2 is shifted toward the right-hand side as pH increases, with significant amounts of unionized ammonia $[NH_{3(eq)}]$ forming when the pH exceeds the pK_a value (pH > 9.5). This means that to remove ammonium ions, the ammonium nitrogen is first converted to unionized ammonia by raising the pH and then stripped from the liquid according to Henry's law (eq 3.3).

Ammonia stripping can be achieved using these principles. It typically requires a large air-to-water (A:W) ratio to achieve a high degree of nitrogen removal, with a minimum A:W ratio for ammonia removal on the order of 1 600 m^3/m^3. A high safety factor typically is used with practical attainable levels of 1 to 3 mg NH_3-N/L.

Full-scale ammonia-stripping towers at South Lake Tahoe, California; at Water Factory 21 of Orange County Water District, California; and in South Africa have been decommissioned because of operational problems and cost. The three most significant problems with air-stripping plants are listed below:

(1) The process is highly temperature-dependent and has failed during cold weather; freezing has been a problem.
(2) Scaling occurs on the tower packing, specifically with use of lime to raise pH.
(3) The process has failed to consistently achieve a low ammonia concentration.

Although some stripping plants remain in operation, most have been replaced by more economical BNR systems.

2.0 PHOSPHORUS REMOVAL PROCESSES

Unlike nitrogen, there is no gaseous form of phosphorus through which it can be removed from wastewater. Consequently, phosphorus must be converted to a particulate (solid) form and removed as a particulate by sedimentation, filtration, or some other solids removal process. Or phosphorus can be concentrated into a sidestream using membrane ion separation treatments, such as reverse osmosis. Table 3.3 summarizes the various options for removing or converting phosphorus species.

The different chemical species must be considered when considering National Pollutant Discharge Elimination System (NPDES) permit requirements and evaluating process options. Typically, phosphorus limits are stated in terms of total phosphorus, which includes all species, dissolved and soluble. In such cases, removal of the chemical or biological bound solid-phase phosphorus is critical in meeting effluent standards. If the discharge limit is based on orthophosphate only, then suspended solids removal is less critical. Chemically and biologically bound phosphorus, however, will be released during the orthophosphate analysis and then will show up in the reading, creating a false measurement (Neethling, et al., 2007).

There are three basic phosphorus removal processes: chemical, biological, and nano. Figure 3.3 gives a basic overview of typical phosphorus removal used in wastewater treatment. The selection of the specific process must be based on a case-by-case evaluation of the system economics, including both capital and operating costs.

TABLE 3.3 Phosphorus species and reactions (courtesy of HDR Engineering Inc.).

Species	Common conversion or removal process
Organic-P	Organic phosphorus can be converted to orthophosphate and polyphosphate; some organics degrade very slowly
Orthophosphate	Most abundant phosphorus species Reactive species in chemical reactions and consumed in biological growth
Polyphosphates	Condensed orthophosphates Possibly reacts with metal salts Can be used for biological growth
Chemical phosphorus	Precipitated phosphates formed by reacting orthophosphate with metal salts, or precipitates as phosphate hydroxides
Biological phosphorus	Phosphorus incorporated into the biomass for growth Excess phosphorus may accumulate under certain conditions

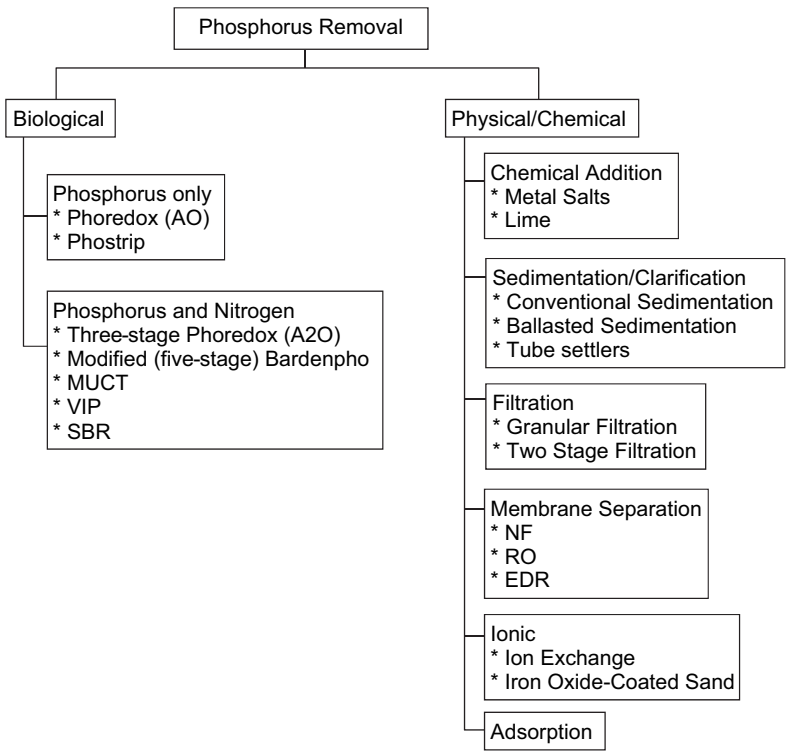


FIGURE 3.3 Overview of typical phosphorus removal processes (EDR = electrodialysis reversal; MUCT = modified the University of Cape Town; NF = nanofiltration; RO = reverse osmosis; and VIP = Virginia Initiative Plant; SBR = sequencing batch reactor) (courtesy of HDR Engineering Inc.).

(1) Convert phosphorus to a chemical species by adding a metal salt or lime. The efficiency of phosphorus removal is dependent on two factors: the chemical equilibrium between the phosphorus liquid and solid phases and the efficiency of the solids removal process. Typically, the latter process controls the removal efficiency.

(2) Incorporate the phosphorus into the biomass. Typically, biomass contains 1.5% to 2.5% (w/w) phosphorus per volatile solids. Under certain conditions, the biomass will accumulate phosphorus levels far in excess of the nutritional requirements of 6% to 8% phosphorus, or up to 20% to 30%—a

process referred to as enhanced biological phosphorus removal (EBPR) (Metcalf and Eddy, 2003). The phosphorus removal efficiency for biological systems depends on the phosphorus content of the sludge removed and the efficiency of the solids separation process.

(3) Nano processes that will remove specific or all pollutants from water at the ion or molecular level, such as reverse osmosis, electrodialysis reversal, or nanofilters, can be used to remove phosphorus. Nano treatment is expensive and has not been used for mainstream phosphorus removal, but could become popular as the limits of both phosphorus and nitrogen are lowered below conventional technology capabilities.

2.1 Chemical Phosphorus Removal

Phosphorus removal by chemical addition is attractive for its simplicity of operation and ease of implementation. It can cause, however, increased sludge production and additional operation and maintenance costs. Chemicals are added to the wastewater at a well-mixed location, followed by flocculation and solids removal by sedimentation, filtration, membrane separation, or similar processes. The chemical reactions favor phosphorus partitioning from the aqueous phase to the solid phase, and will produce low residual phosphorus levels. Phosphorus levels less than 0.1 mg P/L can consistently be achieved with chemical addition at well-designed filtration facilities. Lower concentrations can be achieved with optimal chemical application and complete solids removal.

Chemical phosphorus removal uses reactions between phosphorus in water and other chemical species or compounds, usually multivalent metal ions, to form precipitates of sparingly soluble phosphate that subsequently can be removed from the liquid using a solids separation process. The commonly used chemicals are aluminum [Al(III)], ferric [Fe(III)], and calcium [Ca(II)].

The chemical reaction of phosphorus with aluminum and ferric salts in a liquid environment is complex. The classic model of a metal reacting with a phosphate to produce a metal-phosphate precipitant ($AlPO_{4(s)}$ or $FePO_{4(s)}$) does not occur under the conditions in a wastewater treatment plant (Smith et al., 2008). The precipitant is a complex structure. Several fundamental reactions occur simultaneously:

- The metal reacts with water to produce metal hydroxides. These metal hydroxides (typically shown as the basic chemical form of $Al(OH)_{3(s)}$ or $Fe(OH)_{3(s)}$) actually form hydrated forms and precipitate as an amorphous complex that

will change structure and form with time. These reactions consume alkalinity in the water. Alternative aluminum compounds such as polyaluminum chloride or sodium aluminate significantly reduce the alkalinity demand.

- Phosphate forms a bond with the metal hydroxyl complex. These bonds are strong and bind the phosphate to the structure. The amount of phosphate that binds to the metal hydroxide is still a topic of discussion. Current research suggests that the stoichiometric ratio of metal:phosphorus (Me:P) in the precipitant depends on many factors, including the phosphate concentration in the liquid, chemical dose, age of the hydroxyl complex, mixing, and many other factors (de Haas et al., 2000; Szabo et al., 2008; Yang et al., 2006).
- When the residual phosphorus concentration is high (greater than 1 mg/L), the net Me:P ratio approaches 1:1 mol:mol. As phosphate concentration is reduced, however, the ratio of Me:P increases indicating that more metal salt is required for phosphorus removal (Neethling et al., 1991; Szabó et al., 2008).

The complex metal hydroxides/phosphate chemistry makes it difficult to predict the net chemical reactions and their results. First, the formation of hydroxy-metal complex is not only dependant on the chemical dose and factors such as pH and temperature, but it also depends on mixing intensity, age of the precipitant, and other factors. The dose must therefore often be determined from practical experience for a given application. Second, the reactions produce a significant amount of sludge (approximately 2.9 mg solids/mg Al for alum and 1.9 mg solids/mg Fe for ferric) that must be processed through dewatering and disposal. Third, the reactions consume a significant amount of alkalinity (approximately 5.8 mg as $CaCO_3$/mg Al and 2.7 mg as $CaCO_3$/mg Fe).

Lime also can be used to precipitate phosphorus; however, lime is messy to handle and difficult to use compared to metal salts. A variety of calcium phosphates will form when calcium reacts with phosphate and hydroxide.

A WERF report (1980) showed that the precipitation of hydroxyapatite [$Ca_5(PO_4)_3OH$], the thermodynamically stable calcium-phosphate precipitant, predicts equilibrium phosphate levels far lower than those found in natural waters. Equilibrium with β-tricalcium phosphate shows orders-of-magnitude higher phosphate concentrations, but they still are low. These calculations indicate that the solid precipitant that forms in practical situations is often not the thermodynamically most stable form, but some other metastable chemical compound. In addition, the kinetics of precipitation are slow and some reactions may never quite reach equilibrium.

Even so, for practical application, equilibrium calculations can be used to predict the ultimate equilibrium phosphorus concentration and provide a boundary for dose requirements to meet treatment objectives.

Practical experience with lime addition demonstrates that the treatment becomes effective when pH is raised to approximately 10.0 or higher; pH levels of 10.5 are used to achieve low phosphate levels. Lime dose requirements typically are determined by the bicarbonate alkalinity of the water because, in effect, the wastewater must be titrated to a pH of 10.5 as follows:

$$Ca(OH)_2 + HCO_3^- \rightarrow CaCO_{3(s)} + H_2O + OH^- \quad (3.4)$$

Successful chemical phosphorus removal requires an efficient solids removal process and often includes filtration to achieve low phosphorus concentrations. Because the chemical sludge quantities are high, sedimentation typically is added to reduce the solids loading onto the filters. Chemical clarification processes such as contact clarifiers or sludge blanket clarifiers have been used successfully in chemical phosphorus removal schemes.

2.2 Biological Phosphorus Removal

In the 1950s, Greenburg et al. (1955) proposed that activated sludge could take up phosphate at a level beyond its normal microbial growth requirements. Srinath et al. (1959) reported batch experiments in which soluble phosphorus concentrations could be reduced to below 1 mg/L following vigorous aeration. Levin and Shapiro (1965), however, were the first to report EBPR, in an activated-sludge plant in Washington, D.C. Follow-up work in the United States and South Africa clearly demonstrated that EBPR can occur (Barnard, 1974). Since then, great progress has been made in understanding the fundamentals of EBPR process, especially with the tools of modern microbiology and biotechnology.

The group of microorganisms that are largely responsible for phosphorus removal are known as polyphosphate accumulating organisms (PAOs). The candidate PAOs identified include *Accumulibacter phosphatis* in the *Rhodocyclaceae* group of the *Betaproteobacteria*, *Actinobacteria,* and *Malikia* spp. (Crocetti et al., 2000; Hesselmann et al., 1999; Kong et al., 2005; Oehmen et al., 2007; Spring et al., 2005). Enrichment of PAOs requires alternating anaerobic carbon-rich conditions and aerobic conditions. Under anaerobic conditions, PAOs uptake carbon sources such as volatile fatty acids (VFAs) and store them intracellularly as carbon polymers, or

poly-b-hydroxyalkanoates (PHAs). Under aerobic conditions, these organisms use the internally stored carbon source (PHAs) for growth and excessively store phosphate as intracellular polyphosphate. This results in phosphorus removal from the bulk liquid phase via PAO cell removal in the waste activated sludge (WAS). Typically, biomass in the activated sludge process contains 1.5% to 2.0% phosphorus based on dry weight. In the EBPR process, however, the phosphorus content in sludge can be much higher (Metcalf and Eddy, 2003).

A simplified model of EBPR is shown in Figure 3.4. Acetate and other VFAs are produced from fermentation reactions by facultative organisms in the anaerobic zone, enter the anaerobic zone with wastewater feed, or are deliberately added to the anaerobic basin. The fermentation products are assimilated readily by unique PAOs and stored as poly-β-hydroxybutyrate (PHB) and glycogen. The assimilation and storage is aided by the energy available from the hydrolysis (and release) of polyphosphates previously stored in the cells, thus causing an increase in the soluble phosphate concentration. This accumulation of storage products gives the PAOs a competitive edge for growth and survival. Thus, the anaerobic stage serves two important purposes. First, it provides a fermentation zone to produce simple VFAs used by PAOs. Second,

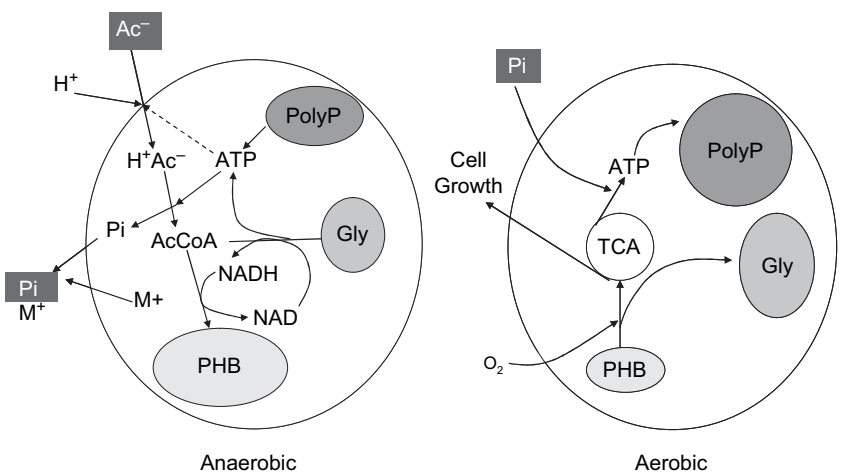


Figure 3.4 Simplified mechanism for phosphorus release and uptake (ATP = adenosine triphosphate; NAD = nicotinamide adenine dinucleotide; NADH = reduced form of NAD; and PHB = poly-β-hydroxybutyrate; TCA = tricarboxylic acid cycle) (adapted from Comeau et al., 1986; Mino et al., 1998; Oehmen et al., 2007).

it provides an environment that gives PAOs the ability to gain carbon substrate for subsequent growth, giving them a competitive edge to ensure their survival in the system.

During the aerobic phase, PHB stored inside the cells is depleted and soluble phosphate is taken up, with excess amounts stored as polyphosphates inside the cells. The PAO population increases during this time because of substrate use and growth. According to this model, the level of polyphosphate accumulation in the cells is, therefore, related to the amount of substrate assimilated and stored in the anaerobic phase.

Another group of microorganisms that often co-occurs in EBPR process is glycogen-accumulating organisms (GAOs), which also proliferate under alternating anaerobic and aerobic conditions. The main difference with GAOs is that they use glycogen as an energy source instead of polyphosphate. As a result, they compete with PAOs for carbon sources under anaerobic conditions without contributing to phosphorus removal. Deterioration of phosphorus removal performance was attributed to the proliferation of GAOs in laboratory- and full-scale EBPR reactors (Cech and Hartman, 1990, 1993; Gu et al., 2005, 2008; Satoh et al., 1994; Saunders et al., 2003). Recent studies of EBPR stability at many full-scale facilities in the United States, however, have demonstrated that effluent phosphorus concentration, the amount of phosphorus removed, and process stability in an EBPR system are not directly related to high abundance of PAO, or mutually exclusive with a high GAO fraction.

Many different process configurations exist where both phosphorus and nitrogen can be removed. The commonly used processes include anaerobic–anoxic–oxic (A2O), the University of Cape Town (UCT), the modified University of Cape Town (MUCT), Virginia Initiative Plant (VIP), and Bardenpho. When operated successfully, the EBPR process is a relatively inexpensive and environmentally sustainable option for phosphorus removal; however, process reliability varies among WWTPs, which can experience from periodic upsets (Blackall et al., 2002; Gu et al., 2004, 2005; Stephens et al., 2004; WERF, 2005). Overextended anaerobic or aerobic hydraulic retention time can negatively affect phosphorus removal. Secondary phosphorus release as a result of an overextended aerobic period has been observed (Gu et al., 2005; Stephens et al., 2004). Process configurations such as UCT or VIP were developed to minimize the amount of nitrate and oxygen entering the anaerobic zone, which was shown to affect the phosphorus removal process negatively for weaker wastewater. In a full-scale study, the advantage of UCT over A2O was demonstrated

by observing the plant phosphorus effluent, uptake, and release kinetic and PAO/GAO populations (Gu et al., 2005). The higher oxygen uptake rate at the front may lead to lower dissolved oxygen and dissolved oxygen-limiting conditions, which would then result in a compromised phosphorus uptake rate at the front of the basin (Drury, 2004; Narayanan et al., 2007).

All biological phosphorus removal schemes include an anaerobic zone in the process. Proper functioning of the anaerobic zone requires the absence of dissolved oxygen and nitrate. Including denitrification in the process reduces the potential for nitrate effects on the anaerobic zone. Various processes use different approaches to eliminate oxygen and nitrate from the anaerobic zone. Some process schemes include a fermentation step to generate VFAs and feed the VFA-rich stream to the anaerobic zone. Chemical addition also can be used to supplement VFAs. Figure 3.5 shows typically used biological and chemical phosphorus removal processes.

3.0 RETURN STREAM EFFECTS

Solids treatment processes are designed to stabilize biosolids and reduce the volume of the solids. Stabilization of solids, specifically through anaerobic digestion, results in the destruction of solids and generates ammonia and phosphorus. The ammonia and phosphorus concentration in the liquid stream is typically high. Ammonia concentrations of 500 to 1 500 mg/L and phosphorus concentrations of 50 to 500 mg/L are not uncommon, with higher phosphorus concentrations found at biological phosphorus removal plants. In addition, return streams from dewatering processes are often intermittent, resulting in a high peak load to the process. Streams originating at anaerobic digestion are typically warm (30–35°C).

In addition to the peak loading, return streams also affect the influent composition of the wastewater, which can alter both biological and chemical processes. Biological processes are sensitive to the composition of wastewater, and high loading can change the characteristics of the influent. In particular, high concentrations can change the BOD/N and BOD/P of the influent. Chemical processes are likewise affected to meet variable demands for the chemical dose.

Attenuating the return streams is critical to achieving low effluent limits. The dynamic loading not only leads to deterioration of the process performance, but could also lead to a process upset as the biological and chemical systems must adjust to changed conditions.

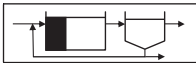
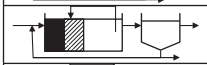
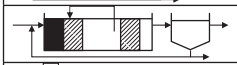
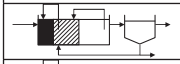
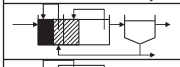
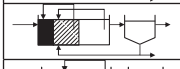
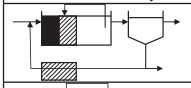
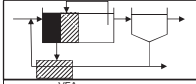
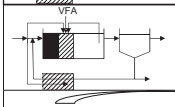
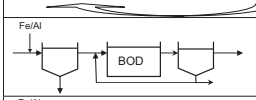
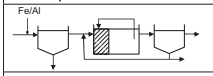
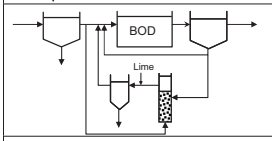
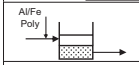
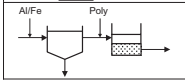
	Process	Biological P removal	Chemical P removal	P removal only	N and P removal	Tertiary
	Phoredox (AO)	X		X		
	Three-stage Phoredox (A2O)	X			X	
	Modified (five stage) Bardenpho	X			X	
	University of Cape Town	X			X	
	Modified University of Cape Town	X			X	
	Virginia Initiative Plant	X			X	
	Johannesburg process	X			X	
	Modified Johannesburg process	X			X	
	West Bank process	X			X	
	Sequencing batch reactor	X			X	
	Primary chemical secondary		X	X		
	Primary chemical any nitrification–denitrification process		X		X	
	Phostrip	X	X	X		
	Direct filtration		X	X		X
	Sedimentation (typ) filtration		X	X		X

FIGURE 3.5 Typical phosphorus removal processes (courtesy of HDR Engineering Inc.).

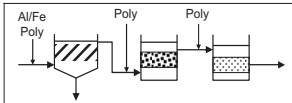
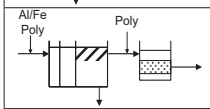
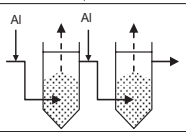
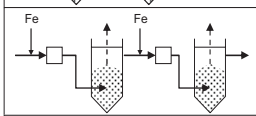
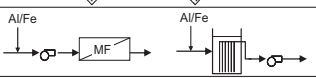
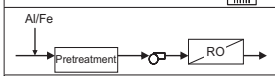
	Process	Biological P removal	Chemical P removal	P removal only	N and P removal	Tertiary
	Enhanced sedimentation/ filtration (trident high solids)		X	X		X
	Ballasted sedimentation/ filtration (Actiflo/CoMag)		X	X		X
	Two-stage filtration (dual filtration)		X	X		X
	Iron-oxide-coated filtration (BluePro)		X	X		X
	Microfiltration		X	X		X
	Reverse osmosis		X	X		X
Anaerobic Anoxic Aerobic						

FIGURE 3.5 (*Continued*)

Many treatment processes are applicable for attenuating return stream effects, including integrated, treatment, and nutrient recovery processes. Figure 3.6 presents an overview of the typically used sidestream processes.

The processes can be divided into three groups: (1) processes to attenuate the peak loading, (2) processes providing dedicated treatment, and (3) processes that are integrated into the mainstream process (see Chapter 9 for more information).

Load attenuation processes typically are cost-effective. These processes simply reduce the instantaneous loading to the mainstream process. Treatment plants often use equalization of the return flows using abandoned or excess basins available

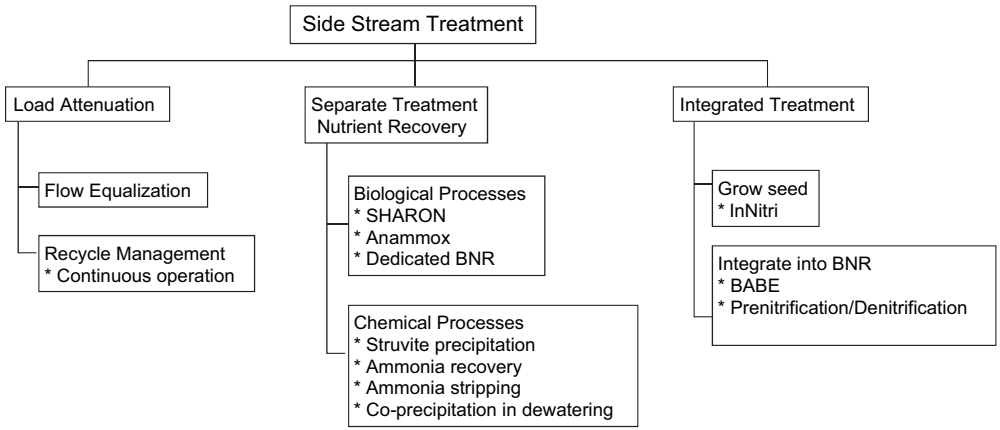


FIGURE 3.6 Overview of typical sidestream treatment processes (BABE = bioaugmentation batch enhanced; BNR = biological nutrient removal; InNitri = inexpensive nitrification; and SHARON = single reactor high activity ammonia removal over nitrite) (courtesy of HDR Engineering Inc./J.B. Neethling).

onsite. Sometimes, the return stream must be treated to prevent precipitation of struvite and other nuisance precipitants. Management options such as continuous operation of the dewatering equipment also will attenuate the return loading.

Many dedicated treatment processes are emerging, designed to treat the high strength load or to recover nutrients from the stream for beneficial use. All processes listed earlier for mainstream nutrient removal can be used for dedicated treatment. In addition, some processes take advantage of typical return stream characteristics (high temperature and high concentrations).

The SHARON process is well suited for reducing the nitrogen load of streams with a high ammonium content (>500 mg NH_4^+-N/L), but not for obtaining strict effluent standards. Stable nitrogen removal via nitrite was achieved in a single-stage, fixed-film, pilot-scale reactor treating high-ammonia strength recycle stream from sludge dewatering at room temperature (20–25°C) and at pH 6.5 to 8.3, suggesting another potential application of denitrification over nitrite. Another relatively new nitrogen removal process is the deammonification processes, such as anaerobic ammonium oxidation (anammox). Special groups of anammox microorganisms are able to oxidize ammonia using nitrite as an electron donor and, therefore, carry out nitrification and denitrification simultaneously. Most identified anammox bacteria belong to Planctomycetes. The anammox activity requires partial nitrification (to

produce nitrite), low dissolved oxygen (<0.6–0.8 mg/L), higher pH (>7.6), long SRT, and adequate NH_4-N/NO_2^-.

Chemical treatment opens up opportunities for nutrient recovery. In particular, controlled struvite precipitation processes, such as DHV's Crystalactor® (Netherlands), Paques' PHOSPAQ® (Netherlands), and Ostara Nutrient Recovery Technologies' PEARL™ process, are emerging processes to recover nutrients. Struvite precipitation is effective for phosphorus control but cannot substantially reduce ammonia loading from a typical return stream. Chemical addition directly to solids treatment processes, such as dewatering, can reduce phosphorus loading. Ammonia recovery using ammonia stripping and capture is used at the Tahoe Truckee Water Reclamation Facility, Reno, Nevada.

Integrated processes are emerging that link return flow treatment with the mainstream process. Two fundamentally different processes are used. A dedicated return stream process can be used to grow nitrifying organisms that can be sent to the mainstream process for seeding (e.g., the In-Nitri® process). This process takes advantage of higher ammonia concentrations and temperatures in the sidestreams. Return streams from solids processing, especially digestion and dewatering, contain relatively high concentrations of NH_4^+-N. Anaerobic digester supernatant is typically warm (30–35°C). The InNitri process consists of a nitrifying system to exclusively treat these sidestreams. The WAS from this system is fed into the mainstream aeration tank, where NH_4^+-N can be nitrified by the constant supply of nitrifiers. The prenitrification and bioaugmentation batch enhanced (BABE) process directs the return flow to a dedicated nitrification basin, where the stream is mixed with biomass from the mainstream process. In this case, the biomass is grown in the mainstream process to produce a stable nitrifier population, and then used to treat the intermittent return flows (Drury et al., 1995; Salem et al., 2002; Sova et al., 2004).

4.0 SELECTION OF NUTRIENT REMOVAL PROCESSES

Nutrient removal requirements typically are plant-specific. Historically, nutrient limits were placed on treatment plants discharging to sensitive water bodies (such as Lake Tahoe, Chesapeake Bay, and others) or for groundwater protection. Nutrient limits can apply to either nitrogen or phosphorus, depending on the location and limiting nutrient. Early nutrient limits set phosphorus to 1 to 2 mg/L and nitrogen to 10 mg/L. A few plants had much lower limits.

Recently, nutrient limits have become more restrictive with implementation of the EPA Ecosystem Nutrient Criteria (U.S. EPA, 2000) and development of total maximum daily loads. In addition, limits for both nitrogen and phosphorus are becoming increasingly more common. Limits often are expressed in terms of total phosphorus or total nitrogen, as opposed to a specific species such as orthophosphate or nitrate or total inorganic nitrogen.

The owner, designer, and operator are challenged to select the most appropriate process. Many application-specific criteria must be considered in the selection of the treatment process:

- Permit requirements and design objectives. Permit requirements could include nitrogen, phosphorus, or both. In addition, the limits could apply to specific species, although total nitrogen and total phosphorus limits are becoming more common. Some permits are seasonal and pose opportunities and challenges to meet.
- Facilities, cost, and operation. The treatment technology often must fit with an existing plant, both liquid processes and solids management. Economical factors (construction and operation and maintenance costs) and client preferences (operator capabilities, complexity, startup and shutdown, redundancy, etc.) must be considered.
- Future requirements. Selecting the process may require considering options to meet a more restrictive permit in the future. Considerations for service area expansion and changing characteristics of wastewater, permit requirements, and solids management should be evaluated.

4.1 Nutrient Removal Levels

The degree of nutrient removal varies with locations, season, and discharge locations. Many regions (e.g., the Chesapeake Bay) or states (e.g., Maryland) have proposed levels of treatment to be accomplished using common terminology such as BNR or enhanced nutrient removal to describe a nutrient limit. Instead of selecting a particular set of nutrient limits that has specific significance to a particular region or state, a general set of treatment levels or objectives are used to describe process selection based on technology. These limits, shown in Table 3.4, form the basis for discussion and identifying process performance for treatment technologies in this section.

The reliability of a technology must be considered when assessing performance. Neethling et al. (2009) introduced a method for using a statistical approach to describe process performance. In this approach, the treatment plant or technology

Table 3.4 Nutrient removal levels (WERF, 2010; HDR Engineering Inc.)*.

Level	Total nitrogen	Total phosphorus	Comment
1	8	1	Nominal nutrient removal achievable with conventional technologies
2	3	0.1	Enhanced removal requires additional treatment to achieve limits
3	1	0.01	Very low limits require best practice and enhanced treatment. May or may not be feasible for certain plants, especially requiring both limits at the same time

*Modifier "N" or "P" are used in the text to denote limits for nitrogen or phosphorus only. For example, Level 2P is only phosphorus limit of 0.1 mg/L TP (total phosphorus), with no nitrogen limit.

performance is tied to the statistical rank to express the probability of achieving a certain performance. This statistic includes the conditions under which the data is collected. Factors such as permit limit, season, interruptions from construction or process upsets, and other conditions that would affect performance must be noted in the performance statistic.

Building on this statistical approach, the term technology performance statistic (TPS) was used at a Water Environment Federation (WEF) Technical Exposition and Conference workshop to assess the performance of full-scale WWTPs (WEF, 2009). The "best achievable" performance is described as the "TPS-14d" value, which is the best performance sustained for a 14-day period and is calculated as the 3.83th percentile rank (14/365 performance) of the three-year data set. This value is considered to be the best the technology can perform under operation conditions and the best achievable on a short-time basis. This is not an appropriate permitting limit because it is exceeded more than 96% of the time. Parker et al. (2009) suggested that the "reliable process" performance, calculated as the number of exceedances in a five-year period, should be used as a measure to evaluate process performance and permit limits. If the 95% value (which can be calculated as the TPS-95% value) is as a monthly limit, then the limit is statistically exceeded three times (months) in a five-year period (5% of 60 months).

These approaches underscore the importance of considering the duration or averaging of performance data when assessing technology capabilities and setting permit limits. Longer averaging periods (monthly or annual) provide significantly greater

opportunity for meeting an effluent limit. Short recurrent limits (daily) provide no room to account for variability and will require large safety factors in design.

The technology presented in this section is based on typical monthly performance achievable.

4.2 Level 1 Nutrient Removal

Many conventional nutrient removal processes can achieve Level 1 removal (see Table 3.4). Most WWTPs designed for nominal biological or chemical nutrient removal can achieve these limits, unless the influent wastewater is unique, containing, for example, elevated nitrogen or phosphorus concentrations or a significant industrial input. Biological processes typically can be designed to meet Level 1 limits without filtration.

Nutrient removal Level 1 can be achieved with various well-established treatment processes. These are summarized in Table 3.5. Many of these can be designed to include primary treatment or not—the table indicates the most commonly used option for a particular process. Primary clarifiers provide an avenue for phosphorus removal by chemical addition.

4.2.1 Level 1N Nitrogen Removal

Level 1N nitrogen removal **(8 mg/L total nitrogen)** can be achieved using various conventional BNR processes or adding nitrification and denitrification processes to existing secondary treatment (BOD) facilities. These processes include the following:

- Mainstream NDN processes, such as the modified Ludzack–Ettinger (MLE), step feed, simultaneous NDN, and others, can achieve Level 1N limits. A secondary anoxic zone is typically not required and an external carbon source is not typically needed.
- Nitrification and denitrification can be added following existing secondary (BOD removal) processes using biofilm or suspended growth processes. An external carbon source typically is required for denitrification.

4.2.2 Level 1P Phosphorus Removal

Level 1P phosphorus removal (1 mg/L total phosphorus) can be achieved with conventional technologies or by adding polishing processes to existing secondary or NDN facilities:

- The EBPR processes such as AO, A2O, Bardenpho, MUCT, VIP, and others can achieve Level 1P limits as a mainstream process.

Table 3.5 Level 1 treatment process trains (8 mg/L total nitrogen/1 mg/L total phosphorus (courtesy of HDR Engineering Inc./J.B. Neethling).

Process	Primary	Secondary	Filter	Post nitrogen	Chemicals
Primary with metal salt, secondary treatment, post NDN	Yes	BOD removal		NDN	MeOH metal
Primary with metal salt, Nitrification activated sludge, post DN, filter	Yes	Nitrification		DN	MeOH metal
Secondary treatment with chemical addition, post NDN, filter	No	BOD removal	Filt	NDN	MeOH metal
Nitrification activated sludge with chemical addition, post DN, filter	No	Nitrification	Filt	DN	MeOH metal
Primary with metal salt, two-stage NDN (without post anoxic)	Yes	NDN			Metal
Two-stage NDN (without post anoxic), filtration	No	NDN	Filt		Metal
Primary with metal salt, four-stage Bardenpho	Yes	NDN			Metal
Four-stage Bardenpho, filtration	No	NDN	Filt		Metal
Three-stage BNR process	Yes/no	NDN EBPR			Metal
Five-stage Bardenpho	No	NDN/EBPR			Metal
MBR with chemical addition to MBR	Yes/no	MBR/NDN			Metal
MBR with EBPR	No	MBR/NDN/ EBPR			Metal

Primary = likely to include primary treatment, usually with chemical addition. Primary can be avoided for most designs if tertiary system can achieve phosphorus limits (typically at higher chemical dose). Biological = biological treatment process, for BOD removal, nitrification, nutrient removal, including solids separation with clarifier. Filt = filtration, typically with chemical (metal salt) addition for phosphorus removal. Post nitrogen = process to remove or polish for nitrogen post secondary treatment, biological, or other. MeOH = methanol or other carbon source added for gentrification. Metal = metal salt (alum, ferric) or other chemical added for phosphorus removal.

BNR = biological nutrient removal; BOD = biochemical oxygen demand; DN = denitrification; EBPR = enhanced biological phosphorus removal; MBR = membrane bioreactor; and NDN = nitrification and denitrification.

- Chemical phosphorus removal can be implemented. Metal salts can be added to a primary clarifier or direct filtration can be used to achieve Level 1P limits. Some facilities add chemicals directly to the activated sludge process. If a high chemical dose is required for the filter, then a solids separation process (clarifier) can be added to reduce the solids loading to the filter.

4.2.3 Level 1 Nitrogen and Phosphorus Removal

Level 1 nitrogen and phosphorus removal can be achieved with conventional technologies or by adding polishing processes to existing secondary facilities. Processes outlined above can be combined to achieve both nitrogen and phosphorus removal:

- The EBPR processes such as A2O, Bardenpho, MUCT, VIP, and others that include denitrification can achieve Level 1 limits as a mainstream process.
- Filters can be designed for simultaneous denitrification and chemical phosphorus removal for Level 1 limits.
- Combinations of Level 1N and 1P processes can be used sequentially.

4.3 Level 2 Nutrient Removal

Level 2 nutrient removal (3 mg/L total nitrogen and 0.1 mg/L total phosphorus) is more challenging and typically requires additional treatment to meet objectives (Table 3.6). Level 1 processes can be enhanced to achieve Level 2 limits.

4.3.1 Level 2N Nitrogen Removal

Level 2N nitrogen removal limits (3 mg/L total nitrogen and no total phosphorus limit) typically will require adding an external carbon source. This can be added to a second anoxic zone in a mainstream process, or to a tertiary polishing process.

- Mainstream NDN processes that will meet Level 2N requirements will require a secondary anoxic zone with external carbon addition as used in a four-stage Phoredox process. A second anoxic stage can be added to conventional processes, such as MLE, step feed, simultaneous NDN, and others, to achieve Level 2N limits.
- Biofilm or suspended growth processes can be added to existing secondary (BOD removal) processes for NDN. An external carbon source typically is required to provide efficient denitrification. This is similar to Level 1N requirements, but requires more robust design and increased carbon doses.

Table 3.6 Level 2 treatment process trains (3 mg/L total nitrogen/0.1 mg/L total phosphorus) (courtesy of HDR Engineering Inc./J.B. Neethling).

Process	Primary	Biological	Filter	Post nitrogen	Chemicals
Primary with metal salt, secondary treatment, filter, post nitrogen removal	Yes	BOD removal	Sed/Filt	NDN	MeOH Metal
Primary with metal salt, nitrification activated sludge, post denitrification, filter	Yes	Nitrification	Sed/Filt	DN	MeOH Metal
Two-stage NDN (without post anoxic), sedimentation/filtration, post denitrification	Yes	NDN	Sed/Filt	DN	MeOH Metal
Four-stage Bardenpho, sedimentation/filtration	Yes	NDN	Sed/Filt		MeOH Metal
Three-stage BNR process; sedimentation/filtration; post gentrification	Yes	NDN EBPR	Sed/Filt	DN	MeOH Metal
Five-stage Bardenpho with sedimentation/filtration	No	NDN/ EPBR	Sed/Filt		MeOH Metal
Membrane bioreactor (MBR) with chemical addition, post denitrification	Yes/No	MBR/ NDN		DN	MeOH Metal
MBR with EBPR, post denitrification	No	MBR/ NDN/EPBR		DN	MeOH Metal

Primary = likely to include primary treatment, usually with chemical addition. Primary can be avoided for most designs if tertiary system can achieve phosphorus limits (typically at higher chemical dose). Biological = biological treatment process, for BOD removal, nitrification, nutrient removal, including solids separation with clarifier. Sed = sedimentation or clarification, typically with chemical (metal salt) addition for phosphorus removal; include conventional or ballasted sedimentation. Filt = filtration, typically with chemical (metal salt) addition for phosphorus removal. Post nitrogen = process to remove or polish for nitrogen post secondary treatment, biological, or other. MeOH = methanol or other carbon source added for gentrification. Metal = metal salt (alum, ferric) or other chemical added for phosphorus removal.

BNR = biological nutrient removal; BOD = biochemical oxygen demand; DN = denitrification; EBPR = enhanced biological phosphorus removal; and NDN = nitrification and denitrification.

4.3.2 Level 2P Phosphorus Removal

Level 2P phosphorus removal (no total nitrogen limit and 0.1 mg/L total phosphorus) typically requires multiple barriers. This can be achieved with Level 1P technologies by adding polishing facilities to lower soluble phosphorus and capture particulate phosphorus. Level 2P requires essentially complete removal of particulate phosphorus using very effective and reliable solids separation processes.

- Level 1P EBPR technologies can be used with enhanced tertiary phosphorus removal. Tertiary removal typically will include coagulation/separation/filtration. In some cases, where biological phosphorus consistently produces soluble phosphorus concentrations below 0.02 to 0.05 mg/L, direct filtration can meet Level 2P limits.
- Level 1P chemical phosphorus removal technologies can be enhanced by adding tertiary processes. Tertiary removal typically will include coagulation/separation/filtration or membrane filtration. Chemical addition can be optimized between the multiple dose points to meet limits.
- Very efficient solids separation is required for the final stage to remove virtually all particles, typically with a combination of sedimentation/filtration or membrane filtration.

4.3.3 Level 2 Nitrogen and Phosphorus Removal

Level 2 nitrogen and phosphorus removal (3 mg/L total nitrogen and 0.1 mg/L total phosphorus) can be achieved by a combination of Level 2N and 2P processes.

4.4 Level 3 Nutrient Removal

Level 3 nutrient removal (1 mg/L total nitrogen and 0.01 mg/L total phosphorus) is at the current limits of technology and below the reliable limits of currently demonstrated processes. These limits at and below technology capability are not appropriate for permit compliance. Some pilot and full-scale examples are known to meet 1 mg/L TN and 0.01 mg/L TP. Except for reverse osmosis, however, there are no known full-scale facilities that meet Level 3 limits for nitrogen and phosphorus consistently. A fraction of the dissolved nonreactive (organic) phosphorus is also nonbiodegradable (the nonbiodegradable dissolved organic phosphorus, nBDOP) and not readily captured in chemical treatment either.

4.4.1 *Level 3N Nitrogen Removal*

Level 3N nitrogen removal limits (3 mg/L total nitrogen and no total phosphorus limit) are challenging because a fraction of the DON is nonbiodegradable (the nonbiodegradable dissolved organic nitrogen, nbDON). There is no reliable method for removing nbDON except reverse osmosis. Meeting Level 3N nitrogen limits requires all of the following (Table 3.7):

- Level 2N capability, designed to produce effluent ammonia and effluent nitrate/nitrite concentrations near detection.
- A low nbDON in the effluent. This fraction cannot be removed with established techniques.
- Molecular exclusion processes such as reverse osmosis.

TABLE 3.7 Potential level 3N unit processes for nitrogen removal (1 mg/L total nitrogen/no total phosphorus limit) (courtesy of HDR Engineering Inc./J.B. Neethling).

Unit Process	NH_4	NO_3	bDON	rDON	pON	Comment
Separation processes	–	–	–	–	Varies	See Table 3.8
Nitrification	++++	–	+++	–	–	Nitrification very efficient; other bacteria degrade bDON
Suspended growth denitrification (mixed)	–	+++	+	–	–	External carbon addition strongly influence denitrification efficiency
Fixed growth denitrification (plug flow)	–	++++	+	–	–	External carbon addition strongly influence denitrification efficiency
Breakpoint chlorination	++	–	–	–	–	Rarely used process
Ammonia stripping	++++	–	–	–	–	Rarely used process
Oxidation	–	–	+	+	–	Strong oxidant, hydroxyl radical, UV show promise to reduce rDON
Reverse osmosis	+	++++	++++	++++	++++	Very efficient molecular exclusion

Scale: + = effective and – = not effective.

bDON = biodegradable dissolved organic nitrogen (biodegradable within timescale of wastewater treatment); pON = particulate organic nitrogen; rDON = refractory or non-biodegradable dissolved organic nitrogen [within timescale of wastewater treatment]; total DON = BDON + RDON; total organic nitrogen = DON + pON.

4.4.2 *Level 3P Phosphorus Removal*

Level 3P phosphorus removal limits (no total nitrogen limit and 0.01 mg/L total phosphorus) are challenging because of the presence of nBDOP. There is no reliable method for removing nBDOP except reverse osmosis. Meeting Level 3N phosphorus limits requires all of the following (Table 3.8):

- Level 2P with enhanced removal efficiency to produce effluent reactive phosphorus (orthophosphate) near detection. Some processes have been shown to be able to approach very low limits (less than 2 ug/L). These include high chemical dose treatment, iron-coated sand dual reactive filtration, and two-stage filtration.

TABLE 3.8 Potential level 3P unit processes for phosphorus removal (no total nitrogen limit/0.01 mg/L total phosphorus) (courtesy of HDR Engineering Inc./J.B. Neethling).

Unit Process	sRP	sNRP	pP	Comment
Metal salt (aluminum/iron)	++++	++	++	Reactions with orthophosphate and metal hydroxide complexes are very efficient sNRP and pP are coagulated and removed with precipitant
Sedimentation and ballasted sedimentation	–	–	+	Effective removal of high solids concentration. Effective to improve filtration
Direct filtration	–	–	++	Removal of particulates depends on filter design. Add polymer for more efficient capture
Sedimentation/ filtration	–	–	+++	Sedimentation allows higher chemical doses and increased removal efficiency
Two-stage filtration	–	–	++++	Effective particle removal with dual barrier
Reactive filtration (iron oxide–coated sand)	+++	?	++++	Reactive removal of sRP and filtration of pP Unknown efficiency for sNRP removal
Membrane	–	–	++++	Very efficient particle separation
Reverse osmosis	++++	++++	++++	Very efficient molecular exclusion

Scale: + = effective and – = not effective.

pP = particulate phosphorus (difference between TP and sTP); sNRP = soluble nonreactive phosphorus (difference between total soluble phosphorus and sRP); sRP = soluble reactive phosphorus.

- High-efficient particle removal to reduce particulate phosphorus to very low limits (<2 ug/L). Some processes capable of highly efficient particle separation are two-stage filtration, multibarrier filtration, and membrane separation.
- A low nBDOP in the effluent. This fraction cannot be removed with established techniques and appears to be resistant to chemical treatment.
- Molecular exclusion processes such as reverse osmosis.

4.4.3 Level 3 Nitrogen and Phosphorus Removal

Level 3 nitrogen and phosphorus removal (1 mg/L total nitrogen and 0.01 mg/L total phosphorus) requires a combination of Level 3N and 3P processes (see Tables 3.5–3.8).

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Chapter 4

Principles of Biological Nitrogen Removal

1.0 INTRODUCTION

Nitrogen (N) is a key element involved in biogeochemical cycles. Its oxidation state can vary from –3.0 for organic nitrogen to +5.0 for nitrate. The important nitrogen species are ammonium-nitrogen (NH_4^+-N, -3), dinitrogen gas (N_2, 0), nitrite-nitrogen

(NO_2^--N, +3) and nitrate-nitrogen (NO_3^--N, +5). Continuous interconversion between various nitrogen species in the environment is the basis of the nitrogen cycle. The principal reactions involved in the nitrogen cycle are nitrogen fixation, ammonification, nitrification, denitrification, and assimilative nitrogen uptake. Because of the various transformations they undergo, nitrogen species are converted rapidly from one oxidation state to another. The various nitrogen species are summarized in Table 4.1.

Although nitrogen is an essential component of the building blocks of life, such as amino acids, excessive deposition of nitrogen species such as ammonium-nitrogen (NH_4^+-N) and nitrate-nitrogen (NO_3^--N) in terrestrial and oceanic ecosystems causes eutrophication and groundwater pollution (Robertson and Kuenen, 1992). Increasing industrialization has resulted in an increase in the global nitrogen flux. Nitrous oxide (N_2O), which is a purported intermediate in both nitrification and denitrification, is a greenhouse gas and, though not as abundant in the atmosphere as CO_2, it significantly contributes to global warming. The deleterious effects of NH_4^+-N include toxicity to aquatic fauna, depletion of dissolved oxygen in receiving waters because of nitrification, and a reduction in chlorine-disinfection efficiency at water treatment facilities (U.S. Environmental Protection Agency [U.S. EPA], 1993). Nitric acid (HNO_3) can be a principal contributor to acid rain. In addition to the well-documented damage to infrastructure, acid rain can increase soil and water acidity. In freshwater, the nitrous and nitric acids produced by nitrification can mobilize toxic aluminum ions and can

TABLE 4.1 Oxidation states of nitrogen (Madigan et al., 1997).

Species	Oxidation state
Organic nitrogen (R-NH_2)	–3
Ammonia (NH_3)	–3
Nitrogen gas (N_2)	0
Nitrous oxide (N_2O)	+1 (average per N)
Nitrogen oxide (NO)	+2
Nitrite (NO_2^-)	+3
Nitrogen dioxide (NO_2)	+4
Nitrate (NO_3^-)	+5

be lethal to flora and fauna (Robertson and Kuenen, 1992). Further, the colonization of building surfaces by nitrifying microorganisms can lead to corrosion and eventual destruction of structures because of the production of nitrous and nitric acids. Yet another problem is the undesirable succession of the natural flora on nutrient-poor land that is exposed to increased mineral nitrogen loadings. Nitrogen pollution of environmental systems is caused by both anthropogenic and nonanthropogenic sources.

Because eutrophication and aquatic toxicity can result from the discharge of nitrogen-containing waters in aquatic environments, it is desirable to remove nitrogen species from wastewater before they flow into sensitive water bodies. Though nitrogen removal from waters is possible using physico-chemical methods (e.g., air-stripping at high pH and breakpoint chlorination for NH_4^+-N removal), biological nitrogen removal (BNR) presents a more cost-efficient and environmentally benign alternative. The biochemical processes of nitrification and denitrification, acting in concert, channel different nitrogen species through a part of the nitrogen cycle. The product is dinitrogen (N_2) gas, which can be stripped rapidly from the BNR reactor. This chapter presents an overview of BNR processes. A detailed discussion on nitrification and denitrification is presented in Chapters 5 and 6, respectively. In addition, sidestream nitrogen removal is presented in Chapter 9.

2.0 SOURCES AND SINKS OF NITROGEN IN WASTEWATER TREATMENT

2.1 Influent Nitrogen Species

Nitrogen species in typical domestic wastewater are predominantly in the reduced state with an average oxidation state of –3, corresponding to that of ammonia (inorganic) or amino acids (organic). Based on an acid–base dissociation constant (*pKa*) value of 9.3 for the ammonia–ammonium pair, most reduced inorganic nitrogen is in the form of protonated ammonium ion (NH_4^+-N) rather than free ammonia (NH_3) (Stumm and Morgan, 1996). Ammonium/ammonia and organic nitrogen collectively are referred to and measured as total Kjeldahl nitrogen. Total Kjeldahl nitrogen can be further classified depending upon whether the reduced nitrogen species are soluble or particulate and biodegradable or nonbiodegradable. Free ammonia rather than ionic ammonium is the true substrate for nitrification.

2.2 Ammonification

Ammonification is a process by which organic reduced nitrogen (in the –3 oxidation state) is converted to inorganic ammonium/ammonia. Heterotrophic bacteria carry out ammonification, which is a prerequisite to nitrification (Grady et al., 1999). The rate of ammonification is a function of the organic nitrogen containing substrate concentration, the heterotrophic biomass concentration catalyzing the ammonification reaction, and the ratio of the carbon to reduced nitrogen concentration of the waste stream (Grady et al., 1999).

2.3 Ammonia Assimilation

Ammonia-nitrogen (NH_3-N) is the preferred assimilative nitrogen source for bacteria (nitrifying or nonnitrifying) in activated sludge because it is in the same oxidation state (–3) as in biomass (approximated empirically by $C_5H_7O_2N$) (Grady et al., 1999; Hoover and Porges, 1952; Rittmann and McCarty, 2001). This means that bacteria do not need to reduce ammonia, unlike all other more oxidized nitrogen species such as dinitrogen gas, nitrite, or nitrate (Grady et al., 1999, Rittmann and McCarty, 2001). The relative nitrogen content of biomass and the corresponding amount of ammonia assimilated is 0.0875 g-N/g of particulate COD formed (Grady et al., 1999). In the absence of ammonia or reduced organic nitrogen (assimilated after ammonification), activated sludge can assimilate more oxidized sources such as nitrite or nitrate but at a significant expenditure of energy (or electron equivalents) required to reduce these species to the –3 oxidation state (Rittmann and McCarty, 2001). The growth of microorganisms or biomass represented by $C_5H_7O_2N$ can be shown in a simplified manner as follows:

$$\text{Organic matter} + O_2 \rightarrow CO_2 + C_5H_7O_2N\ \text{(New biomass)} + \text{Energy} + \text{Other products} \tag{4.1}$$

Biomass present in the wastewater treatment system is oxidized through endogenous respiration, which can be represented by:

$$C_5H_7O_2N\ \text{(Biomass)} + 5\,O_2 \rightarrow 5\,CO_2 + NH_3 + 2\,H_2O + \text{Energy} + \text{Other products} \tag{4.2}$$

Thus, endogenous respiration releases some of the nutrients back in to the wastewater treatment process.

2.4 Stripping

Nonionized free ammonia, NH_3, is significantly volatile and could be removed by stripping from activated sludge in the aerated zones. Typical activated sludge

plants, however, operate at a pH close to 7.0. At this pH value, the liquid phase NH_3 concentration is more than two orders of magnitude lower than the ionized (nonvolatile) ammonium NH_4^+ form. Thus, stripping is expected to contribute minimally to the overall ammonia removal from activated sludge trains.

2.5 Denitrification

As shown above, nitrogen can be removed through incorporation into new biomass growth and by limited stripping that might occur under suitable conditions. The other major route of nitrogen removal from wastewater treatment processes is the biological reduction of nitrate and nitrite to primarily nitrogen gas, N_2, in the denitrification reaction. The atmosphere acts as a nitrogen sink where nitrogen in gaseous form is the principal form of nitrogen.

The overall amount of total nitrogen removed through the system depends on the amount of waste activated sludge (WAS) generated and the denitrification occurring in the process. The amount of WAS, in turn, depends on the solids retention time (SRT) of the activated sludge process.

3.0 NITRIFICATION

Chapter 5 provides the details of nitrification in wastewater treatment. The following sections, however, provide an overview of the nitrification process.

3.1 Biochemistry and Microbiology

Nitrification is the process of biological oxidation of ammonia (which exists mostly as NH_4^+-N in typical wastewater) to nitrite (NO_2^--N) and further oxidation of nitrite to nitrate (NO_3^--N). Ammonia oxidizing bacteria (AOB) carry out the oxidation of ammonia to nitrite, and nitrite oxidizing bacteria (NOB) carry out nitrite conversion to nitrate. Both these reactions should operate at optimal rates for production of nitrate. Ammonia and nitrite oxidizers are referred to as "nitrifiers." Although classified together, AOB and NOB are not related phylogentically (Bock et al., 1991).

Most nitrifiers found in typical wastewater treatment systems are autotrophic because they synthesize cellular material from inorganic carbon (HCO_3^-) under typical operating conditions. Oxidation of ammonia or nitrite provides the energy needed for cell synthesis. These bacteria are obligate aerobes, as they grow only when dissolved oxygen is available. The absence of dissolved oxygen for prolonged periods,

however, is not lethal as these organisms adapt and survive under low dissolved oxygen as well as low ammonia concentrations (Geets et al., 2006; Painter, 1970). In typical BNR systems, nitrifiers successfully survive anaerobic (absence of oxygen and oxidized nitrogen species) and anoxic (absence of oxygen but the presence of oxidized nitrogen species) conditions. The relative abundance and diversity of nitrifying organisms in wastewater treatment systems depends on influent characteristics and operating conditions (Ahn et al., 2008; Siripong and Rittman, 2007).

Heterotrophic nitrification has been reported by some researchers (Joo et al., 2005, 2007; Lin et al., 2006; Su et al., 2006). The microorganisms capable of heterotrophic nitrification include *Thiosphaera pantotropha*, *Bacillus*, *Pseudomonas*, *Alcaligenes*, *Pseudomonas denitrificans*, and *Paracoccus denitirficans*. These bacteria typically carry out aerobic denitrification and contribute to simultaneous nitrification and denitrification (SND). The heterotrophic nitrification process requires a readily available organic substrate, such as acetate, which typically is limited in aerobic zones. As a result, heterotrophic nitrifier population is likely to be insignificant in most municipal wastewater treatment plants (WWTPs) (van Loosdrecht and Jetten, 1998). Ammonia can be used as an inorganic electron donor in the presence or absence of oxygen. In the absence of oxygen, the reaction occurs with nitrite as the electron acceptor in the anammox (anaerobic ammonia oxidation) process. Electrons from ammonium are transferred to nitrite producing nitrogen gas and water (Egli, 2003; Egli et al., 2001; Strous et al., 1999):

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2\,H_2O \tag{4.3}$$

The anammox process adds a significant amount of gaseous nitrogen to the atmosphere (Arp and Bottomley, 2006). To date, anammox bacteria have not been obtained in pure culture. The bacteria capable of anammox include Candidatus *Brocadia anammoxidans*, Candidatus *Kuenenia stuttgartiensis*, Candidatus *Scalindua brodae*, Candidatus *Scalindua wagneri*, and Candidatus *Scalindua sorokinii* (Egli et al., 2001; Kuypers et al., 2003; Schmid et al., 2000, 2003). These organisms are classified under phylum Planctomycetes, class Planctomycetacia, and order Planctomycetales (Perxas, 2005). The anammox process is slow—the doubling time of the anammox bacteria is 10.6 days with the maximum specific growth rate estimated to be 0.003/h (Jetten et al., 2001). Recent research, however, indicates that by providing suitable seed biomass and reactor operating conditions, it is feasible to oxidize ammonia at high rates using the anammox process (Tsushima et al., 2007). The main advantages of the anammox process include (1) significant reduction in nitrification oxygen requirement because only one-half of the influent nitrogen needs to be nitrified, and

only to NO_2^--N; (2) reduction in chemical oxygen demand (COD) or supplemental organic carbon requirement for denitrification; (3) substantial reduction in production of WAS; and (4) elimination of CO_2 emissions that occur during conventional denitrification.

To overcome the slow growth and consequent washout of nitrifiers from high-rate systems, especially at low temperatures, a process named "In-Nitri®" (inexpensive nitrification) has been proposed (U.S. EPA, 2007a). The In-Nitri® process consists of a nitrifying system to exclusively treat sidestreams in treatment plants. Nitrifiers are grown using ammonia from digested sludge, sludge dewatering liquid, or a commercial source. The WAS from this system is fed into the mainstream aeration tank, where NH_4^+-N can be nitrified by the constant supply of nitrifiers. The In-Nitri® process is operated at short SRT and takes advantage of higher ammonia concentrations and temperatures in sidestreams, for example, treatment of warm anaerobic digester supernatant of 30°C to 35°C.

Several new processes have been developed to oxidize ammonia: SHARON (single-reactor high-activity ammonia removal over nitrite); CANON (completely autotrophic nitrogen removal over nitrite); and OLAND (oxygen-limited autotrophic nitrification-denitrification). In the SHARON process, ammonia is oxidized to nitrite rather than nitrate and denitrified, which saves 25% of the oxygen requirement for nitrification and 40% of the external carbon (as methanol) in denitrification, as shown in eqs 4.4 and 4.5 (Jung et al., 2007). The key to success of the SHARON process is the elimination of NOB from the system by operating at low SRTs (1–2 days) and high temperatures (>25°C), where AOB out-compete NOB (Paredes et al., 2007; Van Hulle et al., 2005):

$$NH_4^+ + 1.5\ O_2 + 2\ HCO_3^- \rightarrow NO_2^- + 2\ CO_2 + 3\ H_2O \tag{4.4}$$

$$6\ NO_2^- + 3\ CH_3OH + 3\ CO_2 \rightarrow 3\ N_2 + 6\ HCO_3^- + 3\ H_2O \tag{4.5}$$

The CANON process is completely autotrophic and does not require organic carbon for denitrification (Third et al., 2001). In this process, ammonium is first converted to nitrite under aerobic conditions, and then the nitrite is converted to nitrogen gas in the absence of oxygen (eq 4.6). In the OLAND process, AOB are able to convert ammonia to nitrogen gas under oxygen-limited conditions in a single reactor (eq 4.7) (Kuai and Verstraete, 1998).

$$NH_3 + 0.85O_2 \rightarrow 0.11NO_3^- + 0.44N_2 + 0.14H^+ + 1.43H_2O \tag{4.6}$$

$$2NH_4^+ + 1.5O_2 \rightarrow N_2 + 3H_2O + 2H^+ \tag{4.7}$$

Anammox, SHARON, CANON, and OLAND processes are suitable for treating wastewaters with high ammonia concentrations (e.g., leachate from landfills, anaerobic digestion dewatering liquors), typically operating at warm temperature (>25°C). The flow rate of supernatant from digesters is relatively small; however, it can contribute 10% to 20% of the total nitrogen load to the treatment plant in a BNR system. In other words, in a conventionally operated activated sludge plant (without BNR), the recycle from the digesters can increase effluent ammonia-nitrogen by 50% or more. This stream is an ideal source to implement novel nitrogen removal processes. Additional details on sidestream nitrogen removal are presented in Chapter 9.

3.2 Stoichiometry

The first step of ammonia-oxidation to nitrite-nitrogen in the overall nitrification process can be written as follows:

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2\ H^+ + H_2O \tag{4.8}$$

This is an energy reaction and does not include the production of cell mass. The nitrite produced is then oxidized as follows:

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^- \tag{4.9}$$

The overall energy reaction can be written by summing the above two equations:

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O \tag{4.10}$$

Based on the stoichiometry of the overall energy reaction, 2 moles of oxygen are required to oxidize 1 mole of nitrogen to nitrate, which is equivalent to 4.57 g O_2/g NH_4^+-N oxidized. It should be noted that these reactions do not take biosynthesis into account, and additional equations that include biosynthesis are provided in Chapter 5.

3.3 Kinetics

AOB typically grow slower than NOB, making the first step in nitrification as the rate-limiting step. In the past, kinetics of nitrification was modeled in a single step (NH_4^+-N $\rightarrow$ NO_3^--N). Recent research suggests, however, that this is not appropriate, and modeling of individual oxidation reactions in two steps is necessary (Chandran and Smets, 2000). At higher temperatures (25–35°C) and low SRTs (1–2 days), AOB indeed grow faster than NOB. As a result, NOB are washed out of the system and

only the first step of nitrification can be accomplished, which is exploited in the SHARON process.

3.4 Toxicity

Nitrifiers are less robust than heterotrophs, and their performance is sensitive to several heavy metals and synthetic organic chemicals, as summarized in Table 4.2.

Table 4.2 Organic compounds and heavy metals reported as inhibitory to nitrification (Blum and Speece, 1991; Christensen and Harremoës, 1977; Hockenbury and Grady, 1977; Martin et al., 2005; Painter, 1970; Payne, 1973; Richardson, 1985; Sharma and Ahlert, 1977).

Name	mg/L
Acetone	2000
Acid black dye 1 (AB1)	24
Allyl alcohol	19.5
Allyl chloride	180
Allyl isothiocyanate	1.9
Allyl thiourea	1.2
AM (2-amino-4-chloro-6-methylprimidine)	50
Amino acids	1–1000
Aminoethanol	12.2
Aminoguanidine	74.0
2-Aminophenol	0.27
4-Aminophinol	0.07
Aminopropiophenone	43
Aminotriazole	70.0
Ammonium	1000
Aniline	7.7
1-Arginine	1.7
Benzene	13.0
Benzidine dihydrochloride	50.0

(*continued*)

TABLE 4.2 Continued

Name	mg/L
Benzocaine	100
Benzothiazzole disulphide	38.0
Benzylamine	100
Benzyldimethyldodecylammonium chloride	2.0
Benzylthiuronium chloride	40.0
2.2′ Bipyridine	10.0
Bisphenol A	100
Bromodichloropropane	84.0
2-Bromophenol	0.35
4-Bromophenol	0.83
n-Butanol	8200
Cadmium	14.3
Carbamate	2
Carbon disulphide	35.0
Chlorine	1
Chlorobenzene	0.71, 500
Chloroform	18.0
2-Chloronaphthol	14.3
2-Chlorophenol	2.70
3-Chlorophenol	0.20
4-Chlorophenol	0.73
5-Chloro 1-pentyne	0.59
2-Chloro-6-trichloromethyl-pyridine	11.0
Chromium (III)	10
Copper	230
m-Cresol	01.–100
o-Cresol	11.4
p-Cresol	12.8
Cyanide	16.5

TABLE 4.2 Continued

Name	mg/L
Cyclohexylamine	0.500
Di-allyl ether	100
1,2-Dibromoethane	50.0
Dibromethane	60
1,2-Dichlorobenzene	100
1,1-Dichloroethane	0.91
2,4-Dichloroethane	0.79
1,5-Dichloropentane	13.00
2,3-Dichlorophenol	0.42
2,3-Dichlorophenol	0.61
2,6-Dichlorophenol	8.10
3,5-Dichlorophenol	3.00
1,3-Dichloropropene	0.67
1,3-Dichloropropene	0.48
Dicyandiamide	250
Dicyclohexylcarbodiimide	10.0
Diethyl dithiothiosemicarbazide	0.1
Diguanide	50.0
Dimethylgloxime	140
Dimethylhydrazine	19.2
Dimethyl *p*-nitrosoaniline	19.0
Dimethyl *p*-nitrosoaniline	30
2,4-Dinitrophenol	37.0
Diphenylthiocarbazone	7.5
Dithio-oxamide	1
Dodecylamine	<1
Erythromycin	50.0
Ethanol	2400

(*continued*)

TABLE 4.2 Continued

Name	mg/L
Ethanolamine	100
Ethyl acetate	18
Ethylenediamine	100
Ethyl urethane	1000
Ethyl xanthate	10
Flavonoids	0.01
Guanidine	4.7
Hexamethylene diamine	85
Histidine	5
Hydrazine	58.0
Hydrazine sulfate	200
Hydrogen sulfide	50
8-Hydroxyquiniline mercaptobenzothiazole	1
Lauryl benzenesulphonate	118
Lead	0.500
1-Lysine	4.0
Mercaptobenzothiazole	3
Methanol	160
Methionine	9.0
n-Methylaniline	<1
Methylhydrazine	12.3
Methyl isothiocyanate	0.800
Methyl mercaptan	300
Methyl pyridines	100
2-Methylpyridine	100
4-Methylpyridine	100
Methylthiourea	0.455
Methyl thiuronium sulfate	1
Methylamine hydrochloride	100

TABLE 4.2 Continued

Name	mg/L
Methylene blue	30
Monethanolamine	>200
N-serve	10
Napthylethylenediamine dihydrochloride	23
Nickel	5.0
Ninhydrin	10.0
p-Nitroaniline	10.0
p-Nitrobenzaldehyde	50.0
Nitrobenzene	50.0
4-Nitrophenol	2.60
2-Nitrophenol	11.00
2-Nitrophenol	50.0
Nitrourea	1.0
Panthothenic acid	50
Pentachloroethane	7.90
Perchloroethylene phenol	5.6
Phenolics (substituted)	100
Phenolic acids	0.01
p-Phenylazoaniline	100
Potassium chromate	800
Potassium chlorate	2500
Potassium dichromate	6.0
Potassium thiocyanate	300
n-Propanol	20.0
Purines	50
Pyridine	10.0
Primidines	50
Pyruvate	400
Resurcinol	7.80

(*continued*)

Table 4.2 Continued

Name	mg/L
Skatole	7.0
Sodium azide	23.0
Sodium azide	20
Sodium arsenite	2000
Sodium chloride	35 000
Sodium cyanate	100
Sodium cyanide	1
Sodium dimethyl dithiocarbamate	13.6
Sodium methyl dithiocarbamate	0.90
Sodium pluoride	1218
Sodium methyldithiocarbamate	1
ST (sulfathiazole)	50
Strychnine	100
Sulphides	5.0
Tannin	0.01
Tetrabromobisphenol	100
1,2,3,4-Tetrachlorobenzene	20.0
1,2,4,5-Tetrachlorobenzene	9.80
1,1,1,2-Tetrachloroethane	8.70
1,1,2,2-Tetrachloroethene	1.40
12,3,5,6-Tetrachlorophenol	1.30
Tetramethylammonium chloride	2200
Tetramethyl thiuram disulfide	5
Thiamine	0.530
Thioacetamide	500
Thiocyanates	0.180
Thiosemicarbazide (Aminothiourea)	0.760
Thiourea	1
Thiourea (substituted)	3.6

Table 4.2 Continued

Name	mg/L
1 -Threonine	5
Threonine	50.0
2,4,6-Tribromophenol	7.70
2,4,6-Tribromophenol	50
2,4,6-Tribromophenol	2.5
2,2,2-Trichloroethanol	2.00
1,1,2-Trichloroethane	1.90
Trichloroethylene	0.81
Trichlorophenol	100
2,3,5-Trichlorophenol	3.90
2,3,6-Trichlorophenol	0.42
2,4,6-Trichlorophenol	7.90
Triethylamine	100
Trimethylamine	118
2,4,6-Trimethylphenol	30.0
1-Valine	1.8
Vitamins riboflavin, A-lipolic acid, B-pyridoxine HCL	50
Zinc	11.0

The effects of the substances can be either inhibitory or fatal depending on the compound, its concentration, the duration of exposure, and other environmental conditions in the nitrification reactor. Special mention should be made of the inhibitory effect of gaseous (free or unionized) ammonia [$NH_3(g)$] and unionized nitrous acid (HNO_2). *Nitrosomonas* and *Nitrobacter* are inhibited by free ammonia (150 mg/L) and nitrous acid (Anthonisen et al., 1976; Turk and Mavinic, 1986). Table 4.3 summarizes the range of ammonium and nitrite concentrations that may inhibit nitrification. *Nitrobacter* appears to be more sensitive to free ammonia than *Nitrosomonas*. Turk and Mavinic (1986) found that nitrite oxidation was inhibited at 0.1 to 1.0 mg/L $NH_3(g)$-N (free ammonia) and that ammonia oxidation was inhibited at 5 to

Table 4.3 Ammonium-nitrogen and nitrate-nitrogen concentration range for *Nitrobacter* inhibition as a function of pH (T = 20°C) (reprinted from *Water Science and Technology*, Vol. 25, Randall, C. W. et al., Nitrification Kinetics in Single-Sludge Biological Nutrient Removal Activated Sludge Systems, p. 195, Copyright 1992, with permission from the copyright holders, IWA Publishing).

pH	NH_4^+–N (mg/L)	NO_2^-–N (mg/L)
6.0	210–2100	30–330
6.5	70–700	88–1050
7.0	20–210	260–3320
7.5	7–70	
8.0	2–20	

20.0 mg/L NH_3(g)-N. Ford et al. (1980) found that nitrite oxidation was inhibited at 10 to 150 mg/L NH_3(g)-N.

At low pH, ammonia oxidation is more sensitive to nitrite than nitrite oxidation. Inhibition by nitrite at low pH is likely caused by the presence of free nitrous acid (Beccari et al., 1979). Turk and Mavinic (1986) also found that nitrite-nitrogen levels as high as 100 mg/L caused no discernible inhibition to the treatment process. The conclusion again is that free nitrous acid, rather than nitrite, is likely inhibiting the process.

Alleman (1984) observed elevated nitrite concentration of 27 mg/L in batch nitrification systems and concluded that *Nitrobacter* is more susceptible than *Nitrosomonas* to environmental stresses. He (1984) proposed that reduced temperature, limited oxygen and carbon dioxide, elevated pH, presence of free ammonia, and excess solids wasting reduce *Nitrobacter* growth and nitrite oxidation. He also reported that shock ammonium loading and reduction of nitrate induce nitrite accumulation. Shock loads of ammonium can cause nitrite accumulation because *Nitrosomonas* can adapt its population more quickly than *Nitrobacter*. Mines (1983) observed nitrite concentrations ranging from 19 to 210 mg N/L at free ammonia concentration from 9.5 to 73 mg/L in continuous-flow studies treating high-strength nitrogenous wastewater. Tanaka and Dunn (1982) found that oxygen concentrations approaching zero led to nitrite concentrations of 36 mg/L in a laboratory-scale fixed-film batch nitrification system. They also found that when the dissolved oxygen concentrations increased, the nitrite levels decreased to below 10.0 mg/L.

Salinity can affect nitrification rates. Panswad and Anan (1999) reported a decrease in specific ammonia-nitrogen uptake rate (SAUR) of nitrifying sludge acclimated to varying levels of NaCl. They operated BNR systems acclimated to 0 to 30 g/L of NaCl. After dosing the systems with 70 g/L of NaCl for four days, they observed the SAUR. For sludge not acclimated to NaCl, SAUR dropped from 4.76 to 0.48 mg NH_4^+-N/g MLSS·h within three days. After recovery, SAUR came back up to 4.33 mg NH_4^+-N/g MLSS·h. Sludge acclimated to 30 g/L of NaCl showed a decrease in SAUR from 2.14 to 1.02 mg NH_4^+-N/g MLSS·h but recovered to 2.13 mg NH_4^+-N/g MLSS·h. Sludge acclimated to 5 and 10 g/L NaCl recovered to better SAURs than before the shock. This suggests that nitrifiers are affected by salinity but are capable of recovering from the salinity shock. A summary of salt effects on nitrification is presented in Table 4.4 (Paredes et al., 2007).

Inorganic substances such as cadmium, chromium, cyanide, arsenic, fluoride, nickel, and zinc can lead to nitrification inhibition (Fox et al., 2006; Hu et al., 2002, 2003). Fox et al. (2006) concluded that significant inhibition occurred at 10 mg/L of Zn, whereas complete inhibition occurred at 50 mg/L of Zn. In the same study, only slight inhibition was observed at 1 mg/L of Zn. Hu et al. (2002) found that free cation concentration of nickel and cadmium, and not the total aqueous concentration of the metal, correlated with nitrification inhibition. In addition, it was observed that the addition of chelating agent such as ethylenediamine tetraacetate reduced the inhibitory effect. Excessive use of chelating agents, however, can be inhibitory. Therefore, care needs to be exercised in the selection of chelating agent concentration. Typically, the free ion concentration in activated sludge processes is reduced because of production of exocellular polymers, which bind some of the metals, reducing the overall inhibition capacity of the metals. Hu et al. (2003) investigated the impact of copper, cadmium, nickel, and zinc on nitrification. The objectives of this study were to (1) evaluate the relationship between metal partitioning and metal inhibition for a mixed nitrifying consortium; (2) determine metal internalization kinetics after transient exposure of metals; and (3) develop a mathematical model to describe nitrification inhibition that captures both metal transport and biological toxicity effects. The results of this study indicated that in short-term batch assays (approximately one hour), the specific ammonium oxidation rate decreased as the applied metal dose to nitrifying biomass increased for all metals. The metal molar inhibitory effect toward ammonium oxidation was cation-specific and followed Cu^{2+} Zn^{2+} > Cd^{2+} > Ni^{2+}. It also was observed that nitrification inhibition increased with exposure time; however, sorbed metal concentrations were not good predictors of the effect of metal on

TABLE 4.4 Effect of salt on nitrification (adapted from Paredes et al., 2007).

System examined	Salinity	Observed effect	Reference
Activated sludge	10% sea water	No effect on nitrogen removal	Abughararah and Sherrard, 1993
	70 g NaCl/L	55% Inhibition on nitrification recovery when salt concentration reduced	Panswad and Anan, 1999
	70 g NaCl/L	30% Inhibition on nitrification with salt acclimated sludge	Panswad and Anan, 1999
SBR	78 g NaCl/L	No inhibition for acclimated sludge	Dahl et al., 1997
	40 g Cl^-/L	Inhibition of AOB and NOB	Moussa et al., 2006
Salt adapted sludge in fluidized bed reactor	33 g NaCl/L	Stable nitrification	Vredenbregt et al., 1997
	56 g NaCl/L	Stable ammonium oxidation and nitrite accumulation when a carrier material was used	Vredenbregt et al., 1997
Salt acclimated nitrifying activated sludge	13.7 g NaCl/L 19.9 g $NaNO_3$/L 8.30 g Na_2SO_4/L	100% Full nitrification with applied loads between 1 and 4 g NH_4^+-N/L Higher salt concentration caused ammonium (10%) and nitrite (20%) accumulation	Campos et al., 2002
SHARON reactor (35°C)	12 g NaCl/L	Nitrite accumulation increased 30% with salt addition	Mosquera-Corral et al., 2005
	< 50 g NaCl/L	Stable partial nitrification	Mosquera-Corral et al., 2005

AOB = ammonia oxidizing bacteria; NOB = nitrite oxidizing bacteria and SBR = sequencing batch reactor.

nitrification kinetics. On the contrary, inhibition of ammonium oxidation kinetics correlated well with the intracellular Zn, Ni, and Cd concentrations. The results for copper, however, showed no direct correlation between intracellular or sorbed concentrations and nitrification inhibition. Copper is characterized by high complexation potential, high degree of partitioning to nitrifying biomass, and fast internalization kinetics. It was suggested that the difference in physicochemical behavior of copper compared to other metals studied is because of different biological response. The precise method of copper inhibition on nitrification was not understood, and further research is needed to better understand the mode of copper toxicity or inhibition to ammonia oxidation.

3.5 Biofilm Systems

In addition to suspended-growth systems, a variety of attached-growth or fixed-film systems are used to nitrify domestic and industrial wastewater. In these systems, biomass is attached to solid support media contained within a reaction vessel. The wastewater to be treated is brought in contact with the biofilm, where the local mixing and turbulence determine the transfer of nutrients to the biofilm. The growth of biofilm needs to be balanced from excessive detachment to avoid clogging the reactor while maintaining activity within the bioreactor (Henze et al., 2008). Although the kinetic (growth and oxidation) relationships used in the design of suspended-growth reactors are still valid, the design of attached-growth systems is complicated by mass-transfer limitations of substrate within the biofilm system. The biofilm system can be described by four components consisting of bulk liquid, boundary layer, biofilm, and substratum, as shown in Figure 4.1 (Eberl et al., 2006). In the past, the design of fixed-film processes was mainly based on empirical data derived from pilot or full-scale system; however, recent advances in biofilm modeling has made these models available in commercial process simulators to facilitate design of fixed-film processes (Eberl et al., 2006). Many different types of media (shape, size, and material of construction) are available commercially, and the choice depends on reactor design. Factors that should be considered in the selection of media include specific surface area, density, material of construction, attrition resistance, and suitability for biofilm attachment (Lazarova and Manem, 2000). The larger media have more void spaces and reduced risk of clogging but have lower specific surface area, increasing the overall size of the reactor volume. Smaller-size media are characterized by higher specific surface area, higher risk of clogging, and smaller reactor volume. A balance must be struck between the potential for clogging and reactor size for a given

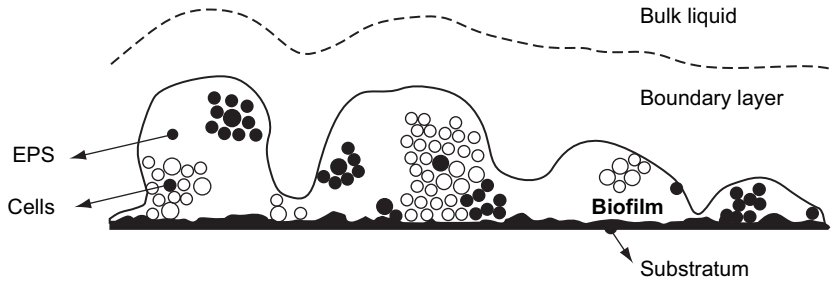

FIGURE 4.1 Four compartments typically defined in a biofilm system: bulk liquid, boundary layer, biofilm, and substratum, where EPS is the extracellular polymeric substance (Eberl et al., 2006).

application. Other features that should be considered in the design of fixed-film reactors include aeration, flow distribution, biofilm control, and solids removal.

In fixed-film nitrification reactors, the competition or interactions between heterotrophic and autotrophic bacteria may be more important than in suspended-growth systems. The presence of significant amounts of organic substrate in the fixed-film reactor can allow the heterotrophic biomass to overwhelm the autotrophs and effectively prevent their growth until the carbon substrate concentration in the bulk liquid is reduced to approximately 20 mg/L or less soluble biochemical oxygen demand ($sBOD_5$) (Boller et al., 1994). Boller et al. (1994) presented an overview of the important parameters that affect nitrification.

Mass transfer of nutrients and competition for dissolved oxygen between heterotrophic and autotrophic bacteria becomes more critical in attached-growth systems. The concentration of substrates such as ammonia-nitrogen and dissolved oxygen within the biofilm and external liquid layer can be significantly lower than in the bulk liquid because of transport limitations. Low concentrations within the biofilm can result in lower rates of nitrification. A diffusion-reaction model that considers both external (liquid film) and internal (biofilm) mass-transfer resistances can be used to accurately describe the processes occurring in biofilms. Previously, it was understood that the external (liquid film) mass-transfer resistance is negligible in comparison to the internal resistance. More recent work, however, suggests that the mass-transfer within the external liquid layer or the boundary shown in Figure 4.1 is equally important to the process (Eberl et al., 2006).

Traditional examples of attached-growth systems include trickling filters, rotating biological contactors, submerged packed-bed reactors, and fluidized bed reactors. Immobilized cells or high-biomass processes also rely significantly on attached-growth biomass. Trickling filters, in which 5- to 20-cm rocks or plastic material are used as static support media, are one of the oldest type of biofilm reactors. The height of the tricking filter may range from 1 to 3 m for rock media and 4 to 12 m when using plastic media (Henze et al., 2008). Typically, attached-growth systems tend to be more resistant to shock loads. When the reactors are enclosed, they are also protected from excess loss in temperature aiding the process. An additional advantage of attached-growth systems is that there is no need for sludge recirculation to maintain the necessary biomass for treatment because the biomass is attached to the solid support in the reactor. From a practical design viewpoint, this means process efficiency is not dependent on the settleability of the biomass, unlike for suspended-growth systems. Short detention times in some of the fixed-film reactors, however, may result in breakthrough of ammonium-nitrogen at peak flows. As with suspended-growth systems, nitrification may be accomplished in a separate unit process or in combination with carbonaceous removal in a single reactor.

During the past decade, the effluent ammonia-nitrogen limits have become more stringent. As a result, many existing plants have been upgraded with the addition of synthetic media to increase nitrification capacity of the system. These integrated fixed-film activated sludge (IFAS) systems are hybrid reactors that use synthetic media completely submerged into water (either fixed in the aeration tank or suspended in the mixed liquor) and recycle sludge from the secondary clarifier. When sludge is not recycled, which is typically the case for separate-stage nitrification processes, suspended media are used in moving bed biological reactors (MBBRs). These systems allow growth and retention of additional biomass in the reactor without the need for an increase in clarification capacity of the system. The additional biomass results in higher SRT, improving carbon removal and nitrification rates. A similar concept is used in a biological aerated filter. The biological aerated filter system provides both biological treatment and solids filtration. In a submerged aerated filter, rigid, corrugated, structured polypropylene media are installed in an aeration tank to provide a high surface area for biomass attachment (500–1150 m^2/m^3 or 150–350 sq ft/cu ft). The media are arranged into cells-in-series in which effluent is contacted with the fully submerged media in the presence of co-current aeration.

4.0 DENITRIFICATION

Denitrification or reduction of nitrate to nitrogen gas under anoxic conditions depends on nitrate being produced in the nitrification process under aerobic conditions. For total nitrogen removal, first nitrification and then denitrification should occur efficiently to achieve the desired effluent quality. Nitrification requires aerobic conditions and consumes alkalinity. Denitrification does not require aerobic conditions and generates NO_3-N as the alternate electron acceptor, which reduces the overall oxygen requirement of the process. Denitrification also returns part of the alkalinity consumed during nitrification. Thus, where feasible, denitrification should be incorporated to reduce total energy footprint and external alkalinity addition. The potential disadvantage is the cost of adding external carbon (e.g., methanol) when wastewater does not contain sufficient amounts of readily biodegradable carbon to meet the effluent total nitrogen limits.

4.1 Biochemistry and Microbiology

Most denitrifiers are facultative, which means that they can use either oxygen or oxidized nitrogen (NO_2^--N or NO_3^--N) as the terminal electron acceptor in respiration. The use of oxygen as the electron acceptor is called "aerobic respiration," and the use of nitrate or nitrite as electron acceptor is termed "anoxic respiration." These microorganisms use similar metabolic pathways. A major difference between aerobic respiration and anoxic respiration is the enzyme catalyzing the final electron transfer occurring in the electron transport chain. Oxygen must be excluded to promote dissimulatory denitrification, which is the process in which nitrate is used as an alternative electron acceptor (Madigan et al., 1997). If both oxygen and nitrate are present, then microorganisms preferentially use oxygen as the terminal electron acceptor because it yields more energy than nitrate or nitrite. There are several advantages of removing wastewater COD through denitrification: (1) reduction in aeration requirement for the process; (2) a slight reduction in the overall sludge production as biomass yield in anoxic conditions is less than the yield in aerobic conditions; (3) recovery of alkalinity; (4) effluent with low nitrates, which reduces negative effects on the receiving water; and (5) a reduction in filaments thus better settling solids.

Microorganisms require nitrogen for protein synthesis. The preferred source of nitrogen is NH_4^+-N because this form is used directly in synthesis. Nevertheless, if sufficient NH_4^+-N is unavailable, some microorganisms can reduce nitrate to ammonium (Gayle and Benoit, 1989). This process is referred to as "assimilatory nitrate

reduction" ($NO_3^- \rightarrow NO_2^- \rightarrow NH_2OH \rightarrow$ organic nitrogen), indicating that nitrogen is incorporated to the cell. This reaction can proceed successfully even under aerobic conditions (Madigan et al., 1997). It is, therefore, distinguished from dissimulatory nitrate reduction (denitrification), which is a respiratory process whereby the microorganism obtains energy. Four steps are involved in dissimulatory biological denitrification (Grady and Lim, 1980):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO\ (g) \rightarrow N_2O\ (g) \rightarrow N_2\ (g) \tag{4.11}$$

The NO_2^-, NO, and N_2O are intermediates in the process. Each step involves a particular reductase enzyme that catalyzes the transfer of electrons to nitrogen. Nitrate reductase, a molybdenum-containing enzyme, converts NO_3^- to NO_2^-, and nitrite reductase catalyzes the conversion of nitrite NO_2^- to NO. Nitric oxide reductase converts NO to N_2O, and in the final step, nitrous oxide reductase produces gaseous nitrogen. The NO and N_2O are both nonionic gaseous forms of nitrogen, and N_2O is especially important in that it is a significant greenhouse gas released from wastewater treatment.

The electrons originate from the substrate, that is, the electron donor. Either inorganic (e.g., hydrogen or sulfur) or organic waste compounds can serve as substrate for denitrification. As a result of denitrification, the electron donor is oxidized while nitrate is reduced. In addition to organic material present in the wastewater, external carbon sources frequently are used to provide a source of electron donors for denitrification. The possible electron transport system of the dissimulatory denitrification is:

$$\begin{aligned} e^- \text{ Donor} \rightarrow \text{NAD} \rightarrow \text{FAD} \rightarrow \text{Quinone} \rightarrow \text{Cytochrome} \\ \rightarrow \text{Nitratereductase} \rightarrow NO_3^- \end{aligned} \tag{4.12}$$

where NAD is nicotineamide adenine dinucleotide and FAD is flavin adenine dinucleotide.

At least 14 bacterial genera are known to contain denitrifying species (Drysdale et al., 1999; Gayle and Benoit, 1989). These include *Bacillus*, *Pseudomonas*, *Methanomonas*, *Paracoccus*, *Spirillum*, and *Thiobacillus*. Denitrification can be accomplished by both heterotrophic and autotrophic organisms (Zumft, 1997). Most of the denitrifying bacteria are heterotrophic, however, meaning that they use carbon from organic compounds for cell synthesis and energy. There are relatively few species of autotrophic denitrifying bacteria, which obtain carbon for cell synthesis from inorganic compounds. One example is *Thiobacillus denitrificans*. This organism oxidizes elemental

sulfur for energy and obtains carbon for cell biosynthesis from dissolved carbon dioxide or bicarbonate (HCO_3^-).

Denitrification can be accomplished using the carbon from influent organics by creating an anoxic zone or separate anoxic reactor at the head end of the process and recycling nitrified mixed liquor into it. This process often is called "preanoxic denitrification." In postanoxic denitrification, an external carbon source can be added to the mixed liquor after the ammonia in the wastewater has been oxidized to nitrate or endogenous respiration is used to reduce the nitrates. When very low total nitrogen levels are desired in the final effluent, a combination of pre- and postanoxic gentrification is often used. External carbon sources include methanol, acetate, ethanol, sugar, butanol, corn syrup, molasses, methane, and industrial wastes such as from food processing, breweries, and biodiesel. The advantage of using methanol over other sources in wastewater is that it is free of contaminants such as nitrogen and phosphorus, has the lowest cost, and can lead to improved process control and operation. The disadvantage of using methanol intermittently appears to be the initial lag period (several days to weeks) for the growth of methanol using denitrifiers (Ginige et al., 2004; Hallin and Pell, 1998; Hallin et al., 1996; Nyberg et al., 1992; Purtschert et al., 1996). The other disadvantage of using methanol is that unlike acetate it cannot be used by the phosphorus accumulating organisms in enhanced biological phosphorus removal when both nitrogen and phosphorus removal are desired (deBarbadillo et al., 2008).

SND can occur in systems operated at low dissolved oxygen concentrations in the bulk mixed liquor. At the outer periphery of the bioflocs, dissolved oxygen is available for heterotrophs for carbon removal and nitrifiers for nitrification. Inside the floc, however, dissolved oxygen may not penetrate and anoxic conditions can exist, leading to denitrification and to SND within the aerobic environment. Under these conditions, potentially, neither nitrification nor denitrification may proceed at optimum rates, as low dissolved oxygen can slow down nitrification and the presence of dissolved oxygen can inhibit denitrification.

In the SHARON process, NH_4^+-N is oxidized to NO_2^--N in a chemostat reactor (no recycle, SRT = hydraulic retention time) and the NO_2^--N is reduced to nitrogen gas by adding a carbon source under anoxic conditions. The net result of this process is a reduction in theoretical oxygen requirement as NO_2^--N is not oxidized to NO_3^--N. There is also a reduction in external carbon source requirement because the reduction step from NO_3^--N to NO_2^--N is eliminated. As discussed earlier, denitrification

can also occur in the anammox process where ammonium provides electrons for the denitrification of nitrite to nitrogen gas:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \tag{4.13}$$

4.2 Stoichiometry

The stoichiometric equations for denitrification depend on the carbon substrate and the source of nitrogen. The energy equations using wastewater and methanol as the carbon substrates and nitrate as the terminal electron acceptor can be written as follows:

$$\text{Wastewater: } 10\ NO_3^- + C_{10}H_{19}O_3N \rightarrow 5\ N_2 + 10\ CO_2 + 3\ H_2O + NH_3 + 10\ OH^- \tag{4.14}$$

$$\text{Methanol: } 6\ NO_3^- + 5\ CH_3OH \rightarrow 3\ N_2 + 5\ CO_2 + 7\ H_2O + 6\ OH^- \tag{4.15}$$

The hydroxide ion formed during denitrification reacts with carbon dioxide in the water to create bicarbonate ions according to the following equation:

$$OH^- + CO_2 \rightarrow HCO_3^- \tag{4.16}$$

The oxidation–reduction half reactions using oxygen, NO_2^--N, and NO_3^--N as electron acceptors can be expressed as follows:

$$0.25\ O_2 + H^+ + e^- \rightarrow 0.5\ H_2O \tag{4.17}$$

$$0.33\ NO_2^- + 1.33\ H^+ + e^- \rightarrow 0.17\ N_2 + 0.67\ H_2O \tag{4.18}$$

$$0.20\ NO_3^- + 1.2\ H^+ + e^- \rightarrow 0.1\ N_2 + 0.6\ H_2O \tag{4.19}$$

The significance of the conversion of nitrate to nitrogen gas is that the overall process oxygen demand is reduced by 2.86 g oxygen/g NO_3^--N reduced [(0.25 × 32)/(0.20 × 14)]. When nitrite is converted to nitrogen gas, oxygen demand is reduced by 1.73 g oxygen/g NO_2^--N reduced [(0.25 × 32)/(0.33 × 14)]. Also, for each equivalent of NO_3^--N reduced, one equivalent of alkalinity is produced, which is equivalent to 3.57 g of alkalinity as $CaCO_3$/g NO_3^--N reduced. The stoichiometric relationships for frequently used carbon sources are presented below (Sorensen and Jorgensen, 1993):

$$\text{Acetic acid: } 5\ CH_3COOH + 8\ NO_3^- \rightarrow 4\ N_2 + 10\ CO_2 + 6\ H_2O + 8\ OH^- \tag{4.20}$$

$$\text{Dextrose: } 0.208\ C_6H_{12}O_6 + NO_3^- \rightarrow 0.5\ N_2 + 1.25\ CO_2 + 0.75\ H_2O \tag{4.21}$$

Ethanol: $5\ C_2H_5OH + 12\ NO_3^- \rightarrow 6\ N_2 + 10\ CO_2 + 9\ H_2O + 12\ OH^-$ (4.22)

Glycol: $0.50\ (CH_2OH)_2 + NO_3^- \rightarrow 0.5\ N_2 + CO_2 + H_2O + OH^-$ (4.23)

Formaldehyde: $1.25\ HCHO + NO_3^- \rightarrow 0.5\ N_2 + 1.25\ CO2 + 0.75\ H_2O + OH^-$ (4.24)

Isoproponol: $0.278\ C_3H_7OH + NO_3^- \rightarrow 0.5\ N_2 + 0.833\ CO_2 + 0.5\ H_2O + OH^-$ (4.25)

Fusel oil (amyl alcohol): $0.167\ C_5H_{11}OH + NO_3^- \rightarrow 0.5\ N_2 + 0.833\ CO_2 + 0.5\ H_2O + OH^-$ (4.26)

Methane: $8\ NO_3^- + 5\ CH_4 \rightarrow 4\ N_2 + 5\ CO_2 + 6\ H_2O + 8\ OH^-$ (4.27)

As with nitrification, the inclusion of biosynthesis changes the stoichiometry. The overall result is an increase in the electron donor (carbon substrate) required per unit mass of nitrate or nitrite reduced.

4.3 Substrate Requirements

Several factors influence substrate consumption in biological denitrification. The first factor is the concentration levels of the electron acceptors present, including nitrate, nitrite, dissolved oxygen, and sulfate (SO_4^{2-}). Most of the dissolved oxygen present must be reduced before denitrification can proceed. Nitrate and nitrite compete on approximately an equal basis for electrons from the substrate. Sulfate can be reduced biologically, but only after almost all the dissolved oxygen, nitrate, and nitrite have been consumed. Hence, nearly complete denitrification can be obtained without appreciable sulfate reduction.

A second factor affecting electron donor requirements is the nature of the donor molecule. Organic compounds are used by bacteria as the source of electrons for energy metabolism, as well as the source of carbon for cell biosynthesis. Inorganic compounds such as molecular hydrogen and sulfur only supply electrons for energy metabolism.

A third factor that affects electron donor requirements is the extent of the denitrification reaction. A shortage of electron donor can cause the conversions depicted in eq 4.15 to stop before nitrogen gas is produced, so that the quantity of NO_3^--N removed exceeds the quantity of nitrogen gas produced. The electron donor requirement, expressed in terms of the mass of substrate consumed per unit mass of NO_3^--N removed, will then vary directly with the percentage removal of nitrate, up to the point of complete conversion. The total concentration of substrate (as methanol)

required to reduce the nitrate, nitrite, and dissolved oxygen present without biosynthesis (C_m) is (McCarty et al., 1969):

$$C_m = 2.47\ NO_3\text{-}N + 1.53\ NO_2\text{-}N + 0.87\ DO \tag{4.28}$$

Where,

C_m = methanol required (mg/L);
NO_3-N = initial nitrate nitrogen concentration (mg/L);
NO_2-N = initial nitrite nitrogen concentration (mg/L); and
DO = dissolved oxygen concentration (mg/L).

Another parameter for evaluating substrate requirements (including the carbon required for growth) is the substrate consumption ratio (SCR) presented below:

$$SCR = \frac{\Delta C}{\Delta NO_{3eq} - N} \tag{4.29}$$

Where,

ΔC = corresponding change in substrate concentration expressed as (g COD/m^3); and
ΔNO_{3eq}-N = equivalent nitrate concentration consumed, based on:

$$(g\ NO_3eq\text{-}N/m^3) \tag{4.30}$$

The oxygen equivalent of the substrate required (COD) can be calculated using the following equation (Metcalf and Eddy, 2003):

$$g\ bsCOD/g\ NO_3^-\text{-}N = 2.86/(1–1.42Y_{obs}) \tag{4.31}$$

Where,

bsCOD = biodegradable soluble COD (g/d); and
Y_{obs} = net biomass yield (g biomass volatile suspended solids [VSS] produced/g bsCOD removed).

The SCR of methanol varies from 3.2 to 6.0 g COD/g NO_{3eq}-N. Substrate consumption ratios reported by Monteith et al. (1980) for industrial organic wastes ranged from 2.2 to 10.2 g COD/g NO_{3eq}-N. Typically, a carbon-to-nitrogen ratio (C/N) of 1.5 to 5 may be required for denitrification to occur effectively. A C/N greater than 4 may be required, however, to obtain more than 95% nitrate removal in municipal wastewater treatment systems. Table 4.5 presents a range of C/N optimal for different carbon substrates (Sorensen and Jorgensen, 1993). Table 4.6 presents information on supplemental carbon sources used for denitrification (deBarbadillo et al., 2008).

Table 4.5 Carbon-to-nitrogen ratio for different carbon sources for denitrification (adapted from Sorensen and Jorgensen, 1993).

Organic substrate	C/N optimum	Unit
As internal source	3.0–3.50	kg BOD_5/kg N
	4.0–5.0	kg COD/kg N
In sludge	1.5–2.5	kg BOD_5/kg N
	2.9–3.2	kg COD/kg N
Methanol	2.3–2.7	kg MeOH/kg N
	3.5–4.1	kg COD/kg N
Acetic acid	2.9–3.5	kg HAc/kg N
	3.1–3.7	kg COD/kg N

BOD = biochemical oxygen demand and COD = chemical oxygen demand.

Table 4.6 Information on supplemental carbon sources (adapted from DeBarbadillo et al., 2008.).

Carbon source	Chemical formula	Specific gravity	Estimated COD content (mg/L)
Methanol	CH_3OH	0.79	1 188 000
Ethanol	CH_3CH_2OH	0.79	1 649 000
Acetic acid (100% solution)	CH_3COOH	1.05	1 121 000
Acetic acid (20% solution)	CH_3COOH	1.026	219 000
Sugar (sucrose) (50% solution)	$C_{12}H_{22}O_{11}$	1.22	685 000
MicroC™	Proprietary product includes 5% methanol	1.16	630 000
UnicarbDN	Glycerin based	1.09	600 000–1 000 000
Primary sludge Fermentate	VFAs (primarily acetic and propionic acids)	1.0	400–800 soluble COD (depending on elutriant)

COD = chemical oxygen demand and VFA = volatile fatty acid.

4.4 Alkalinity Production

The quantity of base produced by denitrification can be calculated from the following balanced reaction, as modified from McCarty et al. (1969):

$$NO_3^- + 1.08\ CH_3OH = 0.065\ C_5H_7O_2N + 0.47\ N_2 + 0.76\ CO_2 + 1.44\ H_2O + OH^- \quad (4.32)$$

Therefore, 3.57 mg/L of alkalinity are produced per milligram per liter NO_3^--N reduced when NO_3^- is used by the denitrifying bacteria for cell synthesis. This alkalinity production is beneficial to the overall process to reduce the external addition of alkalinity where required.

4.5 Kinetics

The rate of denitrification has been found to vary depending on the type and concentration of compound used as the carbon source. The availability of soluble and readily biodegradable substances results in higher denitrification rates. Denitrification is affected by the dissolved oxygen concentration, pH, temperature, and reactor configuration. Researchers have developed several mathematical models for predicting denitrification rates based on Monod kinetic expression shown below (Henze et al., 1987):

$$r_{v,NO} = \left(\frac{1-Y_H}{2.86\times Y_H}\right)\mu_{mH}\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)\eta_g X_{b,H} \quad (4.33)$$

Where,

$r_{v,NO}$ = denitrification rate (g NO_3-N reduced/m^3·d);
μ_{mH} = maximum specific growth rate for heterotrophs (d^{-1});
η_g = fraction heterotrophs using nitrate for electron acceptor;
$X_{b,h}$ = concentration of heterotrophs (mg/L COD);
S_s = concentration of readily degradable organic substrate (mg/L COD);
K_s = half-saturation coefficient for readily degradable substrate (mg/L COD);
S_O = concentration of dissolved oxygen (mg O_2/L);
$K_{o,hi}$ = half-saturation coefficient for dissolved oxygen in heterotrophic growth (mg O_2/L);
S_{NO} = concentration of nitrate (mg N/L);
K_{NO} = half-saturation coefficient for nitrate (mg N/L); and
Y_H = heterotrophic yield (g biomass COD/g substrate COD).

The values for the biokinetic coefficients for Monod-type expressions are not well defined. Table 4.7 summarizes recommended values from two references. The current

Table 4.7 Monod kinetic coefficients for denitrification (Henze et al., 1986).

Coefficient	Symbol	Typical range	Suggested
Maximum specific growth rate of heterotrophs (per day)	μ_H	3– 3	4.0–6.0
Heterotrophic biomass yield (g cell formed/g COD oxidized)	Y_H	0.46–0.69	0.67
Half-saturation coefficient organic substrate (g COD/m^3)	K_s	10–180	10.20
Half-saturation coefficient nitrate-nitrogen (g NO_3-N/m^3)	K_{NO}	0.06–0.5	0.2–0.5
Correction factor for μ_H under anoxic conditions (dimensionless)	η_g	0.5–1.0	0.8
Half-saturation coefficient for dissolved oxygen for heterotrophic biomass (g O_2/m^3)	$K_{o.H}$	0.10–0.28	0.1–0.2
Mass nitrogen per mass of COD in biomass (g N/g COD in biomass)	$i_{x,B}$	0.06–0.12	0.06–0.086
Decay coefficient for heterotrophic biomass (per day)	b_H		0.05

COD = chemical oxygen demand. Baillod and Boyle, 1970.

practice is to use process-simulation models to design denitrification systems, which in the past were based on empirical rate expressions for a given type of substrate.

Temperature has a significant influence on maximum growth rate of denitrifying population, which can be expressed for methanol using denitrifying bacteria by an Arrhenius equation (Nichols et al., 2007):

$$(\mu_{mH})_T = (\mu_{mH})_{20}\,(\theta)^{(T-20)} \tag{4.34}$$

Where,

$(\mu_{mH})_T$ = maximum specific heterotrophic growth rate at any temperature, T;
$(\mu_{mH})_{20}$ = maximum specific heterotrophic growth rate at 20°C; and
θ (Arrhenius coefficient) = 1.13.

The denitrification rate is strongly affected by the kinetic regime of the reactor. Plug-flow reactors and reactors in series will produce higher denitrification rates when the reaction order is greater than zero. This typically will happen when the availability of substrate limits the denitrification reaction.

Denitrifying bacteria grow well under the conditions typically experienced in wastewater—pH between 7 and 8 and temperature between 5°C and 25°C. The maximum rate of denitrification is temperature-dependent, roughly doubling for every 10°C increase in temperature between 5°C and 25°C. Reported values for the temperature coefficient are given in Table 4.8.

TABLE 4.8 Denitrification temperature coefficients (Sutton et al., 1975).

Θ Values	Substrate	Temperature range, °C	Type of system	Reference
1.09	Methanol	6–25 6–16 10–20	Suspended growth 6-day SRT	Sutton et al., 1975
1.07	Methanol	5–25 5–15 10–20	Upflow packed column	Sutton et al., 1975
1.094	Wastewater (exogenous carbon)	17–25	Suspended growth	Barnard, 1975
1.20	Endogenous (no external carbon)	17–25	Suspended growth	Barnard, 1975
1.12	Methanol	5–27	Laboratory batch	Dawson and Murphy, 1972
1.10		10–20		
1.06		15–25	Batch activated sludge, SRT = 2 days	Stensel, 1970
1.13		10–20	Continuous activated sludge	Stensel, 1970
1.15	Methanol	10–20	Suspended growth, SRT = 7.6	Mulbarger, 1971
		10–20	Activated sludge	Johnson and Vania, 1971
	Wastewater	6–25	Separate sludge	Murphy and Sutton, 1975

(*continued*)

TABLE 4.8 Continued

Θ Values	Substrate	Temperature range, °C	Type of system	Reference
	Wastewater	6–25	Single sludge	Murphy and Sutton, 1975
1.08	Raw and settled wastewater	12–24	Suspended growth (first anoxic; SRT = 10–25 days)	Ekama et al., 1984
1.03	Raw and settled wastewater	12–24	Suspended growth (first anoxic; SRT = 10–25 days)	Ekama et al., 1984
1.06	—	—		Dawson and Murphy, 1972

SRT = solids retention time.

Soluble, readily degradable substrates support the highest rates of denitrification. Although methanol is the most typically used soluble substrate, it is not the best on a kinetic basis. Kinetic coefficients for denitrification obtained from reported studies are presented in Tables 4.9 and 4.10.

The New York City Department of Environmental Protection evaluated methanol and ethanol addition to improve denitrification (Fillos et al., 2007). In this study, the following expressions were determined for specific denitrification rate (SDNR) for acclimated biomass, where ethanol had a higher SDNR value:

$$\text{Methanol: } (\text{SDNR})_T = 0.0738\ (1.11)^{(T-20)} \tag{4.35}$$

$$\text{Ethanol: } (\text{SDNR})_T = 0.161\ (1.13)^{(T-20)} \tag{4.36}$$

Where,

SDNR = mg NO_3-N removed/mg VSS/d and

T = temperature, °C.

Hallin et al. (2006) studied the metabolic profiles and genetic diversity of denitrifying population in activated sludge by feeding 10 different carbon sources. They observed changes in the community of denitrifiers depending on the carbon source. A preferred carbon source could not be identified based on their study because the final outcome depends on conditions specific to operation, including the costs of supplying the carbon source. A different study examined the effect of acetate addition on denitrifying population and found that the activity improved rapidly with the addition of acetate; however, the biomass settleability was adversely affected (Ginige et al., 2005).

Table 4.9 Denitrification kinetic coefficients.

Carbon source	COD/N	Y (g VSS/g COD)	μ_{max} (d^{-1})	k_D (mg N/g VSS·h)	Reference
Methanol COD: 1 188 000 mg/L				3	Nyberg et al., 1996
				8.7–13.3	Beccari et al., 1983
				4.28	Bilanovic et al., 1999
				5–6	Bailey et al., 1998
			0.52 (10°C)–1.86 (20 °C)		Stensel et al., 1973
	4.7		0.4–0.5 (13°C)–1 (19 °C)		Mokhayeri et al., 2006
			0.56 (13°C)–6.29 (20 °C)		Dold et al., 2008
	4.1–4.5	0.23–0.25	0.77 (15°C)–2 (20 °C)	32 (15°C) 91 (20 °C)	Christensson et al., 1994 (pure culture)
		0.18	0.52 (10°C)–1.86 (20 °C)		Metcalf and Eddy, 2003
	4.8	0.29	0.34 (10°C)–1.2 (20 °C)	6.07	Onnis-Hayden and Gu, 2008
Acetate				4–7	Naidoo, 1999
				2.08–3.53	Isaac and Henze, 1995
				7.95–10.6	Tam et al., 1992
				3.2	Karlsson et al., 1990
				9.89	Bilanovic et al., 1999
		0.32			Muller et al., 2003
		0.46		3.6	Kujawa and Klapwijk, 1999
		0.22			Lee and Welander, 1996
	3.5		1.2 (13°C)–3.5 (19 °C)		Mokhayeri et al., 2006
		0.35		13.6	Onnis-Hayden and Gu, 2008

(*continued*)

TABLE 4.9 Continued

Carbon source	COD/N	Y (g VSS/g COD)	μ_{max} (d^{-1})	k_D (mg N/g VSS·h)	Reference
Glucose				2.7	Akunna et al., 1993
		0.38			Muller et al., 2003
Ethanol		0.25–0.28	1.89 (15°C)–4.8 (25°C)	46 (15°C) 139 (20°C) (pure culture)	Christensson et al., 1994 (pure culture)
				10	Nyberg et al., 1996
		0.22			Hallin et al., 1996
Acetic acid				27	Akunna et al., 1993
				2.2–2.5	Gerber et al., 1987
Butyric acid				2.0–2.1	
Propionic acid				1.7–2.1	
Formic acid				0.9–1.5	

COD = chemical oxygen demand and VSS = volatile suspended solids.

TABLE 4.10 Industrial byproducts, industrial waste, and fermentation products.

Carbon source	COD/N	Y (g VSS/g COD)	μ_{max} (d^{-1})	k_D (mg N/g VSS·h)	Reference
Hydrolyzed sludge				4.9–7.5 (BH) 6.1–7.3 (BH/PA) 3.9–5.7 (CH)	Hoffmann and Klute, 1990
				0.67–3.09	Isaac and Henze, 1995
	6.9	0.27		11.9–15.9 (TH)	Barlindhaug and Ødegaard, 1996

TABLE 4.10 Continued

Carbon source	COD/N	Y (g VSS/g COD)	μ_{max} (d^{-1})	k_D (mg N/g VSS·h)	Reference
	4.5		0.61	23.6 (BH)	Æsøy and Ødegaard, 1994
Hydrolyzed molasses	4.3–5.8			2.9–3.6	Quan et al., 2005
Corn syrup	4.5		1.3 (13°C)–3.7 (19°C)		Mokhayeri et al., 2006
Olive oil mill	4.6–5.4				Tsonis, 1997
Dairy waste	3.6–3.8	0.22–0.38		3.4–8	Sage et al., 2006
Winery waste				32.6	Bernet et al., 1996
Distillery fusel oils	2.22			13.8	Monteith et al., 1980
Pea blanch water	5.71			10.8	
Wines sludge concentrate	7.3			8.6	
Brewery waste	5.48–6.17			7.8–8.2	
Methanol still bottoms	3.66			7.1	
National starch	3.26			6.6	
Tomato sludge	2.54			6.6	
Distillers fuel oils	5.32			6.6	
Organic acid waste	5.14			5.9	
Methanol heads	2.45			5.3	
Acetic acid waste	1.71			5.2	
Fibers glycol waste	5.98			4.3	
Waste dextrose	8.19			2.9	
Formaldehyde waste	6.21			1.7	

(*continued*)

TABLE 4.10 Continued

Carbon source	COD/N	Y (g VSS/g COD)	μ_{max} (d^{-1})	k_D (mg N/g VSS·h)	Reference
MicroC	5.8	0.52	1.2 (10°C)–3.66 (20°C)	4.7–6.37	Onnis-Hayden and Gu, 2008
Dairy waste	4.7		1.91	6.21	
Brewery waste	4.2		1.08	8.18	
Winery waste	3.4		1.43	6.8	
Beet-sugar production waste	3.4		1.89	5.83	
Methane	4.0–5.9			25 (maximum)	Thalasso et al., 1997
	4.2			2.48–9.47	Houbron et al., 1999
				2.46	Raghoebarsing et al., 2006

COD = chemical oxygen demand.

Therefore, it is important to consider other effects on process operation when selecting the carbon source for denitrification.

4.6 Toxicity

The heterotrophic bacteria that perform denitrification are typically less sensitive to inhibition from toxic chemicals compared to nitrifiers; however, toxicity is still a concern. Oxygen has been found to inhibit nitrite reductase to an even greater extent than nitrate reductase, slowing the rate of nitrite reduction. Hernandez and Rowe (1987) found that nitrite began to accumulate when oxygen was added to a batch denitrifying system and stopped accumulating when the oxygen supply was terminated and the system was flushed with argon gas.

Hochstein et al. (1984) conducted experiments to understand the influence of oxygen on denitrification, using a culture *Paracoccus halodenitrificans*, pure oxygen, and a laboratory-scale reactor operating at 30°C. They found that, in the absence of dissolved

oxygen concentration, the nitrate-limited culture produced nitrogen gas, which confirmed effective denitrification. As the oxygen supply was increased, however, *P. halodenitrificans* first produced nitrous oxide and then nitrite, indicating the inactivation of nitrous oxide reductase by oxygen and diversion of electrons from nitrite to oxygen, ultimately leading to complete loss of denitrification. This study also noted that although nitrate reductase was least sensitive to dissolved oxygen, it was completely inhibited after 3.3 mg/L of dissolved oxygen concentration in the medium.

Excess nitrite concentration can suppress denitrification rates. Rowe et al. (1979) reported that NO_2-N concentrations greater than 14.0 mg/L at a pH of 7.0 inhibited active transport of carbohydrates and amino acids in *Pseudomonas aeruginosa.* They also found that concentrations greater than 350 mg/L completely inhibited active transport by microorganisms in both anoxic environment with NO_3^- as the terminal electron acceptor and oxic environment with oxygen as the terminal electron acceptor. Beccari et al. (1979) suggested that inhibition by nitrite is caused by free nitrous acid (HNO_2). They found that nitrite reduction rates drop sharply for pH values less than 7.5 in contrast to nitrate reduction rates.

4.7 Biofilm Systems

Like nitrification, denitrification can be accomplished in biofilm systems. In fact, denitrification is one of the easiest applications for a wide range of biofilm processes because oxygen transfer will not be a limiting factor, allowing for higher volumetric loadings (Rittmann and McCarty, 2001). The first filter for denitrification was patented in 1970 (U.S. EPA, 2007b). A list of denitrifying filter manufacturers and equipment is summarized elsewhere (U.S. EPA, 2007b). Any of the biofilm systems can work efficiently, as long as oxygen transfer is controlled and plugging of the reactor is avoided. The various systems applied for denitrification include (Rittmann and McCarty, 2001)

- Rotating biological contactors in which the air ventilation is controlled;
- Submerged fixed beds of rocks, sand, limestone, or plastic media;
- Fluidized beds of sand, activated carbon, and pellets of ion-exchange resin;
- Circulating beds of range of lightweight particles; and
- Membrane reactors in which the membrane supplies hydrogen and supports the biofilm media.

All of the denitrification biofilters are submerged in water. When RBC or packed filter media such as plastic or loose carriers are involved, sludge production is removed via secondary settling. For filters with sand or gravel, backwash is used to remove the excess sludge. The most widely used reactor configurations for denitrification include MBBR, biological anoxic filter, and IFAS. Fixed-bed IFAS use media such as Ringlace®, Bloweb®; moving-bed IFAS use media such as Captor®, Linpor® (sponge), Kaldnes®, Hydroxyl®, Entex (plastic). The MBBR reactors use media such as Kaldnes®, Entex®, or other plastic media (Sen and Randall, 2008). Recently, the town of Cheshire, Connecticut (13 200 m^3/d, or 3.5 mgd) implemented an upflow biological anoxic filter with methanol addition to achieve less than 3 mg/L of effluent total nitrogen (Pearson et al., 2008). The MBBR and IFAS technologies were pilot-tested at Norman Cole Jr. Water Pollution Control Plant in Fairfax County, Virginia (Motsch et al., 2007). Both technologies were capable of reducing NO_x-N levels from 7 mg/L to less than 2 mg/L when operating between 18°C and 20°C. Five parts of methanol per part of nitrate-nitrogen were added, which was an intentionally maintained overdose. The nitrate removal rate in the MBBR was equal to 2.5 to 3.0 g NO_x-N/m^2·d at 18.5°C to 20°C, resulting in an average effluent NO_x-N concentration of 0.6 mg/L. The IFAS system was slightly less effective, achieving effluent NO_x-N of 0.86 mg/L.

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Chapter 5

Nitrification

(continued)

1.0 INTRODUCTION

This chapter focuses on suspended growth and attached growth nitrification in activated sludge and presents simplified nitrification design equations as applied to biological nutrient removal (BNR). Nitrification is discussed in detail in this chapter because it is often the rate-determining step in BNR owing to low specific growth rates, growth yields, and high sensitivity of nitrifying bacteria to a wide range of physical, chemical, and environmental disturbances (Grady et al., 1999).

2.0 ACTIVATED SLUDGE NITRIFICATION SYSTEMS

2.1 Single-Sludge Nitrification–Denitrification

This section discusses single-sludge nitrification–denitrification suspended-growth systems. Single-sludge systems are those in which nutrient removal is achieved in a single basin and clarifier. The basin may be divided into several zones to achieve anaerobic or anoxic conditions depending on the treatment goal. Several configurations have been used including predenitrification, postdenitrification, and combined pre- and postdenitrification systems. The more commonly used single-sludge processes are presented in the *Design of Municipal Wastewater Treatment Plants* (Water Environment Federation [WEF] and American Society of Civil Engineers, 2009). Various procedures have been developed for designing nitrogen removal systems (Barnard et al., 1992; Bidstrup and Grady, 1988; Soap and Detergent Association, 1989; TREEO, 1988; WEF, 2009). The objective of these processes is to remove nitrogen from wastewater via microbiological pathways and mechanisms.

A single-sludge system using one anoxic zone can achieve an effluent total nitrogen concentration of 4 to 11 mg/L as nitrogen. Oxidation ditches preceded by anaerobic/anoxic selectors have achieved effluent total nitrogen concentrations of less than

3 mg/L as nitrogen (Mines and Woods, 1994). Typically, supplemental carbon is only needed when postdenitrification systems are used.

2.2 Separate-Sludge Suspended Growth Nitrification

Activated sludge systems in which the removal of biodegradable carbonaceous material and nitrification are promoted in distinct reactors, each subjected individually to secondary clarification, are called separate-sludge nitrification systems. In these systems, the biochemical oxidation of organic matter is achieved upstream in a low solids retention time (SRT) or a high-rate reactor. The operating SRT of this reactor is lower than the minimum SRT required to sustain nitrifying bacteria. As a consequence, the predominant mechanism for removing ammonia in this low-SRT reactor is assimilation into heterotrophic nonnitrifying biomass. Clarified effluent from the low-SRT reactor is subsequently nitrified in a downstream high-SRT (or low-rate) reactor, which results in a high fraction of nitrifying bacteria. Although more complicated to operate than a single-sludge nitrification system, the separate-sludge nitrification system has several positive attributes. These attributes include lower susceptibility to shock loads of both carbonaceous and nitrogenous matter in the influent wastewater (because each reactor is optimized independently for carbon or ammonia oxidation); lower susceptibility of the nitrification process to organic toxicants (because these might be subject to degradation or physical removal in the carbon removal process); and maintenance of an enriched nitrifier inventory, which could be used to "seed" other process reactors in case of nitrification failure (Michael, 2003). Furthermore, separate-sludge systems also maximize ammonia assimilation in the low-SRT reactor leading to reduced ammonia loading to the nitrification sludge and reductions in oxygen and alkalinity consumption. Differences between single-sludge and separate-sludge systems are especially apparent at lower operating temperatures when the kinetic differences between heterotrophic and nitrifying bacteria are much higher (Grady et al., 1999).

2.3 Attached Growth Nitrification

In addition to suspended-growth systems, nitrification can be engineered in attached growth or biofilm systems. Attached growth systems are used to sustain nitrification in wastewater treatment plants because of the inherently lower biokinetics and yield coefficients of nitrifying bacteria relative to heterotrophic bacteria. Growth in biofilm mode affords nitrifying bacteria increased potential against toxic shock loads based on the higher "apparent" SRT of organisms in biofilms compared to bulk-phase SRT. In addition, it is now well-established for several other bacteria that the biofilm mode

of growth renders them intrinsically more resistant to toxicity, inhibition, and starvation (Hengge-Aronis, 2000). It is, therefore, conceivable that similar principles could apply for nitrifying bacteria.

Previous work on characterization of attached growth nitrifying reactors has mostly focused on in-situ microbial ecology and their ecophysiology (Daims et al., 1999; Gieseke et al., 2001, 2005; Hoshino et al., 2001; Manz et al., 1993; Montras et al., 2008; Pynaert et al., 2003; Schramm et al., 2000; Tanaka and Dunn, 1982; Tijhuis et al., 1994). From these studies it has been found that, in most cases, nitrifying bacteria are restricted to the outer reaches of the biofilms. Additionally, a close spatial correspondence between the ammonia (AOB) and nitrite oxidizing bacteria (NOB) also has been revealed (Manz et al., 1993; Schramm et al., 2000). The dominance of nitrifying organisms on the outer fringes of biofilms is consistent with the fact that nitrifying bacteria favor environments with higher dissolved concentrations and that nitrite, as occurring near the regions of the biofilm exposed to the bulk liquid. Further, the close spatial orientation of the AOB and NOB is explained by their link to nitrite, which is produced by the former and consumed by the latter. In more recent studies, however, uniform distribution of AOB has been found in anaerobic biofilms even in regions with little to no dissolved oxygen, thereby indicating active anaerobic metabolism of AOB in such environments (Pynaert et al., 2003).

3.0 FUNDAMENTALS OF NITRIFICATION

3.1 Microbiology and Microbial Ecology

Nitrification is the process of biological oxidation of ammonia (which exists mostly as NH_4^+-N in typical wastewater) to nitrite (NO_2^--N) and the further oxidation of nitrite to nitrate (NO_3^--N). The oxidation of ammonia to nitrite is carried out by AOB and nitrite conversion to nitrate is carried out by NOB. Both of these reactions should operate at optimal rates for the production of nitrate. The most common ammonia-oxidizing organisms in wastewater treatment plants belong to the genus *Nitrosomonas*. Other genera with similar capability include *Nitrosococcus*, *Nitrosospira*, *Nitrosolobus*, and *Nitrosorobrio* (Painter, 1970). *Nitrobacter* spp. are believed to be the most common nitrite oxidizers in wastewater treatment systems. Recent research, however, suggests that nitrospira-like bacteria are the main NOB in wastewater treatment systems (Schramm et al., 1998). Other genera capable of oxidizing nitrite to nitrate for energy include *Nitrococcus*, *Nitrospina*, and *Nitrocystis* (Metcalf and Eddy, 2003). Ammonia and nitrite oxidizers collectively are referred to as *nitrifiers*. Although classified together, AOB and NOB are not related phylogenitically (Bock et al., 1992).

The microbial ecology of AOB and NOB relevant to activated sludge is given in Figure 5.1, which highlights the relationships between AOB. In addition, the recent discovery of ammonia oxidizing archaea in activated sludge suggests that knowledge of ammonia oxidizing organisms is not yet complete and that activated sludge maybe a repository of several novel nitrifying organisms (Francis et al., 2005; Nicol and Schleper, 2006).

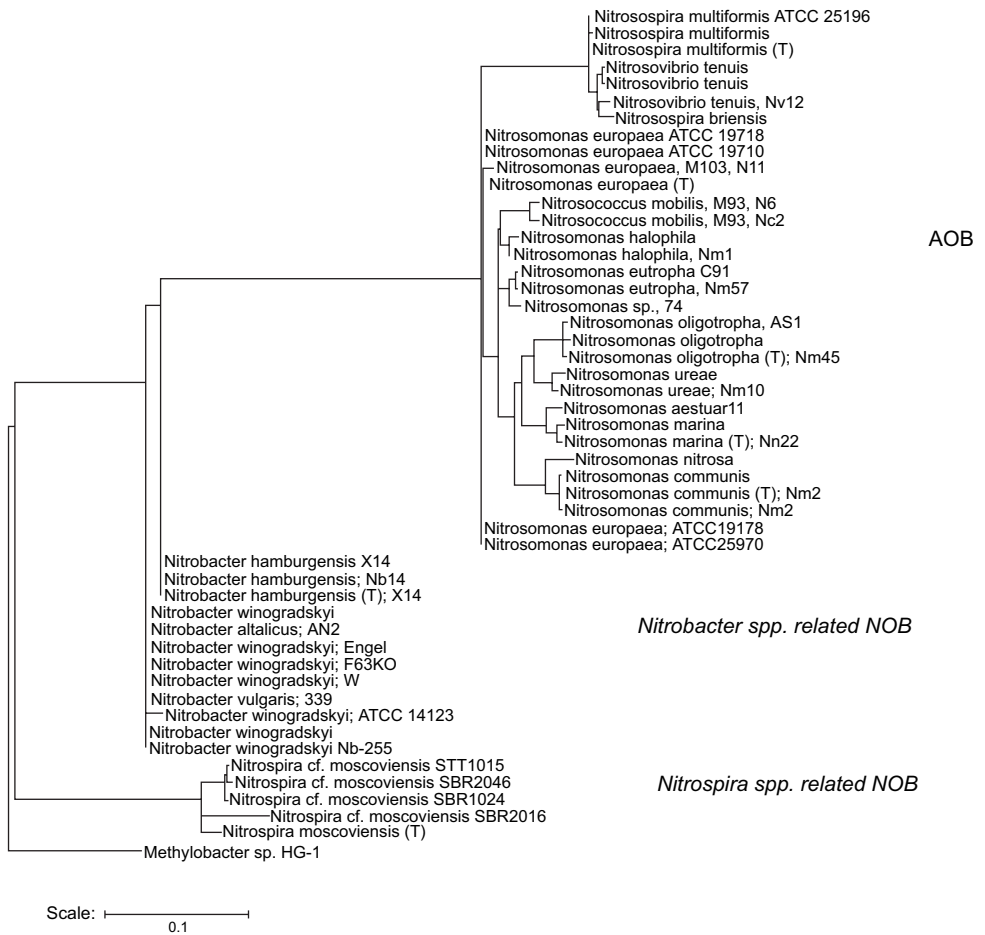

Figure 5.1 Microbial ecology and phylogenetic diversity of ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) relevant to activated sludge.

3.2 Biochemical Pathways and Reactions

Ammonia oxidation to nitrite can be described by the following reactions (White, 1995):

$$2\ H^+ + NH_3 + 2\ e^- + O_2 \rightarrow NH_2OH + H_2O \quad (5.1)$$

$$NH_2OH + H_2O \rightarrow HNO_2 + 4\ H^+ + 4\ e^- \quad (5.2)$$

$$2\ H^+ + 0.5\ O_2 + 2\ e^- \rightarrow H_2O \quad (5.3)$$

The key enzymes involved in the reactions are ammonia monooxygenase, which oxidizes ammonia to hydroxylamine, and hydroxylamine oxidoreductase, which catalyzes the oxidation of hydroxylamine (see Figure 5.2). The first step of ammonia conversion to hydroxylamine does not yield significant energy; the second step of hydroyxlamine conversion to nitric acid provides the energy for metabolic reactions (Hooper et al., 1997). The nitrite oxidation process is shown in Figure 5.3 and eqs 5.4 and 5.5:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2\ H^+ + 2\ e^- \quad (5.4)$$

$$2\ H^+ + 2\ e^- + NAD(P)^+ \rightarrow NAD(P)H + H^+ \quad (5.5)$$

Most nitrifiers found in typical wastewater treatment systems are autotrophic because they synthesize cellular material from inorganic carbon (HCO_3^- under typical operating conditions). Oxidation of the ammonia or nitrite provides the energy needed for cell synthesis. These bacteria are obligate aerobes because they grow only when dissolved oxygen is available. The absence of dissolved oxygen for prolonged periods, however, is not lethal because these organisms adapt and survive under low dissolved oxygen and low ammonia concentrations (Geets et al., 2006; Painter, 1970). In typical BNR systems, nitrifiers must survive anaerobic (molecular oxygen and oxidized nitrogen absent) or anoxic (molecular oxygen absent but oxidized nitrogen present) conditions, which they do successfully. The relative abundance and diversity of nitrifying organisms in wastewater treatment systems depend on influent characteristics and operating conditions (Ahn et al., 2008; Siripong and Rittman, 2007).

3.3 Stoichiometry

The stoichiometry of ammonia and nitrite oxidation are described in detail in Chapter 4 and are not repeated herein. Briefly, two moles of oxygen are required to oxidize 1 mole of nitrogen to nitrate, which is equivalent to 4.57 g O_2/g NH_4^+-N oxidized. Two equivalents of H^+ are produced in the process, which, in turn, reacts with two

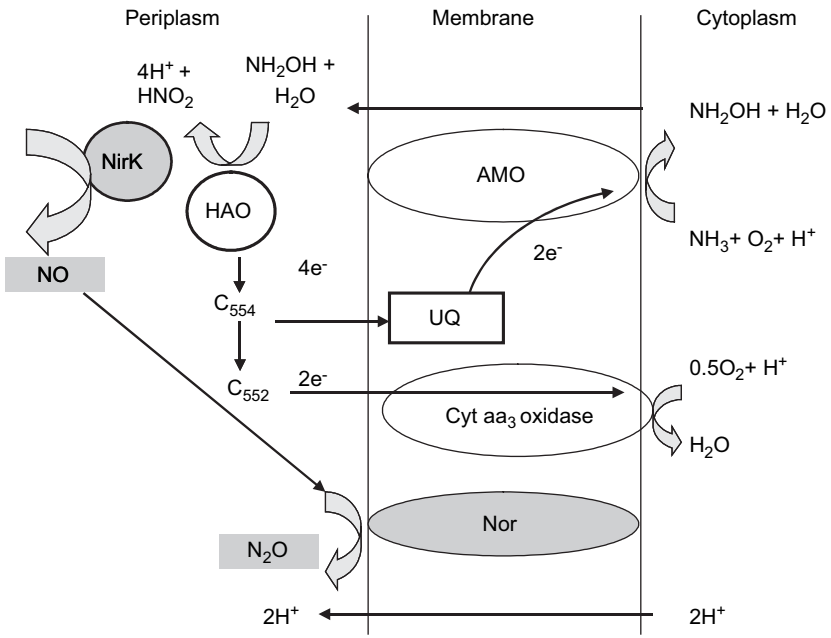

FIGURE 5.2 Biochemical pathways for ammonia oxidation in *Nitrosomonas europaea* (Hooper et al., 1997; With kind permission of Springer Science+Business Media).

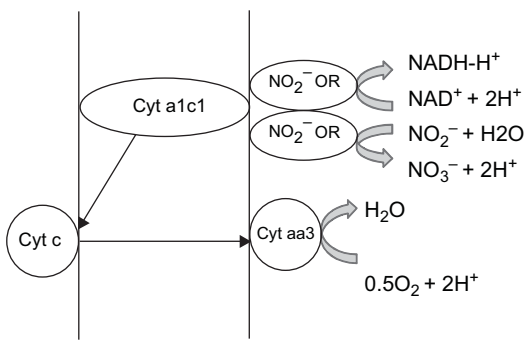

FIGURE 5.3 Biochemical pathways for ammonia oxidation in *Nitrobacter* (Bock et al., 1992; With kind permission of Springer Science+Business Media).

equivalents of bicarbonate in the wastewater. As a result, 7.14 g of alkalinity (as $CaCO_3$) are destroyed per gram NH_4^+-N oxidized.

Because of the predominantly autotrophic mode of growth for nitrifying bacteria, the biomass yield coefficient for nitrification is considerably lower than

that for heterotrophic bacteria (Grady et al., 1999). On the positive side, the low yield results in lower nitrifying biomass production per unit nitrogen oxidized. However, the low yield contributes in part to the high oxygen demand for nitrification. Considering a yield of 0.17 g of nitrifying bacteria per gram NH_4^+-N oxidized, the overall nitrification reaction can be summarized as follows (Gujer and Jenkins, 1974):

$$1.02\ NH_4^+ + 1.89\ O_2 + 2.02\ HCO_3^- \rightarrow 0.021\ C_5H_7O_2N + 1.06\ H_2O + 1.92\ H_2CO_3 + 1.00\ NO_3^- \quad (5.6)$$

The oxygen requirement and alkalinity consumption in nitrification change little even after considering biosynthesis because of low bacterial mass yield. The oxygen requirement decreases to 4.3 g O_2/g NH_4^+-N oxidized, whereas alkalinity consumption increases to 7.2 g as $CaCO_3$/g NH_4^+-N oxidized. In design, however, the values derived from the energy reactions (4.57 g O_2 consumed and 7.14 g alkalinity destroyed per gram NH_4^+-N oxidized) typically are used.

Considering synthesis and oxidation by AOB and NOB separately, Haug and McCarty (1972) reported that oxidation of 100 mg of NH^+-N to NO_3^--N resulted in the production of 14.6 mg of AOB biomass and 2.0 mg of NOB biomass, as follows:

$$55\ NH_4^+ + 76\ O_2 + 109\ HCO_3^- \rightarrow C_5H_7NO_2\ (AOB) + 54\ NO_2^- + 57\ H_20 + 104\ H_2CO_3 \quad (5.7)$$

$$400\ NO_2^- + NH_4^+ + 4\ H_2CO_3 + HCO_3^- + 195\ O_2 \rightarrow C_5H_7NO_2\ (NOB) + 3\ H_2O + 400\ NO_3^- \quad (5.8)$$

The overall electron flow for energy synthesis and biosynthesis for AOB and NOB are summarized in Figures 5.4a and 5.4b (Chandran and Smets, 2000b, 2001).

3.4 Kinetics

Nitrification typically limits overall biological nitrogen removal because nitrifying microorganisms have lower specific growth rates than their heterotrophic counterparts and are more susceptible to environmental factors such as temperature, pH, and the presence of synthetic organic chemicals and heavy metals (Grady et al., 1999). Further, the nitrifying microorganisms can also be inhibited by their own substrates and the intermediates and products of the nitrification process. Therefore, it is essential to obtain accurate estimates of the biokinetics of nitrification to ensure proper design and operation of bioreactors for nitrogen removal.

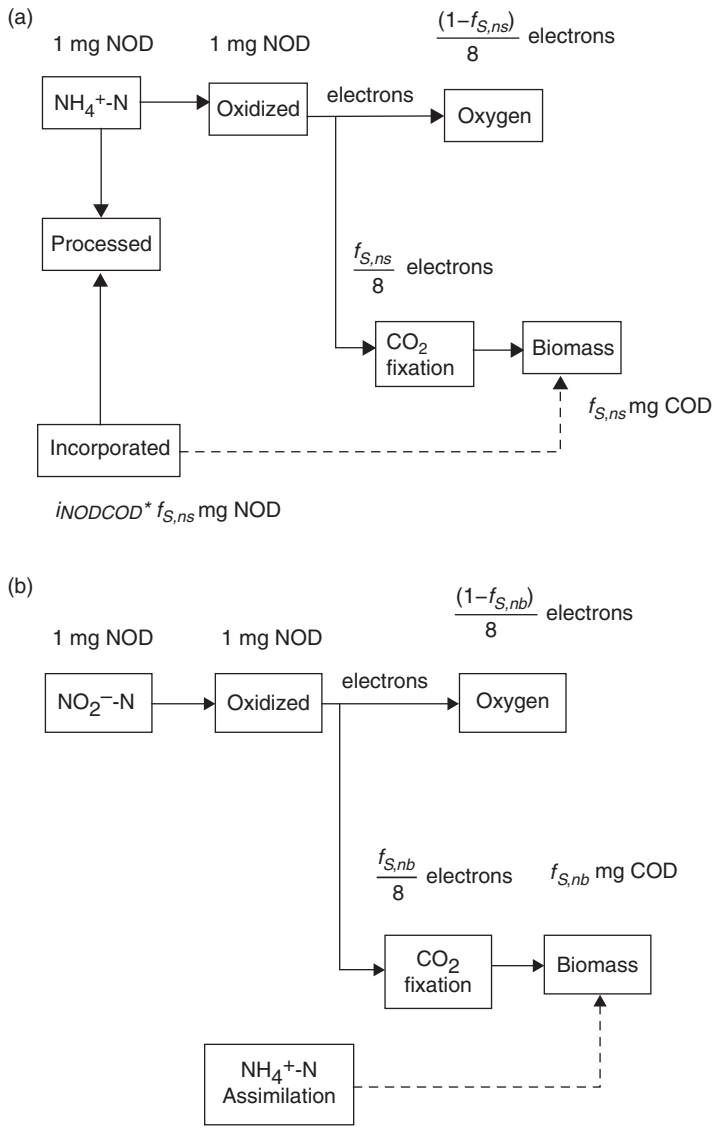

FIGURE 5.4 Electron flow describing energy synthesis and biosynthesis in (a) ammonia oxidizing bacteria (AOB) and (b) nitrite oxidizing bacteria (NOB) (COD = chemical oxygen demand; f_S = fraction of electrons incorporated into biomass; and NOD = nitrogenous oxygen demand) (Chandran and Smets, 2000b, 2001).

The first step in nitrification is the rate-limiting step because AOB typically have lower specific growth rates than NOB. Kinetics of nitrification have, therefore, been modeled in the past as a single step (NH_4^+-N $\rightarrow$ NO_3^--N). Recent research suggests, however, that when both reactions are limiting at different stages of the process, the single-step representation may be inappropriate, and characterization of individual oxidation reactions is necessary (Chandran and Smets, 2000a, 2000b, 2005). At higher temperatures (25–40°C) and very low SRTs (1–2 days), AOB grow faster than NOB. As a result, NOB are washed out of the system and only the first step of nitrification can be accomplished, which is the basis of the SHARON process.

The Monod equation is used to describe the effect of limiting substrates on microbial growth (Monod, 1949). Both ammonium and dissolved oxygen are substrates for AOB growth. The concentrations of either or both of these substrates could be low enough to limit the specific AOB growth rate in wastewater treatment systems. Assuming no alkalinity limitation, the growth rate of AOB can be expressed as:

$$\mu_{AOB} = \mu_{max,AOB}\left[\frac{S_{nh}}{S_{nh} + K_{ns,AOB}}\right]\left[\frac{S_O}{S_O + K_{O,AOB}}\right] \tag{5.9}$$

Where,

μ_{AOB} = specific growth rate of AOB biomass (g biomass formed per g biomass present per day), d^{-1};

$\mu_{max,AOB}$ = maximum specific growth rate of AOB, d^{-1};

S_{nh} = NH_4^+-N concentration, mg N/L;

$K_{ns,AOB}$ = half-saturation coefficient for AOB, mg N/L;

S_O = dissolved oxygen concentration of bulk mixed liquor or wastewater, mg O_2/L; and

$K_{O,AOB}$ = oxygen half-saturation coefficient for AOB, mg O_2/L.

The above equation is a simplification because it does not explicitly consider free ammonia, the true substrate for AOB. When necessary, alternate expressions that consider pH-dependent speciation of free and ionized ammonia can be used to describe ammonia oxidation (Flora et al., 1999). Figure 5.5 shows specific growth as a function of NH_4^+-N concentration, when dissolved oxygen is not limiting. The specific growth rate increases almost linearly (approximating first-order kinetics) with respect to NH_4^+-N concentration near the origin of the plot, where the NH_4^+-N concentration is low. At higher NH_4^+-N concentrations, the specific growth rate approaches an asymptotic value (the maximum specific growth rate), thus exhibiting zero-order behavior. The NH_4^+-N half-saturation coefficient is the NH_4^+-N concentration at which the specific growth rate is one-half of its maximum value. A similar plot could be drawn to depict

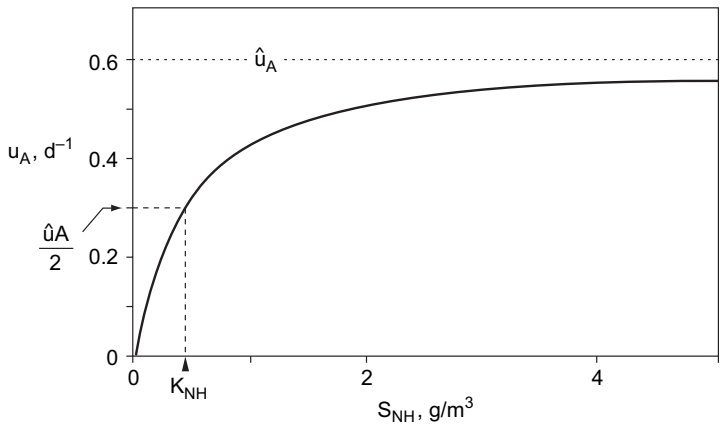

FIGURE 5.5 Relationship between specific growth rate of ammonia-oxidizing bacteria and ammonia–nitrogen concentration as predicted by the Monod equation (dissolved oxygen is assumed to be nonlimiting).

the relationship between specific growth rate and dissolved-oxygen concentration, when NH_4^+-N is not limiting. The oxygen half-saturation coefficient is the dissolved-oxygen concentration where the specific growth rate is one-half of its maximum value.

NOB can use both ammonia and nitrite (nitrous acid) as nitrogen sources. Considering NH_4^+-N as the nitrogen source, the specific growth rate equation can be written as follows:

$$\mu_{NOB} = \mu_{max,NOB}\left[\frac{S_{nh}}{S_{nh} + K_{ns,NOB}}\right]\left[\frac{S_O}{S_O + K_{O,NOB}}\right]\left[\frac{S_{no2}}{S_{no2} + K_{no2,NOB}}\right] \tag{5.10}$$

Where,

μ_{NOB} = specific growth rate of NOB biomass (g biomass formed per g biomass present per day), d^{-1};
$\mu_{max,NOB}$ = maximum specific growth rate of NOB, d^{-1};
S_{nh} = NH_4^+-N concentration, mg N/L;
$K_{ns,NOB}$ = half-saturation coefficient for ammonia for NOB, mg N/L;
S_O = dissolved oxygen concentration of bulk mixed liquor or wastewater, mg O_2/L;
$K_{O,NOB}$ = oxygen half-saturation coefficient for NOB, mg O_2/L;
S_{no2} = NO_2^--N concentration, mg N/L; and
$K_{no2,NOB}$ = NO_2^--N half-saturation coefficient for NOB, mg N/L.

When nitrous acid is the only source of nitrogen, the following kinetic expression can be used:

$$\mu_{\text{NOB}} = \mu_{max,\text{NOB}} \left[\frac{S_O}{S_O + K_{O,\text{NOB}}} \right] \left[\frac{S_{no2}}{S_{no2} + K_{no2,\text{NOB}}} \right] \tag{5.11}$$

If AOB kinetics solely limit overall nitrification kinetics (as opposed to both AOB and NOB kinetics), then overall nitrification process can be described using single-step nitrification models (Chandran and Smets, 2000b). In such a scenario, eq 5.12 can be used to describe the overall nitrification process by modifying the suffix "AOB" to "A" to refer to autotrophic nitrifying bacteria.

Under such conditions, the specific growth rate of nitrifying bacteria is approximately related to the specific rate of NH_4^+-N or NO_2^--N oxidation in a wastewater treatment process by the following expression:

$$q_A = \frac{1}{Y_A} \mu_A \tag{5.12}$$

Where,

q_A = specific NH_4^+-N or NO_2^--N oxidation rate, g N oxidized per g biomass per day and

Y_A = yield of AOB or NOB, g biomass produced per g N oxidized.

The yield coefficient in eq 5.12 is the true growth yield, representing the quantity of biomass that would be formed if all of the energy captured by the bacterial cells were used in cell synthesis.

A decay coefficient (b_A) is used to account for the consumption of cell energy reserves for maintenance requirements and the effects of predation and cell lysis. An overall mass balance on the nitrifying biomass results in the following equation as described in Grady et al. (1999):

$$\theta_{C,A} = \frac{1}{\mu_A - b_A} \tag{5.13}$$

Where,

$\theta_{C,A}$ = mean cell residence time, d^{-1}, and

b_A = endogenous decay coefficient for nitrifiers (g biomass destroyed per g biomass present per day), d^{-1}.

The combined nitrifier decay rate was initially thought to be negligible (Downing and Hopwood 1964). Nevertheless, recent work sponsored by the Water Environment

Research Foundation (WERF, 2003), suggests that the decay rate could be significantly higher in the range of 0.17 d^{-1} at 20°C. The WERF study results correspond with previous results. Kopp and Murphy (1995) reported a b_A value of 0.15 d^{-1} at 20°C using pure cultures. Nowak et al. (1994) and Siegrist et al. (1999) reported decay rates of 0.20 to 0.21 d^{-1}. The WERF study also resulted in the following expression for decay rate variation with temperature for combined nitrifiers:

$$b_{A,T} = 0.17(\theta)^{(T-20)} \tag{5.14}$$

Where,

$b_{A,T}$ = autotrophic decay rate at temperature T (d^{-1});
θ (temperature dependency factor) = 1.029; and
T = temperature in degrees Celsius.

Table 5.1 presents a brief comparison of decay rates found by Manser (2006) in a study where conventional activated sludge (CAS) and membrane bioreactor (MBR) systems were operated in parallel. This table also indicates that the decay rates of heterotrophic organisms determined in the study and shows that the AOB and NOB decay rates are similar and within the range of values reported by other researchers (Kopp and Murphy, 1995). The intent of Table 5.1 is to show that the decay rates of AOB and NOB in MBR system are similar to CAS under similar operating conditions.

3.5 Values of Biokinetic Coefficients

The reported values for nitrification growth rates and half-saturation coefficients fall in a wide range. Several reasons have been proposed for this variability beyond the effects of pH, temperature, and toxins (Atkinson and Rahman, 1979; Baillod and Boyle, 1970; Bakti and Dick, 1992; LaMotta and Shieh, 1978; Mueller et al., 1968; Stenstrom and Poduska, 1980; Stenstrom and Song, 1991). These include the effects of organic loading in single-sludge systems, the concentration of dissolved oxygen

Table 5.1 Estimated aerobic decay rates at 20°C in conventional activated sludge (CAS) and membrane bioreactor (MBR) systems (adapted from Manser, 2006).

System	Decay rate for AOB (d^{-1})	Decay rate for NOB (d^{-1})	Decay rate for heterotrophs (d^{-1})
CAS	0.15 ± 0.02	0.15 ± 0.01	0.28 ± 0.05
MBR	0.14 ± 0.01	0.14 ± 0.01	0.23 ± 0.03

AOB = ammonia oxidizing bacteria; NOB = nitrite oxidizing bacteria.

within the mixed liquor floc, and simultaneous double substrate limiting kinetics. Work by several researchers has shown that the resistance of the floc particle to the mass transfer of oxygen into the floc particle or through the layers of a biofilm can make the rate of oxygen diffusion the rate-limiting step to the overall nitrification process (a more detailed overview of fixed-film nitrification is presented in Chapter 4). Several parameters can affect the concentration of dissolved oxygen within the floc: floc shape and size, mixing intensity, and growth rate of the bacteria within the floc. According to Hanaki et al. (1990), the heterotrophic bacteria in a single-sludge system may assimilate ammonia faster than nitrifiers, thus reducing the ammonia available for the nitrifiers. The heterotrophic biomass also may hinder the transport of ammonia and dissolved oxygen within the floc. This would help explain why nitrification is slower in combined systems for carbon and ammonia oxidation. This concept is illustrated in Figure 5.6 (Monod, 1949). Regardless of the specific mechanism, the apparent effect of mass-transfer limitations is to increase the half-saturation coefficient and increase the minimum dissolved oxygen required for nitrification.

Table 5.2 presents the kinetic parameters and Table 5.3 presents yield data for AOB and NOB from the literature, in CAS processes (Ahn et al., 2008; Chandran

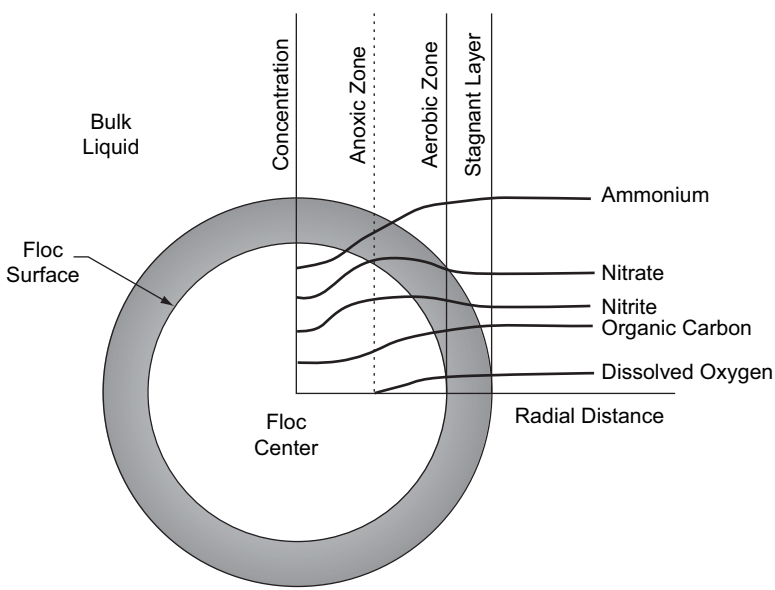

Figure 5.6 Illustration of substrate concentration profiles within a microbial floc showing simultaneous nitrification and denitrification.

TABLE 5.2 Comparison of major kinetic parameters for ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB).

Parameter	Unit	Magri et al., 2007	Hellinga et al., 1998	Hellinga et al., 1999	Carrera et al., 2004	Wett and Rauch, 2003	Van Hulle et al., 2004	Guisasola et al., 2005	Pynaert, 2003	Chandran and Smets, 2000a, 2000b, 2005; Chandran et al., 2008	Iacopozzi et al., 2007
AOB											
$\mu_{max,AOB}$	d^{-1}	4.55	2.10	2.10		4.04	1.0±0.2		0.3–2.2	0.2–0.6	0.6313
b_{AOB}	d^{-1}	0.08				1.00					0.061
$K_{O,AOB}$	mg O_2/L	0.75		1.45		0.40	0.94±0.091	0.74±0.02	0.03–1.3		0.50
K_{ns}	mg N/L	0.88	0.50–7.00	0.468	0.20	0.13	0.75±0.052		0.06–27.5	0.5	2.0
NOB											
$\mu_{max,NOB}$	d^{-1}	1.20	0.02–0.17	1.05	–	3.21	–		0.2–2.5	0.6	1.0476
b_{NOB}	d^{-1}	0.007	–	–	–	0.87					0.061
$K_{O,NOB}$	mg O_2/L	1.22	–	1.10	–	1.00	–	1.75±0.01	0.3–2.5		0.50
K_{no2}	mg N/L	0.004	0.26	0.0014	0.00012	0.30	–		0.1–15	1.5	0.50

Table 5.3 Ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) biomass yield values.

Reference	AOB yield = Y_{AOB} (g COD*x*/g NH_4^+-N)	NOB yield = Y_{NOB}(g COD*x*/g NO_2^--N)	Y_{AOB}/Y_{NOB}
Chandran and Smets, 2000a, 2000b	0.28	0.11	2.61
Guisasola et al., 2005	0.21	0.08	2.62
Wiesmann, 1994	0.147	0.042	3.50
Knowles et al., 1965	0.05	0.02	2.50
Sheintuch et al., 1995	0.14	–	–
Gee et al., 1990a	0.43	0.132	3.25
Gee et al., 1990b	0.40	0.114	3.50
Kopp and Murphy, 1995		0.015	–
Hellinga et al., 1999	0.15	0.041	3.65
Pynaert, 2003	0.04–0.13	0.02–0.08	–

Table 5.4 Ammonia half-saturation constants for ammonia oxidizing bacteria (AOB) ($K_{NH,A}$) and nitrite half-saturation constants for nitrite oxidizing bacteria (NOB) (K_{NO}) in three different processes (SBR = sequencing batch reactor; CAS = conventional activated sludge; MBR = membrane bioreactor; and OUR = oxygen updake rate) (adapted from Manser, 2006).

K_{ns} (mg/L) for AOB			K_{no2} (mg/L) for NOB			
SBR	**CAS**	**MBR**	**SBR**	**CAS**	**MBR**	**Remarks**
9.90 ± 0.50	0.14 ± 0.07	0.13 ± 0.05	9.20 ± 1.1	0.28 ± 0.20	0.17 ± 0.06	
14.1 ± 0.6			2.90 ± 0.3			Estimated from concentration profiles
6.0 ± 0.3	0.11 ± 0.01	0.10	15.2 ± 2.3	0.21 ± 0.02	0.21 ± 0.05	
			4.2 ± 3.0	0.24 ± 0.02		Estimated from OUR profiles

et al., 2008; Manser, 2006). Fluorescent in situ hybridization analysis showed no significant differences between AOB and NOB populations in the CAS and the MBR system (Manser, 2006). Differences in the kinetics, however, were considerable between CAS, sequencing batch reactor (SBR), and MBR systems, suggesting potential influence of the type of process on the kinetic parameters, as shown in Table 5.4. The oxygen half-saturation concentration for an MBR system is lower than for the CAS system (Table 5.4), likely because of improved mass transfer in smaller flocs generated by high level of turbulence within the MBR as a result of operating conditions. Fundamentally,

the basic biokinetics of nitrifying bacteria in different reactor configurations need to be related to the microbial ecology of nitrifying bacteria present, which could govern the measured rates of nitrification (for more discussion on this topic, refer to Ahn et al., 2008). The reader is refererred to the original works by Manser (2006) and Chandran and coworkers for more details on the biokinetics of nitrification obtained from a wide variety of systems (Ahn et al., 2008; Chandran et al., 2008).

Of the kinetic parameters that describe nitrification (or any other process according to Monod kinetics), the half-saturation constants (for ammonia, nitrite, or oxygen) are among the most difficult to estimate with a high degree of precision (Bates and Watts, 1988; Chandran and Smets, 2000a, 2005). This is because these half-saturation constants depend on the intrinsic affinity of the bacteria for these respective substrates and are governed by mass transfer limitations that exist in microbial aggregates, flocs, or biofilms. Consequently, any physical, chemical, or environmental factors that affect floc size distribution or biofilm thickness also affect the "apparent" lumped half-saturation constants (Grady et al., 1999). However, there are techniques to determine experimentally the local transport to diffusivity constants in biofilms and flocs (Bryers and Drummond, 1998).

Any published value of the maximum specific growth for AOB should be used with caution because toxic chemicals in wastewater can inhibit their growth. Wherever possible, wastewater-specific values of this coefficient should be determined experimentally.

The optimum temperature for nitrification is between 30°C and 36°C, with growth possible between 4°C and 50°C (Focht and Chang, 1975; Painter, 1970). At greater than 15°C, AOB grow faster than NOB; at 25°C, AOB can outcompete NOB (Brouwer et al., 1998; Van Dongen et al., 2001).

The optimum pH range is 7.9 to 8.2 for *Nitrosomonas* and 7.2 to 7.6 for *Nitrobacter* (Alleman, 1984; Antoniou et al., 1990). The following expression can be used to relate the maximum growth rate of nitrifiers to pH in the 6.8 to 7.10 range (Blackburne et al., 2007).

$$\mu_{nm} = 0.72\ (3.3)^{(pH-7.10)} \tag{5.15}$$

3.6 Nitrification Biokinetic Estimation Techniques

In a typical assay designed to determine the kinetics of a biological process, the key parameters of interest are the maximum specific growth rate, μ_{max}, the half saturation coefficient, K_S, and if applicable, the self-inhibition coefficient, K_i, pertaining to the growth-limiting substrate. Conventional biokinetic assays involve the evaluation of the specific growth rate at different initial substrate concentrations.

Alternatively, substrate depletion or biomass synthesis is monitored during a batch growth experiment and the resulting data are used to characterize the growth profile. The principal drawback to these approaches is the analytical effort involved. Numerous initial rate experiments are required to fully delineate a single growth profile. Further, low specific growth rates that occur at low substrate concentrations are difficult to determine accurately, and repetitive sampling in itself can be a major source of error.

In recent years, batch respirometry and titrimetry have emerged as facile and robust tools for measuring nitrification kinetics. The fundamental basis of respirometry and titrimetry are the stoichiometric link between the substrate consumption and biomass synthesis with oxygen consumption (respirometry) or alkalinity consumption (titrimetry). There are several reports and treatises devoted to the estimation of nitrification biokinetics via direct substrate measurements, measurement of surrogate analytes such as oxygen, alkalinity consumption, or a combination of both surrogates and nitrogen species (Brouwer et al., 1998; Chandran and Smets, 2000a, 2000b, 2005; Chudoba et al., 1985; Gee et al., 1990; Gernaey et al., 1998; Jones et al., 2005; Knowles et al., 1965; Mauret et al., 1996; Ossenbruggen et al., 1991, 1996; Petersen, 2000; Surmacz-Gorska et al., 1996; WERF, 2003).

Based on the initial conditions imposed, a batch biokinetic assay can be either "intrinsic" or "extant" (Grady et al., 1996). The intrinsic assay creates considerable growth and change in physiological state during the assay itself. The obtained kinetics are, therefore, representative of the maximum capability of the fastest growing members of the microbial consortium and are independent of the biomass concentration and reactor configuration in which they are measured (Grady et al., 1996). In the extant kinetic assay, there are minimal changes in the physiological state of the test microorganisms, and information regarding microbial activity reflects that of the biomass immediately before the assay (Grady et al., 1996). Extant respirometric assays are robust, simple tools for estimating nitrification kinetics that yield nitrification kinetic parameter such as μ_{max}, K_S, Y, and b estimates comparable to those obtained by laborious measurement of ammonia or nitrite depletion methods (Chandran et al., 2008). A recently developed variant of the commonly used respirometric assay allows biokinetic estimation of both nitrification steps (ammonia and nitrite oxidation) in one experiment (Chandran et al., 2008; Chandran and Smets, 2005).

The main limitation of these estimates is that they rarely measure the specific nitrifying biomass concentrations, specifically X_{AOB} and X_{NOB} (Chandran et al., 2008;

Chandran and Smets, 2000a, 2000b, 2001, 2005). Recently, molecular tools targeting 16S rRNA, 16S rDNA, ammonia monooxygenase subunit A (*amoA*) gene DNA, and *amoA* mRNA have emerged as powerful alternates to measure the presence and activity of AOB in natural and engineered systems (Bollmann et al., 2005; Ebie et al., 2004; Egli et al., 2003; Gieseke et al., 2001; Harms et al., 2003; Hoshino et al., 2001; Juretschko et al., 1998; Kowalchuk et al., 1997; Mobarry et al., 1996; Okano et al., 2004; Schramm et al., 1998, Wagner et al., 1998). Similar characterization for NOB has also been conducted using 16S ribosomal ribonucleic acid (rRNA) and 16S recombinant deoxyribonucleic acid (rDNA) and more recently by targeting the nitrite oxidoreductase (*nxr*) gene (Burrell et al., 1998, Daims et al., 2001, Dionisi et al., 2002, Gieseke et al., 2005, Juretschko et al., 1998, Kim and Kim, 2006; Poly et al., 2008; Schramm et al., 1998). However, there are only a handful of studies that actually use such molecular measures for the estimation of nitrification kinetics such as μ_{max}, b, and Y (Ahn et al., 2008; Blackburne et al., 2007; Kindaichi et al., 2006).

3.7 Estimating Maximum Specific Growth Rate Using Respirometry and Molecular Techniques

The maximum specific growth rate, μ_{max}, estimates for both AOB and NOB can be computed using independent measures of ammonia or nitrite oxidation rate (by respirometry) and AOB or NOB abundance (by quantitative polymerase chain reaction, qPCR) (eq 5.16a and 5.16b, after Grady et al., 1999). Estimates of $Y_{true,AOB}$ have already been determined experimentally, and a widely reported value was adapted from literature (see Table 5.5) (Chandran and Smets, 2000a, 2000b; Pirsing et al., 1996; Rittmann and McCarty, 2001; Sharma and Ahlert, 1977; Wiesmann, 1994).

$$\mu_{max,AOB} = \frac{Y_{true,AOB}}{(1 - Y_{true,AOB})} \times \frac{\dfrac{dO_2}{dt_{max,nh}}}{X_{AOB}} \tag{5.16a}$$

$$\mu_{max,NOB} = \frac{Y_{true,NOB}}{(1 - Y_{true,NOB})} \times \frac{\dfrac{dO_2}{dt_{max,no_2}}}{X_{NOB}} \tag{5.16b}$$

Where,

$Y_{true,AOB}$ = true yield of ammonia oxidizing bacteria (mass of AOB COD/mass of ammonia–nitrogen oxidized);

Table 5.5 Summary of biokinetic parameter estimates describing a partial nitrification bioreactor obtained by a combination of respirometry, mass balances and quantitative polymerase chain reaction (qPCR)-based molecular determination of ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) concentrations (COD = chemical oxygen demand)(Ahn et al., 2008)*.

Parameter estimated in this study (average ± standard deviation)		Additional parameters needed for estimation	Source	Type of reactor or biomass
$\mu_{max,AOB}$ (1/d)	1.08 ± 1.03	$Y_{true,AOB}$ = 0.24 mg X COD/mg N oxidized	Chandran and Smets, 2000a, 2000b	Complete nitrifying enrichment culture
$Y_{obs,AOB}$ (mg X COD/mg N oxidized)	0.15 ± 0.06	None		
b_{AOB} (1/d)	0.32 ± 0.34	f_D = 0.2 mg debris COD/mg COD X, $Y_{obs,AOB}$: estimated above	Grady et al., 1999	Activated sludge
$\mu_{max,NOB}$ (1/d)	2.6 ± 2.05	$Y_{true,NOB}$ = 0.1 mg X COD/mg N oxidized	Pirsing et al., 1996; Rittmann and McCarty, 2001; Sharma and Ahlert, 1977; Wiesmann, 1994	Complete nitrification enrichment culture, including activated sludge
$Y_{obs,NOB}$ (mg X COD/mg N oxidized)	0.04 ± 0.02	None		
b_{NOB} (1/d)	0.75 ± 0.80	f_D = 0.2 mg debris COD/mg COD X, $Y_{obs,NOB}$ estimated above	Grady et al., 1999	Activated sludge

*$\mu_{max,AOB}$ = maximum specific growth rate of ammonia oxidizing bacteria, d^{-1}; $Y_{obs,AOB}$ =observed yield of ammonia oxidizing bacteria (mass of AOB COD/mass of ammonia-nitrogen oxidized); b_{AOB} = specific decay coefficient of ammonia-oxidizing bacteria (d^{-1}); f_D = fraction of decayed biomass resulting in biomass debris (COD/COD); $Y_{true,AOB}$ = true yield of ammonia-oxidizing bacteria (mass of AOB COD/mass of ammonia-nitrogen oxidized); $\mu_{max,NOB}$ = maximum specific growth rate of nitrite-oxidizing bacteria, d^{-1}; $Y_{true,NOB}$ = true yield of nitrite-oxidizing bacteria (mass of NOB COD/mass of nitrite-nitrogen oxidized); $Y_{obs,NOB}$ = observed yield of ammonia-oxidizing bacteria (mass of AOB COD/mass of nitrite-nitrogen oxidized); b_{NOB} = specific decay coefficient of nitrite-oxidizing bacteria (d^{-1}); and X = biomass concentration (mass COD/volume).

$Y_{true,\,NOB}$ = true yield of nitrite oxidizing bacteria (mass of NOB COD/mass of nitrite-nitrogen oxidized);

dO_2/dt_{max} = maximum volumetric oxygen uptake associated with ammonia (subscript, *nh*) and nitrite (subscript, NO_2), respectively;

X_{AOB} = ammonia-oxidizing bacteria concentration (mass COD/volume); and

X_{nob} = nitrite-oxidizing bacteria concentration (mass COD/volume).

3.8 Calculation of Observed Biomass Yield Coefficient

The observed biomass yield coefficients (Y_{obs}) for AOB and NOB can be estimated based on respective biomass concentrations (X_{AOB} and X_{NOB}), HRT (τ), SRT (θ_C), and extent of ammonia or nitrite oxidation (eq 5.17a and 5.17b, after Grady et al., 1999).

$$Y_{obs,AOB} = \frac{X_{AOB}\tau}{\theta_C(S_{no2,eff} + S_{no3,eff})} \tag{5.17a}$$

$$Y_{obs,NOB} = \frac{X_{NOB}\tau}{\theta_C S_{no3,eff}} \tag{5.17b}$$

Where,

Y_{obs} = observed yield coefficients, for AOB and NOB, as previously defined;
X = biomass concentrations, for AOB and NOB, as previously defined;
τ HRT (d);
θ_C = SRT (d); and
$S_{no2,eff}$ and $S_{no3,eff}$ = nitrite and nitrate concentrations in the effluent, respectively (mass-N/volume).

3.9 Calculation of Autotrophic Biomass Decay Coefficient

Specific decay coefficients (b) for AOB and NOB were estimated based on their respective true yield and observed yield coefficients, SRT and f_D (fraction of biomass decayed that results in biomass debris = 0.2 mg COD debris produced per milligram COD active biomass decayed (eqs 5.18a and 5.18b, after Grady et al., 1999).

$$b_{AOB} = \frac{\left(\frac{Y_{true,AOB}}{Y_{obs,AOB}}\right) - 1}{\theta_C\left[1 - f_D\left(\frac{Y_{true,AOB}}{Y_{obs,AOB}}\right)\right]} \tag{5.18a}$$

$$b_{NOB} = \frac{\left(\frac{Y_{true,NOB}}{Y_{obs,NOB}}\right) - 1}{\theta_C\left[1 - f_D\left(\frac{Y_{true,NOB}}{Y_{obs,NOB}}\right)\right]} \tag{5.18b}$$

Based on this methodology, the following kinetic and stoichiometric parameters were estimated for a partial nitrification reactor treating synthetic anaerobic digestion centrate (Table 5.5, influent ammonia = 500 mg-N/L). The reactor relied upon selective enrichment of AOB and washout of NOB from the reactor and consequently, the parameter estimate values reported are distinct from that of typical activated sludge.

4.0 SIMPLE STEADY-STATE SUSPENDED GROWTH DESIGN EQUATIONS

4.1 Effluent Ammonia

The effluent ammonia–nitrogen concentration from a nitrifying activated sludge reactor is governed primarily by nitrification kinetics and the aerobic operating SRT. If the operating SRT is significantly higher than the minimum SRT, then the effluent ammonia–nitrogen concentration is not a function of the influent ammonia concentration (Grady et al., 1999; Rittmann and McCarty, 2001). In such a case, the effluent ammonia–nitrogen concentration from a nitrifying reactor configured as a single completely mixed tank is given by:

$$S_{nh,\text{eff}} = K_{S,nh}\frac{\left(\frac{1}{\theta_{C,A}} + b_A\right)}{\left(\mu_{\max,a} - \left(\frac{1}{\theta_{C,A}} + b_A\right)\right)} \tag{5.19}$$

Where,

$S_{nh,\text{eff}}$ = effluent ammonia–nitrogen concentration from a completely mixed nitrification activated sludge reactor (mg-N/L);
$\theta_{C,A}$ = aerobic solids retention time (d);
$\mu_{\max,A}$ = maximum specific growth rate of nitrifying bacteria (1/d);
$K_{S,nh}$ = half-saturation coefficient of nitrifying bacteria (mg-N/L); and
b_A = specific decay constant of nitrifying bacteria (1/d).

For reactors configured in plug-flow mode, or as completely mixed tanks in series, the above equation needs to be combined with mass balances around each tank in series or each zone in a plug-flow reactor to describe the effluent concentrations.

Alternately, process simulators that capture these and additional activated sludge reactions can be used to determine reactor effluent concentrations.

4.2 Nitrogen Incorporated to Waste Sludge

As mentioned earlier, ammonia is the preferred assimilative nitrogen source for bacteria growth. Under ammonia limitation, alternate assimilative sources such as nitrite and nitrate can be used, but these typically lead to a reduction in the biomass yield coefficient (Grady et al., 1999; Rittmann and McCarty, 2001). Ammonia–nitrogen is assimilated broadly by several bacterial classes in activated sludge, under aerobic, anoxic, and anaerobic conditions to support biomass synthesis, a fraction of which is discharged in waste activated sludge. For typical domestic wastewater, the nitrogen assimilated by nitrifying bacteria in activated sludge is negligible (Grady et al., 1999). In such a case, the amount of nitrogen incorporated into heterotrophic biomass (assuming completely aerobic conditions) is given by (Grady et al., 1999):

$$N_{\text{was}} = F\left[\frac{(1+f_D b_H \theta_C) Y_H (S_{SO} + X_{SO} - S_S)}{(1+b_H \theta_C)}\right] i_{N/XB} \tag{5.20}$$

Where,

N_{was} = nitrogen incorporated in waste sludge (mg N/d);
F = wastewater flow rate (L/d);
f_D = fraction of decayed biomass resulting in biomass debris (COD/COD);
b_H = specific decay constant of heterotrophic bacteria (1/d);
θ_C = overall solids retention time (d);
S_{So} = influent soluble biodegradable organic substrate (mg COD/L);
X_{So} = influent particulate biodegradable organic substrate (mg COD/L);
S_S = effluent soluble biodegradable organic substrate (mg COD/L);
$i_{N/XB}$ = nitrogen content of biomass (X), (mg N/mg X-COD); and
Y_H = true biomass yield of heterotrophic bacteria (mg X-COD/mg S COD).

This equation is simplified to represent completely aerobic-activated sludge operation. Appropriate changes in kinetic and stoichiometric parameters and operating SRT should be included to account for operation under a combination of aerobic, anoxic, and anaerobic conditions.

4.3 Nitrifier Sludge Mass

The total mass of nitrifying (AOB and NOB) bacteria in activated sludge is given by

$$X_{B,A,T}V = \theta_{C,A}F\left[\frac{(1+f_D b_A\theta_{C,A})Y_A(S_{N,A}-S_{nh})}{(1+b_A\theta_{C,A})}\right] \tag{5.21}$$

Where,

$X_{B,A,T}$ = total nitrifier biomass concentration (mg COD/L);
V = aerobic volume of activated sludge reactor (L);
F = wastewater flow rate (L/d);
b_A = specific decay constant of autotrophic nitrifying bacteria (1/d);
$\theta_{C,A}$ = aerobic solids retention time (d);
$S_{N,A}$ = nitrogen available for nitrification (mg N/L);
S_{nh} = effluent ammonia nitrogen concentration (mg N/L); and
Y_A = true biomass yield of autotrophic nitrifying bacteria (mg *X*-COD/mg N oxidized).

The amount of nitrogen available for nitrification is obtained by subtracting the nitrogen assimilated for biomass synthesis from the influent TKN and is given by (Grady et al., 1999):

$$S_{N,A} = TKN - \left[\frac{(1+f_D b_H\theta_C)Y_H(S_{SO}+X_{SO}-S_S)}{(1+b_H\theta_C)}\right]i_{N/XB} \tag{5.22}$$

4.4 Oxygen Requirements

Nitrification is an extremely oxygen-intensive process, and each unit of ammonia–nitrogen by mass consumes approximately 4.33 units (accounting for nitrifier biomass growth) of oxygen by mass for oxidation to nitrate (Grady et al., 1999). In high nitrogen-load systems, it may be challenging to supply adequate oxygen for nitrification, for instance, in the influent end of plug-flow reactors or in the influent zones of highly modular reactors-in-series system. In such cases, step-feed configurations may be a viable alternate to redistribute the oxygen requirement over a higher volume of the reactor (Grady et al., 1999). See Chapter 7 for additional discussion on this topic. The oxygen consumption associated with nitrification is given by (Grady et al., 1999):

$$R_{O,A} = F(S_{N,A}-S_{nh})\left[4.57-\frac{(1+f_D b_A\theta_{C,A})}{1+b_A\theta_{C,A}}Y_A\right] \tag{5.23}$$

Where,

$R_{O,A}$ = oxygen requirement for nitrification (mg O_2/d);
$S_{N,A}$ = nitrogen available for nitrification (mg N/L);
S_{nh} = effluent ammonia nitrogen concentration (mg N/L);
f_D = fraction of decayed biomass resulting in biomass debris (COD/COD);
b_A = specific decay constant of autotrophic nitrifying bacteria (1/d);
$\theta_{C,A}$ = aerobic solids retention time (d); and
Y_A = true biomass yield of autotrophic nitrifying bacteria (mg X COD/mg N oxidized).

4.5 Alkalinity Consumption

Nitrification consumes 7.07 g alkalinity (as $CaCO_3$) per gram ammonia–nitrogen consumed by nitrifying bacteria or 7.23 g alkalinity (as $CaCO_3$) per gram nitrate-nitrogen formed, accounting for ammonia assimilation and biomass growth (Grady et al., 1999). The amount of alkalinity consumed during nitrification is given by (Grady et al., 1999):

$$R_{\text{Alk}} = 7.23F(S_{N,a} - S_{nh} - S_{ns}) \tag{5.24}$$

Where,

F = wastewater flow rate (L/d);
$S_{N,A}$ = nitrogen available for nitrification (mg N/L);
S_{nh} = reactor ammonia concentration (mg N/L); and
S_{ns} = soluble biodegradable organic nitrogen (mg N/L).

In addition to providing alkalinity to offset consumption by nitrification, residual alkalinity of 50 mg/L (as $CaCO_3$) typically is provided to ensure adequate buffering (Grady et al., 1999).

5.0 CONSIDERATIONS FOR DIFFERENT NUTRIENT REMOVAL CONFIGURATIONS

5.1 Accounting for Unaerated Zones or Clarifiers

Overall BNR by single-sludge systems is achieved by combined nitrification (under aerobic conditions) and denitrification (under anoxic conditions). From a wastewater treatment design perspective, under completely anoxic conditions, nitrifying bacteria cannot sustain their activity. Thus, the only governing process for nitrification in

anoxic zones of a BNR reactor or clarifiers is anoxic decay. For this reason, the elementary design equations above only account for nitrification in the aerobic section of the activated sludge reactor.

5.2 Single-Sludge Versus Separate-Sludge Systems

Typically treatment of separate-stage nitrification systems is more straightforward compared to single-sludge systems. This is because single-sludge systems are dominated by nitrification in the nitrification stage with minimal heterotrophic activity. Therefore, the elementary equations can be simplified to account solely for nitrification associated substrate consumption and biomass growth and decay. Additional considerations of single- and separate-sludge systems is provided in Section 2.0 of this chapter.

6.0 DYNAMIC BEHAVIOR

The equations provided in this chapter are based on steady-state solutions of differential equations that govern substrate consumption and biomass growth and decay. Steady-state solutions often are used to formulate the initial design of an activated sludge system because of their simplicity. It must be recognized, however, that activated sludge systems are subject to constantly varying influent flow volume and composition, in addition to variations in factors such as temperature and pH. These variations can be described adequately only by using dynamic state modeling. Dynamic states can be described by using the concept of peaking factors for analytical or spreadsheet-based calculations or simulator packages including BioWin, WEST, GPS-X, Aqua-Sim, or custom packages. The specific dynamic variations in effluent ammonia and oxygen requirements are considered next.

6.1 Effluent Ammonia

Dynamic-state modeling is especially important for nitrification since nitrifying bacteria have inherently low kinetics and are inhibited by many physical, chemical, and environmental effects (Chandran and Love, 2008; Grady et al., 1999; Hockenbury and Grady, 1977; Painter, 1970; Sharma and Ahlert, 1977). As a result, the effect of dynamically changing wastewater flow and composition is especially apparent on nitrification performance and associated oxygen or alkalinity consumption.

During peak influent load events at nitrifying wastewater treatment plants, there is a strong correlation between the magnitude and timespan of variables in the

influent and effluent ammonia-N concentrations because of low nitrification kinetics. In contrast, more rapid processes associated with aerobic heterotrophic growth are minimally or not at all affected. Further, the variability in effluent ammonia concentrations is especially severe for nitrification tanks configured as a single completely mixed reactor as opposed to several reactors in series. In the former case, the entire dynamic loading is subjected upon a single reactor, resulting in higher effluent ammonia concentrations. In the latter case, the extent of nitrification shifts to downstream reactors, thereby dampening some of the dynamic variability effects (Grady et al., 1999).

6.2 Spatial and Time-Varying Oxygen Demand

The variability in the degree of nitrification is mirrored in oxygen consumption. Based on the high oxygen consumption associated with nitrification during peak-load events, there simply may not be enough aerator capacity (or number of diffusers) to handle the additional ammonia loading. Therefore, it is common to have periods of high influent load correspond with low dissolved oxygen concentrations in the activated sludge reactors. For a reactors-in-series configuration, the overall oxygen uptake may simply be redistributed with increased oxygen consumption downstream to parallel higher extents of nitrification (Grady et al., 1999).

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Chapter 6

Nitrogen Removal Processes, Configuration, and Process-Sizing Criteria for Combined Nitrification and Denitrification Processes

(continued)

1.0 NITROGEN REMOVAL PROCESSES

There are two types of nitrogen removal processes—biological and chemical. Biological processes include autotrophic nitrification and heterotrophic denitrification as in biofilms and activated sludge, and autotrophic nitrification and autotrophic denitrification as applied in certain sidestream processes (i.e., anammox).

1.1 Heterotrophic Denitrification for Nitrogen Removal

Heterotrophic denitrification can occur at three locations in the wastewater treatment process:

(1) In separate-sludge denitrification processes that treat effluent from a nitrifying activated-sludge, biofilm reactor (i.e., biological aerated filter, moving bed with plastic or sponge media) or in integrated fixed-film activated sludge (IFAS) processes. An external organic carbon source is added as the carbon source for heterotrophic denitrification.

(2) In unaerated zones of single-sludge activated sludge systems, predenitrification filters, and biofilm reactors. Nitrates are either recycled from the downstream aerobic zone to the predenitrification zone or flow to a downstream anoxic zone. The organic carbon in the influent to the reactor (primary effluent or raw influent) or endogenous respiration is used for the carbon source.

(3) In biological flocs and biofilms in the aerobic zone of an activated sludge process. This depends on the operating dissolved oxygen levels in the aerobic zone.

1.2 Autotrophic Denitrification for Nitrogen Removal

Autotrophic denitrification occurs at long mean cell residence times (MCRTs) of typically greater than 20 days and under conditions where organic carbon is limited. This process can be used to treat wastewaters from sidestreams generated following anaerobic digestion (Rosenwinkel and Cornelius, 2005; Rostrom et al., 2001; Seyfried et al., 2001). Autotrophic denitrification results in significant savings in external carbon and sludge production. The ability to use nitrites as an electron acceptor instead of oxygen to oxidize ammonia to nitrogen gas, as in the anammox autotrophic denitrification process, helps reduce oxygen and organic carbon requirements. The downside to this process is the need for accurate control over dissolved oxygen and pH to create conditions that are optimal for the bacteria.

This chapter presents the separate-sludge and single-sludge biological nitrogen removal processes in which heterotrophic bacteria carry out denitrification. The nitrogen removal process includes the steps for nitrification and denitrification and for the synthesis of nitrogen in the biomass. Process kinetics and kinetics-based equations are presented to explain the details of each step of the nitrogen removal process. In some instances, a full-scale example is included to provide the reader with a better context of the material for the kinetics-based equations. This chapter does not cover the mixing, aeration, shear, or hydraulics criteria that need to be integrated with kinetics to develop a complete design approach.

2.0 SEPARATE-SLUDGE (SEPARATE-STAGE) DENITRIFICATION

The purpose of a separate-sludge (in some instances, referred to as separate-stage) denitrification process is to remove nitrate from wastewater, typically by treating effluent from a nitrifying activated-sludge process. When carbon oxidation and nitrification are performed in one stage, the addition of separate-sludge denitrification creates what is known as a two-sludge (two-stage) nitrification–denitrification process. Each sludge system is operated independently. The division of carbon oxidation, nitrification, and denitrification into three separate stages is referred to as a three-stage process.

Separate-stage heterotrophic denitrification processes have some advantages and disadvantages. The biggest advantage is that low effluent total nitrogen concentrations are attainable primarily because the denitrification stage can be optimized separately. Also, separate-stage denitrification is needed for some industrial wastewater that is high in nitrogen but deficient in carbon. This process requires, however, two sets of clarifiers and return sludge pumping systems. In addition, if there is no denitrification in the first stage (as in the modified Ludzack–Ettinger, or MLE, configuration discussed below), then most of the nitrates have to be denitrified with supplemental carbon. This adds to the operating cost.

This section focuses on nitrogen removal process kinetics for single-sludge, separate-stage denitrification processes.

2.1 Characteristics

There are four types of separate-sludge denitrification processes: suspended-growth, moving-bed attached growth, packed-bed attached growth, and fluidized-bed attached growth systems. A flow schematic diagram of each is shown in Figure 6.1. There are some characteristics that all separate-stage denitrification processes share. Specifically, denitrification rates are lower at colder temperatures, at low phosphorus levels that inhibit growth (less than 0.1 mg/L ortho-P), at extreme pH levels, and in the presence of inhibitory chemical compounds. The kinetics-based methodology that follows can account for the effect of temperature. The effect of pH is not clear, however, because of conflicting reports in the literature. The pH effects typically can be ignored if near-neutral pH (6.5–7.5) is maintained (Randall et al., 1992). Denitrification reactions can produce alkalinity, which typically elevate the pH. This may be important if the nitrified effluent has a pH of less than 6.5.

2.2 Suspended Growth

Figure 6.1a shows a schematic diagram of the separate-stage, suspended-growth denitrification process. The process is a variation of the activated-sludge process, which consists of a suspended-growth reactor followed by a clarifier. The primary operational difference (besides methanol addition) in suspended-growth denitrification compared to standard activated sludge is that either the majority of the reactor or the entire reactor is not aerated but instead mixed, typically by mechanical means. Either complete-mix or plug-flow reactors can be used for the anoxic reactor. The schematic in Figure 6.1a shows the anoxic reactor divided into sections, which simulates plug flow. An aeration zone with a short retention time (15–60 minutes)

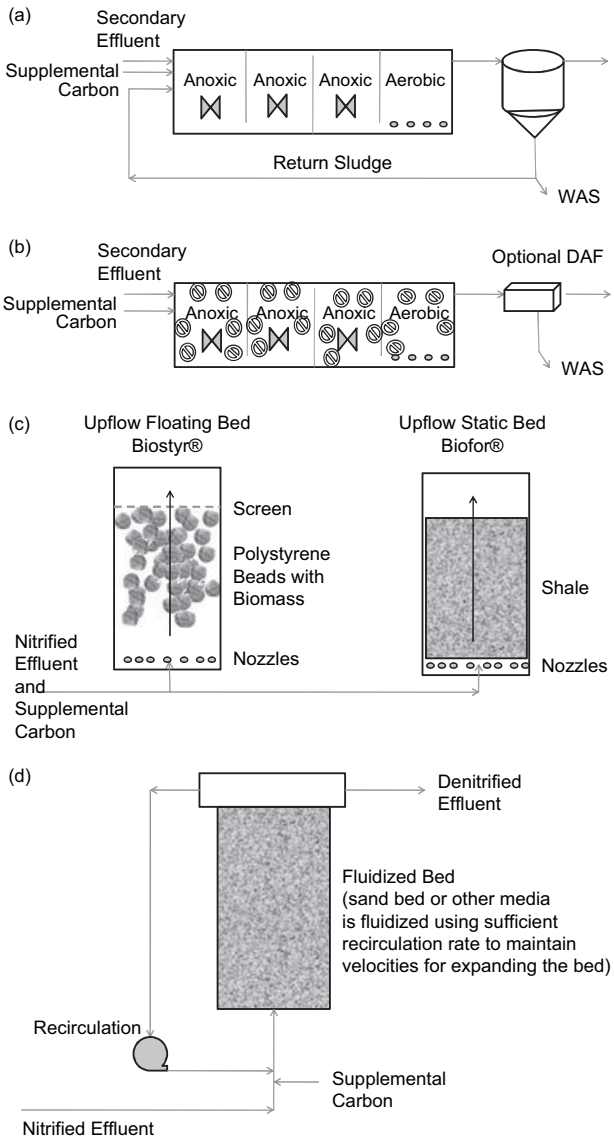

FIGURE 6.1 (a) Tertiary denitrification suspended growth-activated sludge system (Benefield, et al., in development); (b) tertiary denitrification horizontal biofilm reactor (moving-bed biofilm reactor) (c) upflow packed-bed biological anoxic filters (filters can also be downflow sand bed or shale); and (d) fluidized-bed denitrification filter. (DAF = dissolved air flotation; WAS = waste activated sludge).

typically is provided directly before clarification to strip any remaining nitrogen gas (also strips carbon dioxide); to add dissolved oxygen and help prevent denitrification (and possible rising sludge because of nitrogen gas bubbles adhering to the sludge floc) in the clarifier; and to oxidize any excess methanol that remains. Some settled sludge is wasted to maintain the desired solids retention time (SRT) or mixed liquor suspended solids (MLSS) concentration, and the rest is recycled to the anoxic portion of the reactor.

Mixing is required in the anoxic reactor. Proper intensity of mixing is needed to maintain the solids in suspension without mixing in too much dissolved oxygen and to ensure good contact of the denitrifying biomass with nitrates and carbon. Mixing intensity required will vary from system to system, but it is reasonable to assume that 4 to 10 W/m^3 (20–50 hp/million gal.) is required (Randall et al., 1992). Another criterion is to provide complete tank contents turnover every 20 minutes based on the pumping rate of the submersible mixer and the tank volume.

2.2.1 Process-Sizing Criteria

The volume of a suspended-growth denitrification reactor can be determined based on denitrification kinetics or on full-scale or pilot experience. Hydraulic retention time (HRT), SRT, denitrification rate, and methanol requirements typically are the most important considerations for the process.

The sizing of suspended-growth denitrification reactors typically is based on either SRT considerations or a denitrification rate approach. The SRT approach uses basic kinetic information for a rational approach to sizing (Randall et al., 1992). In the SRT approach, the kinetic coefficients should be expressed on a chemical oxygen demand (COD) basis rather than a nitrate basis. This accounts for the fact that COD, rather than nitrate, is typically the limiting factor for denitrification (McClintock et al., 1988; Stensel et al., 1973). The half-rate constant for nitrate is low, approximately 0.1 mg/L; therefore, nitrate does not become limiting until it approaches very low concentrations. McClintock et al. (1988), in a study treating synthetic wastewater, reported that yield coefficients and decay rates were approximately 25% lower when nitrate was used as an electron acceptor compared to when oxygen was used. Stensel et al. (1973) have reported basic denitrification kinetic coefficients on a COD basis using methanol. These coefficients will be used in the design example (see Table 6.1).

The gentrification-rate approach historically has been the most widely used approach. Although it is a relatively simple approach, it requires a specific denitrification rate (SDNR). Reported rates using methanol vary widely (0.10–1.2 g NO_3^--N/g

TABLE 6.1 Denitrification kinetic coefficients using methanol (Stensel et al., 1973).

Parameter	Units	20°C	10°C
Synthesis yield coefficient, $Y_{H,anx}$	g VSS[a]/g COD	0.18	0.17
Endogenous decay coefficient, $k_{dH,anx}$	d^{-1}	0.04	0.05
Maximum specific substrate removal rate, $q_{mH,anx}$	g COD/g VSS·d	10.3	3.1
Half-saturation constant, K_s	g COD/m^3	9.1	12.6

COD = chemical oxygen demand; VSS = volatile suspended solids.

total suspended solids [TSS]·d) because of different temperature conditions and organic substrate concentrations used during the denitrification studies. These design approaches are discussed in detail by Metcalf and Eddy (2003) and in the U.S. Environmental Protection Agency's (U.S. EPA's) *Nitrogen Control Manual* (1993).

2.2.2 *Design Equations*

The design equations used for the SRT design approach using kinetic coefficients on a COD basis are illustrated here. The kinetics equations used are based on organic substrate removal in complete-mix systems and are used in the kinetic approach to design for carbon oxidation activated-sludge processes (Lawrence and McCarty, 1970).

The specific substrate removal can be found from the maximum substrate removal rate according to the following:

$$q_{H,anx} = q_{mH,anx}\left(\frac{S_{anx,eff}}{K_S + S_{anx,eff}}\right) \tag{6.1}$$

Where,

$q_{H,anx}$ = specific substrate removal rate, d^{-1};
$q_{mH,anx}$ = maximum substrate removal rate, d^{-1};
$S_{anx,eff}$ = effluent soluble biodegradable COD concentration out of the anoxic zone, mg/L; and
K_s = half-saturation constant, mg/L;

Denitrification is adversely affected by colder temperatures. Specific substrate removal rates (and denitrification rates) can be corrected for temperature using the following equation:

$$q_T = q_{20}\,\theta^{T-20} \tag{6.2}$$

Where,

θ = temperature correction coefficient, and

T = temperature, °C.

The minimum SRT required can be calculated from the temperature-corrected q using the equation:

$$\frac{1}{SRT_{anx}} = (Y_{H,anx})(q_{H,anx}) - b_{H,anx} \quad (6.3)$$

Where,

$Y_{H,anx}$ = anoxic synthesis yield coefficient, g volatile suspended solids (VSS)/g COD used, and

$b_{H,anx}$ = anoxic endogenous decay coefficient, d^{-1}.

Use of a safety factor between 1.25 and 2.0 is recommended to account for reductions in $q_{H,anx}$ that may occur when some oxygen is introduced. A peaking factor also may be used to account for diurnal peak loads.

$$SRT_{anx,design} = SRT_{anx}\,(SF)(PF) \quad (6.4a)$$

The design SRT for the reactor includes the anoxic zone and a reaeration zone. The reaeration zone removes any excess biodegradable soluble COD that remains after the postanoxic zone. The volume of the reaeration zone is small, and its HRT ranges from 10 to 30 minutes. An HRT of 15 minutes may be used for the design.

$$SRT_{design} = SRT_{anx}\frac{V_{total}}{V_{anx}} \quad (6.4b)$$

Where,

V_{anx} = anoxic volume as determined below.

V_{total} = total of anoxic and reaeration zone volume. The reaeration volume can be assumed to provide an HRT of 15 minutes. The SRT_{design} can be determined after the anoxic volume as described below.

The concentration of COD from methanol maintained in the anoxic reactor must be selected, typically 3 to 5 mg COD/L. This amount will be oxidized easily in the postaeration part of the reactor. The denitrification rate could be increased by using higher methanol concentrations, if desired, resulting in a smaller anoxic basin. There is a tradeoff, however, between costs of higher methanol doses (and increased sludge production) and capital costs for a larger reactor.

The supplemental COD that has to be added as methanol can be computed as follows:

$$\text{Supplemental COD} = [2.86(NO_X N_{inf} - NO_2 N_{eff}) + 1.71(NO_2 N_{inf}) + DO_{inf}][\text{COD Factor}_{anx}] + S_{anx,eff} \quad (6.5a)$$

Where COD Factor_{anx} is the amount of COD consumed for the electron acceptor (dissolved oxygen and oxidized N forms) used in the anoxic process.

Because COD is used for biomass production (sludge yield) and for COD oxidation, it helps determine the amount of COD required based on the electron acceptors consumed.

$$\text{COD Factor}_{anx} = \frac{1}{1 - 1.42\dfrac{Y_{H,anx,methanol}}{1 + b_{H,anx}SRT_{anx} + b_{H,aer}SRT_{reaer}}} \quad (6.5b)$$

Where,

NO_X-N_{inf} = influent nitrate and nitrite–nitrogen (NO_2 and NO_3–N) concentration, mg/L;
NO_3-N_{eff} = effluent NO_3–N concentration, mg/L;
NO_2-N_{inf} = influent NO_2–N concentration, mg/L (effluent is assumed to be 0);
DO_{inf} = influent dissolved oxygen, mg/L; and
COD Factor_{anx} = a conversion factor to determine mg of COD uptake per mg of uptake of electron acceptors.

The SRT_{reaer} has to be determined iteratively after the anoxic volume has been computed. For the first pass of the iteration, it can be assumed to be two days.

The anoxic volume can be determined using the following equation which is based on a mass balance on solids (Lawrence and McCarty, 1970):

$$V_{total} = \left[\frac{Y_{H,anx,methanol}}{1 + b_{H,anx}SRT_{anx} + b_{H,aer}SRT_{reaer}}(S_{suppl\ COD} - S_{anx,eff}) + \frac{Y_{H,anx,inf\ VSS}}{1 + b_{H,anx}SRT_{anx} + b_{H,aer}SRT_{reaer}}(S_{VSS,inf}) + \frac{Y_{H,aer}}{1 + b_{H,anx}SRT_{anx} + b_{H,aer}SRT_{reaer}}(S_{anx,eff} - S_{eff})\right]\frac{Q\ SRT_{design}}{X_{VSS}}$$

$$S_{VSS,inf} = 1.42\ VSS_{inf} \quad (6.6)$$

Where,

V = volume of tank, m^3;
Q = influent flow rate, m^3/d;
X_{VSS} = denitrification reactor VSS concentration, mg/L;
$S_{uppl\ COD}$ = supplemental COD added for denitrification, mg/L;

$S_{VSS,inf}$ = 1.42 times the VSS in the influent to the reactor (secondary effluent);
S_{eff} = reaeration zone effluent soluble COD, mg/L;
$Y_{H,anx,inf\ VSS}$ = 0.3 mg VSS/mg COD present in the VSS; and
$b_{H,aer}$ = aerobic zone decay rate, assumed to be 33% higher than the anoxic zone decay rate.

The concentration of S_{eff} can be assumed to be one-half of $S_{anx,eff}$. It can be computed in an iterative calculation using a mass balance and substrate utilization kinetics across the aerobic cell (Sen and Randall, 2008a). Complex multicell simulation models can automate these calculations.

In some instances, the anoxic volume is sized-based on the SDNR (mg NO_3-N denitrified per mg VSS per day) obtained from pilot studies or from the literature. This is computed as follows:

$$V_{anx} = \frac{(NO_3N_{inf} - NO_3N_{eff})(Q)}{X_{VSS}\ \ SDNR} \tag{6.7}$$

2.3 Attached Growth Biofilm Reactors

Attached growth biofilm reactors for denitrification include moving-bed or cross-flow reactors (Figure 6.1b) and packed- (Figure 6.1c) and fluidized-bed (Figure 6.1d) reactors. This section discusses packed-bed technology.

There are two types of packed-bed processes: gas filled and liquid filled (Soap and Detergent Association [SDA], 1989). In the gas-filled reactor, the enclosed vessel is filled with structured or random media as the growing site for denitrifying microorganisms. Open space is maintained with a nitrogen-enriched atmosphere that is essential for denitrification. The nitrate-bearing wastewater is distributed evenly throughout the media in the same way as in the trickling filter process. Because of constant sloughing of biomass from the media during operation, a clarifier is required to remove excess TSS from the denitrified effluent.

The liquid-filled reactor may further be divided into two categories depending on whether they use high- or low-porosity media. In the high-porosity reactor, 10% to 20% of the liquid volume is displaced by the media and its biofilm. In the low-porosity (packed-bed) reactor, more than 50% of the liquid volume is displaced by the media and its biofilm.

The high-porosity reactor typically is operated in an upflow or cross-flow (horizontal) mode. (The cross-flow reactor previously was known as a moving-bed reactor, and then subsequently called a moving-bed biofilm reactor, or MBBR, which was trademarked by Kaldnes [Reardon, 1993]). Because a constant discharge of excess

biomass is unavoidable, a subsequent clarification step such as clarifier, dissolved air flotation thickener, or filter is required to produce a clear effluent with low TSS.

A low-porosity reactor typically is operated in a downflow mode (i.e., Tetra Tech denitrification filters and IDI Biofor filters) or in an upflow mode (Kruger Biostyr filters). A periodic backwash of the reactor is required to prevent clogging. The use of fine media allows this type of bioreactor to achieve both denitrification and filtration. Therefore, the treated effluent will be low in TSS and oxidized nitrogen. In downflow mode, however, the fine media will retain not only the removed suspended solids and biomass but also the nitrogen gas that is generated. A periodic nitrogen gas release operation (bumping) and filter backwashing will have to be performed to relieve the buildup of head loss caused by trapped gas and solids.

A popular low porosity packed-bed reactor is the downflow deep-bed filter for both denitrification and filtration. This filter, as shown in Figure 6.2, will be used to illustrate the attached growth denitrification.

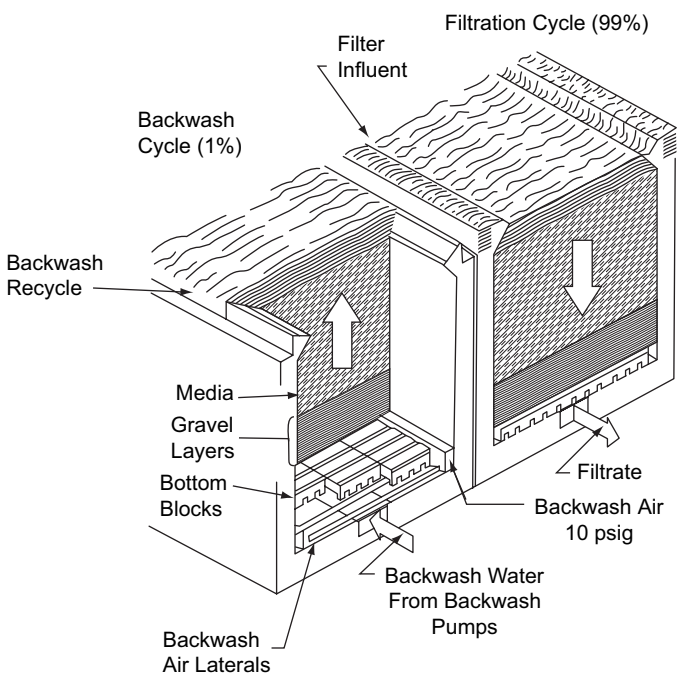

FIGURE 6.2 Cross section of a downflow dentrification filter (psi × 6895 = Pa).

2.3.1 *Process-Sizing Criteria for Attached Growth Biofilm Reactor*

Because the denitrification filter serves both as a filter for removing TSS and as a biological reactor for denitrification, some special considerations must be made (Chen and Slack, 1991). First, a nozzleless filter underdrain system should be used for the denitrification filter application. At the Howard F. Curren Advanced Wastewater Treatment Plant in Tampa, Florida, a nozzle-type filter bottom caused biofouling, clogging, and breakage and eventually led to short-circuiting of backwash air and water and loss of filter media (Pickard et al., 1985). After conversion to a nozzleless underdrain, these undesirable problems were eliminated. Second, a coarse (effective size 1.8–2.3 mm), uniform (uniformity coefficient at 1.35), and spherical (sphericity of 0.8–0.9) media should be used for this application. Again the Tampa plant experience proved that replacement of angular media with round media significantly reduced the frequency of gas bumping and backwashing. Third, air and water backwash is required to keep the denitrification filter clean and free of biosolids accumulation. The degree of filter cleaning, however, should be controlled carefully to avoid excessive scouring of biomass and the resulting long lag time for the denitrification reaction to be established when the filter is put back into operation. Otherwise, a reseed of biomass with backwash water may be required. Fourth, the influent to the filter vessel should be introduced with the least amount of turbulence to minimize the increase of dissolved oxygen in the filter influent, which will affect consumption of the carbon source used for denitrification. A specially designed weir block for the influent trough has been used successfully for this purpose.

Figure 6.2 shows the cross-section of a deep-bed filter and depicts the essential elements of a downflow denitrification filter. Three parts methanol is added per part NO_3-N to provide sufficient carbon for complete denitrification (Savage and Chen, 1975). If complete denitrification is not a requirement, then the quantity of methanol as depicted in Figure 6.3 can be reduced (Redd et al., 1992).

The method of distributing nitrified flow to the filter cells is important to the performance of the denitrification filter system. The HRT in every filter cell should be equal at any given time. Therefore, even distribution of filter influent is important. The incoming flow may vary, but the flow should be split evenly to every individual filter in operation. It is not desirable to use a declining rate filter system for denitrification because of the resulting uneven filtration rate through individual filters.

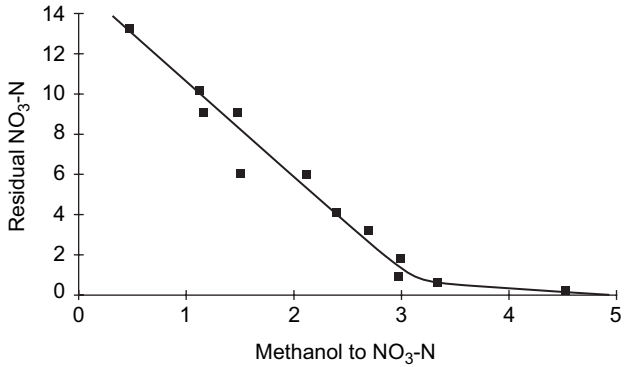

FIGURE 6.3 Nitrate removal efficiency at various methanol dosages.

2.3.2 Design Equations

There are two different but related methods available to engineers for sizing a denitrification filter system: the volumetric nitrogen loading approach and the hydraulic contact time method.

The volumetric approach is probably the most typically used method of the two. In this approach, the denitrification reactor size is calculated based on an appropriate NO_3-N loading per unit reactor volume. A "rule of thumb" approach is used when denitrification kinetic information is lacking or a conservative design is tolerable. The range for the unit volumetric loading rate varies between 240 and 3200 kg NO_x-N/l000 m^3·d (15 to 200 lb NO_x–N/d/l000 cu ft). The selection of a loading rate for the reactor sizing will be dictated by the type of reactor and media used, characteristics of the nitrified water, and reaction temperature.

The hydraulic contact time method is based on the principle that, for a biological system to remove NO_3-N from water, removal efficiency is directly proportional to the HRT in the reactor until a maximum denitrification is approached, at which time the rate of removal levels off. Typical denitrification design curves for a deep-bed filter using coarse sand as the filter media are shown in Figure 6.4 (Savage, 1983). These design curves are only applicable to a specific type of reactor or media and within a certain range of NO_3-N levels. It is advisable that for different types of reactors or for various ranges of nitrate levels, separate design curves may have to be derived from a pilot study to determine their specific denitrification applications.

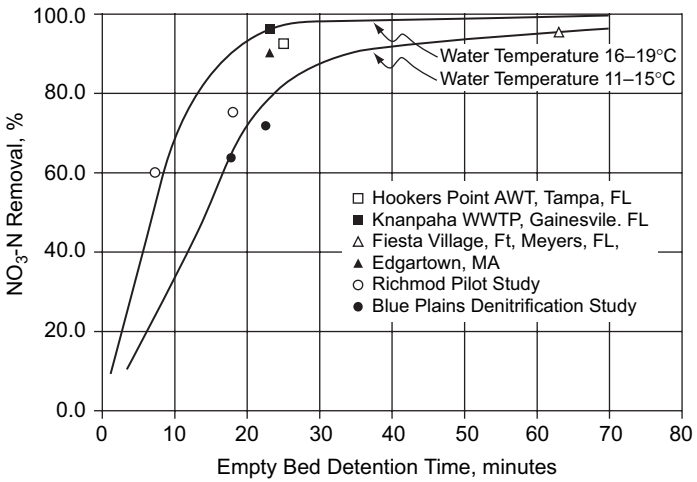

FIGURE 6.4 Typical design curves using hydraulic contact time for a downflow deep-bed filter (Savage, 1983).

Occasionally, the size of a denitrification filter system will not be determined by reaction kinetics but by the hydraulic limitation according to site-specific regulations. For example, in California, Title 22 regulations require that the maximum filtration rate for a water reclamation filter system should not be more than 294 $m^3/m^2 \cdot d$ (5 gpm/sq ft) with one of the filter cells out of service (State of California, 1978). The kinetic rate may allow a filtration rate to be more than 294 $m^3/m^2 \cdot d$ (5 gpm/sq ft); however, the Title 22 regulations dictate the size of the filter system.

Other factors that may affect the sizing of a filter system are the limitation of the filter backwashing and gas bumping frequency. Although backwashing and bumping operations will not affect significantly the denitrification efficiency of a deep-bed filter, in practice, the frequency of filter backwashing should be limited to no more than once per day and gas bumping to no more than once per hour (Savage and Chen, 1972). For a deep-bed denitrification filter, the filter will require backwashing after the solids loading exceeds 5 to 10 $kg/m^2 \cdot$cycle (1–2 lb/sq ft·cycle). When the NO_3-N removal exceeds 0.25 to 0.5 $kg/m^2 \cdot$cycle (0.05–0.1 lb/sq ft·cycle), the filter will need bumping. Filter sizing should be reviewed with these limitations in mind when treating a nitrified stream with high TSS or nitrate concentrations . It is possible that filter size may have to be increased beyond that required strictly for nitrate removal to accommodate excessive solids buildup.

A kinetics-based approach to modeling filters can be undertaken as a second method. In this approach, the filter is segmented into multiple compartments in series. Denitrification is computed within each segment. The denitrification is based on bulk liquid dissolved oxygen and oxidized nitrogen entering each segment and their consumption by biofilm growth. This is used to compute the dissolved oxygen and oxidized nitrogen entering the following segment. Removal in each segment also depends on the biofilm surface area, which is a function of the media and hydrodynamic conditions (liquid velocities in the interstitial space) that prevent agglomeration of particles. The approach has been taken by Choudhury et al. (2010) and Crosswell et al. (2009) for simulating COD removal and denitrification in a deep-bed recirculating denitrification filter. The method gives a better perspective of where the denitrification is taking place in the filter and whether the kinetics in the biofilm will be inhibited by nutrient starvation (i.e., phosphorus) in some segments of the filter.

3.0 SINGLE-SLUDGE NITRIFICATION–DENITRIFICATION

3.1 Characteristics

Single-sludge systems are those in which nutrient removal is achieved in a single basin and clarifier. The basin may be divided into several zones to achieve anaerobic or anoxic conditions depending on the treatment goal. Several configurations have been used including predenitrification, postdenitrification, and combined pre- and postdenitrification systems. The more commonly used single-sludge processes are presented in the *Design of Municipal Wastewater Treatment Plants* (WEF and ASCE, 2009) and U.S. EPA (1993). Various design procedures have been developed for designing nitrogen removal systems (Bidstrup and Grady, 1988; Randall et al., 1992; SDA, 1989; TREEO, 1988; U.S. EPA, 1993; WEF, 2009). The objective of these processes is biological removal of nitrogen from wastewater.

For nitrogen removal, a nitrifying population of microorganisms must first be established for the oxidation of ammonium–nitrogen (NH_4^+-N) to nitrate–nitrogen (NO_3^--N). The design MCRT can be determined by running a simulation model or by using a safety factor and a peaking factor on the minimum MCRT required for nitrification.

As with any type of biological process, a significant amount of nitrogen is removed from the wastewater through incorporation into the biomass. Based on the empirical

formula $C_5H_7O_2N$ for biomass, nitrogen makes up approximately 12% by weight (Hoover and Porges, 1952). Therefore, the maximum amount of nitrogen that can be removed by wasting of the activated sludge (increases with yield which increases with lower SRT) ranges from approximately 7.4 mg/L for high-rate activated-sludge systems to approximately 3.7 mg/L for extended aeration facilities based on the total nitrogen influent loading. The remaining 15 to 25 mg/L is nitrified to NO_x-N.

Biological denitrification systems using one or more anoxic zones are required to meet more stringent effluent requirements for total nitrogen removal. A single-sludge system using one preanoxic zone can achieve an effluent total nitrogen concentration of 4 to 11 mg/L as nitrogen. Both a pre- and a postanoxic zone (aerobic zone in between) are required to reduce the total nitrogen concentration in the effluent to 3 mg/L as nitrogen (Morales et al., 1991; SDA, 1989; U.S. EPA, 1993). Typically, supplemental carbon is needed only when postanoxic zones or postdenitrification systems are used.

This section presents the kinetics-based equations for three types of single-sludge systems: predenitrification systems (MLE), pre- and postdenitrification systems, and oxic-postanoxic. For activated sludge (suspended solids) systems, the method presented here is based on the International Water Association Activated Sludge Model (IWA-ASM). It allows for use of a one-pass and an iterative-calculation process. The iterative process can be implemented in a spreadsheet. The spreadsheet implementation shown here, however, is limited to a single cell (complete mix) anoxic zone followed by a single cell (complete mix) aerobic zone. The spreadsheet can also be combined with a postanoxic and reaeration zone in a separate stage postdenitrification system.

Most plants today include multiple cells within the anoxic and aerobic zones. For the multicell configuration, one of the commercially available process models that are based on the IWA-ASM can be used.

A number of models can be used for IFAS systems, which combine biofilm and suspended solids systems in the same reactor (zone and tank). *Design of Municipal Wastewater Treatment Plant* (WEF et al., 2009) discusses application and verification of the models for an IFAS and MBBR nitrogen removal system design. The IFAS models listed, however, have significant limitations because they do not account for differences in types of media surfaces, shape of carrier particles, or location and mixing factors, which can lead to significant errors (Boltz et al., 2008). Chapter 11 of the manual evaluates results of steady-state and dynamic simulation models for 31 days of plant data taken during December 2006 that were collected at the IFAS system at

Broomfield, Colorado, WWTP. For a more in-depth analysis of differences between media and biological system response, it is necessary to adjust the inputs into modeling tools available on the market (free and commercial) (Sen et al., 2009). These tools allow evaluation of IFAS applications at various temperatures of industrial wastewaters, and differing media types. Also, these tools enable understanding and replication of the differences between fixed-bed media biofilm and moving-bed media (Brown, 2009; Copithorn, 2009; Copithorn and Sen, 2010; Huhtamaki and Huhtamaki, 2009; Smith, 2009).

3.2 Process Kinetics-Based Equations

Figure 6.5 is a schematic of a typical predenitrification system. For the predenitrification (anoxic/oxic) mode of operation, an anoxic zone precedes the aerobic or oxic zone. The carbonaceous oxygen demand is met in the anoxic and aerobic zones. The nitrogenous oxygen demand of the wastewater is primarily met in the aerobic zone. After the nitrates have been formed, the nitrified mixed liquor must be recycled back to the anoxic zone to allow the heterotrophic denitrifiers to accomplish denitrification. Predenitrification systems are economical single-sludge systems to operate because a supplemental carbon source typically is not required. The recycle rates and detention times are dependent on the strength of the wastewater and the temperature. Typical range of values is shown in Table 6.2.

3.2.1 Process Kinetics Equations for Predenitrification

The process volume of the anoxic zone depends on the amount of nitrogen to be removed from the wastewater, the mixed liquor volatile suspended solids (MLVSS),

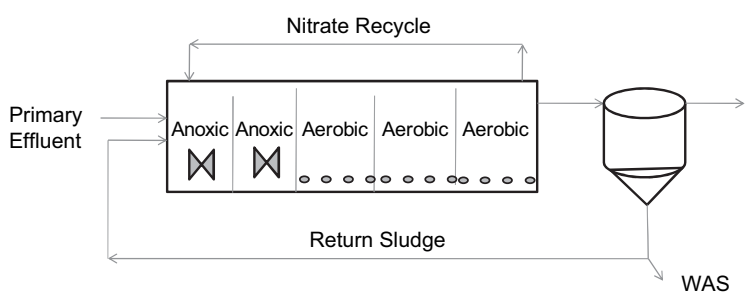

Figure 6.5 Preanoxic, aerobic modified Ludzack-Ettinger configuration in suspended growth activated sludge system (WAS = waste activated sludge).

TABLE 6.2 Typical criteria for nitrification/denitrification systems (20°C MLSS temperature).

Parameter	Predenitrification	Postdenitrification	Combined pre- and postdenitrification
System SRT, days HRT, hours	6–30	6–30	8–40
First anoxic zone	2–8	–	2–6
First aerobic zone	6–12	6–12	6–12
Second anoxic zone	–	2–6	2–5
Reaeration zone	–	–	0.5–1.0
MLSS, mg/L	1500–4000	1500–4000	2000–5000
Nitrate recycle	2–4 Q*		2–4 Q
RAS flow	0.5–1Q	0.5–1 Q	100% (Q design)
Dissolved oxygen, mg/L			
Anoxic zones	0	0	0
Aerobic zones	1–4	1–4	1–4
Mixing requirements			
Anoxic zones, kw/10^3 m^{3b}	4–10	4–10	4–10
Aerobic zones, kw/10^3 m^3	20–40	20–40	20–40
Airflow, aerobic, m^3/min l0^3 m^3	10–30	10–30	10–40

*Energy input is an important parameter; however, the manufacturer should be consulted for determining the number and placement of mixers. Propeller and turbine mixers have been used successfully.

HRT = hydraulic retention time; MLSS = mixed liquor suspended solids; RAS = return activated sludge; and SRT = solids retention time.

and the denitrification rate. Although this is best computed using activated sludge models, if there are multiple anoxic cells in series, then a single-cell anoxic zone can be computed using equations presented in this section. The anoxic zone typically represents approximately 20% to 40% of the total volume (anoxic plus aerobic). It is imperative that the biomass in the anoxic zone be kept in suspension without entraining dissolved oxygen, which inhibits the process. The nitrate recycle pump intakes should be located in such a way that they reduce the return of dissolved oxygen to the anoxic zone.

3.2.1.1 Anoxic Zone Process Kinetics and Kinetics-Based Equations that Control the Nitrogen Removal Process

The anoxic zone kinetics-based method is outlined in the steps below.

(1) Estimate the oxidized nitrogen concentration in the effluent and nitrate recycle returned to the anoxic zone using the following equation:

$$NO_xN_{eff} = \frac{(NO_xN_{gen})(Q)}{(Q + NR + RAS)} \tag{6.8}$$

Where,

NO_x-N_{eff} = nitrate–nitrogen concentration in the effluent and nitrate recycle, mg/L;
NR = mixed liquor recycle flow, m^3/d;
RAS = return activated sludge flow, m^3/d;
Q = influent wastewater flow rate, m^3/d; and
NO_x-N_{gen} = amount of oxidized nitrogen generated by nitrification.

Alternatively, eq 6.8 can be used to determine the nitrate recycle for a specified RAS and NO_x-N_{eff}.

(2) Estimate the COD uptake in the preanoxic zone and the effluent soluble biodegradable COD from the preanoxic zone.

(a) Dissolved oxygen enters the preanoxic zone through the influent (primary effluent), the nitrate recycle, and the RAS. Calculate the dissolved oxygen load entering the preanoxic zone (kg/d).

$$(DO)_{L,preanx} = [(DO_{inf})(Q) + (DO_{RAS})(RAS) + (DO_{NR})(NR)]\left[\frac{1000\ L/m^3}{1000\,000\ kg/mg}\right] \tag{6.9a}$$

If there is no data for DO_{inf}, then assume a value of 2 mg/L at 15°C or less; 1 mg/L at 15°C to 20°C; and 0.5 mg/L at temperatures greater than 20°C. The DO_{NR} can be assumed to be equal to the dissolved oxygen of the mixed liquor in the vicinity of where the nitrate recycle pump is located. This may be equal to the dissolved oxygen at the end of the aerobic zone. The dissolved oxygen of the RAS is difficult to determine without sampling the RAS or the clarifier blanket. In the absence of any data, it may be assumed that it is half the dissolved oxygen level at the end of the aerobic zone.

(b) Calculate the nitrite–nitrogen and nitrate–nitrogen load entering the preanoxic zone (kg/d).

$$(NO_2N)_{L,Preanx} = [(NO_2N_{inf})(Q) + (NO_2N_{RAS})(RAS) + (NO_2N_{NR})(NR)]\left[\frac{1000\ L/m^3}{1\,000\,000\ mg/kg}\right] \quad (6.9b)$$

$$(NO_3N)_{L,preanx} = [(NO_3N_{inf})(Q) + (NO_3N_{RAS})(RAS) + (NO_3N_{NR})(NR)]\left[\frac{1000\ L/m^3}{1\,000\,000\ mg/kg}\right] \quad (6.9c)$$

In the absence of data on nitrite–nitrogen, it may be assumed that all of the oxidized nitrogen forms exist as nitrate–nitrogen. In the MLE configuration, nitrate–nitrogen concentration in the nitrate recycle can be computed using eq 6.8. For the purposes of design, it may be assumed that all of the oxidized nitrogen is nitrate–nitrogen. The concentration of nitrite–nitrogen is 0 mg/L. For the RAS, it may be assumed that the oxidized nitrogen forms in the RAS equals that in the nitrate recycle. This is a conservative assumption because there is some denitrification in the sludge blanket and in the RAS lines.

Equations 6.9a, 6.9b, and 6.9c are summed to determine the COD uptake in the preanoxic zone (kg/d). The calculations are similar to eqs 6.5a and 6.5b.

$$COD\ \ Uptake_{preanx} = [2.86(NO_3N_{L,preanx}) + 1.71(NO_2N_{L,preanx}) + DO_{L,preanx}][COD\ \ Factor_{preanx}] \quad (6.9d)$$

$$COD\ \ Factor_{anx} = \frac{1}{1 - 1.42\dfrac{Y_{H,anx}}{1 + b_{H,anx}SRT_{preanx} + b_{H,aer}SRT_{aer}}} \quad (6.9e)$$

The factor 1.42 represents the milligram of COD incorporated to the biomass per milligram of VSS generated in the anoxic zone.

The effluent COD ($S_{anx,eff}$) from the preanoxic zone can be computed as follows (in mg/L):

$$S_{preanx,bio,eff}, kg/d = \left[(S_{inf} - COD_{anx,unhydolyzed} - SCOD_{nbio})\ Q\left(\frac{1000\ L/m^3}{1000\,000 mg/kg}\right) - COD\ \ Uptake_{preanx}\right]\left(\frac{1}{Q + RAS + NR}\right) \quad (6.10a)$$

$$S_{\text{preanx,bio,eff}}, \text{mg/L} = \frac{S_{\text{preanx,bio,eff, kg/d}}}{Q}\left(\frac{1\,000\,000 \text{ mg/kg}}{1000 \text{ L/m}^3}\right) \quad (6.10b)$$

$$S_{\text{preanx,eff}} = S_{\text{preanx,bio,eff}} + \text{SCOD}_{\text{nbio,eff}} \quad (6.10c)$$

Where, $\text{COD}_{\text{anx,unhydrolyzed}}$ = fraction of particulate COD present in the influent that is not hydrolyzed in the anoxic zone. In the absence of running the detailed simulation models, one can assume this fraction to be 0.5.

$$\text{COD}_{\text{anx,unhydrolyzed}} = (\text{PCOD}_{\text{inf}})(1 - \text{Fraction anoxic hydrolysis}) \quad (6.10d)$$

$$\text{PCOD}_{\text{inf}} = S_{\text{inf}} - \text{SCOD}_{\text{inf}} \quad (6.10e)$$

Where SCOD_{inf} is the SCOD in the influent to the reactor.

The COD $\text{Factor}_{\text{preanx}}$ is used to compute the COD uptake in milligrams of dissolved oxygen, NO_2-N, or NO_3-N denitrified. For example, with NO_3-N, it includes the COD taken up in cell synthesis. This is typically between 0.5 and 2.3 mg per mg NO_3-N (actual number is based on the anoxic sludge yield after adjustment for decay in the cell). It also includes the COD oxidized (2.86 mg COD per mg NO_3-N).

The factor of 2.86 is determined through stoichiometry of the denitrification reaction as follows:

- Valence state of nitrogen (charge) in NO_3^- = 5;
- Number of valence states to change to convert it to N_2 (denitrification) = 5;
- Equivalent weight of each charge on O = 8;
- Equivalent weight of denitrification = 5 × 8 = 40;
- Atomic weight of nitrogen = 14; and
- Oxygen equivalents per mg of N denitrified = 40 ÷ 14 = 2.86.

High levels of nitrate recycle are observed in oxidation ditches where it may be 50 to 200 times the influent flow rate. This will dilute the $S_{\text{anx,eff}}$.

(3) Compute the specific COD uptake and SDNR in the preanoxic zone.

The specific COD uptake rate and the SDNR for the anoxic zone are computed as follows:

$$q_{H,anx} = q_{m,H,anx}\left(\frac{S_{preanx,bio,eff}}{K_{S,H,anx} + S_{preanx,bio,eff}}\right)\left(\frac{NO_x - N_{preanx}}{K_{NOxN} + NO_x - N_{preanx}}\right)\left(\frac{K_{DO,i}}{K_{DO,i} + DO_{preanx}}\right) \quad (6.11a)$$

$$SDNR = q_{H,anx,NO3N} = \frac{q_{H,anx}}{2.86*COD\ \ Factor_{anx}} \quad (6.11b)$$

Where,

$S_{anx,bio,eff}$ = computed in eq 6.10b;

$q_{H,anx}$ = substrate (COD) uptake rate under anoxic conditions; and

SDNR = specific denitrification rate.

Equation 6.11 can be simplified as follows:

$$SDNR = q_{H,anx,NO3N} = \frac{q_{H,anx}}{5} \quad (6.11c)$$

For an actual $Y_{Hanx} = 0.3$ and with 1.42 mg COD/mg VSS, the milligram COD used per milligram NO_3-N denitrified determined through stoichiometry is 4.98. This is close to the value of 5 recommended above. The value of 1.42 is the milligram of COD per milligram VSS incorporated to the biomass for each milligram of VSS generated:

- COD of biomass generated per milligram of COD consumed in denitrification = $Y_{Hanx,\ actual} \times 1.42 = 0.3 \times 1.42 = 0.426$ mg;
- COD oxidized in denitrification = 1 – 0.426 = 0.574 mg;
- Nitrate–nitrogen consumed = 0.574 ÷ 2.86 = 0.2007 mg; and
- COD consumed per milligram of nitrate–nitrogen consumed = 1 ÷ 0.2007 = 4.98.

The observed range of values for $S_{anx,bio,eff}$ in municipal facilities operated with nitrate recycle rates of 1 to 3Q is 20 to 40 mg COD/L. Higher nitrate recycle rates, as achieved in oxidation ditches, will lower it.

The value of $S_{anx,bio,eff}$ can be measured by taking a sample of the mixed liquor, filtering it and measuring the soluble BOD_5. The soluble biodegradable COD is determined by determining the filtered COD for the mixed liquor in the anoxic zone and subtracting the filtered COD of the mixed liquor at the end of the aerobic zone. The soluble, readily biodegradable COD may be determined by adding a coagulant (alum) to the filtered COD and refiltering the solution (Mamais et al., 1993; WERF, 2002).

When using a computational model, the value of *S* is computed. The user will have to enter the quantity of flocculated filtered COD in the influent, the nonbiodegradable

COD in the effluent, and the rate of hydrolysis of biodegradable particulate COD to generate the soluble, readily biodegradable COD that drives the denitrification reactions (WERF, 2002). If biological excess phosphorus removal is included, then the rate of denitrification in an anoxic cell downstream of the anaerobic cell also may be controlled by the rate of poly-beta-hydroxybutyrate use when the soluble, readily biodegradable COD is low.

Where

Influent COD equals 300 mg/L,

Influent SCOD = 150 mg/L;

Anoxic dissolved oxygen = 0.25 mg/L (typical range in plants that are not oxidation ditches is 0.1 to 0.5 mg/L);

Anoxic NO_x-N = 0.5 mg/L (typical concentration of sum total of NO_2N and NO_3-N);

$K_{S,H,anx}$ = 70 mg/L at 25°C (anoxic half-saturation constant expressed in terms of soluble biodegradable COD);

$K_{DO,i,anx}$ = 0.5 mg/L (half-inhibition constant for dissolved oxygen on denitrification);

$K_{NO3\text{-}N}$ = 1 mg/L (anoxic half-saturation constant in terms of nitrate–nitrogen);

Nitrate recycle = 2.5;

RAS = 0.5;

Q = 1.0; and

SDNR = 0.16 mg NO_x-N/mg VSS·d.

The value of SDNR at 25°C is adjusted with an Arrhenius temperature adjustment coefficient. A value of 1.035 can be selected for heterotrophs for the preanoxic zone (observed range of 1.03–1.07):

$$\text{SDNR at } T\ ^\circ\text{C} = \text{SDNR}\ (1.035)^{(T-25)} \tag{6.12}$$

Where T is temperature (°C).

(4) Estimate the anoxic volume required to remove the mass of nitrates and nitrate equivalence of dissolved oxygen calculated in step 2b using the following equation:

$$V_{anx} = \frac{(NO_xN_{gen} - NO_xN_{eff})}{(q_{H,anx,NO3N})(X_{VSS})}\left(\frac{1000\,000\ \text{mg/kg}}{1000\,\text{L/m}^3}\right) \tag{6.13a}$$

$$V_{preanx,d} = (V_{preanx})(SF_{preanx})(PF_{preanx}) \quad (6.13b)$$

Where,

V_{preanx} = preanoxic volume, m^3;

X_{VSS} = VSS of the mixed liquor (assumed to be the same as the aerobic zone); and

$V_{preanx,d}$ = design volume for the preanoxic zone. This includes a safety and a peaking factor for the preanoxic zone. Because heterotrophs are less sensitive to shock loads of inhibitors as compared to nitrifiers, a safety factor could be used that is half the value for the aerobic zone. The peaking factor should be similar to that used for the aerobic zone.

The value of preanoxic volume fraction, Z_1, can be computed as follows:

$$Z_1 = \frac{V_{anx}}{V_{Total}} \quad (6.13c)$$

(5) The sum total of aerobic and anoxic MCRT (SRT) to be used for the design is calculated as follows:

$$SRT_{target} = SRT_{aer,t} \frac{V_{total,t}}{V_{aer,t}} \quad (6.14a)$$

$$V_{total,d} = V_{preanx,d} + V_{aer,d} \quad (6.14b)$$

Where,

SRT_{design} = design SRT of the biological system, d; and

$V_{total,d}$ = sum total of preanoxic and aerobic design volumes.

3.2.1.2 Oxygen Requirements

Oxygen is required to meet both the carbonaceous and the nitrogenous oxygen demand. The total kilogram of oxygen required can be estimated using the following equations:

$$\text{Oxygen required, mg/L} = (COD_{oxidized} + NOD - COD_{Biomass\ syn} - \text{denit credit}) \quad (6.15a)$$

$$\text{Oxygen required, kg/d} = (\text{oxygen required, mg/L})(Q, m^3/d)\ (1/1000)$$

Where,

$COD_{oxidized} = (COD_{inf} - SCOD_{eff})$;

NOD = 4.57 (NO_x-N_{gen}); the NO_x-N_{gen} is computed based on the ammonia that is actually nitrified (Benefield et al., 2010).

$COD_{Biomass\ Syn} = 1.42 \times Biomass_{SYN}$ (based on 1.42 mg COD per mg VSS as biomass); and

Denit credit = 2.86 (NO_x-N_{gen} – NO_x-N_{eff}); NO_x-N effluent is computed in eq 6.8.

3.2.1.3 Alkalinity Requirements

Sufficient alkalinity must be maintained so that the pH does not drop during nitrification, thereby inhibiting the process. Typically, 60 to 75 mg/L of alkalinity as calcium carbonate ($CaCO_3$) is maintained in the secondary clarifier effluent. The pH of the activated sludge tank is typically 6.5 or higher. The effluent alkalinity can be calculated as follows from the anoxic/oxic process (Sen et al., 1990):

$$\begin{aligned} Alk_{eff} = {} & Alk_{inf} + 3.57(TKN_{inf} - NH_4N_{inf} - SorgN_{eff}) - 3.57(N_{SYN}) \\ & - 7.14(NO_x - N_{gen}) + 3.57(NO_x - N_{gen} - NO_x - N_{eff}) \\ & - Alk\ Consumed_{P\ precipitation} + Alk_{supp} \end{aligned} \tag{6.16}$$

Where,

ALK_{eff} = effluent alkalinity, mg/L as $CaCO_3$;
ALK_{inf} = influent alkalinity, mg/L as $CaCO_3$;
$SorgN_{eff}$ = soluble organic nitrogen in the effluent (SKN – NH_4 – N);
N_{SYN} = nitrogen in biomass synthesized, as computed in eq 6.25a;
ALK $consumed_{P\ precipitation}$ = alkalinity consumed in the chemical precipitate formation associated with phosphorus removal;
ALK_{supp} = supplemental alkalinity added to achieve a target for the effluent alkalinity.

The equation is based on the following stoichiometric coefficients (derived below): nitrification consumes 7.14 mg of alkalinity per mg of nitrogen nitrified; denitrification gives back 3.57 mg of alkalinity per mg of nitrogen denitrified; conversion of organic nitrogen to ammonia–nitrogen (ammonification) generates 3.57 mg of alkalinity per mg of nitrogen ammonified; deammonification (synthesis) of ammonia–nitrogen to biomass consumes 3.57 mg of alkalinity per mg of nitrogen nitrified.

Stoichiometry of nitrification:

$$NH_4^+ + CO_3^{2-} + 2\ O_2 = NO_3 + CO_2 + 2\ H_2O$$

This equation shows that 100 mg/L alkalinity (equivalent alkalinity of CO_3^{2-}) and 64 mg/L of oxygen are consumed for 14 mg/L of nitrogen nitrified. This is equivalent to 4.57 mg/L of oxygen and 7.14 mg/L of alkalinity consumed in nitrification.

Stoichiometry of denitrification:

$$2\ NO_3^- + 2\ H^+ + C_6\ H_{12}\ O_6 = N_2 + 2\ H_2O + 6\ CO_2$$

The equation shows that for 28 mg/L (14 × 2 = 28 mg/L) of nitrogen in nitrate, two hydrogen ions (2 × 50 = 100 mg/L) of alkalinity are consumed. This is equivalent to 100 ÷ 28 = 3.57 mg/L of alkalinity generated per mg/L of nitrogen denitrified.

The supplemental alkalinity required, if the secondary effluent alkalinity falls below a certain alkalinity required to maintain the desired pH in the activated sludge tank (i.e., 65 mg/L), can be computed as follows:

$$ALK_{supp} = \text{target effective alkalinity} - ALK_{eff} \text{ without supplement}$$

3.2.2 *Additional Equations for Enhanced Nitrogen Removal Configuration*

This section presents the design criteria and equations and an example and a case history for a combined pre- and postdenitrification system. Figure 6.6 is a schematic of a typical combined pre- and postdenitrification system to achieve low levels of nitrogen removal (enhanced nitrogen removal, or ENR). This layout is typical of an MLE—a postanoxic zone fed with some external substrate such as methanol, ethanol, waste alcohols, or a carbon-rich industrial waste. It is similar to a Bardenpho™ configuration except for the addition of methanol, which increases the denitrification kinetics in the postanoxic zone. The preanoxic zone precedes the aerobic zone. As shown in the example, the MLE portion removes approximately 60% to 75% of the oxidized nitrogen. The postanoxic zone follows the aerobic zone. The postanoxic zone is sized to remove oxidized nitrogen to satisfy a more stringent total nitrogen permit (such as 3–5 mg/L). A reaeration zone with a detention time of 10 to 30 minutes follows to remove some of the supplemental carbon that remains in solution at the end of the aerobic zone and to prevent additional denitrification in the secondary clarifiers.

3.2.2.1 Preanoxic and Aerobic Zone Calculations

The equations for the preanoxic and aerobic zones of the ENR process are similar to those applied for MLE configuration (Benefield et al., 2010).

3.2.2.2 Postanoxic Zone Calculations

The structure of the equations for the postanoxic zone of a combined pre and postdenitrification ENR process are similar to the equations for the preanoxic zone. These equations are used in addition to the equations presented earlier for the preanoxic and aerobic portions of the ENR process. The computational steps are listed below.

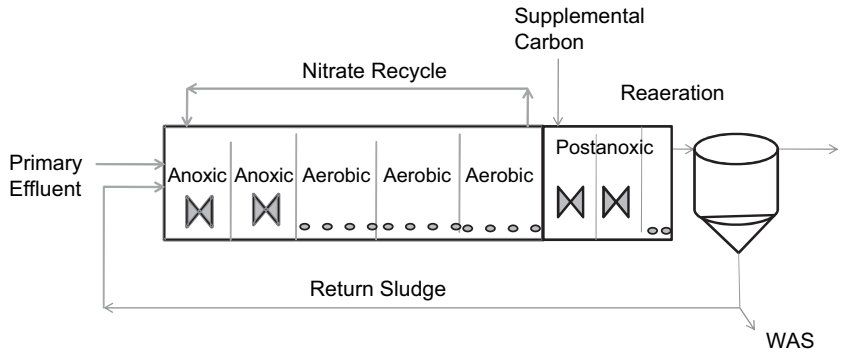

FIGURE 6.6 Combined pre- and postanoxic (enhanced nitrogen removal configuration in suspended growth activated sludge system (WAS = waste activated sludge).

(1) Estimate the dissolved oxygen load that has to be removed in the postanoxic zone:

$$(DO)_{L,postanx} = [(DO_{aer})(Q + RAS)]\left[\frac{1000\ L/m^3}{1000\,000\ mg/kg}\right] \quad (6.17a)$$

Where,

$(DO)_{aer}$ = dissolved oxygen concentration in the mixed liquor leaving the aerobic zone, mg/L.

(2) Calculate the nitrite–nitrogen and nitrate–nitrogen loads that have to be removed in the postanoxic zone:

$$(NO_2 - N)_{L,postanx} = [(NO_2 - N_{MLSS,aer})(Q + RAS)]\left[\frac{1000\ L/m^3}{1000\,000\ mg/kg}\right] \quad (6.17b)$$

$$(NO_3 - N)_{L,postanx} = [(NO_3 - N_{aer} - NO_3 - N_{post-anx})(Q + RAS)]\left[\frac{1000\ L/m^3}{1000\,000\ mg/kg}\right] \quad (6.17c)$$

Where,

$(NO_3\text{-}N)_{postanx}$ = allowable nitrate–nitrogen in the effluent from the postanoxic zone (typically 1 mg/L); and

$(DO)_{aer}$ = dissolved oxygen in the effluent upstream from the aerobic zone;

$(NO_2N)_{aer}$ = nitrite–Nitrogen in the effluent upstream from the aerobic zone; and

$(NO_3\text{-}N)_{aer}$ = nitrate–Nitrogen in the effluent from the upstream aerobic zone.

(3) Calculate the total mass of nitrates to be removed in the anoxic zone:

$$\text{COD Uptake}_{\text{postanx}} = [2.86(\text{NO}_3\text{N}_{\text{L,preanx}}) + 1.71(\text{NO}_2\text{N}_{\text{L,postanx}}) + \text{DO}_{\text{L,postanx}}][\text{COD Factor}_{\text{postanx}}] \quad (6.18a)$$

$$\text{COD Factor}_{\text{postanx}} = \frac{1}{1 - 1.42\dfrac{Y_{\text{H,postanx}}}{1 + b_{\text{H,preanx}}\text{SRT}_{\text{preanx}} + b_{\text{H,aer}}\text{SRT}_{\text{aer}} + b_{\text{H,postanx}}\text{SRT}_{\text{postanx}} + b_{\text{H,aer}}\text{SRT}_{\text{reaer}}}} \quad (6.18b)$$

The supplemental COD required in the postanoxic zone can be computed as follows (in mg/L):

$$S_{\text{postanx, suppl}} = S_{\text{postanx,eff}} + \left(\frac{\text{COD Uptake}_{\text{postanx}}}{Q}\right)\left(\frac{1\,000\,000\ \text{mg/kg}}{1000\ \text{L/m}^3}\right) - S_{\text{aer,eff}} \quad (6.19)$$

The value of the soluble COD in the effluent from the postanoxic zone ($S_{\text{postanx,eff}}$) is determined in step 4 below. It has to be high enough to maintain a satisfactory SDNR.

(4) Calculate the specific COD uptake rate and SDNR in the postanoxic zone. This is shown below.

One of the biggest challenges is correctly estimating the SDNR in an ENR system and its temperature sensitivity, which depend on the type of supplemental carbon used. There are two approaches that can be used to compute the SDNR. In the first approach, rate tests are conducted at actual ENR plants with the bacterial population that has acclimatized to the supplemental carbon source. Without acclimatization, the rates measured will be lower. In the second approach, rates are determined from kinetic coefficients measured in separate-stage denitrification systems.

The second method must be used carefully. Unlike in separate-stage denitrification systems, where the heterotrophic biomass is synthesized principally to denitrify the nitrates, the heterotrophic biomass in ENR systems is also generated in the preanoxic and aerobic zones. Depending on the type of substrate used in the postanoxic zone, some of the biomass generated in upstream zones may not be able to denitrify at the same rates using the external substrate added. The bacteria may not have as many active sites or the enzymes to use the supplemental carbon. Therefore, the rates determined from separate-stage systems have to be adjusted before applying them to the ENR mode of operation.

The following example uses methanol. When methanol is used as the supplemental carbon source, the $q_{m,H,anx}$ (see Table 6.1) for separate-stage denitrification can be used to determine SDNR. Unlike separate-stage denitrification, however, not all of the bacteria undertaking denitrification do so with methanol. Therefore, it is unlikely that a $q_{m,H,anx}$ of 10 d^{-1} at 20°C will occur, which is essentially equivalent to the rate observed with the COD in the primary effluent. This rate must be corrected for an ENR application.

One conservative approach for correction is to use the ratio of NO_3-N or NO_x-N denitrified in the postanoxic zone to the denitrification across the entire plant to determine a fraction for postanoxic denitrification to total denitrification.

$$q_{H,postanx,ENR} = q_{m,H,anx,Separate\ Stage} \frac{PostAnx\ \ Denit}{Overall\ \ Denit} \left(\frac{S_{postanx,bio,eff}}{K_{S,H,anx} + S_{postanx,bio,eff}} \right) \left(\frac{NO_x - N_{postanx,eff}}{K_{NOxN} + NO_x - N_{postanx,eff}} \right) \left(\frac{K_{DO,i}}{K_{DO,i} + DO} \right) \tag{6.20}$$

$$\text{overall denit} = (NO_x - N_{gen} - NO_x - N_{eff})(Q) \tag{6.21}$$

$$\text{postanx denit} = (NO_x - N_{aer,eff} - NO_x - N_{postanx,eff})(Q + RAS) \tag{6.22}$$

$$S_{postanx,eff} = S_{postanx,bio,eff} + SCOD_{nbio,eff} \tag{6.23}$$

$$SDNR = (q_{m,H,postanx,ENR}) \div 5 \tag{6.24}$$

$$SDNR \text{ at } T\ °C = SNUR\ (1.10)^{(T-20)} \tag{6.25}$$

Where,

$S_{postanx,bioeff}$ = 10 mg/L (soluble BOD_5 or soluble readily biodegradable COD remaining in solution at the end of the postanoxic zone);

DO = 0.25 mg/L in the postanoxic zone;

NO_x-N = 1.0 mg/L (typical target concentration);

$K_{S,H,anx}$ = 10 mg/L (anoxic half-saturation constant expressed in terms of soluble biodegradable COD as methanol as per Table 6.1);

$K_{DO,i,anx}$ = 0.5 mg/L (half-inhibition constant for dissolved oxygen on denitrification); and

$K_{NO_3\text{-}N}$ = 1 mg/L (anoxic half-saturation constant in terms of nitrate–nitrogen).

For the first pass of the iteration, one may assume that the postanoxic denitrification is 25% of overall denitrification. This value can be refined in the second pass of

the iterative calculation. The factor of 5 in eq 6.24 represents the milligrams of COD uptake per milligrams of NO_3-N denitrified. It was discussed in the preanoxic zone computations presented earlier.

Incorporating these values, results in an SDNR of 0.12 d^{-1} at 20°C. If we assume that postanoxic denitrification with methanol has a higher temperature sensitivity coefficient of 1.10 as compared to 1.06 for denitrifiers present in the preanoxic zone, the rate drops to 0.055 d^{-1} at 12°C.

The denitrification rate is sensitive to dissolved oxygen. Process design must incorporate good dissolved oxygen control in the aerobic zone upstream and where possible, two postanoxic cells in series to ensure dissolved oxygen uptake in the first postanoxic cell. The methanol dosing should be paced with the diurnal flow pattern and should incorporate bounds to avoid overdosing during wet weather high flows. The pacing may be improved with a feed forward signal from an automated nitrate–nitrogen analyzer and a dissolved oxygen probe and a feedback signal from a nitrate probe. As with any analyzer, however, maintenance and reliability need to be considered. For small plants, it may be more effective to have a slightly larger HRT to ensure adequate denitrification rather than several types of analyzers.

(5) Calculate the postanoxic volume required:

$$V_{\text{postanx}} = \frac{\text{COD Uptake}_{\text{postanx}}}{(q_{\text{H,postanx,ENR}})(X_{\text{VSS}})}\left(\frac{1000\,000\ \text{mg/kg}}{1000\ \text{L/m}^3}\right) \tag{6.26}$$

$$V_{\text{postanxd}} = (V_{\text{postanx}})(\text{SF}_{\text{postanx}})(\text{PF}_{\text{postanx}}) \tag{6.27}$$

Where,

V_{postanx} = postanoxic volume, m^3;
X_{VSS} = VSS of the mixed liquor (assumed to be the same as the aerobic zone), specified by the user; and
$V_{\text{postanx,d}}$ = postanoxic design volume, including a safety and a peaking factor.

(6) Calculate the biomass synthesized as a result of postanoxic COD addition. This can be done by modifying the equation for biomass synthesis in MLE configuration as follows:

$$\text{Biomass}_{\text{SYN,H}} = \frac{Y_{\text{H,anx}}(S_{\text{inf}} - S_{\text{preanx,eff}}) + Y_{\text{H,aer}}(S_{\text{preanx,eff}} - S_{\text{aer,eff}}) + Y_{\text{H,postanx}}(S_{\text{suppl postanx}} - S_{\text{postanx,eff}}) + Y_{\text{H,aer}}(S_{\text{postanx,eff}} - S_{\text{reaer,eff}})}{1 + b_{\text{H,anx}}\text{SRT}_{\text{preanx,d}} + b_{\text{H,aer}}\text{SRT}_{\text{aer,d}} + b_{\text{H,anx}}\text{SRT}_{\text{postanx,d}} + b_{\text{H,aer}}\text{SRT}_{\text{reaer,d}}} \tag{6.28}$$

Where,

$S_{reaer,eff}$ = secondary effluent SCOD (use 2 × filtered BOD_5 if COD data are not available);

$SRT_{postanx,d} = (V_{postanx,d} \div V_{aer,d})(SRT_{aer,d})$

$SRT_{reaer,d} = (V_{reaer,d} \div V_{aer,d})(SRT_{aer,d})$

$Y_{H,postanx}$ = depends on the substrate used. For methanol, the values are shown in Table 6.1.

For the ENR configuration, the effluent oxidized nitrogen levels in the RAS flow entering the preanoxic zone should be used. The denitrification of oxidized nitrogen in the postanoxic zone reduces the oxidized nitrogen levels in the RAS. This will reduce nitrate–nitrogen levels in eq 6.28b; it can be assumed that it is equal to 1 mg/L. The specific denitrification rate should be estimated using the methodology described by Benefield et al. (2010).

3.3 Extending Understanding of Integrated Fixed-Film Activated Sludge Systems

3.3.1 Basics of Media

The IFAS analysis can be initiated by first considering a high-rate conventional activated sludge system operated at the plant where an IFAS upgrade is being considered. The analysis goes through a sequence of steps shown in Figure 6.7 to select the correct type of IFAS media and achieve the effluent quality desired.

The IFAS system can be used for BOD removal, for BOD removal and nitrification, for BOD and nitrogen removal in MLE or ENR modes (ENR mode has a postanoxic zone with methanol feed and a reaeration zone), and or in combination with enhanced biological phosphorus removal. Media may be added to aerobic cells and to anoxic cells if the biomass in the MLVSS is not sufficient for denitrification.

An element of the IFAS process selection is to determine which media fits where. Figure 6.8, which is used in conjunction with Table 6.3, shows how the biofilm specific surface area (biofilm SSA, m^2/m^3) of fixed- and moving-bed media work with maximum fill fractions (mf), resulting in the maximum applied specific surface area (applied SSA, m^2/m^3) that can be achieved.

$$\text{Applied SSA} = \text{Biofilm SSA} \times \text{mf}$$

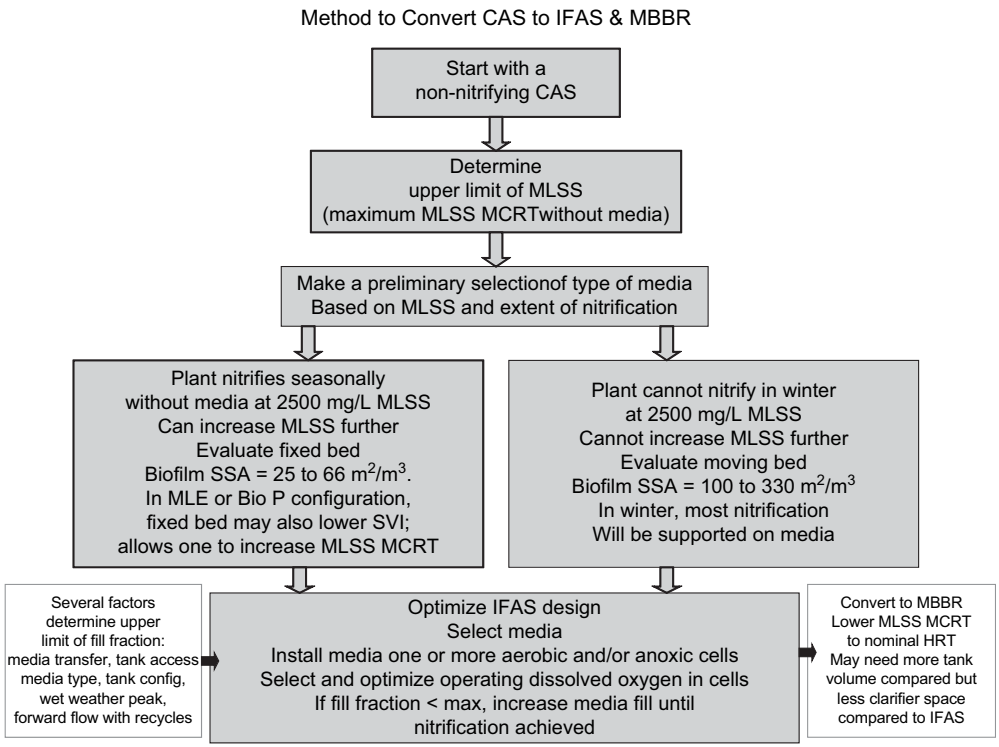

FIGURE 6.7 Method to convert a high-rate conventional activated sludge (CAS) system design to integrated fixed-film activated sludge (IFAS) and moving-bed biofilm reactor (MBBR) (DO = dissolved oxygen; MCRT = mean cell residence time; MLE = modified Ludzack-Ettinger; MLSS = mixed liquor suspended solids) (Copithorn et al., 2008).

The biofilm SSA is a characteristic of the type of media and the environment in which the media is applied. Although there is a reasonable upper limit for each type of media, higher soluble biodegradable COD (or soluble and colloidal BOD_5 concentrations) in the mixed liquor outside the biofilm can increase the thickness of the biofilm and lower the biofilm SSA. Therefore, to keep the biofilm operating optimally, it is important to include certain physical characteristics such as mixing and dilution through recycles. The design method and model used have to account for the effect of aerobic and anoxic mixing and recycles.

Table 6.3 Biofilm specific surface area of various types of media for integrated fixed-film activated sludge (IFAS) and moving-bed biofilm reactor (MBBR) systems (Sen et al., 2006).

Type of system	Media	Media fill volume percentage[a]	Biofilm specific surface area[b] (m^2/m^3)	Recommended MLSS (mg/L)	Minimum aerobic HRT (h) at 12°C
Activated sludge	None	0	0	3000	7
IFAS–fixed bed	Bioweb, Accuweb	70–80	50–100	3000	5
IFAS–moving bed–sponge	Linpor, Captor	20–40	100–150	2500	4
IFAS–moving bed–plastic	K1 (Kaldnes), Entex, Hydroxyl	30–60	150–300[2]	2500	4
MBBR–K12	K1 Kaldnes	40–67	200–335[2]	< 1000	3

[a] External volume of frame for cord-type fixed-bed media; external volume of cuboids or cylinders with biofilm for moving-bed media. Fill volume fraction is not the fraction of liquid volume in the activated sludge tank displaced by the media.

[b] Media with a biofilm specific surface area of 500 m^2/m^3 for 100% fill volume has been used as a reference. Different manufacturers have different volume-specific surface area

HRT = hydraulic retention time; and MLSS = mixed liquor suspended solids.

The biological portion of the IFAS simulation incorporates the interaction between the biofilm and the mixed liquor. This interaction is not as important in MBBR and pure biofilm models. In an IFAS model, however, the biofilm is continuously seeding the mixed liquor in the activated sludge system with heterotrophs, nitrifiers, and inert suspended solids. Particulates from the mixed liquor are trapped and hydrolyzed by the biofilm. The mixed liquor enhances the rate of organics (soluble biodegradable COD) removal, which helps reduce the COD concentration outside the biofilm. This enhances the nitrifier fraction in the first few layers of the biofilm. Several IFAS models take this into account.

3.3.2 Addressing Limitations in the Current Generation of Integrated Fixed-Film Activated Sludge Simulators

Several of the simulators available use the equations developed for biofilms in pure biofilm systems. Full-scale testing of the simulators show that these equations have

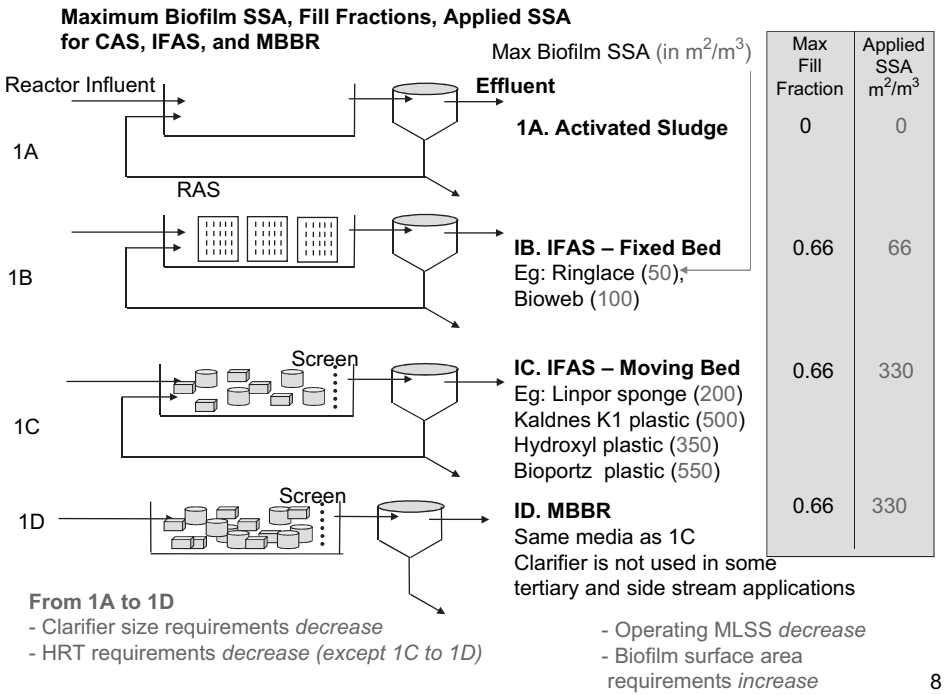

Figure 6.8 Understanding the relationship between maximum biofilm SSA (m^2/m^3), maximum fill fraction, and applied SSA (m^2/m^3). HRT = hydraulic retention time; IFAS = integrated fixed-film activated sludge; and MBBR = moving-bed biofilm reactor (Sen et al, 2006).

limited accuracy when simulating (1) behavior of fixed-bed media; (2) behavior of moving-bed media at higher specific surface areas; (3) effect of locations and mixing; (4) effect of higher substrate concentrations as in industrial wastes; (5) performance in multiple aerobic cells; and (6) performance at low temperatures (Boltz et al., 2008; Copithorn, 2009; McGehee et al., 2009). Further, fixed-bed cord media systems cannot be verified at bench scale because it is not possible to simulate accurately the hydrodynamics. Reviews of models from various manufacturers and designers have shown inaccuracies in the assumptions made by the users while attempting to overcome the limitations in the applicability of equations used in the model (Copithorn, 2009). Copithorn and Sen (2010) discuss the differences in biofilms growing on fixed-bed, moving-bed sponges, moving-bed plastic, and other types of media; their effect

on IFAS design; and method and techniques for improving accuracy of IFAS simulations that look at a combination of simulators and design and operations tools.

The difficulties in IFAS modeling using the various commercial simulators led to the development of a Microsoft.NET module (2009) that can be run in conjunction with various simulators to improve accuracy (Copithorn et al., 2009). The module accounts for the differences in types of media (fixed and moving bed) in terms of surface roughness (M_n) and hydrodynamic forces (G) and modifies the biofilm detachment coefficients. It extended the applicability of commercial simulators to lower temperatures (3–10°C) and media with higher specific surface areas (greater than 1000 m^2/m^3).

In summary, to accurately simulate an IFAS, it is often necessary to take the biofilm diffusional model found in the simulators and incorporate corrections for hydrodynamic considerations associated with media shape; soluble biodegradable COD in the bulk liquid; location within the reactor; mixing patterns (aerobic and anoxic); and differences in the density of the biofilm that sloughs off and its effect on the SVI of the mixed liquor.

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Chapter 7

Chemical Phosphorus Removal

(continued)

1.0 PRINCIPLES OF CHEMICAL PHOSPHORUS REMOVAL

The basic principle of chemical phosphorus (P) removal relies on the transformation of soluble phosphorus to a particulate form, which is then by solid–liquid separation processes, typically sedimentation, filtration, or membrane separation. The separation could occur at single or multiple locations with the aid of coagulants or flocculants.

Some phosphorus is removed in a conventional secondary wastewater treatment plant (WWTP) in primary and secondary treatment processes without the aid of coagulants and flocculants. Primary settling removes a fraction of the particulate form based on the efficiency of the primary clarifiers. In secondary treatment, phosphorus is incorporated into biomass and removed from wastewater through secondary sedimentation with waste biomass. As such, the quantity of phosphorus removed by a conventional secondary treatment process is a function of biomass yield and production.

The process total effluent phosphorus concentration, $C_{TP,eff}$, can be estimated as

$$C_{TP,\,eff} = C_{SP,eff} + X_{eff} m_{PX} \tag{7.1}$$

Where,

$C_{SP,eff}$ = concentration of soluble phosphorus from a process (mainly soluble orthophosphate), mg/L;

X_{eff} = process effluent suspended solids concentration, mg/L; and

m_{PX} = phosphorus content in suspended solids dry mass, mg P/mg suspended solids in the process.

For conventional activated sludge, m_{PX} is 20 to 25 mg P/g volatile suspended solids (VSS) (2–2.5%). For chemical phosphorus removal, m_{PX} varies between 40 and 100 mg P/mg suspended solids (4–10%). Equation 7.1 emphasizes the contribution of suspended solids to the process total effluent phosphorus concentration and the need for effective solids removal. For example, if the process effluent suspended solids concentration is 20 mg/L with a phosphorus content of 5% (50 mg P/g suspended solids), then a total phosphorus concentration less than 1 mg P/L cannot be achieved. Several cations typically are used for the precipitation of phosphorus from wastewater:

- Aluminum,
- Iron,
- Calcium, and
- Magnesium.

Under the right conditions, calcium will precipitate phosphorus, and the hydrous oxides of aluminum and iron will either sorb or coprecipitate orthophosphate. The International Union of Pure and Applied Chemistry (IUPAC) definition of coprecipitation is adopted here. "The simultaneous precipitation of a normally soluble component with a macro-component from the same solution by the formation of mixed crystals, by adsorption, occlusion or mechanical entrapment" (IUPAC, 1987). The term "simultaneous precipitation" used by IUPAC is a mechanistic definition and should not be confused with the process description of simultaneous precipitation used by practitioners and described in greater detail in a subsequent subsection. For this reason, soluble orthophosphate is the primary phosphorus species affected by chemical addition. Soluble orthophosphate is the colorimetryically determined phosphorus using the standard assay after filtration and without digestion, according to Standard Methods, 4500-P (American Public Health Association et al., 2005). This analytical quantity primarily is the actual orthophosphate molecular species ($H_2PO_4^-$ and HPO_4^{2-} at circum-neutral pH) but could also include nanoparticulate phosphorus associated with tiny colloids that potentially pass through 0.45 µm filters. Accurate analysis of its removal can be carried out only if its concentrations are measured and reported. Unfortunately, soluble orthophosphate rarely is determined in practice. All other phosphorus species (such as condensed polyphosphates, colloids, and particulates containing phosphorus) are removed by mechanisms including adsorption, coagulation, flocculation, sedimentation, or filtration or via biologically mediated removal. These mechanisms will not be discussed in detail in this chapter.

Table 7.1 lists examples of chemical solids that may be formed during phosphate removal. Ferric phosphate is not known to form within the pH ranges typical for wastewater treatment (Smith et al., 2008). The researchers used chemical equilibrium calculations and electron microscopy images to demonstrate that $FePO_4(s)$ is only stable at pH values of less than 4 for iron and in the range found in typical domestic wastewater for phosphorus. The nature of the precipitates formed during chemical phosphate removal depends on the cation used, the oxidation-reduction potential, and the overall efficiency of the phosphorus removal process. There are many factors that will affect this efficiency as will be described in a subsequent subsection. Exact stoichiometric composition of phosphate coprecipitates involving Al or Fe is not fully known, the metal:P stoichiometry in solids has been measured with values close to 1 (Smith et al., 2008). Some authors have suggested that all three cations

Table 7.1 Possible precipitates and coprecipitates formed during phosphate removal.

Cation	Precipitate
Al(III)	Aluminum phosphate [$AlPO_4$]*
	Aluminum hydroxide [$Al(OH)_3$], hydrous aluminum oxide (HAO) [$Al_2O_3 \cdot xH_2O$]
Fe(II)	Vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$]
	Ferrous hydroxide [$Fe(OH)_2$]*
Fe(III)	Strengite [$FePO_4 \cdot 2H_2O$][1]
	Ferric hydroxide [$Fe(OH)_3$], hydrous ferric oxide (HFO) [$Fe_2O_3 \cdot xH_2O$], magemite [γ-Fe_2O_3]
Ca(II)	Tricalcium phosphate [$Ca_3(PO_4)_2$]
	Hydroapatite [$Ca_5(OH)(PO_4)_2$]
	Dicalcium phosphate [$CaHPO_4$]
	Calcium carbonate [$CaCO_3$]
Mg (II)	Struvite [$MgNH_4PO_4 \cdot 6H_2O$]

*These precipitates are not common at typical pH ranges of 6 to 8 used in wastewater treatment.

(aluminum, iron, and calcium) can be present in a coprecipitate with other ions such as magnesium, sulfate, and bicarbonate (Arvin and Petersen, 1980; Hsu, 1973). Variability in precipitate composition led to suggestions that phosphate ion also is removed by adsorption on other chemical precipitates (Leckie and Stumm, 1970). Even though exact metal:P stoichiometry is not known, this chapter will explain the factors that can help optimize this ratio and guide the practitioner through design examples.

2.0 PHOSPHORUS SPECIES IN WASTEWATER

Phosphorus species found in wastewater are summarized in Table 7.2, which was adapted from Sedlak (1991) and the Water Environment Research Foundation (WERF) (2007). As indicated, various forms of phosphorus are present in typical municipal wastewater, and the speciation varies depending on the commercial, industrial, and municipal components; the collection system design; and the duration of travel before it reaches the treatment facility. Some of the listed species, such as polyphosphates and organic phosphates, are also produced during biological treatment. The species of phosphorus in the wastewater must be known to use chemical addition for removal.

Contribution of total suspended solids (TSS) concentration of the biological treatment effluent to the effluent total phosphorus concentration is illustrated in Figure 7.1 (Water Environment Federation [WEF] et al., 2006). The figure also illustrates the significance of the phosphorus content of the mixed liquor and the effluent TSS on the effluent total phosphorus concentration. This figure emphasizes the need for properly operating solids–liquid separation systems for reliable phosphorus removal. Although the soluble phosphate concentration may be less than 0.1 mg/L, if the TSS in the effluent is 10 mg/L and the phosphorus content of the mixed liquor is 0.06 mg/mg-VSS, then effluent total phosphorus concentration is expected to be approximately 0.5 to 0.6 mg/L.

The minimum achievable orthophosphate concentration is still undetermined and is quite controversial and depends on theoretical, state of practice, and permit-limit considerations. The U.S. Environmental Protection Agency (U.S. EPA) (2007) and Smith et al. (2008) have suggested that the minimum orthophosphate concentration ranges from 0.002 to 0.005 mg/L with considerable sampling and analytical uncertainty. In theory, even lower concentrations are likely achievable. In practice, however, the minimum achievable orthophosphate is likely in the range reported by

Table 7.2 Phosphorus species in wastewater (adapted from Sedlak 1991 and WERF 2007).

Category	Species	Solid/liquid	Comment
Orthophosphate	PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4	Liquid	pK_a = 2.15, 7.2, 12.35, respectively. Most dominant form of phosphorus, hence, term "orthophosphate" often used interchangeably with "soluble phosphorus"
Polyphosphates/ condensed phosphates	Pyrophosphate, tripolyphosphate, metaphosphate, intracellular polyphosphate granules	Liquid/solid	Large orthophosphate chains. Precipitate in condensed complex molecule form. Hydrolysis results in orthophosphate release. Hydrolysis and polyphosphate formation release and capture high energy (phosphate bonds) most common in biological systems (e.g., biological phosphorus removal systems)
Organic phosphate	Sugar phosphates, phospholipids, nucleotides, other cellular material	Solid/liquid	Can be in particulate or soluble form. Can be released through decay of organic material
Chemically bound phosphorus	Phosphorus precipitates containing Fe, Al, Ca; struvite; vivianite; phosphorus adsorbed onto metal hydroxides, other complexation species	Solid/liquid	Includes both precipitates and phosphorus coprecipitated or adsorbed onto precipitates and metal hydroxides. Dependent on pH and temperature. If the particulate matter is colloidal in nature and can pass through a 0.45 μ filter, it will be measured as soluble phosphorus

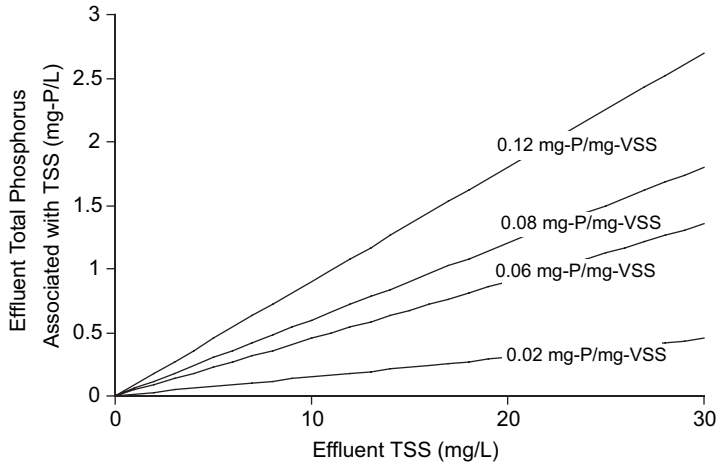

FIGURE 7.1 Contribution of effluent total suspended solids (TSS) to total phosphorus in the effluent for different phosphorus contents in the mixed liquor suspended solids (assuming that the VSS/TSS ratio is 75%) (Water Environment Federation et al., 2006).

these authors after considering sampling and analytical artifacts inherent to such low measurements and the molar ratios required. Likely the reliable range of residual orthophosphate that could be attained consistently for advanced technologies is an order of magnitude greater (0.01–0.05 mg/L) after accounting for considerable process variability of full-scale chemical removal plants. The total phosphorus achievable will also depend on other phosphorus species as discussed earlier. Particulate phosphorus has to be completely removed using technologies such as microfiltration or ultrafiltration membranes. If effluent total phosphorus levels are lower than what could be achieved by filtration technologies, then adsorption technologies using media or reverse osmosis need to be used. The U.S. EPA Region 10 (2007), WERF (2007), and Neethling et al. (2007) have shown that available technologies and approaches could be combined to meet the permit requirements and achieve average effluent total phosphorus concentrations as low as 0.07 mgP/L as in the case of Breckenridge S. D. Farmers Korner WWTP, Colorado. The challenge is that chemical phosphorus removal needs to complement biological phosphorus removal to ensure that chemical consumption could be minimized and other biological processes are not limited because of nutrient deficiency.

3.0 CHEMICAL REMOVAL OF PHOSPHORUS

Phosphorus removal mechanisms include

(1) Precipitation,
(2) Surface complexation (coprecipitation and adsorption), and
(3) Solid–liquid separation.

Overall, precipitation tends to be a lesser mechanism in Fe and Al chemical treatments, although it is the dominant mechanism in Ca-mediated removal. In Fe and Al treatment, the predominant mechanism is coprecipitation. In these systems, phosphate removal is thought to occur simultaneously with hydrous metal hydroxide precipitation via a surface complexation mechanism. Essentially, the phosphate complexes to the surfaces of the hydrous metal oxide as the metal precipitates. In this way, phosphate is occluded into the bulk structure of the solid phase. It is possible, however, to form colloidal metal oxide precipitates; therefore, the solid–liquid separation step is crucial for achieving low-level residual phosphorus. The mechanisms of removal are presented further for the different chemicals used in phosphorus removal.

3.1 Chemicals Used in Phosphorus Removal

3.1.1 Calcium

Phosphate precipitation with lime was the earliest used method of phosphorus removal. Calcium forms several insoluble compounds with phosphate (see Table 7.1), among which hydroxyapatite $Ca_5(PO_4)_3(OH)$ appears to be the most important (Menar and Jenkins, 1972). Additionally, calcium carbonate can form, depending on pH, wastewater alkalinity, and calcium dose. Figure 7.2 shows that significant phosphate removal can be achieved only at higher pH values. Most reports indicated that removal of phosphate to values less than 1 mg P/L requires values of pH of 10.5 to 11 (Buzzell and Sawyer, 1967; Menar and Jenkins, 1972; Spiegel and Forrest, 1969). For this reason, lime is used either in primary treatment or following biological treatment. The dose of lime and the amount of solids produced are functions of total alkalinity of wastewater according to the following reaction:

$$Ca(OH)_2 + HCO_3^- \leftrightarrows CaCO_3 + H_2O + OH^- \qquad (7.2)$$

These factors do not depend significantly on phosphate concentration. According to eq 7.2, the required lime dose (in mg $Ca(OH)_2$/L) is approximately 1.5 times the total alkalinity (as mg $CaCO_3$/L). The U.S. EPA (2007) describes the operation of a high-lime process at the Upper Occoquan Sewage Authority (UOSA), Occoquan,

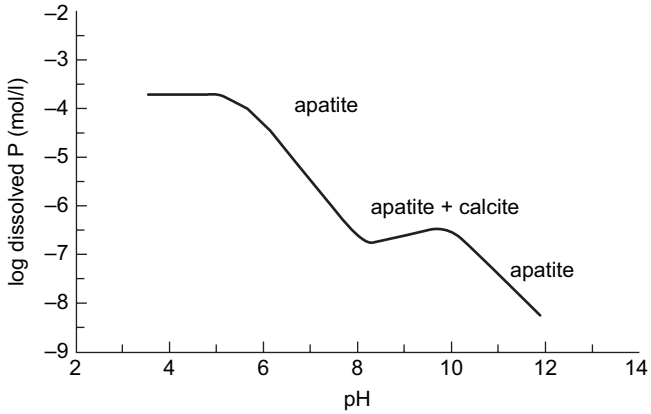

FIGURE 7.2 Equilibrium solubility for calcium phosphate system (adapted with permission from Jenkins, D., and Hermanowicz, S.W. [1991] Principles of Chemical Phosphorus Removal. In *Phosphorus and Nitrogen Removal from Municipal Wastewater*: Principles and Practice. Sedlak, R. I., Ed. Copyright CRC Press, Boca Raton, Florida).

Virginia, to reduce phosphorus to less than 0.10 mg/L, to capture organics from secondary treatment, to precipitate heavy metals, and to serve as a barrier for viruses. This process has been in operation for three decades. In this process, lime slurry is added to rapid mix basins (to achieve pH of 11) and anionic polymer is added in flocculation basins followed by chemical clarification, first-stage recarbonation to lower pH to 10, recarbonation clarifiers to collect precipitated calcium carbonate, second-stage recarbonation to lower pH to 7, and storage in ballast ponds.

3.1.2 Magnesium

Magnesium can be an important precipitant of phosphorus in an anaerobic digester. Magnesium in the presence of ammonium ions and orthophosphate can precipitate as magnesium ammonium phosphate (MAP) or struvite [$MgNH_4PO_4{\cdot}6H_2O$]. When sludge from the biological phosphorus removal process enters an anaerobic digester, polyphosphates associated with the biomass are released as orthophosphate. If this orthophosphate is not precipitated, then it would represent a significant phosphorus recycle stream. This typically does not happen if magnesium is present in sufficient stoichiometric quantities because "struvite," or MAP, forms in or downstream of the digesters (1 mole of magnesium removes 1 mole of phosphate in the presence of ammonium ions). Several processes are being developed to recover MAP, which will be discussed in a subsequent subsection.

3.1.3 Ferrous Iron

The main source of ferrous iron [Fe(II)] is spent pickle liquor containing $FeCl_2$ or $FeSO_4$ and originating from metal-processing operations. It is a potentially convenient and economical source of precipitating agent, but it may contain hazardous materials (such as heavy metals) that can either pass through with the effluent or accumulate in the sludge. Commercially available technical-grade iron salts (both Fe(II) and ferric iron, or Fe(III)) may also contain a certain amount of heavy metals.

Recht and Ghassemi (1970) conducted an extensive study of phosphate precipitation with Fe(II) in the absence of dissolved oxygen. They concluded that optimum removal occurred at pH 8, with residual orthophosphate at 0.4 mg P/L. On either side of the optimum pH, orthophosphate residual concentrations were much greater: 8 mg P/L at pH 7 and 3.5 mg P/L at pH 9. At pH 8, a reaction time of two hours was required to achieve maximum removal. Although the initial iron:phosphorus molar ratio was 1:1, not all Fe(II) was removed from the solution. The precipitate formed in their experiments was identified as vivianite, $Fe_2(PO_4)_3{\cdot}8H_2O$. Theoretically, orthophosphate precipitation with Fe(II) provides a more advantageous stoichiometry. Results of two full-scale applications of Fe(II) to raw wastewater in Mentor, Ohio, and Texas City, Texas, however, showed that the majority of removal occurred in the aeration tanks where Fe(II) likely was oxidized to Fe(III) (Recht and Ghassemi, 1970). Low phosphate removal in primary treatment was attributed to inadequate reaction time of Fe(II), formation of poorly settling precipitate, or complexation of Fe(II) by organic matter.

Fe(II) also is dosed to an aeration tank containing activated sludge, which allows for its conversion to an oxidized Fe(III) species. The dosing of iron or aluminum to an aeration tank is referred to as "simultaneous precipitation" (simultaneous chemical removal of orthophosphate along with biological processing of wastewater). Frossard et al. (1997) used X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, and scanning electron microscopy to investigate phosphorus species in one activated sludge sample subject to simultaneous precipitation with $FeSO_4$. They determined that 43% of the total iron was accounted for as vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$]. The amount of reduced versus oxidized species of iron present likely depends upon the overall aerobic conditions present in the aeration tank. If exposed to sufficient aerobic conditions in an aeration tank, Fe(II) oxidizes to Fe(III). Leckie and Stumm (1970) indicated that ferric iron Fe(III) formed by oxidation of Fe(II) is more effective for phosphate precipitation than Fe(III) added directly from a stock solution. Recht and Ghassemi (1970) found that the speed of phosphate precipitation increased significantly in the presence of oxygen as Fe(II) was oxidized to Fe(III). Similarly to Leckie and Stumm (1970),

they claimed that phosphate removal efficiency with oxidized Fe(II) was better than that for an equivalent dose of Fe(III) from stock solution. The practical efficiency of phosphorus removal, however, is also affected by the settling characteristics of the coprecipitate. Leckie and Stumm (1970) reported that the coprecipitate formed by oxidized Fe(II) in clean water was inferior to those from Fe(III).

When the sludge from chemical phosphorus removal is sent to an anaerobic digester, much of the coprecipitated phosphate can remain in the anaerobically digested solids. The predominant species of iron in the anaerobic digester is Fe(II). Any oxidized species of iron likely is converted microbially to the reduced form, and the phosphate can be precipitated as vivianite (Stabnikov et al., 2004; Zhengkai et al., 2006). The amount of phosphate that redissolves versus the amount that remains in the solids depends upon the amount of iron initially added, the solubility product of ferrous phosphate, and the competing counterions (mainly sulfide) that are also precipitated by the Fe (II). Wild et al. (1997) suggested that the amount of iron available for precipitating phosphate depends on the amount of iron used to initially remove sulfide as FeS. The precipitation reactions in an anaerobic digester are important because they can constitute the presence or absence of orthophosphate in the recycle stream from anaerobic digestion, the presence of which is an input variable for chemical or biological phosphorus removal in the liquid stream.

3.1.4 Ferric Iron and Aluminum

Because there are many similarities between the chemistry of orthophosphate coprecipitation or sorption with Fe(III) and aluminum [Al(III)], these two agents will be discussed together. Ferric iron is used as ferric chloride ($FeCl_3$) or ferric sulfate [$Fe_2(SO_4)_3$]. Aluminum for phosphate removal is used as either alum [$Al_2(SO_4)_3{\cdot}18H_2O$], sodium aluminate ($NaAlO_2$), or polyaluminum chloride (PAC). The last chemical is often used when enhanced solids removal is also a treatment objective because their orthophosphate removal efficiency is lower than the nonpolymerized constituents (Fettig et al., 1990; Gillberg et al., 1996; Ratnaweera et al., 1992; Szabó et al., 2008). More recently, polymeric aluminum or iron silicate sulfates have been discussed (Boisvert et al., 1997; Sagberg et al., 2006; Wang and Tang, 2001; Zouboulis and Moussas, 2008). Polyaluminum silicate sulfate (PASS) and polyferric silicate sulfate (PFSiS) have been referred to as polymeric flocculants that, although inferior as coagulants compared to nonpolymerized constituents, resist shear stress, enhance aggregation, form larger flocs, and enhance flocculation and clarification of the chemical sludge formed. Sagberg et al. (2006) demonstrated significant reductions in overall chemical costs using a combination

of ferric chloride and PASS. Ferric chloride was added where mixing was maximized, and PASS was added at a location where conditions for flocculation were more optimal in a downstream section of a tapered aeration grit chamber. Regardless of the form used, Fe^{3+} or Al^{3+} cations are the coprecipitating or sorption agents.

The addition of acidic ferric iron or aluminum solution to wastewater in the presence of sufficient alkalinity results in the rapid precipitation of hydrous ferric or aluminum oxides (HFO or HAO). Soluble orthophosphate is removed simultaneously with the HFO/HAO precipitation by either precipitation of iron phosphates, coprecipitation, or adsorption of phosphate onto existing HFO particles. The removal of phosphate can occur via many different pathways:

(1) Adsorption of phosphate onto HFO or HAO or coprecipitation into the HFO or HAO structure;
(2) Coprecipitation of phosphate into the HFO or HAO structure;
(3) Precipitation of ferric or aluminum phosphate; and
(4) Precipitation of mixed cation phosphates (i.e., Ca, Mg, Fe, or Al phosphates, or hydroxyphosphates).

In the case of ferric iron, Smith et al. (2008) indicated that ferric phosphate precipitation only occurs near pH of 3.5 with no evidence of occurrence greater than pH of 5. In the pH range of 6 to 8 typical of wastewater treatment, surface complexation dominates, and phosphate either sorbs onto preformed HFO or it coprecipitates simultaneously as the formation of HFO occurs. The basis of the phosphate complexation model is that iron and phosphorus share a surface oxygen (see eq 7.3). The overall reaction is presented symbolically (charges omitted) for a reaction at a metal oxide surface in eq 7.3. The surface oxygen, which is underlined in eq 7.3, take part in surface binding and oxygen sharing. This type of reaction can be termed a "ligand exchange reaction" where phosphate exchanges for hydroxide, or water, at the mineral surface. This arrangement can be pictured as O_3P-O-Me, where Me can be either Al or Fe(III).

$$\equiv \mathrm{Me}\underline{\mathbf{O}}\mathrm{H} + \mathrm{HOPO_3} \rightarrow \equiv \mathrm{Me}\underline{\mathbf{O}}\mathrm{PO_3} + \mathrm{H_2O} \qquad (7.3)$$

Water must be a byproduct of the reaction to account for the extra oxygen released during ester bond formation. The three solid lines (≡) are the standard symbol for a surface reactive site (Dzombak and Morel, 1990).

Equation 7.3 presents one possible reaction. The exact reaction depends on the nature of oxygen at the surface, in particular, the number of Me atoms sharing each oxygen. Each Me that is bound to an oxygen draws some of the electron density from

the oxygen atom. The reactivity of the surface oxygen depends on how much of its valence electron density it shares. This aspect is summarized by the multisite surface complexation (MUSIC) model as applied to phosphate/goethite interactions by Geelhoed et al. (1997) (Hiemstra et al., 1996). The MUSIC model assumes a crystalline oxide. In applying these concepts to amorphous oxides, which occurs when minerals are precipitated rapidly as in wastewater, the assumption is that the short-range order in an amorphous material is similar to the long-range order in a crystalline substance.

Modeling can be performed to predict the speciation of the metal and phosphate chemical equilibrium. The first step of equilibrium modeling is to solve for the solution and solid-phase species present. A set of possible reactions and associated equilibrium constants are given in Table 7.3. Reaction 1 in Table 7.3 can be used to test for precipitation of amorphous hydroxide precipitate. Reactions 2 to 5 determine the minimum solubility for the hydroxide mineral phase; the "U-shaped" solubility diagram. For aluminum and Fe(III), most wastewater systems will be supersaturated compared to the mineral phase, and HAO or HFO will precipitate. Fe(II)

TABLE 7.3 Chemical reactions of PO_4^{3-}, Al(III), Fe(III), and Fe(II) (from National Institute of Standards and Technology [NIST], 2001).

		Log equilibrium constants[b]		
Reactions[a]		**Al (III)**	**Fe(III)**	**Fe(II)**
(1)	$Me^{n+} + nOH^- = Me(OH)_n(s)$	33.7	38.6–42.7	14.43
(2)	$Me^{n+} + OH^- = Me(OH)^{n-1}$	9.0	11.81	4.6
(3)	$Me^{n+} + 2OH^- = Me(OH)^{n-2}$	17.9	23.4	7.5
(4)	$Me^{n+} + 3OH^- = Me(OH)^{n-3}$	25.2	NA	13
(5)	$Me^{n+} + 4OH^- = Me(OH)^{n-4}$	33.3	34.4	10
(6)	$Me^{n+} + HPO_4^- = Me(HPO_4)^{n-2}$	6.12	8.3	2.46
(7)	$Me^{n+} + H_2PO_4^- = Me(H_2PO_4)^{n-1}$	2.71	3.47	0.55
(8)	$Me^{n+} + 2H_2PO_4^- = Me(H_2PO_4)_2{}^{n-2}$	4.82	6.03	1.82
(9)	$Me^{n+} + 3H_2PO_4^- = Me(H_2PO_4)_3{}^{n-3}$	NA	8.1	NA
(10)	$(7–2n)Me^{n+} + (4 - n)PO_4^{3-} = Me_{7-2n}(H_2PO_4)_{4-n}(s)$	18.34	21.76–26.4	37.76

[a]For the reactions $n = 3$ for Al(III) and Fe(III), $n = 2$ for Fe(II).

[b]Where appropriate ranges are indicated for the equilibrium constant values. The ionic strength of the values given is zero if possible or the lowest ionic strength listed in NIST if zero is not available.

is much more soluble, and hydroxides should not tend to precipitate under reducing conditions. The other possible solid phase is the metal phosphate (Reaction 10). In wastewater systems, Fe(III) and Al(III) are expected to exist only at low pH, but Fe(II) PO4(*s*) is likely to be supersaturated under reducing conditions.

In terms of soluble phosphate, the complexation tends to keep phosphate in the solution. In supersaturated systems the residual metal concentrations are low because most metal has precipitated, and most of these aqueous phosphate complexes tend to occur at low concentration reactions (i.e., Reactions 6–9, Table 7.3).

There are many possible approaches to evaluating surface complexation at oxide surfaces. An example method for HFO-phosphate surface complexation is given here. Once HFO is found to precipitate, a surface complexation model calculation is run to determine how much phosphate is bound to the surface and other available oxygen binding sites as the precipitate is formed. The surface complexation model, shown in Table 7.4, shows the stoichiometry of the surface reactions based on Geelhoed et al. (1997). These possible surface reactions are based on spectroscopic studies and theoretical surface structural considerations (i.e., MUSIC model). The stoichiometries of the reactions are not curve-fit exercises but are based on physical and chemical constraints. These possible reactions on known goethite are assumed to be valid reactions possible on the HFO surface. Even though the iron oxide formed here is amorphous and not crystalline, it is reasonable that similar types of binding arrangements (Fe to O) will occur at their surface (Smith and Ferris, 2001). These are the active phosphate binding sites. The values for the equilibrium constants in Table 7.4 are given as a range of values between those determined by Geelhoed et al. (1997) and Smith et al. (2008).

TABLE 7.4 Possible reactions (charges omitted) and equilibrium constants for surface complexation of phosphate (adapted from Geelhoed et al. 1997 and Smith et al. 2008).

Reaction*		Log *K*
(1)	$2H^+ + PO_4^{3-} + 2(\equiv FeO) \leftrightarrow (\equiv FeO)_2H_2PO4$	27.6–30
(2)	$3H^+ + PO_4^{3-} + 2(\equiv Fe_3O) \leftrightarrow (\equiv FeO)_2H_3PO4$	33.8–35.5
(3)	$H^+ + PO_4^{3-} + \equiv FeO \leftrightarrow \equiv Fe_3OHPO4$	15.5–20.5
(4)	$H^+ + PO_4^{3-} + \equiv FeO \leftrightarrow \equiv FeOH$	9.2
(5)	$H^+ + PO_4^{3-} + \equiv Fe_3O \leftrightarrow \equiv Fe_3OH$	9.2

* ≡FeO is a singly coordinated surface oxygen, meaning that the surface oxygen is bound to only one iron whereas $\equiv Fe_3O$ represents a surface oxygen bound to three irons.

Soluble phosphorus is the sum of all phosphorus species not bound to the iron oxide surface or precipitated. To quantify a value for this, it is necessary to determine how much phosphate capacity exists. Using the same assumptions as Geelhoed et al. (1997), the concentration of these binding sites is assumed to have the same value. These need to be related to the total iron concentration (FeT) in the precipitate, as follows:

$$S1T = S2T = ASF \times (FeT \text{ in HFO}) \tag{7.4}$$

Where,

S1T = binding capacity for Site 1;
S2T = binding capacity for Site 2; and
AST = active site factor (ASF).

The ASF, a critical factor, is related to available binding sites before, after, and during precipitation and represents a fraction of the reactive surface oxygen per bulk Fe in the HFO. Best-fit values for ASF tend to range from 0.2 to 1.2.

The value of the area factor parameter is linked to the mixing conditions (*G* value) and the age of the floc (HRT) through a kinetic function:

$$ASF = f(G, HRT) \tag{7.5}$$

When combined with expressions describing diffusion limitations within the floc, this function forms the kinetic part of the model. The exact forms of the functions and their parameters have not yet been determined and need to be the subject of further investigation.

3.2 Design and Operating Variables Important for Phosphorus Removal

Because ferric iron and aluminum are more commonly used to remove orthophosphate in practice, a more detailed analysis is provided to understand the removal capabilities for these chemicals. The following subsections will focus on dose requirements, minimum achievable orthophosphate concentration, and removal mechanisms.

3.2.1 Dose Requirements

The overall dose requirements for phosphorus removal will depend on the phosphorus limit required in the permit and the design features of the WWTP. An important operations parameter is the observed metal dose added to the orthophosphate removed molar ratio for a plant. This parameter will vary depending on the type of processes used for removing orthophosphate and particulate phosphate and the total and orthophosphate residual required to attain permit limits.

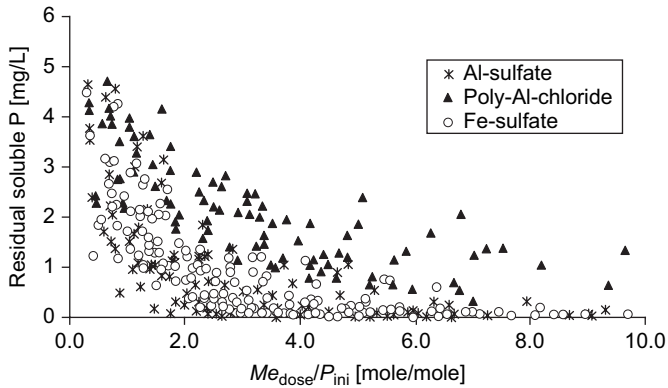

FIGURE 7.3 Residual soluble phosphorus applying different types of coagulants (different raw wastewater samples; initial pH = 6.8 to 8.7; initial phosphorus = 0.9 to 7.4 mg/L; initial total suspended solids = 50 to 2050 mg/L; and initial chemical oxygen demand = 200 to 4000 mg/L; 500 samples) (reproduced from Szabó et al., 2008).

Szabó et al. (2008) observed that the molar ratio for iron and aluminum were similar to achieve a certain orthophosphate residual (Figure 7.3). Fettig et al. (1990) suggested that aluminum is somewhat more effective at orthophosphate removal for similar molar ratios. Szabó et al. (2008) suggested that HAO and HFO have similar coprecipitation and adsorption capacities. They also suggested that the residual orthophosphate achieved and the molar ratios for orthophosphate removal for these two materials depend more on design and operations variables (see subsequent subsections) and wastewater characteristics than the inherent chemistry of these chemicals to remove the orthophosphate ion. Design and operational effects on metal dose and phosphorus removal and Szabó et al. (2008) laboratory data are provided in Figure 7.4. Typically, as the orthophosphate residuals decrease, the molar ratio of coagulant added to phosphorus removed increases. For plants that need to remove orthophosphate to less than 0.1 mg/L, the overall plant-wide metal ion added to orthophosphate removed molar ratio is in the broad range of 2 to 4 moles of Fe or $Al_{added}/P_{removed}$ after taking into account phosphorus requirements for biological growth (Fettig et al., 1990; Gates, 1991; Rabinowitz et al., 1987; Takács et al., 2006; U.S. EPA, 2007). For plants that need to achieve orthophosphate residuals less than 0.1 mg/L, the optimized molar ratio can increase significantly and can exceed 6 moles Fe or $Al_{added}/P_{removed}$ (U.S. EPA, 2007). Conversely, the molar ratio requirement for both aluminum and ferric iron will decrease as the desired orthophosphate residuals increase (for orthophosphate

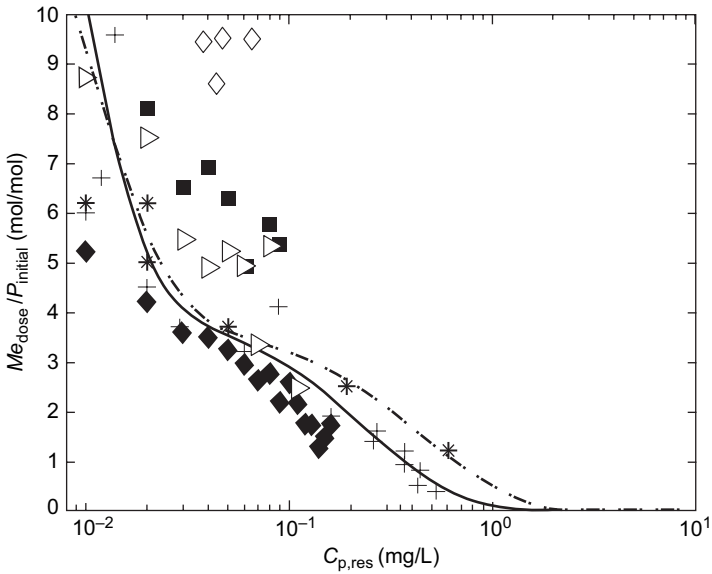

FIGURE 7.4 Ratio of metal dose to initial soluble phosphorus concentration as a function of residual soluble orthophosphate concentration. Full-scale plant data shown as solid symbols: ♦ = Plant A (simultaneous precipitation with iron removal including biological phosphorus uptake); ■ = Plant B (tertiary phosphorus removal with iron); ◊ = Plant C (tertiary phosphorus removal with aluminum); Δ = Plant D (tertiary phosphorus removal with aluminum). Laboratory data for initial orthophosphate less than 1 mg P/L: + = iron; ✳ = aluminum (Szabó et al., 2008). Data less than 0.05 mg/L orthophosphate is less than quantification limits for Plant A , B, and D. Each data point shown for Plant A, B, and D represents an average of molar ratio of metal dosage-to-initial phosphorus ($Me_{dose}/P_{initial}$) to achieve the residual phosphorus concentration ($C_{p,res}$) value for the plant.

residuals of approximately 1 mg/L or greater) and will approach unity (Fettig et al., 1990; Gates, 1991; Rabinowitz et al., 1987; Smith et al., 2008; Szabó et al., 2008).

When an excess dose of metal salt [Fe(III) or Al(III)] is added, metal hydroxide will precipitate in addition to metal phosphate precipitating (Ferguson and King, 1977; Kavanaugh et al., 1978). It is likely that the proportion of phosphorus being removed as a metal salt precipitate is very small and most of the phosphorus will be removed by coprecipitation/adsorption to HFO and HAO precipitates (see Section 3.1.4). In this case, residual phosphate concentration can be calculated from equilibrium equations if the appropriate equilibrium constants are known or estimated using an empirical equation (eq 7.6) as discussed later in this section.

3.2.2 *Role of pH*

The role of pH in orthophosphate removal is one of the most explored parameter in chemical phosphorus removal (Altundogan and Tümen, 2001; Fettig et al., 1990; Gates et al., 1990; Gillberg et al., 1996; Goldberg, 1985; Jenkins and Hermanowicz, 1991; Li and Stanforth, 2000; Lijklema, 1980; Luedecke et al., 1988; Rabinowitz et al., 1987; Smith and Ferris, 2001; Smith et al., 2008; Stumm and Morgan, 1996; Szabó et al., 2008; Takács et al., 2006; Xiaofang et al., 2007). Despite this literature, confusion remains about the role of pH in chemical phosphorus removal. Literature suggests that for a constant molar ratio of ferric or aluminum ion added to phosphorus removed, the minimum phosphorus is achieved at acidic pH in the range of 3 to 5 with increasing residuals as pH increases (Altundogan and Tümen, 2001; Fettig et al., 1990; Gillberg et al., 1996; Li and Stanforth, 2000). Smith et al. (2008) suggest that for similar molar ratios, lower phosphate residuals are obtained at lower pH values. A pH range of between 5 and 10 was evaluated.

The adsorption of phosphate onto HFO and HAO was described as a ligand exchange mechanism, where the phosphate exchanges a hydroxyl ion, resulting in increased pH (Altundogan and Tümen, 2001; Goldberg, 1985; Xiaofang et al., 2007). Altundogan and Tümen (2001) also showed the reverse: desorption of orthophosphate from bauxite with an increase in pH as a similar ligand exchange of orthophosphate ions by hydroxyl ions. Thus, the overall pH effect of decreasing sorption of orthophosphate with increase in pH can be described as a competitive adsorption for HFO or HAO sites between orthophosphate and hydroxyl anions. Lijkema (1980) explains the ligand exchange mechanism and shows a decreasing sorption capacity as the pH increases from 5 to 8.5. Xiaofang et al. (2007) and Smith et al. (2008) explored this concept further and suggested that specific surface area played an important role on adsorption capacity. Although pH can affect the chemical dosage needed for orthophosphate removal, for most treatment plants pH does not limit the extent of orthophosphate removal. Readers are referred to Takács et al., 2006, for data for plants showing the ability to remove orthophosphate to as low as 0.01 mg/L at the typical WWTP operating at pH of between 6 and 7.5. Although Lijkema (1980) shows the pH effects for iron, the same ligand exchange mechanism applies to aluminum.

3.2.3 *Role of Other Counteranions*

Goldberg (1985) describes a generalized ligand exchange model for adsorption onto goethite (α-FeOOH) where orthophosphate and any other anion competitively adsorb

onto the surface. For example, the role of a counterion such as sulfate is similar to the mechanisms explained above for orthophosphate at different pH, where competition exists between counteranions and orthophosphate for the adsorption sites. Geelhoed et al. (1997) also investigated this phenomenon as competitive adsorption and found that sulfate was adsorbed onto goethite surface and competed with phosphate adsorption when the two ions were simultaneously present at a pH range of 2 to 6. At neutral pH, there was little competition for adsorption sites and phosphate adsorption dominated over sulfate adsorption. In summary, the role of counteranions on phosphate adsorption needs further study.

3.2.4 Role of Particulate or Colloidal Solids

The presence of particulate material can affect orthophosphate sorption (Fettig et al., 1990; Szabó et al., 2008). This is significant for removal of orthophosphate in the primary clarifiers or during simultaneous precipitation in the aeration tank. Fettig et al. (1990) used synthetic wastewater and increased turbidity while maintaining a constant initial orthophosphate concentration. They observed a 25% decrease in sorption capacity of orthophosphate when turbidity was increased from approximately 90 to 350 NTU. They also observed a decrease in sorption capacity in the presence of humic material. Szabó et al. (2008) observed a decrease in phosphate adsorption with an increase in COD of raw wastewater as described in Figure 7.5. Wastewater treatment facilities that use iron or aluminum in upstream wastewater treatment processes should expect to see a decrease in orthophosphate sorption because of the presence of particulate or colloidal COD. Szabó et al. (2008) hypothesized that carboxylic and phenolic groups on the organic matter compete with phosphate for binding sites on the surface of the hydrous metal oxides.

3.2.5 Role of Mixing

Lijklema (1980) showed that orthophosphate adsorption onto aluminum was influenced by mixing. Gillberg et al. (1996) showed in laboratory testing that rapid mixing significantly increased the percentage of orthophosphate removed compared to slow mixing. These authors compared the ratio of orthophosphate removed by coprecipitation versus the same amount of orthophosphate removed by sorption on freshly formed hydrous metal oxides. A higher ratio would suggest a greater importance of mixing versus a lower ratio. The ratios observed ranged from 2 to 4, which suggests that good mixing could lower coagulant dosages to one-half to one-quarter of coagulant dosages needed with no mixing. They conducted a series of tests using various chemical coagulants. From these tests they found that aluminum salts had

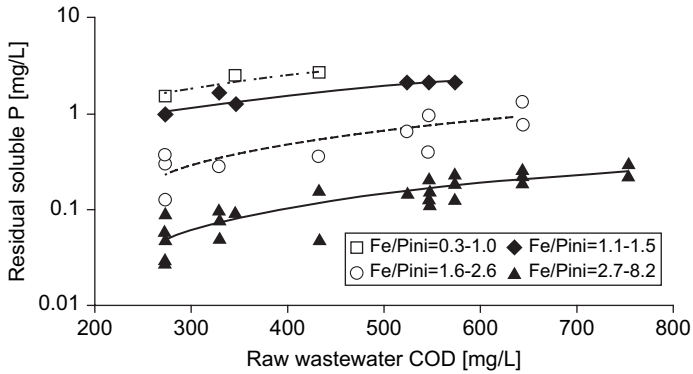

Figure 7.5 Residual soluble phosphorus concentration in terms of raw wastewater chemical oxygen demand (COD) concentration (raw wastewater: initial pH = 7.5 to 8.5; initial PO_4-P = 3.1 to 5.2 mg/L; and initial total suspended solids = 80 to 260 mg/L) (from Szabó et al., 2008).

a higher ratio than iron salts, thus concluding that mixing was more important for aluminum salts than iron salts. Furthermore, the ratio increased with an increase in pH, suggesting that rapid mixing for both iron and aluminum was more important at higher pH compared to lower pH. This observation would agree with the competitive sorption concept and the ligand exchange model explained in the earlier subsection. Hydroxyl ions outcompete orthophosphate ions for HFO and HAO sites as pH increases. Rapid mixing would thus be more important at higher pH to provide orthophosphate ions with the ability to adsorb on HAO or HFO sites before sorption of hydroxyl ions. Szabó et al. (2008) observed that an increase in mixing intensity (G) resulted in a decrease in residual orthophosphate at a constant molar ratio (Figure 7.6). The curve was logarithmic and for $G > 200\ s^{-1}$ mixing was not as important as for $G < 200\ s^{-1}$. Sagberg et al. (2006) described the importance of mixing for orthophosphate precipitation in a full-scale process using pressurized air to inject the coagulant into a static mixer. They emphasized that strong mixing conditions were needed to reduce coagulant dose.

3.2.6 Role of Contact Time

Lijklema (1980) showed that HFO flocs continued to sorb orthophosphate over nearly 1000 hours of contact time. Szabó et al. (2008) showed the importance of HFO adsorption kinetics on orthophosphate removal. The authors ran batch and continuous reactor

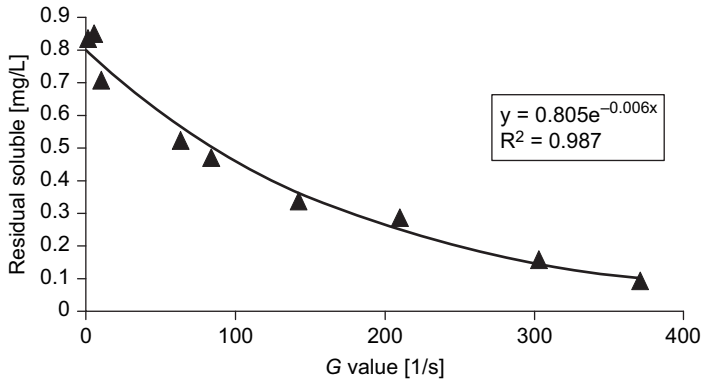

FIGURE 7.6 Effect of *G* value on phosphorus removal (ferric chloride, initial P = 4.1 mg/L; Fe–dose, initial phosphorus = 1.8 mole/mole; time of sampling = 11 minutes after coagulant addition) (from Szabó et al., 2008).

experiments. They showed that after more than 100 hours of contact time, the orthophosphate ions continued to adsorb onto HFO floc particles. The relationship was logarithmic in both studies, and the amount sorbed decreased with increase in contact time (Lijklema, 1980; Szabó et al., 2008). Szabó et al. (2008) repeated these experiments in two abiotic continuous flow reactors that simulated a tertiary clarification process (System A) with a short reaction step of HRT (equals SRT) of 18 minutes and a clarifier of HRT of 4.5 hours versus an activated sludge aeration tank (System B) with a longer HRT (4.7 hours) and SRT (5.5 days) and a similar clarifier HRT (4.5 hours). They determined that System B consistently outperformed System A by (1) producing lower orthophosphate residuals and (2) producing a lower standard deviation in residuals. The authors suggested that the longer contact time produced a lower residual. The recycling of sludge may have contributed to reducing the standard deviation in the residual orthophosphate by maintaining a large mass of HFO in the system thus overcoming transient variations in influent iron to orthophosphate molar ratios. Simultaneous precipitation in aeration tanks and solids contact clarifiers provide a longer solids contact time with orthophosphate ions and should benefit from adsorption of orthophosphate that could occur over several hours to several days in these processes.

3.2.7 *Role of Aging*

Aging studies with HFO showed that the sorption capacity of HFO flocs decreased by 25% after as little as 30 minutes of aging was conducted (Szabó et al., 2008).

Lijklema (1980) described the sorption capacities of fresh HFO particles versus one-day old HFO particles and showed that one-day old flocs possessed approximately half the orthophosphate sorption capacity of fresh HFO flocs. Kang et al. (2003) evaluated fresh ferrihydrite versus aged material (goethite and hematite) prepared from the same ferrihydrite stock source. All three materials had similar particle size. The ferrihydrite particles, however, possessed a larger specific surface area that was 10 times that of goethite and hematite. The sorption capacity of the ferrihydrite was determined to be 10 and 20 times greater than goethite and hematite, respectively, on a mass basis. The sorption capacity of all the materials was similar on a unit-area basis, suggesting the validity of using a surface complexation approach to evaluate sorption onto HFO flocs. Smith et al. (2008) also showed that fresh HFO had six times the surface area of two-year-old HFO and suggested a surface complexation approach to modeling the sorption reaction. Berkowitz et al. (2006) evaluated the aging of HAO flocs. They suggested that HAO transformed into gibbsite with 20% gibbsite formed after 20 days of aging. They showed that the surface area of HAO flocs decreased by 50% with aging over 120-day-old flocs with a corresponding 50% loss in sorption capacity.

3.2.8 Role of Alkalinity

Szabó et al. (2008) evaluated the role of alkalinity on coprecipitation of orthophosphate. They showed that for similar pH range, higher alkalinity water possessed a lower orthophosphate removal capability than lower alkalinity water. They proposed that higher alkalinity resulted in the rapid formation of HFO because of greater H^+ capturing capacity. This capacity results in a kinetic advantage in the formation of HFO over the coprecipitation of phosphate in HFO.

For both Al(III) and Fe(III), optimum pH (corresponding to minimum metal phosphate solubility) is approximately 6.8 and is relatively broad. In contrast, Recht and Ghassemi (1970) reported an optimum pH of 6.0 for phosphate precipitation from distilled water with Al(III) and a pH of 3.5 to 4.0 for precipitation with Fe(III). The difference in optimum pH can be attributed to the influence of other chemical species present in wastewater. Hsu (1973) reported that the addition of Ca2+ resulted in a change from a well-defined optimum pH of 4 without Ca2+ to a broad pH range of 4 to 8 at 2 mmol/L Ca2+. Similar calcium effects were reported by Grohman et al. (1984), who studied ferric phosphate precipitation from "clean" solutions. Arvin and Petersen (1980) incorporated the effects of calcium and bicarbonate to a complex semiempirical model of phosphate precipitation. Despite these studies, the mechanism of calcium effect is not fully understood.

Composition of metal phosphate precipitate has a significant effect on the required metal dose. The ratio of metal dose to initial soluble orthophosphate concentration closely approximates the overall precipitate (or precipitate mixture) composition because the residual soluble metal concentrations are small (at least for ferric and aluminum additions). Figure 7.7 shows the ratio as a function of residual phosphate concentration for batch and continuous experiments with aluminum for a pH in the range 6 to 7.5. Figure 7.8 illustrates the effect of the initial TSS concentration in treated water on the ratio of metal dose to soluble orthophosphate as a function of residual phosphate concentration. As shown, as the concentration of TSS increases

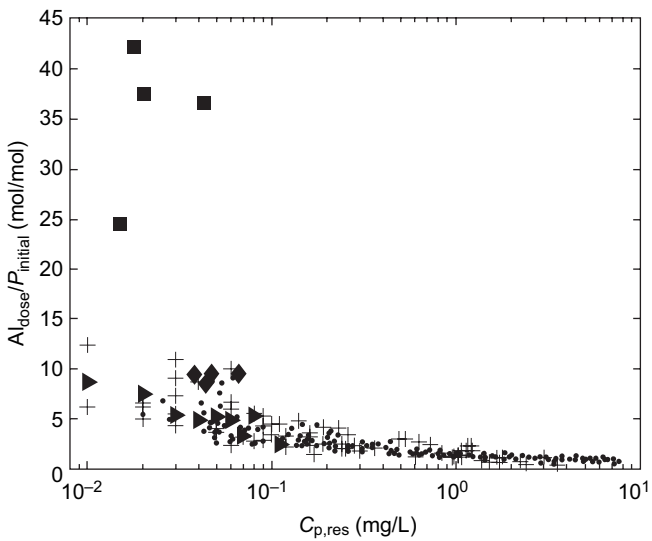

FIGURE 7.7 Ratio of Al(III) dose to initial orthophosphate concentration as a function of residual soluble orthophosphate concentration. Full-scale plant data shown as solid symbols: ♦ = Plant C (tertiary phosphorus removal with aluminum); ■ = Plant D (tertiary phosphorus removal with aluminum); ▼= Plant E (tertiary phosphorus removal with aluminum). Laboratory data: + = jar test data for initial TSS between 0 and 350 mg/L (Szabó et al., 2008); • = batch and continuous flow tests (Gates, 1991). Data less than 0.05 mg/L orthophosphate is less than quantification limits for Plant E. Each data point shown for Plant E represents an average of molar ratio of aluminum dosage-to-initial phosphorus ($Al_{dose}/P_{initial}$) to achieve the residual phosphorus concentration ($C_{p,res}$) value for the plant.

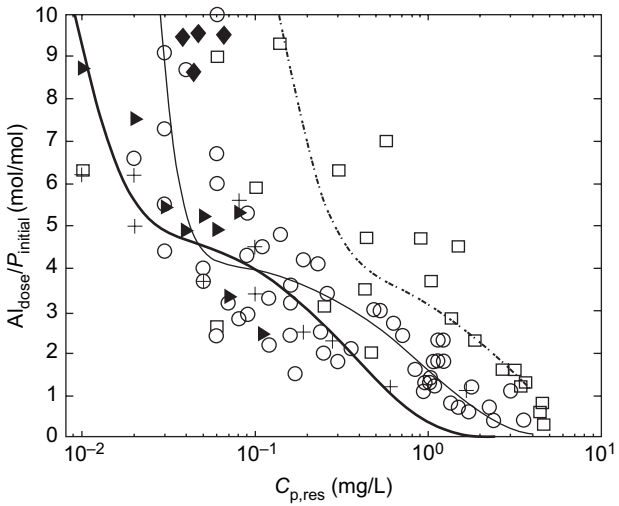

FIGURE 7.8 Ratio of Al(III) dose to initial orthophosphate concentration as a function of residual soluble orthophosphate concentration. Full-scale plant data shown as solid symbols: ♦ = Plant C (tertiary phosphorus removal with aluminum); ■ = Plant D (tertiary phosphorus removal with aluminum); ▼ = Plant E (tertiary phosphorus removal with aluminum). Laboratory data: + and dark solid line = initial total suspended solids (TSS) concentration between 0 and 100 mg/L; ○ and solid line = initial TSS concentration between 100 and 350 mg/L; □ and dashed line = initial TSS concentration between 350 and 2100 mg/L (Szabó et al., 2008). Data less than 0.05 mg/L orthophosphate is less than quantification limits for Plant E. Each data point shown for Plant E represents an average of molar ratio of aluminum dosage-to-initial phosphorus ($Al_{dose}/P_{initial}$) to achieve the residual phosphorus concentration ($C_{p,res}$) value for the plant.

the aluminum dose needed to meet the desired residual phosphorus concentration increases. The data also imply that it becomes more difficult to achieve lower phosphorus concentrations as the TSS concentration increases. A similar relationship was found in the effect of the initial phosphorus concentration in treated water on the ratio of metal dose to soluble orthophosphate as a function of residual phosphate concentration (see Figure 7.9).

Figure 7.10 presents the ratio of metal dose to initial soluble orthophosphate concentration as a function of residual phosphate concentration for Fe(III) for

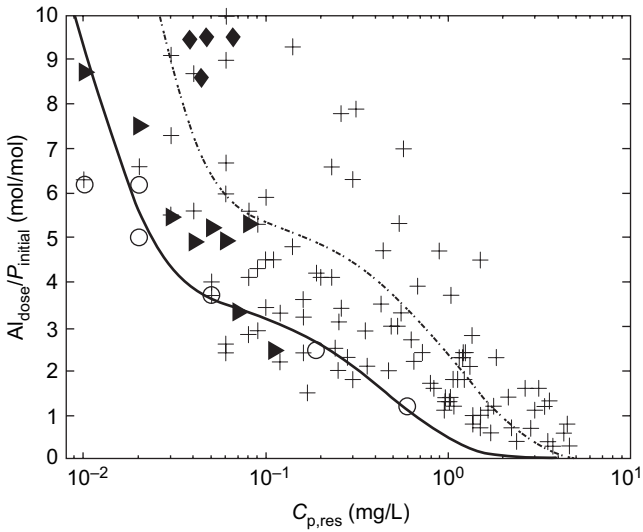

FIGURE 7.9 Ratio of Al(III) dose to initial orthophosphate concentration as a function of residual soluble orthophosphate concentration. Full-scale plant data shown as solid symbols: ♦ = Plant C (tertiary phosphorus removal with aluminum); ■ = Plant D (tertiary phosphorus removal with aluminum); ▼ = Plant E (tertiary phosphorus removal with aluminum). Laboratory data: + and dashed line = initial phosphorus concentration greater than 1 mg P/L; ○ and dark solid line = initial phosphorus concentration less than or equal to 1 mg P/L (Szabó et al., 2008). Data less than 0.05 mg/L orthophosphate is less than quantification limits for Plant E. Each data point shown for Plant E represents an average of molar ratio of aluminum dosage-to-initial phosphorus ($Al_{dose}/P_{initial}$) molar dosages to achieve the residual phosphorus concentration ($C_{p,res}$) value for the plant.

laboratory- and full-scale activated sludge systems for pH 6.5 to 7.5. The figure also includes the data collected by Gates (1991) through batch and continuous flow experiments. Improvements in analytical techniques now allow measurement of lower phosphorus concentrations; the "wall effect" observed in the dataset from Gates (1991) is not present in recently collected laboratory and field data.

For both metals, the relationships corroborate the chemical mechanism of phosphate precipitation. At high residual phosphate concentrations (i.e., low metal doses) the ratio in the precipitate remains essentially constant, indicating stoichiometric precipitation (i.e., ASF equals approximately 1.0 in eq 7.5). At high metal doses, the

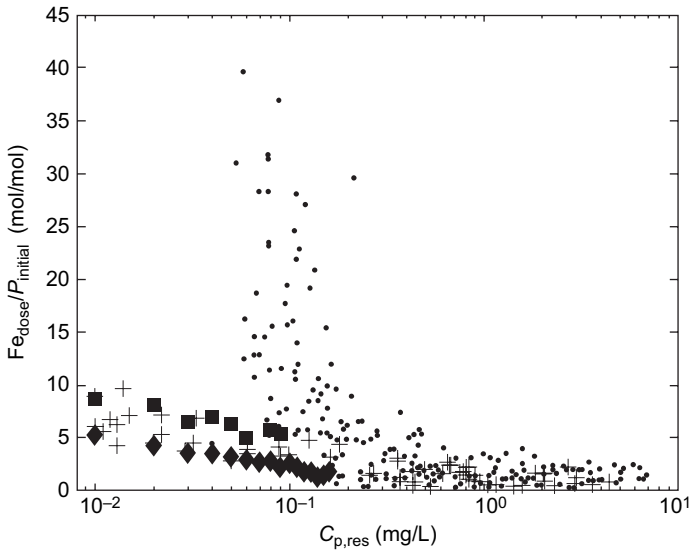

FIGURE 7.10 Ratio of Fe(III) dose to initial orthophosphate concentration as a function of residual soluble orthophosphate concentration. Full-scale plant data shown as solid symbols: ♦ = Plant A (simultaneous precipitation where molar dosage includes phosphorus required for biological growth); ■ = Plant B (tertiary phosphorus removal with iron). Laboratory data: + = jar test data for initial TSS between 0 and 350 mg/L (Szabó et al., 2008); • = batch and continuous flow tests (Gates, 1991). Data less than 0.05 mg/L orthophosphate is less than quantification limits for Plant A and B. Each data point shown for Plant A and B represents an average of molar ratio of iron dosage-to-initial phosphorus ($Fe_{dose}/P_{initial}$) molar dosages to achieve the residual phosphorus concentration ($C_{p,res}$) value for the plant.

phosphate solubility limit is approached, and the excess of Al(III) or Fe(III) precipitates as metal hydroxide, resulting in a dramatic increase of the Me/P ratio. At residual phosphate concentrations of less than approximately 1 mg P/L, the Me/P ratio increases as a result of either additional phosphate adsorption or substitution of orthophosphate for OH in the precipitate (Goldshmid and Rubin, 1978; Hsu, 1973; Luedecke et al., 1988). Figure 7.11 illustrates the effect of the initial TSS concentration in the treated water on the ratio of metal dose to soluble orthophosphate as a function of residual phosphate concentration. As shown, as the concentration of TSS increases the iron dose needed to meet the desired residual phosphorus concentration increases. More importantly, the

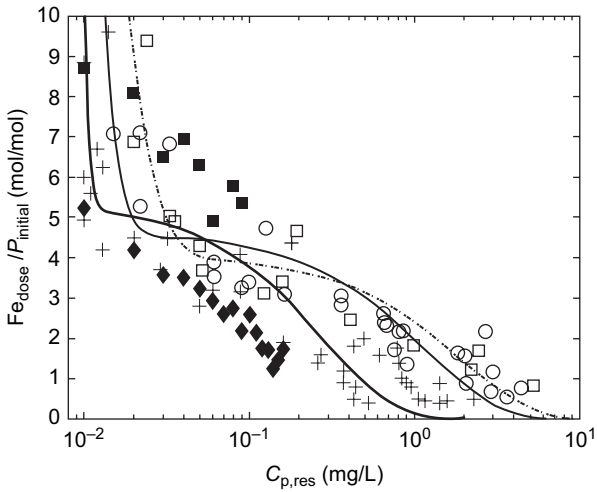

FIGURE 7.11 Ratio of Fe(III) dose to initial orthophosphate concentration as a function of residual soluble orthophosphate concentration. Full-scale plant data shown as solid symbols: ♦ = Plant A (simultaneous precipitation with iron removal including biological phosphorus uptake); ■ = Plant B (tertiary phosphorus removal with iron). Laboratory data: + and dark solid line = initial total suspended solids (TSS) concentration between 0 and 100 mg/L; ○ and solid line = initial TSS concentration between 100 and 350 mg/L; □ and dashed line = initial TSS concentration between 350 and 2100 mg/L (Szabó et al., 2008). Data less than 0.05 mg/L orthophosphate is less than quantification limits for Plant A and B. Each data point shown for Plant A and B represents an average of molar ratio of iron dosage-to-initial phosphorus ($Fe_{dose}/P_{initial}$) molar dosages to achieve the residual phosphorus concentration ($C_{p,res}$) value for the plant.

data implies that it becomes more difficult to achieve lower phosphorus concentrations as the TSS concentration increases. This effect was not as pronounced as for aluminum (Figure 7.8). A similar relationship was found in the effect of initial phosphorus concentration in treated water on the ratio of metal dose to soluble orthophosphate as a function of residual phosphate concentration (see Figure 7.12). For the reasons stated above, the Gates (1991) data is not included in these figures.

Although the exact mechanism of precipitate formation is not fully understood, Figures 7.7 through 7.12 can be used to estimate and calculate the metal dose necessary to achieve the required residual soluble orthophosphate:

$$Me_{dose} = (Me/P)\,(C_{P,ini} - C_{P,res})\ [g\ Me/mol\ Me] \tag{7.6}$$

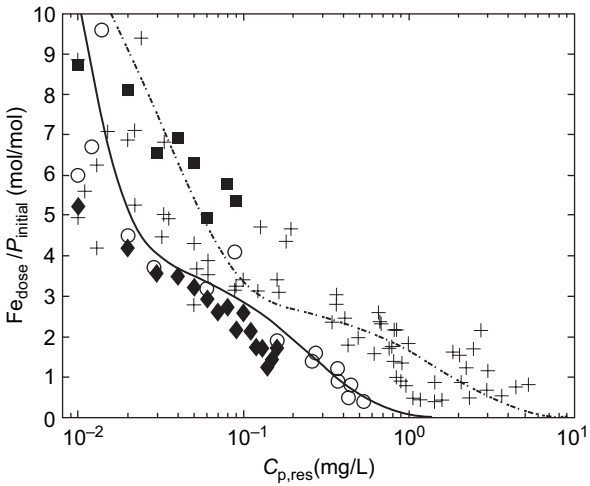

FIGURE 7.12 Ratio of Al(III) dose to initial orthophosphate concentration as a function of residual soluble orthophosphate concentration. Full-scale plant data shown as solid symbols: ♦ = Plant A (simultaneous precipitation with iron removal including biological phosphorus uptake); ■ = Plant B (tertiary phosphorus removal with iron). Laboratory data: + and dashed line = initial phosphorus concentration greater than 1 mg P/L; ○ and dark solid line = initial phosphorus concentration less than or equal to 1 mg P/L (Szabó et al., 2008). Data less than 0.05 mg/L orthophosphate is less than quantification limits for Plant A and B. Each data point shown for Plant A and B represents an average of molar ratio of iron dosage-to-initial phosphorus ($Fe_{dose}/P_{initial}$) molar dosages to achieve the residual phosphorus concentration ($C_{p,res}$) value for the plant.

Where, Me/P is the required doses for residual phosphate concentration presented in Figures 7.7 through 7.12.

Practice has shown that to achieve residual phosphorus concentrations of greater than 1 mg/L, an Me/P value of approximately 1 mol/mol is needed. For concentrations less than 1 mg/L, the Me/P dose are presented in Figures 7.8, 7.9, 7.10, or 7.12. Alternatively, batch tests can be conducted to determine site-specific dosage.

For biological treatment systems, influent concentration includes soluble orthophosphate concentration and a portion of soluble nonorthophosphate and particulate phosphorus concentration. The latter two fractions of total phosphorus are

partially hydrolyzed during treatment and converted to orthophosphate requiring an additional metal dose.

3.3 Sludge Generation

Chemical addition to both primary and secondary treatment for phosphorus removal results in more primary sludge production and less secondary sludge production. Additional sludge production in primary treatment is generated by chemical sludge, enhanced removal of influent suspended solids, and soluble total organic carbon after chemical addition. Reduced sludge production in secondary treatment may be because of lower biochemical oxygen demand (BOD) loads in primary effluent that has been chemically treated. In primary treatment, TSS and BOD removal without chemical addition are approximately 50% and 30%, respectively. Chemical addition can improve TSS removal to 70% or greater and BOD removal to approximately 50% if implemented for chemically enhanced primary treatment (CEPT) purposes (U.S. EPA, 1987). In addition to TSS, CEPT also removes colloidal material and phosphorus. Site-specific bench tests need to be conducted to establish the chemical type and dose and to evaluate removal goals. Attention must be given not to remove too much phosphorus, which is a nutrient needed in downstream biological processes. Anionic polymer typically is added during CEPT to facilitate and enhance flocculation and rapid removal of the solids. Sludge generation calculations are demonstrated later in this chapter as part of the design example.

3.4 Chemical Storage and Feed

Ferric, ferrous, and alum compounds are acidic, so storage and handling issues are of concern. Fiberglass-reinforced plastic or polyethylene tanks can be used to store ferric chloride, ferrous chloride, ferric sulfate, ferrous sulfate, or alum. Recommended metering pumps include peristaltic, solenoid, or diaphragm types. Carrier water should be avoided if possible; the chemical will react with the carrier water and cause plating in the chemical feed lines. If it is necessary to add carrier water for mixing or dilution, then it should be added as close to the injection point as possible to minimize the plating effects (WEF et al., 2006). The pump heads should be polyvinyl chloride. Piping, valves, and fittings should be polyvinyl chloride or chlorinated polyvinyl chloride. Personnel should wear personal protective equipment (PPE) when handling chemicals. The PPE should include, but not be limited to, gloves, respirators, goggles, aprons, and face shields.

Plant personnel should obtain a specification data sheet or certified analysis for any chemicals to be used in the process to assess if the increased load of chemical impurities on the treatment plant is acceptable. This is particularly important for land disposal of biosolids or in water reclamation facilities. Typically it is not necessary to use high-purity chemicals in chemical feed application because technical grade from a reputable manufacturer is sufficient. Use of pickle liquor from some industrial sources has a higher probability for containing metal contaminants, however, so it is important to obtain specifications for the delivered chemical to ensure these contaminants do not have an adverse effect on plant operation or permit.

3.5 Chemically Enhanced Separation Technologies

Figure 7.13 shows a typical WWTP and the recycle streams that are generated at the solids handling facilities. The quality of these streams varies based on the technology used in the solids processing operations. For example, sludge thickening using belt filter dewatering typically generates two times more recycle flow (filtrate) compared to centrifuge dewatering because of the amount of wash water used. Total recycle

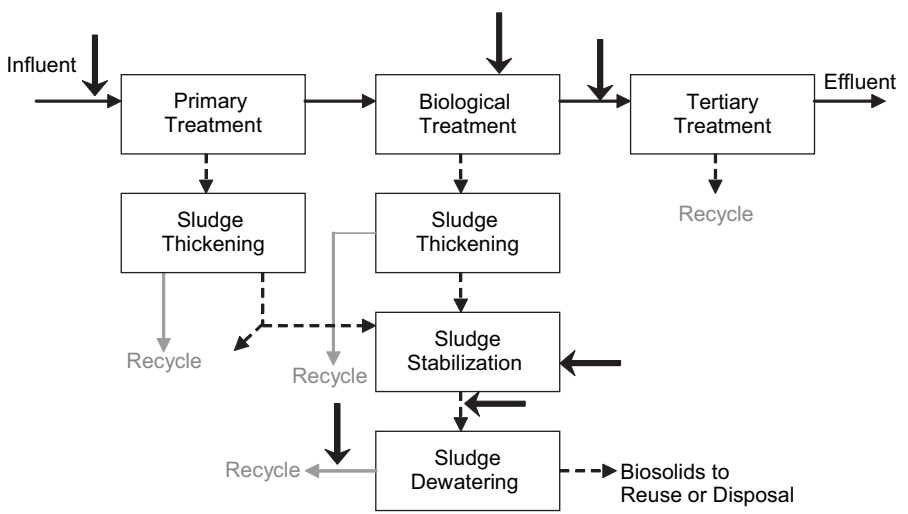

FIGURE 7.13 Typical wastewater treatment flow scheme and the liquid and solids handling sidestream generation. Chemical addition shown can be implemented individually or can be combined.

streams can generate 20% to 30% of plant influent. Recycle streams from the solids processing units typically contain high ammonia and phosphorus concentrations, especially if the recycle stream was collected following sludge digestion. These concentrations can be as high as 900 to 1100 mg/L of ammonia and 100 to 150 mg/L of phosphorus, depending on digestion efficiency and struvite and phosphorus precipitates formation in the digestion system and the associated appurtenances. Therefore, 50% to 60% of the released phosphorus can be retained in dewatered biosolids or taken out in the form of struvite precipitates, the remaining returning back to the head of the plant.

Agencies that have implemented or conducted full-scale tests of chemical phosphorus removal include District of Columbia Water Sanitation Authority (DCWASA) in Washington, D.C.; City of Coeur D'Alene, Coeur D'Alene, Idaho; Hayden Area Regional Sewer Board, Hayden, Idaho; Clean Water Services, Oregon; and Alexandria Sanitation Authority, Alexandria, Virginia. In all cases, chemical addition points are similar to those shown in Figure 7.13. This includes several types of chemical phosphorus removal schemes used in solids–liquid separation technologies:

(1) Multipoint removal;
(2) Coprecipitation during primary and tertiary clarification:
    - Conventional clarification and
    - Contact clarification and ballasted flocculation;
(3) Simultaneous precipitation; and
(4) Direct filtration.

Successful chemical phosphorus removal depends on the formation of stable particulates with complexed, coprecipitated, or adsorbed phosphorus species and well-operated solids–liquid separation units that effectively capture phosphorus without release or resolubilization. Coupling chemical phosphorus removal with enhanced biological phosphorus removal (EBPR) can reduce the chemical costs. The U.S. EPA (2007) indicated that facilities that relied on EBPR for phosphorus removal also used multipoint or subsequent chemical addition and tertiary processes to reduce the amount of phosphorus to be removed. In this way, the facilities improved efficiency of the chemical phosphorus removal processes and significantly reduced the costs of chemicals additions. In Fairfax County, Virginia, chemical dosing was cut in half after EBPR was implemented (U.S. EPA, 2007).

3.6 Separation Processes

Depth filtration typically is used as a tertiary filtration step that follows secondary treatment and is aided by chemical addition. Total phosphorus concentrations in the final effluent can be reduced to very low levels through removal of particulate phosphorus and chemically bound soluble phosphorus. Conventional deep bed sand filters, mixed-media gravity filters, continuous backwash filters, and variations of these technologies are used. For example, at the Upper Blue Sanitation District's Farmers Korner Wastewater Treatment Facility, Breckenridge, Colorado, biological secondary treatment is followed by chemical coagulation and flocculation with polymer and alum addition, clarification via tube settlers, and filtration though mixed media bed filters. The final effluent monthly average total phosphorus concentration is approximately 0.05 mg P/L.

Continuous backwash filtration systems use adsorption filtration and moving-bed filtration technology preceded by chemical addition and a prereactor zone. The filtration system can be operated as a single- or dual-pass filtration system. Ferric chloride ($FeCl_3$), which creates iron oxide–coated sand promoting an active filtration system, is used before filtration. As a result, the process combines the removal mechanisms of coprecipitation and adsorption onto iron oxide–coated sand. The theoretical details of this proposed mechanism are discussed in section 3.1.4 for HFO particles within the water column. The fundamental physical and chemical processes should not vary significantly if the HFO is coating other particles. The filtration system acts as a fluidized-bed reactor, facilitating the precipitation of iron as a coating on the sand and creating a reactive filter media. Iron oxide–coated sand is continually formed, abraded, and regenerated within the moving-bed filter.

Membrane filtration systems use membranes as the filtration medium and potentially can lead to good total phosphorus removal depending on the phosphorus species. Neethling et al. (2007) evaluated several chemically enhanced separation technologies. Ultrafiltration coupled with alum addition was included, and it showed very efficient particulate phosphorus removal because of superior ability to remove suspended and some colloidal material. Removal of soluble phosphorus fractions were not as consistent or as effective as other tertiary treatment processes studied. These findings emphasize the significance of additional contact for effective coagulation and flocculation of the colloidal fraction similar to the multiple-stage filtration and adsorption processes where more contacting surface area and

contacting time are provided. In the event that very low total phosphorus concentrations are required—less than solubility limits and what could be achieved by adsorption filtration—reverse osmosis can be implemented.

Separation systems in series can be implemented if there are very low phosphorus concentrations beyond which can be achieved using a single-step filtration or clarification. In this process, the first step removes coarser particulate material and phosphorus, and the second step serves as a polishing unit that targets phosphorus removal by using additional dosing and contact time or finer media. Commercial products such as Dual-Stage Blue Pro from Blue Water Technologies, Spokane, Washington; DynaSand D2 from Parkson Corp., Fort Lauderdale, Florida; and Trident HS from Siemens, Warrendale, Pennsylvania, consist of separation technologies installed in series. For example, D2 consists of a two DynaSand units operated in series with a lamella settler to thicken the backwash stream. The Trident HS consists of a high-rate settling unit, adsorption clarification, and mixed media or upflow moving-bed (HSC) filter as the final separation step. These separation technologies can be coupled with conventional clarification units or with high-rate ballasted clarification systems such as Actiflo from Veolia Water, Houston, Texas, or DensaDeg from Degremont Technologies, Richmond, Virginia, depending on site-specific conditions and needs, such as available footprint, chemical costs, and final water quality requirements.

Leaf et al. (2007) reported effluent total phosphorus concentrations at the Hayden WWTP of as low as 0.009 mg/L during steady-state operation with a maximum value of 0.018 mg/L from the second stage filter. This was achieved with the dual-pass filtration system and chemical addition. The first-stage filter received a chemical dose of 15 mg Fe/L (44 mg $FeCl_3$/L), and the second-stage filter received a chemical dose of 10 mg Fe/L (29 mg $FeCl_3$/L). The reject stream from the filters was returned to the front of the WWTP. With a feed rate of 0.95 ML/s (0.25 mgd) to the filters, the system was operating with a hydraulic load of 8.5 m/h (3.5 gpm/sq ft).

3.7 Resource Recovery

Some examples of technologies that rely on the chemical phosphorus removal principles presented are listed below. These technologies target controlled separation of phosphorus-containing products and could be implemented within an existing plant in place of or in addition to chemical addition at the primary, secondary, and tertiary treatment steps.

Crystallization is a process that allows for forced precipitation of calcium phosphates by the addition of crystallization adjuvants in a specially designed fluidized-bed reactor with formation of salt pellets. Crystallization is favored by seeding grains (sand or anthracite) with strict control of precipitation conditions by addition of sodium hydroxide or lime. When applied to concentrated solutions (>100 mg P/L) the resulting high crystallization rate provides short retention time and relatively small reactors. The Crystalactor® process, developed by DHV Water BV, Netherlands (1998), is an example of crystallization processes. Although complex, this technology is used in several full-scale installations in the Netherlands (Giesen, 1999).

Researchers identified the process of struvite formation using magnesium addition with pH adjustment (Burns and Moody, 2002). Researchers used MgO as the magnesium source and X-ray diffraction to confirm the presence of struvite (magnesium ammonium phosphate hexahydrate) in the product. Chemical analysis of total nitrogen and total phosphorus indicated the fertilizer value of the recovered materials. The researchers also recovered nonstruvite material, and based on the X-ray diffraction peaks they identified them as the mineral brushite [$CaPO_3(OH)\cdot 2H_2O$]. Commercialization of these technologies are ongoing. The technologies can be as simple as chemical dosing, contact, clarification, and solids handling. Some examples of commercialized struvite recovery processes are provided below.

One of the newer struvite recovery technologies is Ostara™. This technology uses magnesium chloride and caustic followed by granule formation at the City of Edmonton's Gold Bar WWTP, Edmonton, Alberta, Canada. The plant achieves phosphorus removal rates of greater than 80% on average.

The Phosnix® process, developed by Unitika Ltd, Japan, is based on an air-agitated column reactor with complementary chemicals dosing equipment (i.e., $Mg(OH)_2$ or $MgCl_2$ and NaOH for pH control to 8.5–9.5) ensuring fast nucleation and growth of struvite pellets. Like the similar Phosnix® processes, it works preferentially with phosphorus-concentrated wastewater (e.g., supernatant liquor from sludge anaerobic digestion or specific industrial streams) offering removal efficiencies of more than 90%. The process is used in some full-scale installations in Japan, where recovered struvite is sold (Katsuura and Ueno, 1998).

The REM NUT process was developed in the mid-1980s to remove and recover phosphate, ammonium, and potassium ions from wastewater in the form of a premium quality slow-release fertilizer (i.e., ammonium and potassium struvite,

$MgNH_4PO_4$ and $MgKPO_4$) (Liberti et al., 1984). Its basic configuration process relies on two unit operations:

(1) Selective ion exchange for removal of nutrients (NH_4^+, K^+, HPO_4^{2-}) from wastewater and their concentration in the ion exchangers regeneration eluate.
(2) Chemical precipitation of nutrients in the form of struvite after addition of Mg^{2+} at a controlled pH; the supernatant solution is recycled.

4.0 DESIGN EXAMPLES

4.1 Chemical Phosphorus Removal Process Design

The process design of chemical phosphorus removal is dependent on several factors. The most important factors are

- Wastewater characteristics such as phosphorus concentrations, TSS, pH, and alkalinity;
- Chemicals used for precipitation, such as aluminum, calcium, or iron; and
- The point of chemical addition, for example, primary treatment, secondary treatment, or tertiary treatment.

Wastewater characterization involves determining constituent parameters under varying diurnal and seasonal loading conditions such that chemical type, chemical requirements, and feed rates can be designed to satisfy both peak and minimum requirements for best phosphorus removal. Because the chemicals added to remove phosphorus may also be involved in other reactions, such as alkalinity consumption, reaction with sulfides, and coagulation of suspended solids, chemical doses in excess of those estimated using wastewater characteristics and precipitation chemistry of phosphorus often must be provided.

Selection of the chemical used for phosphorus removal depends on the cost of the chemical, alkalinity consumption, quantities of sludge generated, and safety in handling and use (Jenkins and Hermanowicz, 1991). Typical forms of the three cations used for phosphorus removal are aluminum sulfate (alum) and sodium aluminate for aluminum; ferric chloride, ferrous chloride, and ferrous sulfate for iron; and lime for calcium. Lime addition for phosphorus removal from wastewater, however, is not typical in current designs because of drawbacks such as high

sludge production rates, high pH requirement, and large investments in equipment, operation, and maintenance (Jenkins and Hermanowicz, 1991). Hence, use of calcium for phosphorus removal from wastewater is not discussed further in this section.

The ability to achieve the required effluent phosphorus limits is strongly dependent on the point of chemical addition in the treatment process. The potential points of chemical addition in the treatment process are before primary treatment (preprecipitation), before secondary treatment prior to either the aeration basins or the secondary clarifiers (simultaneous precipitation), and postsecondary treatment or postprecipitation. The addition of chemicals before primary treatment requires a mixing tank for dissolution of chemicals. Chemicals required for phosphorus removal are much higher than stoichiometric requirements because of chemical consumption for suspended solids coagulation. Similarly, postsecondary addition of chemicals to remove phosphorus requires a mixing tank for chemical dissolution and tertiary clarification of filtration for solids removal. Jenkins and Hermanowicz (1991) stated that either a combination of primary and secondary chemical addition or tertiary treatment is necessary to achieve effluent phosphorus concentrations of less than 1.0 mg P/L. Addition of chemicals to secondary treatment reduces the active fraction of the mixed liquor suspended solids. Operators may need to maintain a higher mixed liquor concentration to achieve comparable biological activity with metal addition.

Examples provided below outline the procedures for process design of phosphorus removal using metal salts addition before primary clarification or to the aeration basin. The chemical doses are determined using Figures 7.7 through 7.12 and eq 7.6. These design examples can be used as a starting point either to design a new chemical phosphorus removal system or to retrofit an existing WWTP. The final design should be based on pilot-scale trials and possibly full-scale trials of these example process designs to account for the variations in the characteristics of the wastewater being treated.

4.1.1 Phosphorus Removal by Alum Addition to Raw Wastewater and Aeration Basin

This example presents the basic steps in the design of phosphorus removal by alum addition during primary and secondary treatment stages. Because secondary treatment by activated sludge or other biological processes requires phosphorus for biomass growth, it is undesirable to remove very high levels of total phosphorus in the

primary clarifiers. The wastewater characteristics and effluent requirements for this design example are as follows:

- Wastewater average flow = 1.89×10^7 m^3/d (5 mgd),
- Wastewater peak flow = 4.73×10^7 m^3/d (12.5 mgd),
- BOD_5 = 250 mg/L,
- Total suspended solids = 270 mg/L,
- Total phosphorus = 8 mg P/L,
- Orthophosphate = 5 mg P/L,
- pH = 7.0,
- Alkalinity = 250 mg/L,
- Effluent total phosphorus limit ≤ 0.5 mg P/L,
- Effluent TSS limit ≤ 15 mg/L, and
- Effluent BOD_5 limit ≤ 15 mg/L.

4.1.1.1 Alum Dose Determination

The aluminum dose to be added can be determined by using eq 7.6 and Figures 7.7 to 7.9. Because the soluble orthophosphate form is removed by chemical precipitation, the dose of aluminum required to remove orthophosphate in primary treatment is as follows:

$$Al_{dose} = (Al/P)\,(C_{P,in} - C_{P,res})\,[(26.98\text{ g Al/mol})/(30.97\text{ g/mol P})] \qquad (7.7)$$

Where,

Al_{dose} = aluminum dose,
$C_{P,in}$ = concentration of phosphorus in influent, and
$C_{P,res}$ = concentration of residual phosphorus.

Figure 7.7 shows that for $C_{P,res}$ of less than 0.1 mg/L, the Al/P ratio increases steeply. It is economical to keep the Al/P ratio low; therefore, a $C_{P,res}$ of 0.1 mg/L can be selected.

$C_{P,res}$ = 0.1 mg/L,
Al/P ratio = 3 (from Figure 7.7), and
$C_{P,in}$ (ortho P) = 5 mg/L (given).

Therefore,

Al_{dose} = 3 (5 – 0.1) [(26.98 g Al/mol)/(30.97 g/mol P)]= 13 mg/L; and
Al_{dose} = 15 mg/L.

For secondary treatment, the influent $C_{P,in}$ includes all the remaining phosphorus because the nonorthophosphate and particulate phosphorus are partially hydrolyzed and converted to orthophosphate during biological treatment. Some of the phosphorus is used for biomass growth; however, determining $C_{P,in}$ as all the remaining phosphorus in the primary effluent is a conservative approach:

$$C_{P,in} = 8 - (5 - 0.1) = 3.1 \text{ mg/L} \tag{7.8}$$

Similar to primary treatment, eq 7.6 and Figure 7.7 can be used to determine the aluminum dose to be added to secondary treatment to obtain effluent soluble phosphorus of 0.1 mg/L, which is required because the TSS in the effluent contains approximately 2% to 2.5% particulate phosphorus. Therefore, if effluent TSS is 15 mg/L and phosphorus content is 2.5% in the TSS, then particulate phosphorus concentration in the effluent is 0.375 mg/L.

To achieve an effluent total of phosphorus of less than or equal to 0.5 mg/L, the effluent soluble phosphorus must be less than 0.125 mg/L (0.5–0.375).

- $C_{P,in}$ = 3.1 mg P/L;
- $C_{P,res}$ = 0.1 mg P/L;
- Al/P = 2;
- Al_{dose} = 2 (3.1 – 0.1) [(26.98 g Al/mol)/(30.97 g/mol P)] = 5.2 mg/L (Use Al_{dose} = 6 mg/L); and
- Total Al_{dose} = 15 + 6 = 21 mg/L.

4.1.1.2 Chemical Requirements and Storage

The amount of aluminum required, in kilograms per day, is equal to

$$\begin{gathered}\text{Flow (L/d)} \times \text{Dose (mg/L)} \times 10^{-6} \text{ kg/g} = \\ (1.89 \times 1.7 \text{ L/d})\ (21 \text{ mg/L})\ (10^{-6} \text{ kg/g}) = 397 \text{ kg/d}\end{gathered} \tag{7.9}$$

Aluminum typically is added as alum, $Al_2(SO_4)_3$ 14 H_2O = 594.3 g/mol,
Percentage aluminum in alum = (2 × 27 × 100)/594.3 = 9.08%

Therefore,

Amount of alum required = (397 × 100)/9.08 = 4377 kg/d

Using 50% alum by weight, unit weight = 1.33 kg/L (11.1 lb/gal). The volume of 50% alum solution required at average flow is equal to

$$4377/(0.5 \times 1.33) = 6575 \text{ L/d}$$

The volume of 50% alum solution required at peak flow is equal to

$$(6575 \times 4.73 \times 10^7)/1.89 \times 10^7 = 16\,455 \text{ L/d}$$

Alum storage tanks are sized either as 1.5 times the largest shipment or 10-day storage at peak flow rates.

Ten-day storage at peak levels = 10(16 455 L/d) = 165 000 L (43 830 gal)

A 190 000-L (50 000-gal) storage tank that can accommodate alum solution storage from 12 tank trucks (15 000 L or 4000 gal per tank truck) with 7570-L (2000-gal) free space is needed. The storage tank should be provided with temperature control higher than −1°C (30°F) (below which alum crystallizes), recirculation pumps, and secondary containment for possible spills during unloading from tank trucks and overflow spillage.

4.1.1.3 Sludge Generation

The amount of primary sludge generated can be estimated as follows. Additional primary sludge removed because of alum addition (improved TSS removal from 50% to 75%) is equal to

$$\begin{aligned}&(0.75 - 0.5) \times \text{Influent TSS} \times \text{flow} \times 10^{-6}\\ &\quad = 0.25 \times 270 \times 1.89 \times 10^7 \times 10^{-6}\\ &\quad = 1277 \text{ kg/d}\end{aligned} \tag{7.10}$$

$Al_{0.8}(H_2PO_4)(OH)_{1.4}$ (MW = 142.4) is assumed to represent the precipitate formed after aluminum addition, and $Al(OH)_3$ (MW = 78) is the excess aluminum hydroxide formed.

Al dose = 15 mg Al/L = 15/27 = 0.555 mmol Al/L

Phosphorus removed = 4.9 mg P/L = 4.9/31 =0.158 mmol P/L

Stoichiometric Al required, r = (0.8 mmol Al/mmol phosphorus removed) × 0.158 = 0.126 mmol Al/L

Excess Al added = 0.555 – 0.126 = 0.428 mmol Al/L

$Al_{0.8}(H_2PO_4)(OH)_{1.4}$ sludge = 0.158 × 142.4 = 22.5 mg/L

$Al(OH)_3$ sludge = 0.428 × 78 = 33.4 mg/L

Total chemical sludge produced = 22.5 + 33.4 = 55.9 mg/L

Chemical sludge because of alum addition (55.9 mg/L)
= flow × 55.9 × 10^{-6} = 1.89 × 10^{7} × 55.9 × 10^{-6} = 1058 kg/d

Total increase in primary sludge production = 1277 + 1058 = 2335 kg/d

Waste activated sludge (WAS) from biological treatment is reduced by alum addition in the primary treatment because BOD removal in the primary treatment is increased from approximately 30% to 50% (U.S. EPA, 1987).

Secondary sludge production (WAS P_X) = WAS + mass of effluent TSS

WAS P_X, kg VSS/d (without alum) = Y_{obs} × Flow × BOD removal × 10^{-6}

Assume observed yield, Y_{obs} = 0.5 g VSS/g BOD

Primary effluent BOD (without alum) = 250 × (1 – 03) = 175 mg/L

Primary effluent BOD (with alum) = 250 × (1 – 0.5) = 125 mg/L

Secondary effluent BOD = 15 mg/L

WAS P_x, kg VSS/d (without alum) = 0.5 × 1.89 × 10^{7} × (175 – 15) × 10^{-6} = 1514

WAS P_x, kg VSS/d (with alum) = 0.5 × 1.89 × 10^{7} × (125 – 15) × 10^{-6} = 1041

Decrease in WAS because of alum addition to primary treatment
= 1514 – 1041 = 473 kg VSS/d

Decrease in WAS because of alum addition to primary
treatment = 473/0.85 (assume TSS/VSS ratio = 0.85) = 556 kg TSS/d

Similar to primary sludge, the chemical sludge composition is because of two components: aluminum phosphate sludge and aluminum hydroxide sludge.

Al dose = 6 mg Al/L = 6/27 = 0.222 mmol Al/L

Phosphorus removed = 3.0 mg P/L = 3.0/31 = 0.097 mmol P/L

Stoichiometric Al required, r = (0.8 mmol Al/mmol P removed) × 0.097 =
0.077 mmol Al/L

Excess Al added = 0.222 – 0.077 = 0.145 mmol Al/L

$Al_{0.8}(H_2PO_4)(OH)_{1.4}$ sludge = 0.097 × 142.4 = 3.8 mg/L

$Al(OH)_3$ sludge = 0.0145 × 78 = 11.3 mg/L

Total chemical sludge produced = 13.8 + 11.3 = 25.1 mg/L

Chemical sludge because of alum addition (25.1 mg/L) =
flow × 25.1 × 10^{-6} = 1.89 × 10^{7} × 25.1 × 10^{-6} = 475 kg/d

Reduction in secondary sludge produced = 556 – 475 = 81 kg TSS/d

Therefore, the net effect of chemical addition to both primary and secondary treatment processes is an increase in primary sludge production by 2335 kg/d (5146 lb/d) and a decrease in secondary sludge production of 81 kg/d (179 lb/d).

4.1.2 Phosphorus Removal by Ferric Chloride Addition to Raw Wastewater before Primary Treatment

The following example illustrates the steps involved in process design for phosphorus removal in a typical WWTP (described in the previous design example), with the addition of ferric chloride to before primary treatment. This process design involves the use of Figures 7.10 to 7.12 and eq. 7.6 to determine the dose of ferric iron required.

4.1.2.1 Ferric Iron Dose Determination

Because soluble orthophosphate form is removed by chemical precipitation, the dose of iron required to remove orthophosphate in the primary treatment is as follows:

$$Fe(III)_{dose} = (Fe/P)\,(C_{P,in} - C_{P,res})\,[(55.85\text{ g Fe/mol})/(30.97\text{ g/mol P})] \qquad (7.11)$$

Figure 7.11 shows that for $C_{P,res}$ less than 0.2 mg/L, the Fe/P ratio increases steeply. It is economical to keep the Fe/P ratio low. Hence, the following can be selected:

$C_{P,res}$ = 0.2 mg/L can be selected.

For $C_{P,res}$ = 0.2 mg/L, Fe/P = 4.

If $Cp_{,in}$ (orthophosphate) = 5 mg/L (given), then Fe_{dose} = 4 mol P/mol Fe × (5 – 0.2) × [(55.85 g Fe/mol)/(30.97 g/mol P)] = 34 mg/L.

Primary effluent phosphorus concentration = 8 – 4.8 = 3.2 mg P/L

It is possible to achieve lower effluent phosphorus concentrations after secondary treatment involving biological processes because a certain amount of phosphorus present in the primary effluent would be incorporated into the biomass for growth. Phosphorus removal by secondary treatment will not be discussed in this design example.

4.1.2.2 Chemical Requirements and Storage

The amount of ferric iron required, in kilograms per day, is

Flow (L/d) × dose (mg/L) × 10^{-6} = 1.89 × 10^7 × 34 / 10^6 = 643 kg/d

Ferric iron typically is added as $FeCl_3$; formula weight = 162.3 g/mol. Therefore,

Percentage ferric iron in dry $FeCl_3$ = (55.85 × 100)/162.3 = 34.4%.
Therefore,
Amount of $FeCl_3$ required = (813 × 100)/34.4 = 1870 kg/d
Using 30% $FeCl_3$ solution by weight, unit weight = 1.34 kg/L (11.2 lb/gal).
Volume of 30% $FeCl_3$ solution required at average flow =
2363/(0.3 × 1.34) = 4650 L/d
Volume of 30% $FeCl_3$ solution required at peak flow = (5877 × 4.73 × 10^7)/
1.89 × 10^7 = 11 635 L/d

$FeCl_3$ solution storage tanks are sized either as 1.5 times the largest shipment or as 10-day storage at peak flow rates.

Provide 10-day storage at peak levels = 10 × 14 708 = 116 350 L

A 120 000-L storage volume that can accommodate $FeCl_3$ solution storage from eight tank trucks (15 000 L /tank truck) is needed. The storage tank should be provided with temperature control greater than –50°C (–58°F) (below which 30% $FeCl_3$ solution freezes), recirculation pumps, and secondary containment for possible spills during unloading from tank trucks and overflow spillage.

4.1.2.3 Sludge Generation

The amount of primary sludge generated can be estimated as follows:

Additional primary sludge removed because of $FeCl_3$ addition (improved TSS removal from 50% to 75%) =

$$\begin{aligned}&(0.75 - 0.5) \times \text{Influent TSS} \times \text{Flow} \times 10^{-6}\\ &= 0.25 \times 270 \times 1.89 \times 10^7 \times 10^{-6}\\ &= 1277 \text{ kg/d}\end{aligned} \quad (7.12)$$

$Fe_{1.6}(H_2PO_4)(OH)_{3.8}$ (MW = 251 g/mol) is assumed to represent the precipitate formed after ferric iron addition, and $Fe(OH)_3$ (MW = 106.8) is the excess ferric hydroxide formed.

Fe dose = 34 mg Fe/L => 34/55.85 = 0.610 mmol Fe/L

Phosphorus removed = 4.8 mg P/L => 4.8/31 = 0.155 mmol P/L

Stoichiometric Fe required, r = (1.6 mmol Fe/mmol P removed)
× 0.155 = 0.248 mmol Fe/L

Excess Fe added = 0.610 – 0.248 = 0.362 mmol Fe/L

$Fe_{1.6}(H_2PO_4)(OH)_{3.8}$ sludge = 0.155 × 251 = 39 mg/L

$Fe(OH)_3$ sludge = 0.362 × 106.8 = 39 mg/L

Total chemical sludge produced = 39 + 39 = 78 mg/L

Chemical sludge resulting from $FeCl_3$ addition (78 mg/L) =
Flow × 78 × 10^{-6} = 1.89 × 10^7 × 78 × 10^{-6}= 1474 kg/d

Total increase in primary sludge production = 1277 + 1474 = 2751 kg/d

Ferric chloride addition to raw wastewater before primary treatment for phosphorus removal increases the primary sludge production by 2751 kg/d (6073 lb/d).

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Chapter 8

Biological Phosphorus Removal

(continued)

1.0 INTRODUCTION

Phosphorus is an essential nutrient for biological growth. Consequently all biological processes remove phosphorus from wastewater naturally. Each pound of volatile suspended solids (VSS) (dry weight) produced in such systems contains 1.5% to 2.5% phosphorus. Assuming a phosphorus content of 2%, if 0.5 mg of VSS is produced per milligram of biochemical oxygen demand (BOD) removed, and then approximately 1.0 mg/L of phosphorus is converted to cell mass per 100 mg/L of BOD removed. Traditional sludge wasting reduces phosphorus by approximately 1 to 2 mg/L. Enhanced biological phosphorous removal (EBPR) or chemical addition can be used to remove phosphorus in excess of metabolic requirements. This chapter outlines EBPR process fundamentals. The application of simulation models to examine the dynamic behavior of EBPR systems is addressed in the chapter on modeling.

2.0 MECHANISM OF ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL

2.1 Overall Mechanism

Enhanced biological phosphorus removal relies on the selection and proliferation of a specialized microbial population capable of storing orthophosphate in excess of their biological growth requirements. These organisms, collectively called phosphate-accumulating organisms (PAOs), can sequester up to 0.38 mg P/mg VSS (Henze et al., 2008). As a result, mixed liquor from an EBPR system can contain 0.06 to 0.15 mg P/mg VSS (Henze et al., 2008). Although the operating conditions that enhance EBPR efficiency are known, it is not clear whether increased phosphorus removal is achieved because of a higher fraction of PAOs in mixed liquor suspended solids (MLSS) or a higher phosphorus content of individual PAOs, or both.

The EBPR process scheme consists of an anaerobic zone followed by an aerobic zone. By definition, an anaerobic zone contains neither dissolved nor combined oxygen such as nitrate and sulfate. In the anaerobic zone, the PAOs, which mediate EBPR, sequester a select number of organic compounds in the form of volatile fatty acids (VFAs) for intracellular storage, typically as polyhydroxybutyrate (PHB) or polyhydroxyvalerate (PHV), designated collectively as polyhydroxyalkanoates (PHA). The energy required for PHA storage is generated through breakdown of another internal storage product, polyphosphate (poly-P) molecules. This results in the release of phosphorus and magnesium and potassium ions to the anaerobic medium. In addition, breakdown of glycogen, another form of internal carbon storage, generates the substantial amount of reducing power required for PHA storage (Erdal et al., 2004; Filipe et al., 2001a; Mino et al., 1987). The external manifestation of these complex reactions is an increase in phosphate concentration in the anaerobic stage. In essence, anaerobic conditions provide PAOs a competitive advantage. They remove much or all of the organic substrate in the anaerobic zone leaving little or no substrate for the other organisms in the subsequent aerobic zone.

In the aerobic zone, the PAOs metabolize the internally stored PHA and do not need to compete for external food. The energy obtained from the oxidation of PHA is used to take up all of the ortho-P released in the anaerobic zone and additional phosphorous present in the influent to renew the stored polyphosphate pool. Phosphorus uptake in excess of metabolic requirement is possible because the energy released by PHA oxidation is significantly greater than the energy required for PHA storage. It is

Table 8.1 Key enhanced biological phosphorus removal reactions in the anaerobic and aerobic zones.

Process or compound	Anaerobic zone	Aerobic zone
Readily biodegradable substrate (volatile fatty acids)	Taken up and stored as polyhydroxyalkanoates	Used
Phosphate	Released	Taken up and stored
Magnesium and potassium	Released	Taken up
Polyhydroxyalkanoates	Stored	Oxidized
Glycogen	Used	Restored

clear that the anaerobic-aerobic sequencing of the single sludge mass is a prerequisite for developing a healthy PAO population.

Net phosphorus removal is realized when the phosphorus-rich sludge is wasted from the system. In addition, some of the energy and carbon is used to restore the glycogen pool for the reactions to continue when mixed liquor is recirculated to the head of the anaerobic zones. The events that take place in the anaerobic and aerobic stages are summarized in Table 8.1.

2.2 Microbiology

In conventional aerobic systems, PAOs are slow growing and are suppressed by faster growing organisms (non-PAOs). When an anaerobic zone is placed ahead of the aerobic zone, however, the PAOs quickly are activated because of their unique ability to use internally stored polyphosphate as an energy source to sequester VFAs. This provides them a competitive advantage over non-PAOs because the need for them to compete for external food in the aerobic zone is eliminated.

The PAOs are a subset of heterotrophs, which make up the greater majority of the activated sludge biomass found at secondary treatment plants. The PAO fraction in the mixed liquor volatile suspended solids (MLVSS) is determined by the amount of readily biodegradable substrate they are able to access in the anaerobic zone. This in turn is determined by which is limiting, available substrate or phosphorus, assuming sufficient nutrients are present. As a result, the PAO content of the MLVSS is directly proportional to the bioavailable substrate-to-phosphorus ratio in the anaerobic zone. This ratio determines the size of the anaerobic zone and EBPR effectiveness. The effect of phosphorus-substrate limitation on system performance is discussed in a later section.

In an acetate-fed sequencing batch reactor (SBR), Furumai et al. (2001) found PAOs represented up to 15% of the MLVSS. Although PAOs prefer oxic conditions, they can grow in the absence of oxygen when other electron acceptors, such as nitrate (NO_3^-), are present. Hence, PAOs can perform excess phosphorus removal under both anoxic and aerobic conditions.

There is no consensus as to which organism is primarily responsible for EBPR. Several investigators have identified *Acinetobacter* as the predominant PAO (Brodisch, 1985; Brodisch and Joyner, 1983; Buchnan, 1983; Florenz and Hartemann, 1984; Fuhs and Chen, 1975). Brodisch and Joyner (1983) concluded that microorganisms other than *Acinetobacter* may be responsible for EBPR. Lotter (1985) found significant levels of *Aeromonas* and *Pseudomonas* capable of storing polyphosphates. Other organisms capable of mediating EBPR include *Moraxella*, *Klebsiella*, *Enterobacter*, *Accumulibacter phosphatis* in the *Rhodocyclaceae* group of the *Betaproteobacteria*, *Actinobacteria*, and *Malikia* spp. (Bitton, 2005; Crocetti et al., 2000; Hesselmann et al., 1999; Kong et al., 2005; Oehmen et al., 2007; Spring et al., 2005).

Pure culture studies to determine *Acinetobacter* growth kinetic coefficients on aerobically grown cultures using substrates such as acetate and ethanol have demonstrated maximum growth rates (μ_{max}) of 4 to 30/days; dry cell yields (Y) of approximately 0.4 g/g chemical oxygen demand (COD); and endogenous decay rates (b) of 1 to 5 g/g·d (Ensley and Finnerty, 1980; Hao and Chang, 1987). Cells grown under such conditions have high phosphorus contents of approximately 4% to 7%. Hao and Chang (1987) reported a maximum of phosphorus content of 4% to 8%. Values of μ_{max} and b obtained in these experiments are far higher than observed in EBPR activated sludge systems. For example, Wentzel et al. (1988a) determined the kinetic growth coefficients of an *Acinetobacter* culture "weaned" from an EBPR activated sludge system by feeding a synthetic substrate. Batch tests with this enriched culture gave a μ_{max} of 0.75 to 0.95 per day without phosphorus limitation, 0.35 per day with phosphorus limitation, and b of 0.03 to 0.04 per day. The culture showed all of the attributes of typical EBPR activated sludge system.

Tandoi and Jenkins (1987) grew *A. calcoaceticusl woffi* AC-7 (isolated from anaerobic/aerobic activated sludge system) on an acetate mineral salt synthetic medium in a two-stage chemostat under both completely aerobic and alternating anaerobic-aerobic conditions. Their reported values (μ_{max} = 0.84/d; Y = 0.13 g VSS/g COD) were similar to the Wentzel et al. (1988a) study. Aerobic chemostat operation gave significantly higher values (μ_{max} = 4.8/day; Y = 0.22 g VSS/g COD).

It is now known that PAO selection cannot be guaranteed by providing favorable conditions for growth (anaerobic conditions and rapidly biodegradable substrate). Another group of organisms called glycogen accumulating organism (GAO) also consumes VFAs but is incapable of excess phosphorus uptake (Liu et al., 1997). Hence, GAO competition can diminish EBPR effectiveness. Further discussion on this is presented in a later section.

2.3 Biochemistry

The biochemistry of EBPR is difficult to study because of the complexity of the process. Jenkins and Tandoi (1991) indicated that available biochemical models are based on experiments with activated sludge systems operated under aerobic-anaerobic cycles. In these mixed cultures, it is impossible to isolate the effects of the PAOs and their biochemistry. It is known, however, that the biochemical reactions of the EBPR process are characterized by the cyclical formation and degradation of stored organic compounds (e.g., PHA) coupled with the degradation and formation of polyphosphate granules. For these reactions to occur, the single sludge mass must be subjected to alternating anaerobic and aerobic conditions. Some of the key biochemical reactions associated with the EBPR process reported in the literature are summarized below:

- Addition of wastewater or a simple carbon source results in phosphorus release and simultaneous carbon uptake and storage (Fukase et al., 1982). Carbon compounds that trigger phosphorus release include acetate, propionate, butyrate, lactate, propionate, glucose, fermented sludge, and septic wastewater (Barnard, 1984; Gerber et al., 1986; Oldham, 1985; Paepcke, 1983; Potgieter and Evans, 1983).
- The phosphate released by PAOs in the anaerobic zone originates from the organisms' polyphosphate reserves (Arvin, 1985; Marais et al., 1982).
- Various organic and energy storage products, collectively termed poly-β-hydroxyalkanoate (PHA), have been found in PAOs. Of these, poly-β-hydroxybuterate (PHB) has been mostly commonly associated with EBPR (Fukase et al., 1982; Timmerman, 1979). Other reported storage products include polyhydroxyvalerate and glycogen (Comeau et al., 1987; Fukase et al., 1982).
- Presence of nitrate or dissolved oxygen in the anaerobic zone will prevent and reverse the uptake-release reactions in the zone (Barnard, 1976; Comeau et al.,

1986; Jenkins and Tandoi, 1991). As Grady and Filipe (2000) pointed out, this potentially could affect EBPR capability in three ways:

(1) All PAOs can use dissolved oxygen as their terminal electron acceptor. In the absence of dissolved oxygen, some PAOs use nitrates. When this happens, they exhibit aerobic metabolism, which will reduce PHA storage;
(2) In the presence of nitrate, denitrifying organisms with higher maximum specific growth rate will displace PAOs; and
(3) Because of the presence of an oxygen source, anaerobic fermentation would be inhibited leading to lower VFA production.

- The ratio of organic substrate uptake and phosphorus release has not been established. With acetate as the carbon source, the acetate uptake to phosphorus release molar ratio ranges from 0.6 to 0.7, and up to 1.9 (Arvin, 1985; Fukase et al., 1982; Rabinowitz and Oldham, 1985). Rabinowitz and Oldham (1985) also found that the ratio depends on the type of substrate in decreasing order: sodium acetate, propionic acid, glucose, acetic acid, and butyric acid.

Various models have been proposed to describe the biochemical pathways for EBPR (Arun et al., 1988; Comeau et al., 1986; Mino et al., 1987). The exact mechanism is still elusive and a topic of debate. Many of the key aspects and phenomena required for the successful growth of PAOs and design of EBPR systems have been established.

3.0 FACTORS AFFECTING ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL PERFORMANCE

Enhanced biological phosphorus removal is a complex process encompassing different environmental conditions and complimenting and competing biochemical reactions. This section discusses the many factors that could singly or in combination affect EBPR efficiency.

3.1 Integrity of the Anaerobic Zone

The anaerobic zone of an EBPR bioreactor is expected to perform two functions. The primary function is PAO selection, which is a relatively rapid reaction if adequate rapidly biodegradable substrate is available. In some instances, the anaerobic zone also is required to perform a secondary function, that of VFA generation through

fermentation. This is a slower reaction requiring a longer anaerobic hydraulic retention time (HRT).

By definition, anaerobic conditions are defined as zones with less than 0.2 mg/L dissolved oxygen. The oxidation reduction potential (ORP) can also be used to confirm the presence of anaerobic conditions. Typical ORP values are in the range of −300 mV or less. Field testing, however, would be required to establish site-specific ORP value for anaerobic conditions. Ideally, anaerobic conditions must be maintained throughout the design anaerobic volume for reliable EBPR. Sources of dissolved oxygen and nitrates, summarized in Table 8.2, can threaten the integrity of the anaerobic zone (Jeyanayagam, 2007).

The introduction of nitrate or dissolved oxygen to the anaerobic zone causes a reduction of the actual anaerobic volume. Consequently, the effective anaerobic solids retention time (SRT) and HRT will be reduced. This will decrease the anaerobic contact time between the PAOs and the substrate (VFAs), which could potentially compromise phosphorus removal (Jeyanayagam, 2007). In addition, the presence of nitrate and dissolved oxygen will provide competing organisms with access to the substrate. For example, 1.0 mg of nitrate-N will take up readily biodegradable organics needed for the removal of 0.7 mg of phosphorus by supporting denitrification. Likewise, the presence of 1.0 mg of dissolved oxygen will use up the substrate needed for the removal of 0.3 mg phosphorus by facilitating normal heterotrophic activity (BOD oxidation).

Table 8.2 Common sources of dissolved oxygen and nitrates (Jeyanayagam, 2007).

Source	Introduces
Preaeration[a]	Dissolved oxygen
Influent screw pumps[a]	Dissolved oxygen
Free-fall over weirs[a]	Dissolved oxygen
Excessive turbulence[a]	Dissolved oxygen
Aggressive mixing in the anaerobic zone	Dissolved oxygen
Return activated sludge flow	Nitrates, dissolved oxygen
Backflow from aerobic to anaerobic zone	Dissolved oxygen
Internal mixed liquor recycle[b]	Nitrates, dissolved oxygen

[a]Upstream of the anaerobic zone.

[b]In nitrogen removal systems.

3.2 Substrate Availability

The key factor that determines the amount of phosphorus stored in the activated sludge is the amount of readily biodegradable organic matter in the anaerobic zone. There must be a large excess beyond that needed to deplete the electron acceptors (dissolved oxygen and NOx) in the anaerobic zone because the bacteria preferentially will metabolize the organic matter and reduce the amount of stored PHA. This would impact PAO selection and EBPR performance.

The type of organic compound in the anaerobic zone is also important; it must be soluble and readily biodegradable. Because biodegradability is a function of the length of the carbon chain, short-chain VFAs are ideal sources. In particular, acetic acid (two carbons) through valeric acid (five carbons) are considered to be the prototype of readily available organic compounds for EBPR. Although all of these VFAs are usable for EBPR, their relative effectiveness varies. Abu-Ghararah and Randall (1991)indicated that of all of the VFAs commonly generated during municipal wastewater fermentation, acetic acid is the most efficient based on mass of phosphorus uptake per COD consumed.

Of the VFAs listed, only valeric acid has a COD consumed-to-phosphorus removed ratio higher than 45:1, the commonly assumed minimum ratio required for EBPR in North American municipal wastewater. This implies that a significant fraction of the organics in wastewater may not be available for EBPR, which results in higher COD requirements for phosphorus removal. Also note that EBPR could not be accomplished with one-carbon compounds, such as formic acid, because their polymerization is thermodynamically unfavorable for the bacteria.

According to Ekama and Marais (1984), more than 25 mg/L as VFA is required in the anaerobic zone to accomplish significant EBPR. In practice, the amount needed is a function of the influent phosphorus. Hence the VFA-to-total phosphorus (TP) ratio is an indication of the EBPR capability of the system. It is now thought that readily biodegradable COD (rbCOD) is a better measure because this fraction represents the influent VFAs and organic compounds that could potentially be fermented to VFAs in the anaerobic zone of the bioreactor. The rbCOD is an estimate of the truly soluble COD.

The five-day carbonaceous BOD ($cBOD_5$) to total phosphorus ratio is often used as a first approximation of the adequacy of carbon substrate for EBPR. Data from several full- and pilot-scale studies, presented in Figure 8.1, show the relationship between the effluent total phosphorus concentration achieved as a function of $cBOD_5$:TP of

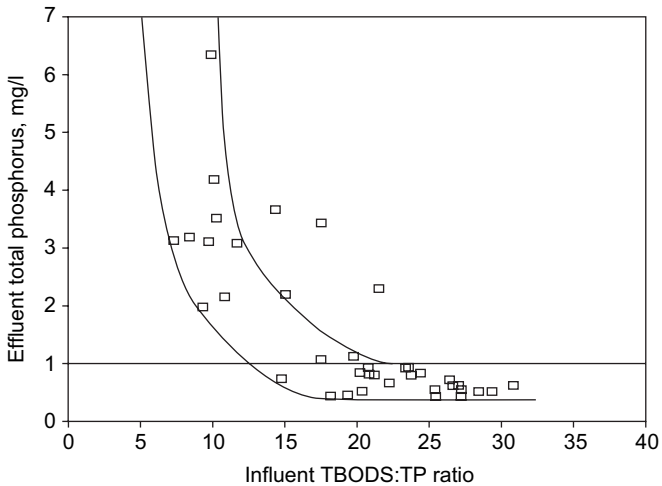

FIGURE 8.1 Effect of influent total BOD (TBOD):TP ratio on effluent TP (from Randall, C.W., et al. [1992] *Design and Retrofit of Wastewater Treatment Plants for Biological Nutrient Removal*. Technomic Publishing Co., Inc., Lancaster, Pa., with permission).

the influent to the anaerobic zone. A $cBOD_5$:TP of 20:1 or greater is needed to reliably achieve an effluent total phosphorus concentration of 1.0 mg/L or less without effluent filtration. Even lower effluent concentrations of phosphorus could have been achieved with chemically enhanced clarification or effluent filtration (Randall et al., 1992).

Because COD is a more consistent measurement and a close approximation of ultimate BOD for most municipal wastewater, the total COD (TCOD) to total phosphorus ratio would be an accurate indicator of available substrate for EBPR. The TCOD:TP and total BOD ($TBOD_5$):TP results shown are conservative relative to what could be accomplished with good design and operation.

The ratios typically used to quantify minimum substrate-to-phosphorus ratios are summarized in Table 8.3. These ratios refer to bioreactor influent and should account for recycle loads and removals in primary clarifiers. Typically, recycle flows represent additional phosphorus load while primary clarifiers remove cBOD. As a result, primary effluent (bioreactor influent) will contain lower substrate-to-phosphorus ratio relative to raw influent.

Table 8.3 Minimum substrate to phosphorus requirements for enhanced biological phosphorus removal.

Substrate Measure	Substrate-to-phosphorus ratio[a]	Remarks
$cBOD_5$	25:1	Provides a rough/initial estimate. Based on typically available plant data
$sBOD_5$	15:1	Better indicator than $cBOD_5$
COD	45:1	More accurate than cBOD. Not measured by all plants
Volatile fatty acids (VFA)	7:1 to 10:1	More accurate than COD. Involves specialized lab analysis
rbCOD	15:1	Most accurate. Measures VFA formation potential. Accounts for VFA formation in the anaerobic zone. Specialized laboratory analysis

[a]Minimum requirements.

$cBOD_5$ = five-day carbonaceous biochemical oxygen demand; $sBOD_5$ = five-day soluble BOD; COD = chemical oxygen demand; and rbCOD = readily biodegradable COD.

The composition of influent phosphorus affects EBPR efficiency. In particular, corrosion inhibitors used by water treatment plants can be a significant source of polyphosphate, which is not readily reactive and is difficult to remove. For example, when the Xenia, Ohio, water treatment plant switched its corrosion control chemical from a 25 poly-P/75 ortho-P formulation to one containing 75 poly-P/25 ortho-P, the city's two wastewater plants discharged elevated levels of total phosphorus (Jeyanayagam, 2007). This was corrected by switching the corrosion inhibitor to the original formulation. It should be noted that the effluent ortho-P values were consistently low indicating that the higher effluent total phosphorus primarily was because of the increased influent polyphosphate.

Municipal wastewater fermented in the collection system typically is a good source of VFAs for EBPR operation. The seasonal variation of influent VFA can be tracked by observing the $cBOD_5$:COD. Typically, a higher ratio implies higher VFAs. Figure 8.2 illustrates changes in $cBOD_5$:COD of raw wastewater at the Hampton Roads Sanitation District's (Hampton Roads, Virginia) York River Treatment Plant when it was being operated as an EBPR process with anaerobic digestion and recycle of belt filter press filtrate. The $cBOD_5$:COD of the raw influent varied from 0.37 to 0.73 during the 12-month period, with higher values typically found in the warmer

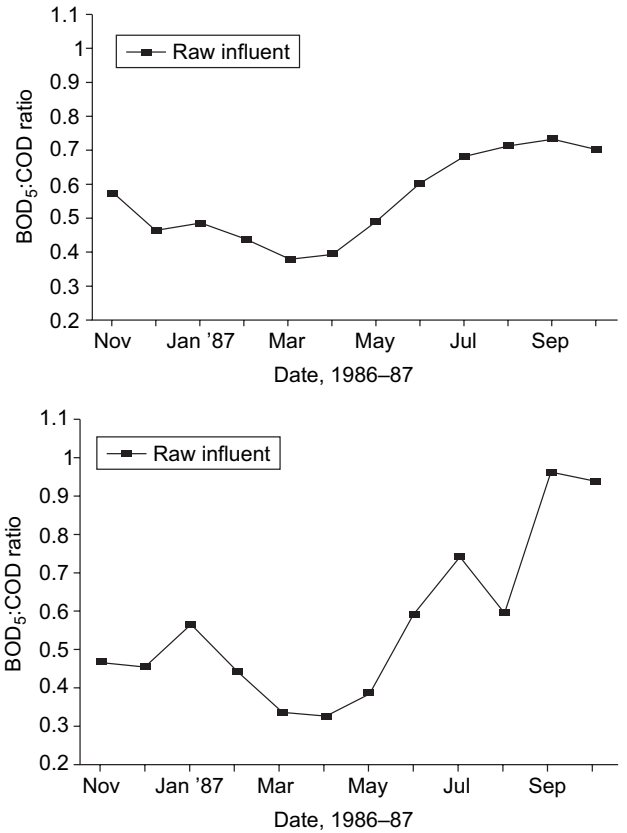

FIGURE 8.2 Seasonal variation in BOD_5:COD ratio at York River BNR plant (from Randall, C.W., et al. [1992] *Design and Retrofit of Wastewater Treatment Plants for Biological Nutrient Removal*. Technomic Publishing Co., Inc., Lancaster, Pa., with permission).

months. This emphasizes the need to determine seasonal variation of influent VFAs for design purposes.

Sewer fermentation is inhibited by dissolved oxygen entrainment, wet weather high flows, and cold temperatures including snow melt. Although adequate VFAs may be available in the plant influent to meet summer phosphorus limits, sewer system fermentation cannot be relied upon as a reliable and consistent source of carbon substrate year round. In such cases, the anaerobic zone may need to be sized to support additional fermentation. Plant recycles such as supernatant from primary sludge gravity thickening also may contain sufficient VFAs for EBPR. Other sources

of carbon augmentation include onsite VFA generation via sludge prefermentation, industrial wastewater containing VFAs, or acetic and propionic acids. Often it may be simpler and more cost-effective to provide a standby chemical feed system.

3.3 Phosphorus versus Substrate Limitation

Wastewater characteristics determine EBPR reaction rates. If substantial concentrations of readily available organics such as acetic, propionic, and butyric acids are present in the bioreactor influent, then reaction kinetics will be faster and will result in smaller anaerobic volume or HRT requirements. The overall EBPR reactions, however, will be limited by either the available phosphorus or the storable organic substrate. All wastewaters are either phosphorus or substrate limited with respect to EBPR. If phosphorus is limiting, then available organics will not be completely removed in the anaerobic stage and soluble organics will enter the aerobic stage. If available substrate is limiting, then phosphorus removal will be limited and the desired effluent phosphorus concentration may not be achievable.

Available organics can be limiting for three reasons: (1) The influent wastewater does not contain adequate total organics, as measured by BOD or COD (i.e., low cBOD:TP or COD:TP); (2) the wastewater organics have not undergone sufficient fermentation to generate VFAs, as confirmed by the rbCOD:TP or VFA:TP; and (3) high influent total phosphorus to the bioreactor because of recycle loads from sludge operations. This can also be caused by industrial discharges containing phosphorus.

In EBPR systems, phosphorus removal is accomplished by wasting phosphorus-rich waste activated sludge. Therefore, the degree of phosphorus removal is a function of the percentage of phosphorus in the MLVSS and the operating SRT. When the PAOs are placed in the anaerobic zone with the wastewater, they will grow to reach an equilibrium concentration dictated by the limiting factor, either phosphorus or rapidly biodegradable substrate. Thus, either phosphorus or COD will determine the fraction of PAOs in the activated sludge population and the phosphorus content of the MLVSS as summarized below:

- Substrate limitation—The activated sludge will be dominated by the PAOs and the phosphorus content of the MLVSS will be high. However, because COD (substrate) is limiting, all the removable phosphorus will not be removed, which will cause elevated effluent phosphorus.
- Phosphorus limitation—This implies there is adequate substrate to sequester all of the removable phosphorus and the soluble phosphorus in the effluent

will be very low unless secondary release occurs in either the activated sludge basin or the secondary clarifier. The excess organic substrate will result in the growth of non-PAOs, leading to low PAO fraction and low phosphorus content of the MLVSS. This was substantiated by Liu et al. (1997) who reported GAO dominance over PAOs at high organic loadings.

Paradoxically, if the percentage of phosphorus in the MLVSS is high, then effluent phosphorus concentration may also be high. If the percentage of phosphorus is low, then effluent phosphorus will be low for a properly designed and operated EBPR system. Thus, the available COD:P in the wastewater influent to the anaerobic zone determines both the percentage of phosphorus in the MLVSS and the effluent phosphorus concentration, and both parameters are inversely related to COD:TP. Full-scale operating data, shown in Figure 8.3, confirms the relationship between COD:TP and MLVSS phosphorus content. Other researchers also have shown that influent COD:P correlates well with EBPR biomass total phosphorus content and phosphorus

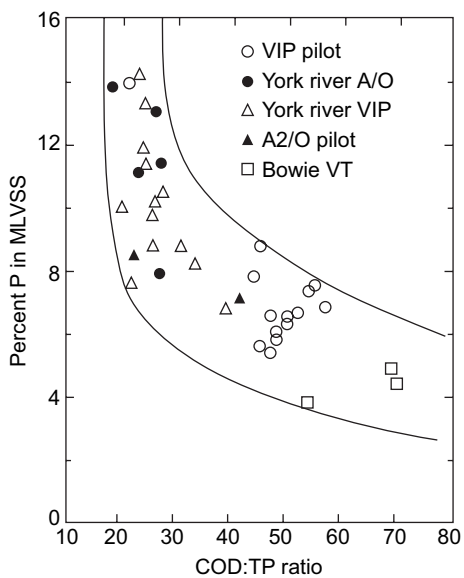

Figure 8.3 Effect of influent COD:TP ratio on percentage of phosphorus in MLVSS (from Randall, C.W., et al. [1992] *Design and Retrofit of Wastewater Treatment Plants for Biological Nutrient Removal*. Technomic Publishing Co., Inc., Lancaster, Pa., with permission).

removal functions (Kisoglu et al., 2000; Liu et al., 1997; Punrattanasin, 1999; Schuler and Jenkins, 2003).

Because they are both functions of COD:P, there also tends to be a correlation between MLVSS percentage of phosphorus and effluent soluble phosphorus, but it may be weak at times. For example, during the York River VIP™ (Virginia Initiative Plant) demonstration, the phosphorus content varied from less than 7% to more than 14%, yet the average effluent soluble phosphorus showed a modest variation (0.49–1.16 mg/L) when the process was not affected by excessively high flows or incomplete nitrification conditions. This may be because the system was phosphorus rather than COD limited most of the time. In contrast, when the plant was operated as a two-stage EBPR plant with excess phosphorus, there was an increase of effluent soluble phosphorus from approximately 2 to 4 mg/L, and the corresponding MLVSS phosphorus content increased from 10% to 13%.

3.4 Adequate Amounts of Cations

In the anaerobic zone, as the polyphosphate granules called volutin (containing phosphate, potassium, and magnesium) are hydrolyzed, phosphorous release occurs. Because each phosphate molecule (PO_4^{3-}) contains three negative charges, it is not possible for the charged molecules to pass through the cell membrane. When the phosphate molecules bond with the positively charged magnesium (Mg^{+2}) and potassium (K^{+1}), however, they become neutralized and are able to be transferred across the cell wall.

According to Patterkine et al. (1991), the removal of 1 mole of phosphorus requires, at a minimum, 0.25 moles of magnesium and 0.23 moles of potassium. Fortunately, the quantities of these two cations present in municipal wastewater exceed EBPR requirements. Hence, they are unlikely to be limiting. However, they need to be considered when treating industrial wastewater or high fractions of industrial wastewater mixed with domestic wastewater.

3.5 Aerobic Zone

Although anaerobic conditions are important for PAO selection, it is in the aerobic zone that phosphorus removal occurs. The long held assumption is that the only two key requirements for EBPR are an anaerobic zone and the presence of VFAs in that environment. Recent full-scale observations have shed light on the critical role played by the aerobic zone in achieving reliable EBPR (Narayanan, et al., 2006). Following anaerobic PAO selection as the MLVSS enters the aerobic zone, two of the three driving forces are encountered. These include PAOs with high stored PHA and

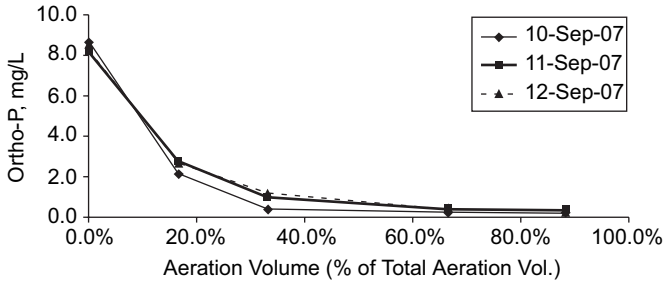

FIGURE 8.4 Phosphorus uptake profile in aerobic zone (Jeyanayagam, 2007).

high levels of soluble phosphorus in the surrounding wastewater. At this point, if the third and final driving force (dissolved oxygen) is provided in adequate amounts, rapid phosphorus uptake kinetics would be ensured. Jeyanayagam (2007) reported similar findings as shown in Figure 8.4. This research showed a rapid phosphorus uptake kinetics in the first 20% of the aeration volume and much lower rates in the subsequent sections. The data also reveals almost complete EBPR in the first half of the aeration volume.

When poor initial phosphorus uptake occurs because of dissolved oxygen limitation, it may not be possible for phosphorus removal to "catch up" in the subsequent aerobic zones even if adequate dissolved oxygen is maintained. This is because two of three causative factors, PHA level and bulk liquid ortho-P concentration, would be significantly lower resulting in higher effluent ortho-P levels (Narayanan, et al., 2006). In the same full-scale study, Narayanan et al. (2006) concluded that staging the aerobic zone enhances EBPR because of improved plug flow conditions. This may be attributed to higher reaction rates caused by the concentration gradient.

3.6 Hydraulic Considerations

Barnard et al. (2004) noted the importance of eliminating hydraulic bottlenecks in achieving low effluent phosphorus levels. The influent to the anaerobic zone and return sludge has different densities and their momentum may carry them in different directions resulting in poor mixing. This will reduce the contact duration between PAOs and the substrate. Consequently, the effective anaerobic HRT will be less than the design HRT. Because VFA production is rate-limiting, this potentially could lead to reduced VFA production in the anaerobic zone and lower EBPR efficiency. Properly sizing and locating mechanical mixers in the anaerobic zone could prevent

this problem. Even flow split to final clarifiers is critical to allow the full capacity of all units to be realized. Poor performance of an overloaded clarifier typically cannot be compensated by good performance of an underloaded clarifier.

3.7 Secondary Phosphorus Release

Biological sludge generated by the EBPR process contains two types of phosphorus—metabolically bound phosphorus and stored polyphosphate granules called volutin. The first is a result of normal microbial synthesis; the second is a temporary storage product that is depleted (phosphorous release) in the anaerobic zone and restored (phosphorus uptake) in the aerobic zone as part of the EBPR mechanism. This "primary" anaerobic release is associated with concomitant carbon (VFA) uptake and storage (PHA) and is desired and necessary for PAO selection. The secondary phosphorus release occurs without carbon storage (Barnard, 1991). Hence, this phosphorus release is not linked to PAO selection and will not be taken up in the aerobic zone. Significant secondary release will cause elevated effluent phosphorus. Although the stored polyphosphate, being unstable, is most commonly associated with secondary phosphorus release, conditions that cause cell lysis will result in the release of metabolic phosphorus as well. Table 8.4 lists the location and potential causes of secondary release in EBPR processes.

Table 8.4 Location and potential causes of secondary phosphorus release.

Location	Cause of phosphorus release
Primary clarifier	Cosettling of primary and enhanced biological phosphorus removal sludges
	Poor solids capture during thickening and dewatering operations may return phosphorus rich solids to the primary clarifier where secondary release could occur
Anaerobic zone	Volatile fatty acids depletion because of oversized anaerobic zone
Anoxic zone	Nitrate depletion because of oversized anoxic zone
Aerobic zone	Long solids retention time leading to cell lysis
Final clarifier	Septic conditions caused by deep sludge blanket

(*continued*)

Table 8.4 Continued

Location	Cause of phosphorus release
Return activated sludge piping	Septic conditions
Primary sludge gravity thickener	Septic conditions caused by deep sludge blanket
Sludge storage	Septic conditions because of poorly or unaerated sludge storage Because of cell lysis in long aerated storage
Anaerobic digestion	Anaerobic conditions and cell lysis
Aerobic digestion	Mostly due to cell lysis
Dewatering	No significant release. Phosphorus released in upstream processing will be in filtrate/centrate
	Poor solids capture may return phosphorus rich solids to the primary clarifier where secondary release could occur

Return streams from sludge operations (e.g., dewatering) can affect EBPR performance significantly. Figure 8.5 illustrates the recycle streams that are generated at typical wastewater treatment plant solids handling facilities. The quantity and quality of these streams vary based on the technology used in the solids processing operations. For example, anaerobic digestion is likely to release more phosphorus than aerobic digestion. However, sludge dewatering using belt filter press typically generates two times more recycle flow (filtrate) compared to centrifuge dewatering because of the amount of wash water used in the dewatering operation. The total recycle flow can amount to 20% to 30% of the plant influent flow and can reduce process HRT. In addition, recycle flows also will affect hydraulic design. Recycle mass loads from both dewatering methods, however, would be about the same.

The type of sludge treatment process used will determine recycle stream characteristics. Composting, thermal drying, and advanced alkaline stabilization produce minimal recycle loads. Use of anaerobic digesters is of particular concern at EBPR facilities. Jardin and Popel (1994) observed that polyphosphate hydrolysis was complete within 2 to 3 days retention in the anaerobic digester. Consequently, the recycle stream from anaerobically digested sludge dewatering operation can contain 100 to

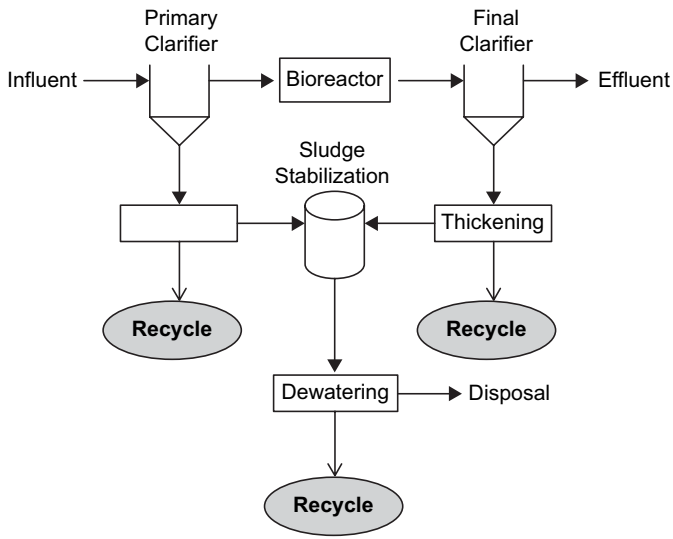

FIGURE 8.5 Recycle streams from a typical wastewater treatment plant.

800 mg/L of phosphorus and 900 to 1100 mg/L of ammonia. The actual recycle loads will depend on how much of the released phosphorus and ammonia are chemically precipitated, primarily as struvite ($MgNH_4PO_4$). Other relevant precipitates include brushite ($CaHPO_4 \cdot 2H_2O$) and vivianite [$Fe_2(PO_4)_3 \cdot 8H_2O$]. This can lead to an apparent reduction in the extent of phosphorus solubilization in the anaerobic digester. At the Hampton Roads Sanitation District's York River Treatment Plant, approximately 70% of the phosphorus entering the digesters was precipitated as struvite and other phosphorus-containing precipitates and disposed of with the dewatered sludge. No detrimental effects of the struvite formation were reported over the four-year demonstration period (Randall et al., 1992).

Return streams often occur intermittently in many facilities, causing significant variation in nutrient loadings and significant short-term peak loads that could overwhelm the EBPR process. For example, if dewatering operations occur over one shift, five days per week, the instantaneous recycle loading could potentially be four times the loading generated by a 24/7 operation. The complex microbial consortium has a limited ability to quickly respond to influent variations by self-adjustment. The period of acclimation is directly influenced by mean cell retention time (MCRT), MLSS, and the magnitude and duration of peak loads. Within limits, higher MCRT and MLSS enhance microbial diversity and system robustness. Extremely high and persistent

loadings can be stressful to the biological process because recycled phosphorus, most of which is bioavailable, will reduce bioreactor influent $cBOD_5$:TP. This could potentially convert a typically phosphorus-limited (excess substrate) EBPR system to a substrate-limited condition with a likelihood of elevated effluent phosphorus levels.

3.8 Solids Handling Considerations

By implementing appropriate solids handling and processing practices, secondary phosphorus release can be eliminated or minimized at the source. The following is a list of key design and operational approaches:

- Ideally, primary sludge and EBPR waste sludge should be handled and processed separately. However, this may not always be practical. Blending the primary and waste activated sludges should be moved as far downstream as possible in the sludge treatment train. Following blending, the sludge should be processed quickly before significant release could occur.
- Maintaining a shallow sludge blanket in primary clarifiers may prevent nitrogen and phosphorus solubilization. It will also improve clarifier performance, particularly during high wet weather induced flows. This will result, however, in a relatively thin underflow (<1.5%). Sen et al. (1990) found that at the Bowie, Maryland, wastewater treatment plant, maintaining the sludge blanket at least 1 m (3.3 ft) below the overflow weir allowed only a fraction of the released phosphorus to escape with the supernatant.
- Secondary release in final clarifiers is a common problem at many biological nutrient removal (BNR) facilities, particularly in the warmer months when septic conditions are readily established in the sludge blanket. This may be avoided by implementing an effective wasting strategy and maintaining a shallow blanket. Doing so will eliminate anoxic conditions and the potential for floating sludge and subsequent sludge blanket washout from denitrification. Some facilities maintain high dissolved oxygen concentration in the bioreactor effluent to minimize potential for denitrification within the sludge blanket. This may not be always viable, however, because the internal recycle necessary for denitrification in the bioreactor will recycle oxygen to the anoxic zone and reduce denitrification. Also, this practice is not energy efficient.
- The EBPR bioreactor should be designed with the flexibility to waste sludge from the end of the aerobic zone of the bioreactor to keep the sludge “fresh”

and to minimize the likelihood of releasing phosphorus downstream. Other benefits include continuous wasting and removing biomass containing the highest phosphorus content from the end of the aeration zone (Rabinowitz and Barnard, 2000).

- Sludge wasted from the clarifier may be aerated to inhibit and delay phosphorus release during subsequent processing.
- Gravity thickening of EBPR sludge likely will cause phosphorus release and should be avoided. Gravity belt thickening, centrifugation, or dissolved air flotation should be used for waste activated sludge (WAS) thickening. Sludge wasted from the bioreactor may be more economically thickened with a dissolved air flotation unit because of the dilute solids concentration. If cothickening is practiced, it should be completed immediately after blending to avoid phosphorus release.

3.9 Solids Capture

Effluent total phosphorous consists of two components—soluble phosphorus and particulate phosphorus. Efficient EBPR can reduce the effluent soluble phosphorus to approximately 0.1 mg/L. Particulate phosphorus, which represents solids-associated phosphorus, depends on effluent total solids and its phosphorus content as illustrated in Figure 8.6 (Water Environment Federation [WEF] et al., 2005). For example, if the effluent TSS is 10 mg/L (75% VSS) and the phosphorus content of the mixed liquor is 0.06 mg/mg VSS (6%), then effluent particulate phosphorus concentration would be 0.45 mg/L. Hence, controlling the effluent solids is important in achieving low effluent total phosphorus.

3.10 Primary Settling

Primary clarification in the process train will modify the characteristics of the bioreactor influent. It is important to understand how this affects EBPR performance. Primary settling typically removes 50% to 70% of the influent TSS, which includes inert solids. As a result, the bioreactor MLSS and the final clarifier solids loading will be lower.

The BOD removal that occurs in primary clarifiers (typically, 30–40% of the influent BOD), reduces the substrate-to-phosphorus ratio entering the bioreactor, making the wastewater less amenable to EBPR. This potentially could lower the

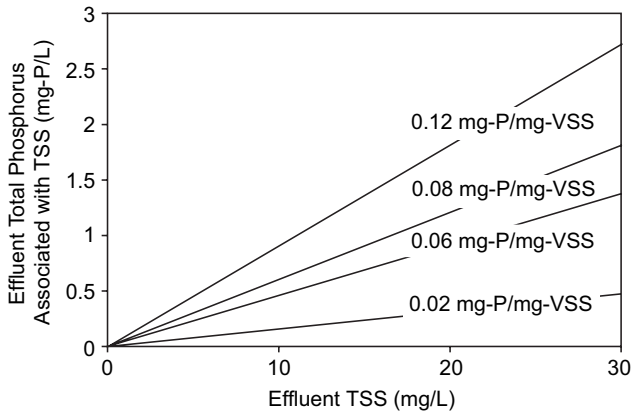

FIGURE 8.6 Contribution of the effluent TSS to the total phosphorus in the effluent for different phosphorus contents in the MLSS (assuming that the VSS/TSS is 75%).

phosphorus removal capability of the downstream EBPR process particularly if adequate VFAs are not present in the influent. Fermentation in the anaerobic zone is crucial for generating VFAs for EBPR. At the Hampton Roads Sanitation District's York River plant, recycles originate from the primary sludge gravity thickener, the secondary sludge flotation thickener, and the belt filter press dewatering an anaerobically digested mixture of the primary and waste activated sludges. Based on the reported data, Randall et al. (1992) made the following observations:

- The decrease in $cBOD_5$:TP and COD:TP from raw influent to combined influent is because of significant phosphorus recycle, which resulted in a 49% increase in total phosphorus in the combined influent. This occurred despite the formation of struvite and other phosphorus-containing precipitates in the anaerobically digesting sludge causing 70% of the phosphorus entering the digester to be incorporated into the digested sludge. The corresponding 11% increase in COD was modest; no increase in BOD_5 was noted.
- The primary clarifier removed a higher percentage of organic matter than nutrients from the combined flow. It removed the 33% of the BOD_5 and 40% of the COD but only 19% each of total phosphorus and total Kjeldahl nitrogen. The resulting nutrient concentrations to the biological process were 11.1 mg/L

total phosphorus and 29.0 mg/L total nitrogen, whereas the BOD_5 and COD concentrations were 139 and 249 mg/L, respectively. Primary settling reduced the $cBOD_5$:TP and COD:TP compared to those calculated for the combined influent by 18% and 26%, respectively.

In essence, the bioreactor influent was changed from phosphorus limiting to COD limiting. Consequently, The EBPR process could not produce an effluent total phosphorus concentration of 1.0 mg/L or less. An average of 9.4 mg/L total phosphorus and 2.4 mg/L soluble phosphorus, however, were removed by biological mechanisms, except for high-flow or acclimation periods. The MLVSS phosphorus contents were as high as 15% on a dry weight basis. Apparently the process was using approximately 26.5 mg/L COD to remove 1 mg/L of phosphorus. Furthermore, during the latter stages of the demonstration, it simultaneously removed reduced total nitrogen to a two-month average concentration of 5.7 mg/L, removed an average of 10.4 mg/L phosphorus, and discharged an average soluble phosphorus concentration of 2.3 mg/L. The design factors given earlier would predict a COD requirement of 660 mg/L for these removals, yet the actual COD removal averaged only 234 mg/L. The BOD_5 removal, however, averaged 218 mg/L. This shows that all of the influent organics were in readily biodegradable form, probably acetic acid, and much higher than predicted removals were possible. The actual average $cBOD_5$:P removal was 21:1.

It appears that substrate-limited EBPR systems can remove considerably more nutrients than predicted but cannot produce an effluent total phosphorus concentration of less than 1.0 mg/L at the same time. The results also indicate that stored substrate can be used simultaneously for both nitrogen and phosphorus removal.

Some plants have minimized the effect of primary settling by providing a bypass around the primary clarifiers in an effort to direct some of the screened wastewater to the anaerobic zone, skipping primary clarification. Such a feature can be used as needed to increase $cBOD_5$:TP. It should be noted, however, that higher suspended solids because of partial bypass of primaries would result in higher MLSS and increased solids flux on secondary clarifiers, which could potentially hinder settling.

3.11 Solids and Hydraulic Retention Times

SRT and HRT are two very important operational parameters in a biological system. Because solids are separated and recycled, organisms are exposed to fresh substrate multiple times, effectively achieving a relatively long contact time. Because the

influent substrate flows through the bioreactor just once, its contact with the organism is significantly less. Depending on individual biochemical reactions, the SRT (i.e., sludge age) in the system dictates the rate at which the biological system operates.

Because the PAO population changes as a function of COD:P, EBPR systems virtually are independent of biomass SRT in the range from 2 to 40 days (Barnard, 1991). Wentzel et al. (1988b) have noted that this phenomenon may be at least partially attributed to the low endogenous decay rate of PAOs, measured as 0.05 day^{-1} on a COD basis compared to 0.24 day^{-1} for aerobic heterotrophic bacteria. This means that at longer SRTs, a proportionally larger part of the active biomass will consist of PAOs; consequently, the phosphorus content of the biomass increases with an increase in SRT.

The system SRT and bioreactor influent COD:P determine the phosphorous content of the MLVSS as illustrated by Figure 8.7. As the observed yield increases (caused by a decrease in SRT), for a constant COD:P, biomass phosphorus content decreases because of a larger number of non-PAOs present in the MLVSS. In other words, at lower SRT values, less phosphorus is stored per unit mass of biomass. Conversely, at longer SRTs, the yield will be lower and sludge will be enriched by PAOs because of their lower endogenous decay rate, resulting in higher biomass phosphorus values. If the feed COD:P is lowered (i.e., increased phosphorus or decreased COD in the feed) at the same SRT and observed yield, then PAOs will be become dominant (as long as COD is nonlimiting), and the biomass phosphorus content will increase. As the feed phosphorus content increases, more of it can be stored in the biomass, assuming the feed COD is sufficient, resulting in PAO enrichment.

The interaction of SRT, substrate-to-phosphorus ratio, and biomass phosphorus content can also be interpreted as shown in Figure 8.8 (Stensel, 1991). In a system with longer SRT and lower MLVSS phosphorus content, more substrate (BOD_5) is required per unit of phosphorus removed. This relationship is substantiated by a pilot study conducted by Fukase et al. (1982), which indicated an increase in $cBOD_5$:P removal from 19 to 26 as the SRT was increased from 4.3 to 8 days.

The above observations reveal a need to operate as close as possible to the minimum SRT to meet overall process goals. Operating at longer SRTs may impose greater substrate requirements for phosphorus removal and could potentially lead to substrate limitation and phosphorus noncompliance.

Extensive field and laboratory experience reveal that EBPR systems can operate at SRT values greater than three days. At SRT values between three and four days, effluent quality declines, and chemical polishing may be needed. At SRT values greater

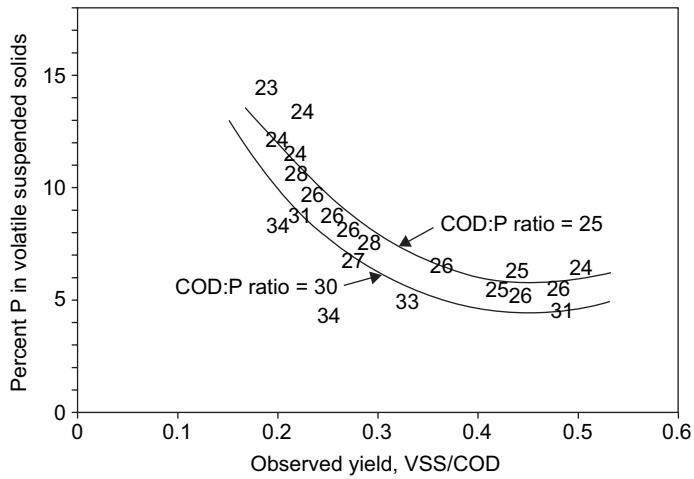

FIGURE 8.7 Effect of EBPR biomass observed yield and SRT on mixed liquor volatile suspended solids phosphorus content.

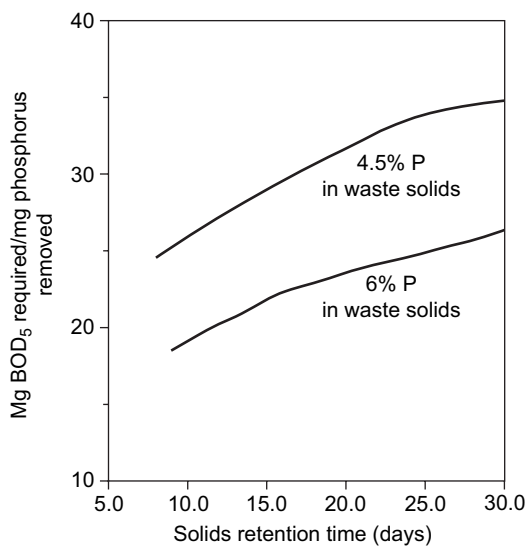

FIGURE 8.8 Calculated BOD_5 required to remove 1 mg phosphorus (Stensel, 1991).

than four days and at temperatures greater than 15°C, nitrification will tend to occur, and process configurations that include anoxic zones for denitrification of nitrate in the recycle flows must be used to protect the integrity of the subsequent anaerobic zone. As the SRT is increased to a level where endogenous reactions become significant (i.e., increased biomass decay), secondary release of phosphorus may lead to decreased performance at given feed VFA and COD values.

To explain the SRT and EBPR performance, several researchers conducted experiments under various operating conditions. McClintock et al. (1993) showed that, at a temperature of 10°C and an SRT of five days, EBPR function of a given activated sludge system would "washout" before other heterotrophic functions do. The washout SRT is a design parameter that defines a critical SRT point below which the mass wasting rate exceeds the growth rate such that no net growth of biomass occurs (Grady et al., 1999). Mamais and Jenkins (1992) showed that there is a washout SRT for all temperatures over the range of 10°C to 30°C. This indicates that, if the SRT-temperature combination is below a critical value, then EBPR ceases before other heterotrophic functions. Erdal et al. (2003, 2004) investigated this phenomenon and showed that in EBPR systems, the main effect of SRT is on PHA and glycogen polymerization reactions. Ordinary heterotrophs (non-PAOs) do not exhibit glycogen metabolism and were not affected in the same manner, even at shorter SRTs.

Anaerobic phosphorus release and aerobic uptake must also be considered in selecting the overall system and individual zone HRT values. Full- and pilot-scale data show that the sensitivity of EBPR performance to changes in the anaerobic nominal HRT is a function of the substrate-to-phosphorus ratio in the anaerobic zone (Randall et al., 1992). In phosphorus-limiting conditions, the change in EBPR performance with a change in anaerobic HRT was relatively small. At lower TCOD:TP (COD-limiting conditions), changes in anaerobic HRT had greater effect on EBPR performance. Polymerization of PHA continues even after the bulk solution VFAs are exhausted within the first hour of the anaerobic period. Hence, if sufficient anaerobic HRT is not allowed, an adequate amount of PHA will not be stored and made available to support the desired phosphorus uptake in the aerobic zone. The effect of excessive aeration (long aerobic HRT) was found to reduce EBPR efficiency. This is attributed to depletion of glycogen reserves in the aerobic stage, which limits PHA storage in the anaerobic zone. This occurs because some of the carbon substrate would be used to replenish the glycogen reserves, thereby reducing EBPR efficiency (Erdal, 2002).

At full-scale plants, VFA uptake is a relatively rapid reaction, requiring an anaerobic zone SRT of as low as 0.3 to 0.5 days. For the majority of the cases, this corresponds to a nominal anaerobic zone HRT of 0.75 hour or less. Depending on the concentration of the mixed liquor biomass concentration, however, the required HRT will vary for different systems. For example, the HRT of the anaerobic zone of a University of Cape Town (UCT) system should be approximately twice that of an anaerobic/oxic (A/O) system. This is because in the UCT process, biomass is transferred from the anoxic to the anaerobic zone via a mixed liquor recycle rather than return activated sludge (RAS), which has a higher MLSS concentration. For the same degree of VFA uptake in the two systems, the same solids inventory (mass of MLSS solids) should be present in the anaerobic zone of the two systems. Therefore, both systems should have approximately the same anaerobic SRT but will require different anaerobic volumes (HRTs) because of differences in the MLSS concentrations.

The fermentation of readily biodegradable organic matter is a slower process, typically requiring an anaerobic zone SRT of 1.5 to 2 days. This corresponds to an anaerobic zone HRT of one to two hours or more. If the influent wastewater contains significant concentrations of VFAs, then a relatively short anaerobic zone SRT and HRT can be used. If, on the other hand, significant fermentation is required in the anaerobic zone to generate VFAs, then a longer anaerobic zone SRT and HRT should be considered. The above HRT and SRT values are guidelines and site-specific values should be determined based on wastewater characteristics and process configuration.

3.12 Glycogen-Accumulating Organism Competition

As stated previously, provision of an anaerobic environment and adequate VFAs does not guarantee PAO selection. Cech and Hartman (1993) were the first to report the link between loss of EBPR and microbial competition. The responsible organism, initially called "G-bacteria," is now commonly referred to as GAOs. Like PAOs, GAOs also take up VFAs and store internally as PHA. The main difference between the two organisms is the energy source used in the anaerobic zone to accumulate PHA. The PAOs use stored polyphosphate and release phosphorus in the anaerobic zone, and GAOs use stored glycogen and do not release phosphorus. In addition, as indicated by Erdal et al. (2004), two organisms store different forms of PHA. The main storage product is PHB in PAOS and PHV in GAOs. Based on a review of full-scale data, Stevens (2004) concluded that the presence of GAOs can coexist with PAOs without

affecting EBPR. The process would be unstable, however, and any increase in the GAO population could quickly lead to loss of phosphorous removal capability.

Liu et al. (1997) linked relative dominance of PAOs and GAOs to phosphorus-to-carbon ratio (P:C). When excessive phosphorus was provided (P:C = 20/100), PAOs outcompeted GAOs. At a lower P:C of 2/100, GAOs were dominant. Both organisms coexisted at median P:C. Ahn et al. (2007) suggested that the amount of anaerobic phosphorus released per acetate uptake could be a good indicator of PAO population change. Their laboratory-scale study showed that higher organic loadings favor glycogen-accumulating metabolism (GAM) over phosphorus-accumulating metabolism (PAM). They concluded that when phosphorus release to acetate uptake ratio was less than 0.4 mM P/mM C, GAM became dominant over PAM.

Grady and Filipe (2000) introduced the application of ecological engineering principles to provide PAOs a competitive advantage over GAOs. They suggested maintenance of a pH of above 7.3 or the use of longer anaerobic SRTs, or both, to allow PAOs to outcompete GAOs.

The relative PAO and GAO fractions can be quantified using the method proposed by Lopez-Vazquez et al. (2007). This practical method relies on the determination of the anaerobic phosphorus release to HAc ratio. The study predicted a maximum phosphorus release to acetate ratio of 0.51 P-mol/C-mol if only PAOs were present. If all other EBPR requirements (e.g., adequate VFAs, sufficient anaerobic contact) are met, then significantly lower phosphorus release to acetate ratio may indicate potential GAO interference. Barnard and Scruggs (2003) have also proposed a batch test to determine the presence of GAOs.

3.13 pH

The optimum pH range for EBPR appears to be 7.5 to 8.0 (Stensel 1991). As shown in Figure 8.9, Tracy and Flammino (1985) found no appreciable effect on EBPR between 6.5 and 7.0. At pH of 6.5, PAO activity declined, and at pH of 5.2, there was minimal activity. This result has been confirmed by Chapin (1993). Filipe et al. (2001a) concluded that GAOs are relatively insensitive to the aerobic zone pH, and PAOs are inhibited by low pH values. For this reason, it is essential to maintain a pH greater than 7.0 in the aerobic zone. Another study completed by the same authors showed that when the pH of the anaerobic zone is less than 7.25, GAOs are able to take up acetate faster than PAOs (Filipe et al., 2001b). Based on these observations, the authors suggested operating the EBPR system at an elevated pH as a means of minimizing competition between PAOs and GAOs.

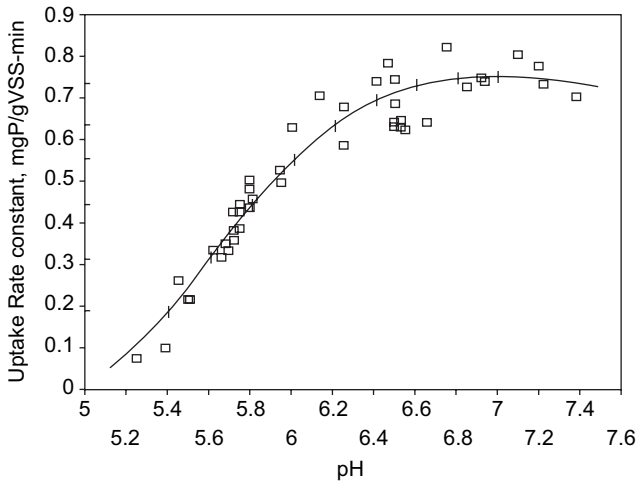

FIGURE 8.9 Effect of pH on the phosphate uptake rate constant (Tracy and Flammino, 1985).

3.14 Temperature

Research by McClintock et al. (1993) revealed that TCOD:TP in the process influent also influences the temperature effects on EBPR processes. The researchers showed that temperature has a stronger effect on the system operated at a five-day SRT when COD was limiting than when phosphorus was limiting. EBPR was completely lost at 10°C in the five-day SRT system when COD was limiting, whereas healthy phosphorus uptake was evident under phosphorus limitation.

The effects of temperature on the efficiency and kinetics of EBPR systems have been investigated for the past two decades, but the studies have yielded contradictory results. Early researchers reported that EBPR efficiency was unchanged at lower temperatures than at higher temperatures, over the range 5°C to 24°C (Barnard et al., 1985; Daigger et al., 1987a; Ekama et al., 1984; Kang et al., 1985; Sell, 1981; Siebritz, 1983). More recently, researchers have found that cold temperatures adversely affect EBPR performance (Beatons et al., 1999; Brdjanovic et al., 1997; Choi et al., 1998; Jones and Stephenson, 1996; Marklund and Morling, 1994). Contradictory to previous findings, Helmer and Kunst (1997) and Erdal (2002) reported that, despite the slowing reaction rates, EBPR performance can be significantly greater at 5°C compared to 20°C. Citing work reported by other investigators, Stensel (1991) attributed better cold weather EBPR performance to a population shift to slower growing psychrophilic

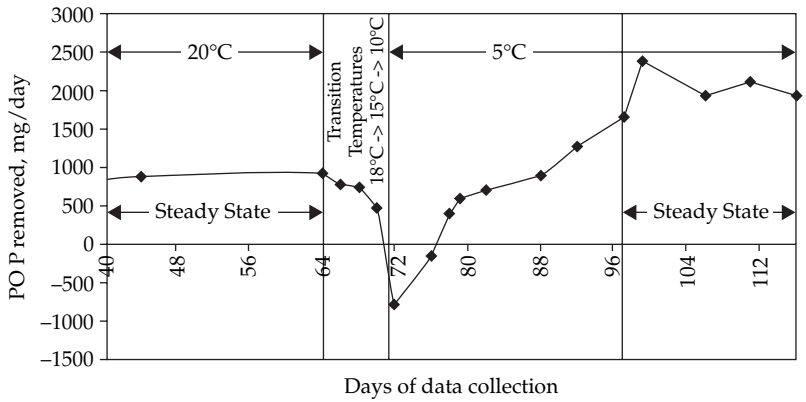

FIGURE 8.10 Effect of acclimation on cold-temperature performance of enriched EBPR populations (Erdal et al., 2002).

organisms with higher yield. The findings of Erdal et al. (2002), presented in Figure 8.10, show the importance of cold weather acclimation and the resulting improved EBPR performance.

Erdal et al. (2002) indicated that efficient EBPR can be achieved, as long as SRT values of 16 and 12 days are provided for 5°C and 10°C, respectively. System performance was not affected between 16 and 24 days and 12 and 17 days SRT for 5°C and 10°C, respectively. High SRT operations increased the endogenous glycogen use, thereby consuming the available reducing power used for PHA formation in anaerobic stages.

Glycogen metabolism was found to be the most rate-limiting step in EBPR biochemistry at temperatures below 15°C (Erdal et al., 2002). The investigators found that the pilot EBPR systems removed phosphorus until complete shutdown of glycogen use and replenishment was observed. Despite the presence of available energy sources (polyphosphate and PHA), the shutdown of the glycogen metabolism was the major reason for washout. This biochemical response at washout SRTs prevented acetate use and PHA formation. While PAOs washed out of the system, ordinary heterotrophs continued to grow in the aerobic zone using the acetate unconsumed in the anaerobic stage.

The washout aerobic SRT is influenced by COD:P. Under COD-limiting condition (Low COD:P), Erdal et al. (2003) obtained 1.2 days at 10°C and 2.1 days at 5°C. These values were lower than those reported under phosphorus limitation, 2.5 days at 10°C and 3.0 days at 5°C (WEF et al., 2005).

Influent conditions influence system performance and washout point of EBPR systems; COD:P, SRT, and temperature are the parameters that define the EBPR biomass makeup and system performance.

In contrast to the behavior at colder temperature conditions, EBPR performance tends to slow down or diminish completely at warmer temperatures. Similar to the case for cold temperature effects, however, researchers report contradicting results. Mamais and Jenkins (1992) investigated long- (13.5–20°C) and short-term (10–33°C) effects of temperature in continuous flow, bench-scale activated sludge systems. The optimum temperature for aerobic phosphorus uptake was reported to be between 28°C and 33°C. Jones and Stephenson (1996) suggested that the optimum temperature was 30°C for anaerobic release and aerobic uptake of phosphate. They also reported reduced EBPR efficiency at 50°C compared to 40°C. Brdjanovic et al. (1997), in a laboratory-scale sequencing batch reactor, determined the short-term effects of temperature on EBPR performance and kinetics at 5°C, 10°C, 20°C, and 30°C. In the absence of acclimation, the optimum temperature for anaerobic phosphorus release and acetate uptake was found to be 20°C. A continuous increase was obtained, however, for temperature values up to 30°C for aerobic phosphorus uptake. The stoichiometry of EBPR was found to be insensitive to temperature changes.

Investigating the effect of temperature (20°C, 25°C, 30°C, 32.5°C, and 35°C) on EBPR performance, Panswad et al. (2003) showed that anaerobic release, aerobic uptake, and biomass phosphorus content all decreased with increase in temperature. At 35°C, no significant phosphorus release or uptake was observed and the cell phosphorus content (2.4%) approached values closer to those of non-EBPR systems. Wang and Park (1998) also reported lower EBPR performance at higher temperature because of longer anaerobic contact times, which caused a decrease in phosphorus content and PHA storage by PAOs.

Based on full-scale plant data and laboratory-scale investigation, Rabinowitz et al. (2004) reported decreased rate of EBPR at temperatures above approximately 30°C. This was attributed to reduced rates of phosphorus release and uptake.

Degrading EBPR performance observed at warmer temperatures is related to increased competition for substrates in non-aerated zones of the biological phosphorus removal systems (i.e., increased competition from non-PAOs that can accomplish anaerobic PHA storage and increased denitrification in anoxic zones). This emphasizes the importance of adequate feed COD:P that must be maintained to support PAO growth and the anaerobic contact time for uptake of VFAs by the PAOs.

In summary, cold temperatures appear to give selective advantage to PAOs to outcompete their mesophilic competitors. At high temperatures, the same bacteria prefer to use and accumulate glycogen to a greater extent. Some researchers believe that it is a population shift from PAOs to GAOs that causes a decline in EBPR efficiency at higher temperatures. In either case, increased GAM (GAO proliferation or glycogen dependency) could potentially lead to complete EBPR failure.

3.15 Wet Weather Operations

All biological processes perform at optimum efficiency when influent conditions are stable. In reality, flows and loads fluctuate over time. Most biological systems are designed with a safety factor and are able to accommodate a peaking factor of approximately two without any detrimental process effects. Wet weather flows can impose significantly higher peaking factors. In addition, depending on collection system characteristics, the plant can experience sustained wet weather flows exceeding 24 hours.

In addition to excessive hydraulic peaks, wet weather flows are associated with influent concentrations that are highly variable and unpredictable. Influent flows and loads during wet weather is influenced by the characteristics of the rain event such as duration, intensity, and duration of dry period preceding the rain event; by type of collection system (separate or combined); use of flow equalization; and collection system storage provided. There are several ways in which wet weather affects EBPR performance:

(1) Concentration of organic matter in the incoming wastewater during a storm event can be quite low, thus not providing sufficient soluble organic readily biodegradable carbon. This will lower the bioreactor influent rbCOD:TP and will be detrimental to PAO selection.
(2) The HRT in the anaerobic zone is decreased by the high incoming flowrate of the wastewater.
(3) A large storm will flush the collection system of settled organic matter, thus eliminating sewer fermentation, which is often a source of VFAs.
(4) Lower temperatures and high oxygen levels associated with storm flows significantly limit the potential for fermentation and production of VFAs.
(5) Final clarifiers are often the weak link in a biological system. During wet weather peak flow conditions, a net transfer of solids occurs from the bioreactor to the clarifiers, resulting in an increase in sludge blanket depth. If

this condition continues, the increasing blanket depth could potentially lead to solids washout. Significant solids washout has multiple process effects including elevated effluent total solids, elevated effluent total phosphorus, and loss of nitrification.

There are several corrective measures that can be implemented to achieve stable phosphorus removal under wet weather conditions:

(1) Inclusion of step-feed capability in the bioreactor to bypass all but a fixed portion of the flow around the anaerobic zone, thereby preserving the anaerobic retention time for PAO selection.
(2) Addition of a supplemental source of VFAs directly to the anaerobic zone. Supplemental VFAs can be produced at a wastewater treatment plant by fermentation of the primary sludge (Oldham and Abraham, 1994; Rabinowitz, 1994). Alternatively, a supply of VFAs (acetic or propionic acid) can be kept onsite to assist EBPR during storm flows.
(3) Addition of final clarifiers that can be brought online to deal with wet weather peak flows. If this is not possible, polymers can be added to the operational final clarifiers to enhance their solids separation and handling capability.

4.0 FILAMENTOUS BULKING AND FOAMING

Filamentous bulking and foaming are two major operating problems associated with EBPR facilities. They negatively affect effluent quality and create serious housekeeping and odor problems. An in-depth examination of the topic may be found in Eikelboom, 2000; Jenkins et al., 2004; Wenner, 1994; and WEF et al., 2005. This section contains a brief discussion of causes and potential corrective strategies of bulking and foaming in EBPR systems.

4.1 Filamentous Bulking

The presence of some filamentous organisms provides a backbone to the floc structure, which helps sludge settle in the final clarifiers and produces a clear effluent. Excessive filaments, however, are associated with poor settling sludge and high effluent solids. A variety of operating conditions, singly or in combination, can cause

the growth of filamentous organisms in EBPR systems. These include low dissolved oxygen, low or high food-to-microorganism ratio (F:M), sulfides, and low pH values.

Filament identification is the first step in resolving the problem. Typically, operational controls focus on removing the conditions responsible for bulking or killing filamentous organisms to control their number. Some common strategies include

- Using selectors to provide growth advantage to floc formers;
- Chlorinating RAS;
- Adding nutrients;
- Correcting the dissolved oxygen concentration in the bioreactor; and
- Correcting the pH.

4.2 Filamentous Foaming

Although *Nocardia* sp. is the most commonly found organism responsible for filamentous foaming, others (such as *Microthrix parvicella* and Type 1863) can also cause foaming. Because many of the organisms that cause foaming look similar, the term "nocardiafoams" is used to refer to them collectively.

The presence of some foam in the activated sludge bioreactor is normal. In a well-operated process, 10% to 25% of the bioreactor surface will be covered with a 50- to 80-mm (2- to 3-in.) layer of light tan foam. Under certain operating conditions, foam can become excessive and affect operations.

Three types of problem-causing foams are stiff white foam, brown/dark tan foam often incorporating scum, and very dark brown or black foam. If allowed to accumulate, stiff white foam can be blown by wind onto walkways and create hazardous working conditions. It can also create an unsightly appearance, produce odors, and transmit pathogens. If greasy or thick scummy foam builds up and is conveyed to the secondary clarifiers, it will tend to build-up behind the influent baffles and create additional cleaning requirements. It can also plug the scum-removal system.

Foaming typically is associated with warmer temperatures, grease, oil, fats, and long SRT. Because foaming is a surface phenomenon, it typically has a longer SRT than the underlying MLSS. Plants prone to foaming often receive oil and grease waste from restaurants with poorly performing or missing grease traps; have poor or no primary scum removal; recycle scum; and have bioreactors and final clarifiers that are not properly designed to remove scum and foam.

The most effective strategy to deal with foaming is to eliminate conditions that encourage growth of nocardiafoams. This is not always easy, however, because exact cause-and-effect relationships have not been fully established. The following is a listing of foam and scum control methods that can be implemented in EBPR systems:

- Design inter- and intrazone baffles to promote free-flow surface foam and scum.
- Eliminate dead ends, sharp corners, and quiescent zones in channels or bioreactors where there is a potential for foam and scum to accumulate.
- Selectively waste preferential removal of foam and scum organisms from the aeration basin as part of the WAS stream. Collected foam should not be recycled to avoid reseeding the foam-causing organisms.
- Design secondary sedimentation tank inlet wells and flocculation wells to allow for passage of floating material.
- Install an effective scum removal system on secondary sedimentation tanks, preferably a full radius skimmer.
- Avoid opportunities for recycling foam and scum organisms to the mainstream treatment train from sidestream solids processing facilities.
- Apply chlorine (0.5–1% solution) spray at localized points of foam and scum collection or accumulation to kill nocardiafoams and prevent them from causing problems in either mainstream or sidestream treatment processes. The chlorine dose should be controlled carefully to avoid EBPR inhibition, which can take several days to recover.
- Add polymers to destroy the hydrophobic properties of the foam and allow it to mix with the sludge so that it can be removed with the waste sludge. The addition of polyaluminum chloride has also been shown to be effective in controlling foaming (Melcer et al., 2009).

5.0 PREFERMENTATION

Prefermentation refers to the conversion of complex organic material present in wastewaters to short-chain VFAs under anaerobic conditions. In this and other

manuals, the process is also referred to as fermentation. Prefermentation occurs in many collection systems before wastewater reaches the treatment plant. The degree of sewer fermentation is affected by several factors, primarily the HRT and wastewater temperature. Typically, long, flat sewers favor VFA generation, whereas short steep sewers decrease the retention time and create conditions for reaeration of the wastewater. Force mains encourage acid fermentation because little or no reaeration takes place. High infiltration during storms dilutes the wastewater, reduces the retention time, and increases reaeration, thereby reducing in-pipe fermentation. Cold temperatures also affect sewer fermentation.

When adequate VFAs are not available through sewer fermentation, engineered prefermentation facilities may be implemented to augment VFA supply. In a typical municipal wastewater, the soluble BOD fraction is 40% to 60% of the total BOD. This means a significant amount of the organic matter is in particulate form and potentially can be converted to VFAs. By ensuring a reliable and consistent supply of VFAs, primary sludge fermentation stabilizes the EBPR process and significantly increases denitrification rates in BNR processes. Fermenters are a particularly attractive option for large plants in temperate and cold climates that receive low-organic-strength wastewater; plants located in hilly areas with no opportunity for sewer fermentation; and plants that want to meet stringent effluent total phosphorus limits using EBPR only.

Acid fermentation laboratory experiments performed at the University of Capetown (initial VSS concentrations of 300 to 40 000 mg/L and turnover of 9 to 19 days after the start of fermentation) reported the following findings (Wentzel et al., 1988b):

- The lag phase before acid formation varied from 0 to 7 days, peak acid concentration was obtained 6 to 9 days after the start of fermentation, and production followed a first-order reaction.
- A maximum yield of approximately 0.125 kg VFA as COD was obtained per kilogram initial VSS as COD. For an SRT of three to four days, the yield was 0.075 kg/kg. The VFAs were produced in proportions of 1:1:0.08:0.07 for acetic, propionic, butyric, and valeric acids, respectively.
- Several observations were made when four reactors in series were operated semi-continuously using primary sludge at VSS concentrations between 37 000 and 57 000 mg/L: (1) there was no lag period for acid production;

(2) between 6% and 10% of the VSS (as COD) was solubilized to VFA (as COD); and (3) approximately 50% to 70% of the 0.45-μm-filtered COD was VFA. The acetic:propionic: butyric: valeric acid ratio of the VFA was 1:1:0.3:0.1. Of the total VFA generated, 43% was acetic, 41% propionic, and 16% butyric and valeric.

- The series system had no significant advantage over a single reactor with equal retention time.

The fundamentals of biological prefermentation design and operation have been described in considerable detail by Barnard (1991), and his observations are summarized in the remainder of this section.

In a prefermenter, the fermentation step is independent of the activated sludge system, and carbon available in the incoming raw wastewater is fermented to generate short-chain VFAs.

Without any incidental fermentation in the sewers or deliberate fermentation in primary sedimentation tanks, it is difficult to produce sufficient VFAs in the anaerobic zone of an EBPR activated sludge plant when the influent is weak and mixed liquor temperatures are low. At influent BOD values of less than 200 mg/L and temperatures below 12°C to 15°C, secondary release (phosphorus release without substrate storage) is more than the uptake possible through the production of VFAs, and enlargement of the anaerobic zone becomes counterproductive.

Thus, although it has been found that with stronger wastes and high winter temperatures there may be merit in enlarging the anaerobic zone, for weaker wastes and lower winter temperatures, the smaller the anaerobic basin the better, provided sufficient VFA is produced in a prefermentation step. The anaerobic zone then becomes merely a contact zone for the uptake and storage of VFAs with the release of phosphate.

Gerber et al. (1986) found that when acetates were fed to sludge from a nutrient removal plant, primary release of phosphate began immediately even in the presence of nitrates and dissolved oxygen. If sufficient VFAs are available, then total exclusion of air and NOx is not required, and strict anaerobic conditions may be counterproductive. Because no more fermentation is required, oxygen or nitrate will allow only some organisms to use the substrate. However, secondary release under anaerobic conditions would require more VFAs for the uptake of the released phosphate. It is not yet clear which is more harmful—excessive anaerobiosis or some oxygen or nitrate. The following factors should be considered in promoting prefermentation and extracting of VFAs:

(1) Dewater the underflow from gravity thickeners. In Kelowna, British Columbia (Canada), initial attempts to elutriate VFAs from thickener

underflow consisted of passing the underflow over a static screen to remove coarser material (Barnard, 1984). This process works only when spraying water on the screen to continuously wash the sludge. This resulted, however, in too much solid material passing through the screen. An alternative method could be to use a dewatering device such as a centrifuge or belt filter press, with return of the liquid to the anaerobic basin. This refers to the dewatering of thickened primary sludge and not of digested sludge.

(2) Return the thickener overflow directly to the anaerobic basin. This would be normal practice in combination with the BNR plants but does not optimize the elutriation of VFA. In the thickening process, liquid containing VFA is expelled continuously. As the sludge thickens and optimal VFA production is reached, however, less liquid is expelled and much of the VFA is not passed to the activated-sludge unit unless the next step is sludge dewatering.

(3) Recycle solids in the primary settling tank (PST) or gravity thickener. One of the simplest ways of producing VFAs is to allow a sludge blanket to form within the PST and to slowly recycle the sludge to the inlet. This concept is the basis of the "activated primary sedimentation tank" or a-PST (Barnard, 1984). Figure 8.11 is a schematic of an a-PST arrangement. The constant recycling process inoculates the incoming solids with actively fermenting organisms, elutriates the VFAs formed in the sludge blanket. It also prevents formation of methane and hydrogen sulfide through constant exposure to air with every recycle. Such recycle may also be applied to the gravity

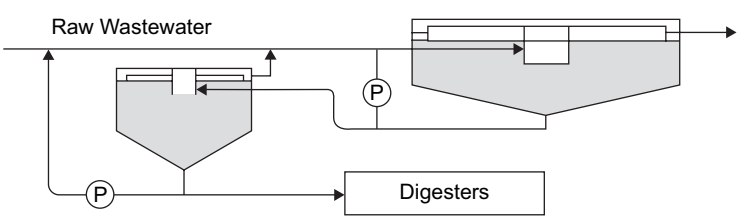

FIGURE 8.11 The activated primary sedimentation tank (from Barnard, J.L. [1984] Activated Primary Tanks for Phosphate Removal. *Water SA*, 10, 121, with permission).

thickener or from the thickener back to the PST. Barnard (1984) provides further details regarding this operation.

(4) Recycle solids in primary settling tanks or gravity thickeners. This eventually will lead to a slow buildup of methanogenic organisms. The sludge should be wasted completely at regular intervals. These intervals vary from one location to the next and even from season to season and must be optimized for each individual plant.

(5) Use a completely mixed fermenter. The sludge removed daily from the PST can be discharged to a completely mixed fermentation unit. The VFA-rich fermenter overflow is sent to the primary clarifier and primary sludge is wasted from the fermenter (Rabinowitz and Oldham, 1985). The fermenter HRT is calculated based on primary sludge feed rate. The SRT is a function of the mass of solids in the fermenter and the wasting rate. Provision should be made for emptying the fermenter at regular intervals to prevent development of methanogenic organisms, which tend to develop and build up slowly in spite of the adverse conditions. Alternatively, regular aeration of the fermenter for short periods can counteract the development of methane organisms. This has been successfully implemented at treatment plants in Johannesburg, South Africa.

(6) Use a batch fermenter. At Pietermaritzburg, Natal (South Africa), four small redundant digesters are used for batch treatment of the primary sludge. The PST underflow is pumped for two days to one batch unit. The pumping automatically is switched to the second, the third, and the fourth. At the other end of the batch units, pumps automatically transfer sludge to the thickener. The thickened sludge is then discharged to the digesters, and the VFA-rich liquid is discharged to the BNR plant. This has the advantage of full automation and achieves odorless optimization of the process.

6.0 PROCESS CONFIGURATIONS

Achieving EBPR requires cycling the microbial consortium (sludge) between anaerobic and aerobic conditions for the appropriate length of time. Table 8.5 summarizes the available process configurations and key characteristics.

TABLE 8.5 Key features of available enhanced biological phosphorus removal alternatives.

Process	Zones	Internals recycles	Key features
Anaerobic-oxic (AO)	AN-OX	None	• TP removal • Mainstream AN and OX zones
PhoStrip	OX-AN	None	• TP removal • Mainstream OX and sidestream AN zones • Biological and chemical removal
Phoredox (A^2/O)	AN-AX-OX	• Nitrate (OX to AX)	• TP and TN removal
University of Cape Town (UCT)	AN-AX-OX	• Nitrate (OX to AX) • Anaerobic (AX to AN)	• TP and TN removal • RAS to AX; AN zone protected • Larger AN because of lower MLVSS
Modified UCT (MUCT)	AN-AX1-AX2-OX	• Nitrate (OX to AX1) • Anaerobic (AX2 to AN)	• TP and TN removal • RAS to AX1 greater protection of AN zone • Larger AN because of lower MLSS
Virginia Initiative Plant	AN-AX1-AX2-OX	• Nitrate (OX to AX1) • Anaerobic (AX2 to AN)	• Similar to MUCT except: • Nitrate recycle mixed with RAS • AN and AX zones are staged
Five-stage Bardenpho	AN-AX1-OX-AX2-Reair	• Nitrate (OX to AX1)	• TP and TN removal • 2nd anoxic (AX2)
Oxidation ditch	AN-OX	None	• TP and TN removal • AN zone precedes oxidation ditch. • Simultaneous nitrification/denitrification (SND)

(*continued*)

TABLE 8.5 Continued

Process	Zones	Internals recycles	Key features
Johannesburg	PreAX-AN-OX	• Nitrate (OX to AX)	• TP and TN removal • PreAX zone for RAS denitrification and to protect AN zone
Westbank	PreAX-AN-AX-OX	• Nitrate (OX to AX)	• TP and TN removal • PreAX zone for RAS denitrification and to protect AN zone
Schreiber	AN-OX (Temporal zone distribution)	None	• TP removal • Air is cycled to achieve AN-OX conditions • Incidental TN removal
Sequencing batch reactor	AN-OX (Temporal zone distribution)	None	• TP removal • Air is cycled to achieve AN-OX conditions • Incidental TN • No clarifiers
Phased isolation ditch (BioDenipho)	AN-OX (Temporal zone distribution)	None	TP removal Air is cycled to achieve AN-OX conditions Incidental TN removal

AN = anaerobic; AX = anoxic; OX = oxic; PreAX = preanoxic; reair = reaeration; TP = total phosphorus; and TN = total nitrogen.

7.0 PROCESS MONITORING

A brief review of the key parameters used for monitoring the EBPR process is provided in this section. A detailed discussion of the topic is presented in Chapter 11 and in WEF et al., 2005.

7.1 Dissolved Oxygen

Dissolved oxygen is a measurement of the oxygen dissolved in a liquid stream. In the EBPR process, adequate dissolved oxygen should be available for rapid phosphorus uptake in the aerobic zone. If it is present in the anaerobic zone, however, it could potentially inhibit VFA production and PAO selection.

Many facilities use online instrumentation for continuous monitoring of dissolved oxygen in the aeration zones. Often, this information is used to control aeration and reduce energy costs. The dissolved oxygen concentrations in the bioreactor influent, anaerobic zone, internal recycle, and RAS streams typically are not monitored, but should be checked if EBPR is reduced.

7.2 Oxidation-Reduction Potential

Oxidation-reduction potential (ORP) is a measurement of the oxidation or reduction potential of a liquid. A positive ORP value is associated with oxidation reaction, and a negative value indicates reducing conditions. Hence, ORP can be used to indicate the type of environment (i.e., aerobic or anaerobic). Because certain wastewater characteristics and type of ORP probe (silver versus platinum) will affect readings, typical values cannot be assigned for aerobic and anaerobic conditions. A field correlation should be performed before ORP values are used to control the system. Once this is done, an operator can measure the ORP to quickly determine if the tank is aerobic, anoxic, or anaerobic. Control systems can be programmed to control recycle rates, aeration, or other devices to meet the desired environmental conditions in the tank.

7.3 Nitrate-Nitrogen

Like dissolved oxygen, the presence of nitrate in the anaerobic zone can inhibit PAO selection. Nitrate is generated during nitrification in the aerobic zone and can enter the anaerobic zone with RAS. It can also be in the backflow from the aerobic to the anaerobic zone. Industrial discharges can also be potential source of nitrates.

If lower EBPR performance occurs, nitrate should be measured in the bioreactor influent, anaerobic zone, and RAS. This information should be reviewed in conjunction with anaerobic phosphorus release to determine if there is a correlation.

7.4 Total Phosphorus

Total phosphorus includes soluble and particulate forms and should be monitored as required by the plant's discharge permit. In addition, it should also be measured as often as practical in the influent, sidestream, and clarified effluent. By reviewing the total phosphorus data in conjunction with the orthophosphorus values, it would possible to identify the process (EBPR or solids capture) that can be improved to lower the effluent total phosphorus levels. It is important that enough data is collected when the facility is running well to form a reliable baseline of information.

7.5 Orthophosphorus

Orthophosphorus is the soluble form of phosphorus and is directly implicated in phosphorus release and uptake reactions of the EBPR process. Hence, by measuring orthophosphorus at targeted locations in the bioreactor, it is possible to assess EBPR performance.

7.6 Chemical Oxygen Demand

COD is considered to be a better measure of the organic content of a sample than $cBOD_5$. At approximately 3 hours, the COD analysis is much faster than the standard 5-day BOD test.

As proposed by Ekama et al. (1984), the influent COD can be subdivided into biodegradable and nonbiodegradable fractions. The unbiodegradable fractions typically will pass through the treatment system or eventually be wasted from the system in the form of particulate matter in the MLSS or primary sludge. The biodegradable fraction may be broken into rbCOD and slowly biodegradable COD. The rbCOD fraction is the most important in the EBPR process because it is susceptible to fermentation to form VFAs within the short retention time (one to two hours) in the anaerobic zone.

Mamais et al. (1993) developed a rapid physical-chemical method to determine rbCOD in municipal wastewater. This method is based on the assumption that rbCOD is equal to soluble effluent COD from an activated sludge plant treating wastewater. Park et al. (1997) also described this method.

7.7 Volatile Fatty Acids

Performance of an EBPR process is related directly to the amount and type of VFAs available in the anaerobic zone. Approximately 7 to 10 mg/L VFA is required to remove 1 mg/L phosphorus. Samples for VFA analysis should be collected from the bioreactor influent before the introduction of RAS. Samples also should be collected on the elutriate from prefermentation facilities to determine the performance of these units in generating additional VFAs that are directed to the anaerobic zone.

7.8 Soluble Biochemical Oxygen Demand

Soluble BOD (sBOD) is the BOD of the filtrate of a sample. The bioreactor influent sBOD is a more accurate measure of the rapidly biodegradable substrate than total BOD. The same sample should be used for sBOD and total phosphorus analyses so that $sBOD_5$:TP can be developed. Review of this data over time will allow a facility to

determine if the variation in EBPR performance is the direct result of changes in the amount of food available to the system.

sBOD:TP is a rough indication of substrate availability and is not as good an indicator as rbCOD:TP or VFA:TP. It can be used, however, by plants that do not have the resources to perform rbCOD or VFA analysis. The key disadvantage of using sBOD is that it takes five days to obtain the results. Hence, it cannot be used for making timely process decisions. Instead, it could be used to identify long-term trends.

7.9 Biological Phosphorus Removal Potential Test

Although the various substrate-to-phosphorus ratios ($cBOD_5$:TP. rbCOD:TP, VFA:TP, etc.) provide an indication of the amenability of the wastewater to EBPR, these ratios may not be reliable because of site-specific conditions. Consequently, plants with supposedly favorable ratios have shown disappointing EBPR performance.

To overcome this drawback, a bench-scale procedure was developed by Park et al. (1999) to assess the EBPR potential. This test can be performed when it is suspected that the influent wastewater strength is affecting performance or when secondary phosphorus release is occurring in the anaerobic reactor. The test compares the amount of phosphorus release obtained from samples with and without supplemental acetate addition. Thus it is an indication of the EBPR potential of the "wastewater only" sample. Details of the tests are outlined in Park et al. (1999).

8.0 DESIGN CONSIDERATIONS

8.1 Anaerobic Zone

The anaerobic zone is expected to sustain two important reactions that are central to the success of EBPR process: PAO selection and VFA generation. The anaerobic zone can be sized based on SRT and HRT requirements as outlined below:

- PAO selection is the primary function. This is a relatively rapid reaction if adequate rapidly biodegradable substrate (VFA) is available. The associated anaerobic SRT is approximately 0.3 to 0.5 days, and the corresponding nominal anaerobic HRT is 30 to 45 min.
- VFA generation through fermentation is a secondary function of the anaerobic zone. It is not required to perform this function if other sources of VFAs, such as sewer fermentation and primary sludge fermentation, are available.

Fermentation in the anaerobic zone is a slower reaction requiring an anaerobic SRT of 1.5 to 2 days and an anaerobic HRT of approximately one to two hours.

Barnard (1984) emphasized the need to correctly size the anaerobic zone. If it is too large, then VFAs would be exhausted, and carbon uptake and storage as PHA would cease. Anaerobic phosphorus release will continue, however, and there would not be adequate stored PHA available to remove this additional phosphorus (secondary phosphorus release) in the subsequent aerobic zone.

Good design practice calls for assessing the need to provide a variable anaerobic volume. This typically is done by incorporating "swing zones" that can be operated as anaerobic or oxic (or anoxic in BNR systems) volumes. Such a feature would allow the anaerobic volume to be varied in response to operating conditions to ensure that the target effluent phosphorus level is achieved consistently.

8.2 Aerobic Zone

Actual phosphorus removal occurs in the aerobic zone. Nitrification, however, typically is the controlling process and would dictate the aerobic volume requirements. Phosphorus uptake is a rapid reaction requiring adequate dissolved oxygen. As stated previously, dissolved oxygen limiting conditions in the initial sections of the aerobic zone can cause poor initial phosphorus uptake. It may not be possible for phosphorus removal to "catch up" in the subsequent aerobic zones even if adequate dissolved oxygen is maintained. Hence, for the EBPR process, the most important factor is the provision of adequate initial dissolved oxygen. Designers should consider tapered aeration to ensure that air delivery matches oxygen demand.

Oversizing the aerobic zone, however, will lead to excessive aerobic HRT, which may result in secondary phosphorus release. This requirement will need to be balanced with nitrification needs.

8.3 Baffles

Baffles play an important role in enhancing the EBPR process. Two types are baffles are used in EBPR bioreactors:

(1) Interzone baffles for separating the anaerobic and oxic zones.
(2) Intrazone baffles placed within a zone to enhance reaction kinetics.

8.3.1 *Interzone Baffles*

In EBPR bioreactor configurations, interzone baffles are provided to protect the integrity of the anaerobic zone. Baffle design should consider the following:

- Because of density differences, the water surface in the aerobic zone will be considerably higher than the water surface in the nonaerated (anaerobic) zone. This could initiate a backflow of high dissolved oxygen stream into the anaerobic zone, which will reduce the available substrate and could potentially stimulate filamentous growths and cause *Nocardia* foam. In addition, foam will be trapped in the upstream aerated zone because of the increase in water surface.
- Head loss is the most effective way to segregate zones by providing a drop in water surface across the top baffle. Baffle openings should be sized to ensure a forward flow of 0.15 m/s (0.5 ft/sec) at minimum flow. Fully submerged baffles with the top approximately 25 mm (1 in.) below the water surface would allow the free flow of surface scum and foam without an opportunity to accumulate. Alternatively, when baffles extend well above the water surface, slots should be cut at the top for the scum and foam to pass as shown in Figure 8.12.
- Bottom baffle openings must be provided to facilitate tank draining. The opening should be small enough to avoid significant forward flow.

8.3.2 *Intrazone Baffles*

Intrazone baffles typically are provided to enhance the reaction rates within a zone. In an EBPR system, intrazone baffles are provided to improve plug flow conditions. As shown in Figure 8.13, Stensel (1991) indicated that an anaerobic stage divided into discrete stages would result in more rapid substrate uptake kinetics (because of the higher initial F:M) than a completely mixed zone. Consequently, the anaerobic volume can be decreased by staging it. Similar benefits have been reported by staging the aerobic zone (Jeyanayagam, 2007; Narayanan et al., 2006).

8.4 Aeration Requirements

The use of an anaerobic zone as the first treatment stage in an EBPR flow configuration results in a reduction of the oxygen requirements (McClintock et al., 1993). This phenomenon has been termed anaerobic stabilization, but the biochemical

FIGURE 8.12 Interzone baffle with provision for the passage of scum and foam (courtesy: Malcolm Pirnie, Inc.)

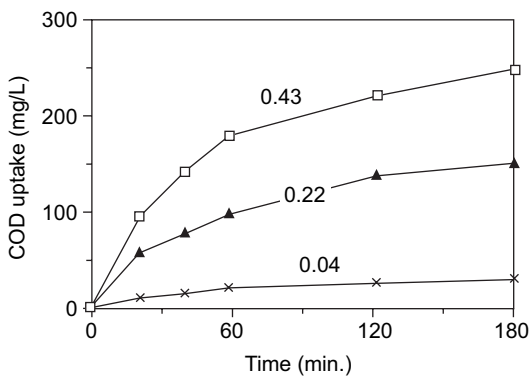

FIGURE 8.13 Effect on initial F/M on COD uptake in anaerobic zone (Stensel, 1991).

mechanisms involved are not fully understood. It has been repeatedly documented, however.

In the study by McClintock et al. (1993), mass balance techniques were used to determine and compare the oxygen requirements of a conventional, fully aerobic activated-sludge system and a UCT/VIP™ system placed side by side and treating

the same wastewater. Both units were operated at three temperatures and two SRTs (six experiments). The results showed that the EBPR system required less oxygen than the conventional system. The oxygen mass balance for the conventional system was within 4.5% of the theoretical amount for five out of six experiments. This shows that the procedures used were reliable and accurate. The oxygen mass balance for the EBPR system was less than the theoretical amount by an average of 16.7%. Data from several other studies that support the existence of anaerobic stabilization have been published previously (Brannan, 1986; Daigger et al., 1987a; Randall, 1985).

An additional observation was that the total oxygen used by the BNR system, which included denitrification and EBPR, was an average of 31% less than the total oxygen used by the fully aerobic conventional system.

8.5 Mixing Requirements

The goal of mixing in an anaerobic zone is to keep the MLSS suspended while minimizing surface turbulence that could transfer oxygen from the atmosphere. Therefore, the minimum power input necessary to keep the solids suspended should be used, and the stirring mechanism should be designed to avoid vortexing. Alternatives include submersible, vertical, and pulsed air mixers. Power input should be sufficient to maintain a velocity of 0.3 m/s (1.0 ft/sec) throughout the zone. Because horizontal velocities can be difficult to quantify in a reactor with a single-point mixing device, a more practical criterion is complete turnover of the cell contents every 20 min, based on the primary pumping rate of the mixer.

A formula for determining mixing requirements as a function of the MLSS concentration has been developed from information presented by Reynolds (1982) and is as follows:

$$P/V = 0.00094\ (\mu)^{0.3}\ (\text{MLSS})0.298 \tag{8.2}$$

Where,

μ = absolute viscosity in centipoises = 1.0087 at 20°C;
P/V = power units per unit volume, kW/1000 L; and
MLSS = mixed liquor suspended solids concentration, mg/L.

However, this formula should be used only for nearly square zones with a depth of no more than 6 m (20 ft).

Although energy input of approximately 4 W/m^3 is adequate for mixing without causing excessive turbulence, the actual power requirement will depend on the shape

and size of the anoxic and anaerobic zones and the type of mixer. Mixer manufacturers should be consulted for sizing the mixer.

8.6 Prefermentation

Following is a compilation of key prefermenter design and operational considerations:

(1) When designing a plant with EBPR, the return of organic carbon in the form of BOD or COD to the biological process should be considered. This is not more than would typically be expected when thickening primary sludge, but if extensive fermentation is required, then the return of COD may be substantial and must be reflected in the calculations for the BNR process.

(2) The mechanical equipment used should be simple and easily accessible. This is particularly important because the fermenter must be enclosed for odor control. A corrosive atmosphere is encountered within the fermenter that attacks metal and concrete. Because a high degree of stirring is not desired, external pumps may be considered. The concrete cover may be designed to be in contact with the liquid to prevent corrosion. Alternatively, an aluminum cover may be provided.

(3) Provision should be made for venting the air space to an odor-control unit. The effluent from a prefermenter should be handled with care to minimize odor problems.

(4) The recycling of sludge in the fermenter leads to the buildup of a fibrous gooey substance that is difficult to handle. It also clogs pumps and accumulates in the digesters. Though a fine screen in the sludge line to the fermenter will help, the best location for this screen is on the recycle line because most of the fibrous mass seems to reform in the fermenter. Because the substance is odorous and difficult to handle, a press is required to squeeze the liquid out and return it to the fermenter or the PST. The remainder of the fibers could be wasted to the screenings. Because most of these fibers would end up in the digesters, the cost of removing them is worthwhile because of the additional benefit.

(5) Sufficient redundancy should be provided to ensure that production and supply of VFA is not interrupted. Two or more fermenters and at least two thickeners should be considered. Alternatively, provision could be made for recycling around the primary sedimentation tanks, of which there should be more than one.

(6) Rabinowitz and Oldham (1985) observed that although the VFAs kept increasing as the SRT of the fermenter increased up to 10 days, optimal phosphate removal was observed at an SRT in the fermenter of between 6 and 8 days.

(7) When using two primary sedimentation tanks as shown in Figure 8.14, there are many possible ways in which the wastewater treatment plant could be operated. In this case, the sludge is separately recycled back to the influent of each tank, the pumps are connected directly to the underflow of each tank, and the lines are interconnected by two-way valves. Thus, any of approximately 12 operating combinations is possible. For example, the underflow of tank one can be pumped to tank two while the underflow of tank two is pumped to the digesters or recycled and then pumped to the digesters. As a result, it is possible to keep fermentation going in one tank while cleaning the other unit.

(8) The key parameter for monitoring the performance of primary sludge fermenters is the VFA concentration in the fermenter supernatant. This is best measured by gas chromatography or high-performance liquid chromatography, which provides accurate information about the concentration of individual VFAs present. The distillation method is a reasonable method for

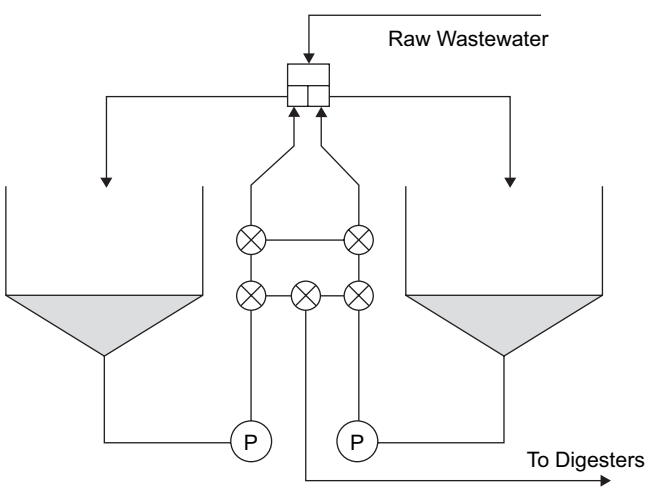

Figure 8.14 Arrangement of two activated primary tanks (from Barnard, J.L. [1984] Activated Primary Tanks for Phosphate Removal. *Water SA*, 10, 121, with permission).

measuring the total VFA concentration, but tends to be inaccurate at concentrations below 100 mg/L. The concentration of soluble COD in the fermenter supernatant provides a reasonable indication of the VFA concentration. The redox potential in the sludge blanket can indicate the level of anaerobic activity in the fermenter and whether optimal conditions for acid fermentation or methane and sulfide formation are being maintained. The pH of the sludge blanket can indicate good VFA production but is somewhat influenced by the natural alkalinity of wastewater.

(9) The two principal control parameters for the operation of primary sludge fermenters are the SRT and HRT. These are discussed below:

- The literature does not provide a clear indication of the SRT requirements for prefermentation. This is probably because the type and condition of the sludge arriving at different plants vary greatly. Some sludges may contain easily degradable solids; others may contain more complex proteins. The solids or the liquid arriving at the plant may be fresh or may have undergone sewer fermentation. In addition, wastewater strength and temperature may vary. The fermenter SRT is controlled by adjusting the solids inventory and the sludge wastage rate. By increasing the fermenter SRT, the growth of slower growing fermentative organisms is favored, and more complex molecules and higher acids are produced. Conversely, decreasing the SRT favors the growth of faster growing organisms, resulting in simpler biochemical pathways and the production of acetic acid and, to a lesser extent, propionic acid.
- The fermenter HRT is controlled by adjusting the primary sludge and elutriation water pumping rates. Elutriation water is added to wash and separate the released soluble VFAs from the particulate matter and remove them as an overflow stream. Increasing the HRT increases the available time for the conversion of solubilized substrates to VFAs. The HRT should be increased if there is insufficient hydrolysis of the particulates. A too long HRT results in the production of complex molecules and higher acids. Primary of final effluent can be used as elutriation water.

8.7 Supplemental Carbon Addition

As stated previously, the presence of rapidly biodegradable substrate (as VFAs) is a prerequisite for EBPR. Fermentation in the collection system and in the anaerobic

zone of the bioreactor is the most common source of VFAs. If naturally occurring VFA content is insufficient, a supplemental source would be required to sustain EBPR. The supplemental chemical dosage requirement is in the order of 7 to 10 mg/L VFA per mg/L phosphorus removed.

Acetic acid (CH_3COOH) is the most effective VFA for EBPR. Abu-Ghararah and Randall (1991) showed that of the carbon sources investigated, acetic acid was associated with the highest phosphorus uptake of 0.37 mg/L P per mg/L COD used and the lowest substrate requirement of 16.8 mg COD/mg P removed. Acetic acid is commonly available as 100% (glacial), 84%, and 56% solutions. A summary of the chemical properties is presented in Table 8.6 (WEF et al., 2005). Unless dilute acetic acid nearing the properties of water is used, the design of storage facilities must include freeze-protection measures. Glacial acetic acid storage could require provisions for heating. In warm climates, it may be necessary to consider an inert gas blanket or floating cover because of the low flash point. Because of corrosivity concerns, 316 stainless steel typically is used for the construction of storage tanks, piping, and appurtenances. The design of storage and chemical handling facilities must meet all applicable code requirements (National Fire Protection Association, Department of Transportation, Occupational Safety and Health Administration, etc.).

Because of the expense of adding pure chemicals such as acetic acid, some plants have considered industrial wastes as supplemental carbon source. These include sugar wastes, molasses, and waste acetic acid solution from pharmaceutical

TABLE 8.6 Properties of acetic acid (Water Environment Federation et al., 2005).

Chemical formula	**CH_3COOH**		
COD equivalent, mg/L	1.07 × acetic acid, mg/L		
Molecular weight	60.05 g/mol		
Description	Colorless liquid, strong vinegar odor		
Solution strength	100% (glacial)	56%	20%
Specific gravity	1.051	1.061	1.026
Density, kg/L (lb/gal)	1.05 (8.76)	1.06 (8.85)	1.03 ((8.56)
Flash point, °C (°F)	42.8 (109)	63.3 (146)	80.6 (177)
Freezing point, °C (°F)	16.6 (61.9)	−23 (−9.4)	−6.5 (20.3)

COD = chemical oxygen demand.

manufacture. When using such sources, it is important to ensure they are free of contaminants and debris.

8.8 Supplemental Metal Salt Addition

When the required level of phosphorus removal cannot be accomplished by EBPR alone, addition of phosphorus-precipitating chemicals, such as alum, ferric chloride, and ferrous sulfate can be used. Chemical dosage should be carefully controlled to ensure that EBPR is not inhibited. Simultaneous use of the two processes reduces the amount of chemical needed to achieve the required effluent phosphorus concentration. There is a tendency, however, to steadily increase the chemical addition rather than trust the EBPR process, which eventually will starve the EBPR process and lead to washout of the system. This can be avoided by first maximizing the EBPR process and then initiating chemical addition only as a last resort.

The metal salt can be added at several locations including the primary clarifier, bioreactor, and secondary clarifier influent. The following should be considered when combining EBPR and chemical phosphorus removal:

- Chemical addition to the primary clarifier also will enhance cBOD removal and decrease the substrate available for EBPR.
- Chemical addition to the clarifier following biological phosphorus removal will minimize chemical requirements. It will also reduce potential interference with the EBPR process.
- When metal salts are added to the bioreactor or clarifier influent, it will result in chemical solids accumulation in the MLSS and a reduction of the active biomass fraction. This may require the operating MLSS to be increased, which could result in clarifier solids loading. If added at the end of the aerobic zone, then the chemical can potentially also improve clarification. An added advantage is that the salt, which is trapped with the biomass, will help fix phosphorus in the digesters, thus reducing recycle and struvite formation potential.
- It will cause increased sludge production and alkalinity consumption.
- When ferric is used, the ferric oxide formed during VSS measurement could overestimate the VSS content.
- To be effective ferrous salts must be added before aeration so that they can be converted to ferric. This will impose additional oxygen demand.

A detailed discussion of chemical phosphorus removal is presented in Chapter 9.

8.9 Final Clarifiers

Several facilities have reported improved sludge settleability with conversion to EBPR. This may be attributed to the storage products glycogen and polyphosphate, which have reported densities of 1.25 to 1.29 g/mL and 1.23 g/mL, respectively (Ford et al., 1983; Friedberg and Avigad, 1968). These values are higher than that of activated sludge at 1.04 to 1.06 g/mL (Dammel and Schroeder, 1991). As noted by Harper et al. (2005), however, a measurable improvement in EBPR sludge settleability would occur only if the increase in density caused by the storage products can overcome factors that typically are responsible for poor settleability. This factors include filamentous growth, poor bioflocculation, and nitrogen gas.

Final clarifier design is crucial to the successful operation of an EBPR system. The clarifier must provide effective clarification because the biomass suspended solids contain phosphorus and must be removed to levels significantly less than the TSS permit values to achieve total phosphorus compliance. For example, to achieve an effluent phosphorus concentration of 1.0 mg/L when the biomass suspended solids contain 4.5% phosphorus, the effluent suspended solids cannot exceed 15 mg/L, assuming an effluent soluble phosphorus concentration of 0.3 mg/L. The resolubilization of phosphorus in the sludge blanket also can be a problem, but the effects can be minimized by operating at a shallow sludge blanket depth. Some facilities have found that a deep side water depth allows clarifiers to be operated without upflow of the released phosphorus through the sludge blanket. The resolubilized phosphorus will exit the clarifier via either the RAS or the WAS instead of in the effluent overflow. The following features are often included to improve clarifier performance:

- Baffles;
- Energy dissipating inlets;
- Efficient sludge collection mechanism; and
- Standby polymer feed system (particularly for wet weather solids control).

Stress testing and computational fluid dynamic models can be used to identify performance bottlenecks. More information on clarifier design, operation, and testing may be found in WEF (2005).

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Chapter 9

Sidestream Nitrogen Removal

1.0 INTRODUCTION

Dewatering of anaerobically digested biosolids returns high ammonia loadings to the wastewater treatment process in the form of the dewatering filtrate or centrate liquor. This liquor typically is referred to as reject water. Nitrogen loadings as high as 15% to 30% of the total nitrogen load of a typical wastewater treatment plant (WWTP) can be returned depending on the efficiency and operating conditions of the anaerobic digestion process being used. The advent of advanced digestion technologies providing improved solids destruction likely will increase recycled nutrient loadings. Loading can increase significantly in centralized dewatering facilities that digest or dewater biosolids from multiple facilities. Dewatering reject liquors are typically from mesophilic anaerobic digestion and at a temperature of 25°C to 35°C; have a biodegradable carbon to nitrogen ratio (C/N ratio) of approximately 0.1; and have an alkalinity to ammonia–nitrogen ratio of 2.5 to 3.5.

Other solids processing sidestreams may be present in a facility. These sidestreams are poor candidates for inclusion in a sidestream treatment system, however, because of their lower nitrogen content and temperature compared to anaerobic digestion liquor. As a result, these sidestreams should be sequestered from the reject water stream.

Treatment of the dewatering reject liquor load in the main plant will reduce its overall C/N ratio and alkalinity available. This could trigger a need for additional facilities for carbon and alkalinity addition and could increase operational complexity in the main plant. Treating the warm, high-ammonia sidestream separately from the main plant flow can allow the plant to use these characteristics of the reject water flow to remove the nitrogen load while minimizing electrical power and chemical usage. Doing this can also allow an increase in the alkalinity to influent nitrogen ratio and the carbon-to-influent nitrogen ratio of the main plant, thereby reducing the need for supplemental alkalinity and carbon facilities.

Introduction of sidestream or reject water treatment (these terms are used interchangeably), with the associated reduction in power and chemical consumption, can reduce the carbon footprint of the facility, enhancing the sustainability of the overall wastewater treatment process. Passive strategies that target equalization of the nitrogen loadings can also provide for some process enhancements; it is difficult, however, to access the significant operating cost savings that sidestream nitrogen treatment allows.

There are two types of biological sidestream nitrogen treatment processes:

(1) Nitrogen elimination with bioaugmentation of the main plant process and
(2) Nitrogen elimination with no bioaugmentation of the main plant process.

Figure 9.1 provides an overview of sidestream nitrogen treatment processes. The preferred process configuration depends on the combination of loadings, treatment performance requirements, and economics of treatment, which varies by plant and by season. Sidestream nitrogen treatment processes have seen significant application in Europe. An extensive list of facilities practicing some form of sidestream nutrient removal is provided in Jardin et al. (2006). These processes have not been used extensively in the United States, however, except at large facilities or those with centralized dewatering facilities. This is because of lower energy and chemical costs and more limited application of total nitrogen removal requirements in the United States. As nitrogen discharge requirements expand and energy and treatment chemical costs increase, however, more U.S. utilities are examining the potential for sidestream nitrogen removal processes.

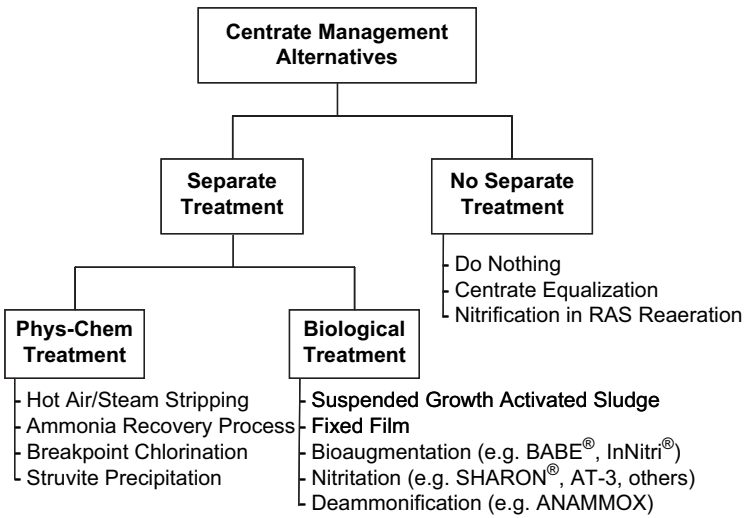

FIGURE 9.1 Overview of centrate treatment processes (RAS = return activated sludge; and BABE = Bioaugmentation batch-enhanced) (Constantine et al., 2005).

It is important to understand the benefits and tradeoffs of different sidestream nitrogen treatment options. Physicochemical treatment, with the exception of breakpoint chlorination, provides ammonia and typically phosphorus removal, thus providing nutrient recovery and load reduction. The bulk of the biological treatment processes provide nitrogen load reduction and enhanced treatment economics. Bioaugmentation processes provide load reduction and enhancement of the main plant's treatment process. Bioaugmentation-type processes, however, do not offer the cost advantages of some of the biological processes that cannot provide bioaugmentation.

2.0 SIDESTREAM NITROGEN REMOVAL TREATMENT PROCESSES

2.1 Bioaugmentation Processes

Bioaugmentation processes are used to produce an enriched culture of nitrifying bacteria grown from the treatment of dewatering reject liquor. The produced nitrifiers are directed to the main plant's nitrification or nitrogen removal process to enhance its

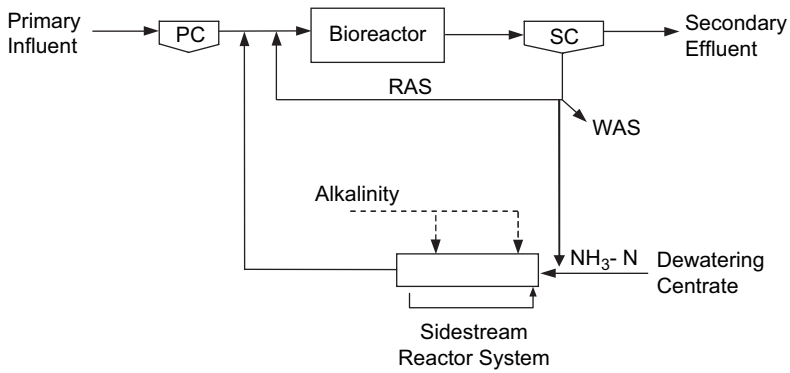

FIGURE 9.2 Typical nitrifying bioaugmentation process flow diagram (RAS = return activated sludge; PC = primary clarifier; SC = secondary clarifier; and WAS = waste activated sludge).

nitrification capacity and reliability. To maximize bioaugmentation capacity, the operating conditions of the dewatering reject liquor process will allow for growth of the maximum mass of ammonia (AOB) and nitrite oxidizing bacteria (NOB). It will also allow the growth of organisms that can function in both reject water process and activated sludge process of the main plant. Thus, two characteristics of a successful bioaugmentation process are a low operating solids retention time (SRT) and the introduction of mixed liquor into the bioaugmentation reactor from the activated sludge process of the main plant.

Several proprietary and nonproprietary nitrifier bioaugmentation processes have been described in detail in the literature (Constantine et al., 2005; Fillos et al., 2005; Katehis et al., 2002; Ramalingam et al., 2007; Siegrist, 1996). Figure 9.2 shows a simplified schematic of a bioaugmentation type process. The addition of return activated sludge (RAS) to the reactor provides several process benefits in addition to providing a constant, yet diverse nitrifier seed source from the main plant:

- Carbon dioxide generated from respiration of the heterotrophic biomass introduced via the RAS stabilizes the process, allowing the use of chemicals such as lime and caustic soda, rather than soda ash, which is more difficult to handle, for supplemental alkalinity addition.
- Constantine (2005) showed that the addition of RAS allows the nitrifiers in the bioaugmentation batch-enhanced reactor to grow within activated sludge flocs,

thereby improving settleability. Recent pilot testing of InNitri at the Ina Road Water Pollution Control Facility, Tucson, Arizona, showed that solids capture was problematic, although the specific reason for this occurrence was inconclusive.

- The RAS flow can be used to cool down the bioaugmentation reactor contents to the minimum level necessary to achieve the required level of nitrification. Large temperature differentials between the sidestream reactor and the main plant reactor may reduce bioaugmentation efficiency. Providing cooling of the reactor (particularly in sidestream nitrification–denitrification configurations) using the main plant's RAS eliminates the need for a heat exchanger to maintain the sidestream reactor contents at temperatures below 36°C to 38°C, where the biological oxidation of ammonia and nitrite may be negatively affected.

Conversion of ammonia to nitrate (nitrification) is typically the preferred operating mode of sidestream treatment process targeting nitrifier bioaugmentation into the activated sludge of the main plant. Nitritation (the conversion of ammonia to nitrite), rather than complete nitrification, can reduce operating costs because the oxygen consumption is reduced by approximately 25% by stopping the nitrification process at nitrite. Preventing oxidation of nitrite to nitrate also results in a 40% reduction in supplemental carbon required to denitrify the reject water flow. It must be recognized, however, that when the main plant's nitrification process is limited, such as when a sustained bleed through of ammonia is occurring, using a bioaugmentation process that provides for preferential nitritation can result in imbalance between AOB and NOB. This can result in elevated nitrite levels in the secondary process effluent.

The New York City Department of Environmental Protection (NYCDEP) uses a bioaugmentation configuration with nitritation that it developed in the mid-1999s. The process uses free ammonia and free nitrous acid toxicity in the sidestream system to force nitritation and prevent biological conversion of the reject water ammonia to nitrate. Nitrifying biomass produced in the sidestream reactor is used to seed the main plant resulting in nitrogen removals in excess of 50% while operating the main plant at very low SRTs (one to three days). The process has been used at the NYCDEP 26th Ward Water Pollution Control Plant since the mid-1990s. A more detailed review of this process, including operating results, is provided in Katehis et al. (2002). Molecular probing of the activated sludge from the main plant from this configuration has shown a reduction in diversity of the ammonia oxidizing species (Ramalingam et al., 2007).

Successful implementation of this process configuration requires a plug flow reactor that can introduce supplemental alkalinity in multiple locations along the length of the reactor and can modify the aerated fraction of the reactor in response to seasonal temperature changes and influent loading conditions. An internal recycle from the end to the head of the reactor recirculates nitrite rich flows that, in conjunction with operating pH setpoints, controls free ammonia levels within the bioaugmentation reactor. The process has the flexibility of being converted to a full nitrification process (e.g., if the nitrite levels in the main plant's effluent increase substantially) by increasing the internal recirculation rate, thereby reducing ammonia and free ammonia levels throughout the reactor.

Sidestream bioaugmentation processes are less cost-effective when compared with processes where bioaugmentation is not necessary. This occurs because maintaining conditions conducive to generation of nitrifiers that can function in the main plant's activated sludge process results in nitrification. Typically 60% to 80% of the ammonia is converted to nitrite, the remainder being converted to nitrate. Biological process modeling using activated sludge modeling (ASM) (i.e., ASM No. 2, ASM No. 3) equation sets is necessary to support the sizing of bioaugmentation reactor systems. The performance of these systems is a function of the operation of the main plant's bioreactors. The required hydraulic retention time and SRT of the bioaugmentation reactor will vary depending on the nitrifier population in the RAS slipstream being provided to the reactor.

Sidestream bioaugmentation processes using dewatering liquor can also be extended to the specialized heterotrophic biomass, such as by integrating denitrifying methanol degrading bacteria. Incorporation of denitrification can also reduce supplemental alkalinity requirements. This occurs because the inherent alkalinity in reject waters from anaerobically digested biosolids dewatering is typically only adequate for oxidation of approximately half of the ammonia load in the centrate. A case study to illustrate design and performance of a bioaugmentation process for dewatering reject water follows.

The sidestream nitrogen treatment reactor at NYCDEP's 26th Ward WPCP is a continuous-flow plug flow reactor without sludge retention. It is operated aerobically at dissolved oxygen and pH levels that enhance preferential production of nitrite (Anthonisen, 1976; Katehis et al., 2002; Wett, 1998, 2007). The temperature in the reactor is a function of the temperatures and flow of the waste activated sludge and dewatering centrate introduced into the reactor. Temperatures range from 17°C in the winter to 30°C in the summer. Minimal changes in temperature occur across the reactor length under typical full-scale conditions. The operating pH of the reactor

is maintained at above neutral levels (7.5–7.8) in the front portion of the reactor, where ammonia concentrations are high, to maintain elevated free unionized ammonia levels (NH_3). The pH is monitored at multiple points along the plug flow reactor and is allowed to drop to below neutral levels in the latter portion of the reactor, where nitrite levels are elevated, thereby resulting in elevated concentrations of free nitrous acid (HNO_2). Bicarbonate limitation is induced in the effluent end of the reactor (Wett, 2005). The combination of selective mechanisms results in oxidation of 50% to 80% of the ammonia to nitrite, the balance being converted to nitrate.

Care is exercised to avoid a significant pH depression in the back end of the plug flow reactor because this leads to conversion of the residual carbonate alkalinity to CO_2. The CO_2 is lost through stripping, reducing the buffering capacity of the sidestream reactor's mixed liquor, thereby making pH control within the reactor challenging when caustic soda (preferred supplemental alkalinity chemical at this site) or lime is used. The heterotrophic biomass, which continues to respire endogenously, helps provide a low level of CO_2 to the system. This counters the stripping effect allowing for enhanced stability of the pH control process. The treated stream from the sidestream system, which now includes elevated levels of ammonia and nitrite oxidizing autotrophs, is then used to seed a portion of the first-stage aeration tanks (Constantine et al., 2005). The seed promotes selective nitritation in the first-stage aeration tanks (Katehis et al., 2002; Ramalingam et al., 2007). Figure 9.3 shows typical data from the application of bioaugmentation at a New York City wastewater treatment plant.

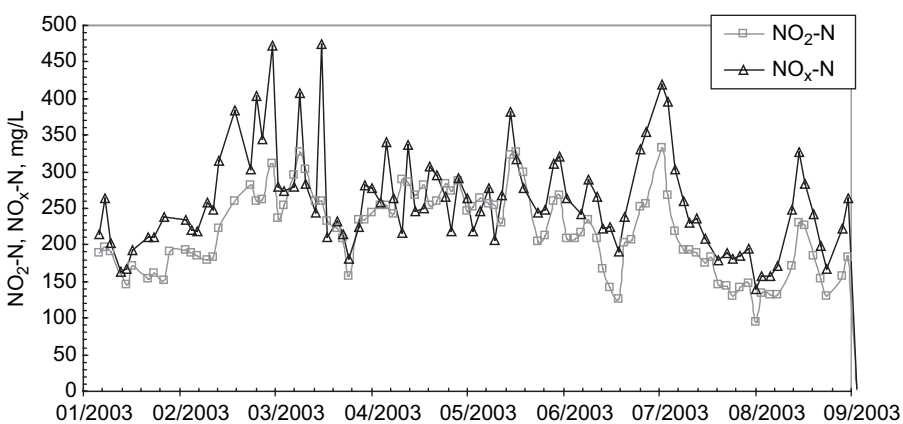

FIGURE 9.3 Preferential nitritation in the sidestream reactor at the New York City Department of Environmental Protection's 26th Ward Water Pollution Control Plant (adapted from Fillos et al., 2005).

2.2 Nonbioaugmentation Processes

2.2.1 Nitritation/Denitritation

More stable nitritation performance, and thus more economical treatment of the dewatering reject water ammonia load, can be achieved if the constraints introduced by bioaugmentation are eliminated. The dewatering reject liquor reactor's operating conditions can be set to minimize nitrate formation, thus minimizing aeration energy consumption and supplemental carbon demand to achieve overall nitrogen removal. Several methods are used to minimize nitrate formation:

- Controlling temperature and SRT to use the higher growth rate of AOB relative to nitrite oxidizers as temperatures increase beyond 30°C.
- Allowing free ammonia inhibition because free ammonia levels increase with increasing pH at a given combined ammonia and ammonium concentration. Ammonia oxidizers are less sensitive to free ammonia than NOB.
- Enabling free nitrous acid inhibition because as nitrite levels increase, operation at subneutral pH levels results in strong inhibition of nitrite oxidizers before ammonia oxidizers are affected.
- Operating at low dissolved oxygen levels because ammonia oxidizers have a greater affinity for oxygen.

Because the effluent stream does not need to be directed to the aeration tanks, it can be sent to the headworks. This allows the produced nitrite to mitigate odors in the headworks and in the primary treatment process. Multiple proprietary and nonpropietary reactor configurations that use the above concepts for prevention of nitrite oxidation have been developed.

One of the earliest documented examples of a nitritation/denitritation process is the SHARON (single reactor high activity ammonia removal over nitrite) process. Delft University of Technology and Grontmij jointly developed the process, which uses the temperature- and SRT-control approach to achieve stable nitritation. When compared to conventional nitrification-based dewatering reject water treatment processes, as a nitritation/denitritation process, the SHARON process configuration reduces the oxygen and COD requirements by 25% (reduced from 4.6 to 3.4 $kgO_2/kgNH_4$-N) and 40%, respectively.

The SHARON process consists of a continuous-flow, completely mixed reactor without sludge retention (Hellinga et al., 1998). By operating the SHARON reactor at an appropriate temperature (e.g., 30°C) and at a sufficiently low retention time (e.g., one-day aerobic SRT), nitrite oxidizers are washed out of the system. With only ammonia oxidizers present, the reject water ammonia is preferentially oxidized to nitrite. Alkalinity requirements often can be fully met through the denitritation step that is carried out in the same reactor. A range of carbon sources can be used to drive the denitritation process, including methanol, ethanol, or recycled carbon sources such as glycerol from biodiesel production and distillery wastes. Methanol is often used because of its low biomass yield and relatively low cost, although there are flammability concerns, and market volatility and availability can affect cost.

There are several documented advantages of the SHARON process:

- Sidestream tankage requirements are smaller than the bioaugmentation processes;
- Significant savings are realized in oxygen and COD (e.g., supplemental carbon in mainstream if practicing N-removal) compared with processes using conventional nitrification/denitrification; and
- Relatively simple to operate and maintain.

There are multiple full-scale SHARON plants currently operating, with relatively long-term operation (greater than three years) in the cities of Rotterdam, Utrecht, Zwolle, and Beverwijk in the Netherlands. The SHARON at Utrecht has been in operation since 1997. The first facility in the United States is a 7.0 ML/d (1.85-mgd) full-scale facility located at New York City's Wards Island WPCP.

An alternative nitritation/denitritation process for facilities not requiring bioaugmentation was originally developed for the city of Strass WWTP in Austria in the early 1990s (Wett, 1998). The process uses a high sludge age sequencing batch reactor to oxidize ammonia to nitrite (nitritation), followed by reduction of the produced nitrite to nitrogen gas (denitritation). A supplemental carbon source is needed to drive the denitritation process. In the Strass WWTP, primary sludge is used to drive the denitritation process. Unlike the SHARON process, the sludge age in the reactor is relatively high (greater than 20 days), but the high solids concentration in the reactor allows for improved denitritation rates at reduced reactor volume. The key feature of the Strass process is the innovative process control strategy. A simple, yet highly effective, pH-based control mechanism is used to control the intermittent aeration

system (Wett, 1998). During an aeration interval, acidification because of nitritation occurs. When the lower pH-setpoint is reached, the aeration stops and alkalinity/pH recovers. At the upper pH-setpoint, aeration is switched on again resulting in a characteristic sawtooth profile of the pH. Following this control strategy, frequency and length of aeration intervals self adjusts to the feedrate and concentration of reject water. The operating conditions used in the process allow for reliable nitritation/denitritation:

- Operating temperatures of 25°C to 35°C;
- Near neutral pH; and
- Intermittent aeration at low dissolved oxygen concentrations (<1 mg/L).

The Strass process is flexible and robust and has higher reaction rates and reduced supplemental carbon requirements as demonstrated by a decade of operation in Austria. A presedimentation process to remove solids from the centrate stream before sidestream treatment may be necessary to avoid excessive solids loading in clarification. Careful pH control is equally critical because the process needs to be able to respond to small changes in pH (less than 0.1 pH unit).

2.2.2 Nitritation/Anammox Processes

Anaerobic ammonium oxidation (anammox) is achieved by a highly specialized group of bacteria belonging to the planctomycete group, which convert ammonia and nitrite to nitrogen gas and nitrate while producing alkalinity (Jetten et al., 1999):

$$NH_3 + 1.32\ NO_2^- + H+ \rightarrow 1.02\ N_2 + 0.26\ NO_3^- + 2\ H_2O \quad (9.1)$$

The microorganism responsible for this reaction occurs naturally in benthic sediments and landfills, locations where ammonia and low levels of nitrite coexist under anaerobic conditions. Several process configurations that combine nitritation and anammox exist and can be categorized either as having "separate" or "integrated" nitritation and anammox steps (Wett, 2005). Figure 9.4 illustrates a separate process configuration that uses two reactors (Constantine, 2005).

In the first step of the separate process, a nitritation reactor is operated without addition of supplemental alkalinity, which results in the conversion of approximately half of the ammonia in the dewatering centrate to nitrite. The combined nitritation/anammox process typically does not require supplemental alkalinity or carbon addition in the nitritation reactor to maintain process stability. This is similar for other processes that use anammox biomass. The effluent from the nitritation reactor, which

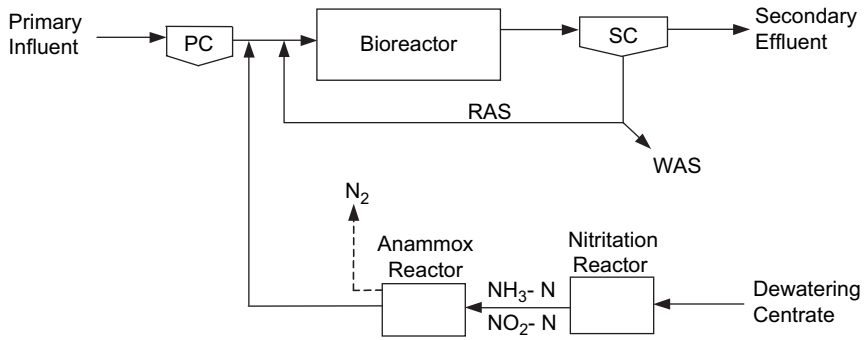

FIGURE 9.4 Process flow diagram for a combined nitritation–anammox process.

typically is composed of approximately equal parts of ammonia and nitrite (1.3:1 for the ratio of nitrite to ammonium is optimal), is fed into the anammox reactor, which is operated at relatively high temperatures (25–40°C). The anammox bacteria present in this second reactor convert ammonia and nitrite to nitrogen gas via the following simplified reaction:

$$NH_4^+ + NO_2^- \xrightarrow{\text{Anammox Biomass}} N_2 + 2H_2O \tag{9.2}$$

Compared with conventional nitrification (including most bioaugmentation processes), deammonification processes reduce the oxygen requirements by 63% and eliminate the need for supplemental carbon for denitrification. Supplemental alkalinity addition during the nitritation step typically is not required but is dependent on the ammonia-to-alkalinity ratio of the influent dewatering liquor. A full-scale separate stage nitritation–anammox process has been operational at the Dokhaven WWTP in Rotterdam, South Holland, Netherlands, since 2005.

In an integrated nitritation/anammox mode, a sequential batch reactor is used with intermittent aeration to avoid a buildup of nitrite to toxic levels. This pH-based control system determines the length of aeration intervals depending on the production of H^+ ions or nitrite (Wett, 2005). During the subsequent aeration break the nitrite produced is depleted autotrophically. The process is operated at an SRT of at least 25 days to prevent washout of slowly growing anaerobic ammonia oxidizers. The partial nitritation of ammonia (approximately one-half of the ammonia is oxidized to nitrite) reduces aeration costs with the subsequent anammox activity during the unaerated portions of the cycle eliminating the need for an external organic carbon substrate such as methanol. A full-scale integrated nitritation/anammox process has

been in operation at the Strass WWTP in Austria since 2003 (Wett, 2005). Multiple nitritation/anammox reactors currently are in operation throughout Europe using granulated suspended growth and moving bed biofilm reactor configurations (Joss et al., 2009; Szatkowska et al., 2007).

2.2.3 Physiochemical Treatment

Extensive work on physicochemical treatment processes was carried out in the late 1980s and early 1990s with processes such as induced struvite precipitation, hot air stripping, ion exchange, distillation, and breakpoint chlorination. Of these processes, induced struvite precipitation is the sole option that has proven widely applicable and commercially viable. Hot air ammonia stripping and recovery has been used where upstream high-lime treatment is practiced (for biosolids conditioning) because the pH of the dewatering liquor needs to be raised to levels in excess of 10 to facilitate efficient mass transfer. The high alkalinity and buffering capacity in the dewatering reject liquor requires that large quantities of base be used to increase the pH of the solution, limiting its viability.

Struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4{\cdot}6H_2O$) is typically a nuisance for WWTPs operating anaerobic digested biosolids dewatering because it precipitates on piping and pumps in the dewatering facility. It is also an excellent fertilizer with the ability to release nutrients over an extended period of time, reducing costs to the agricultural user, while also reducing nutrient runoff from farmland.

Struvite precipitation had limited applicability because orthophosphate and magnesium often are present in relatively low levels in anaerobically digested dewatering liquor, at approximately 1/10 the mass loading of the ammonia–nitrogen component. The stoichiometric requirements for the precipitation of one gram of NH_4-N as struvite are 1.7 g/L of Mg^2+ and 2.2 g/L of PO_4-P.

Addition of phosphorus, typically in the form of phosphoric acid, limits the practical applicability of struvite precipitation. Increased usage of enhanced biological phosphorus removal processes in wastewater treatment greatly reduces the need for phosphorus addition and allows greater recovery of struvite. Magnesium, typically in the form of magnesium chloride, is still required. The economics of magnesium chloride addition are viable, however, allowing for the reported removal of up to 50% of the ammonia in the dewatering liquor, until phosphate becomes limiting. With finite commercially accessible phosphorus deposits available, phosphorus will be the limiting nutrient for agriculture in the future. As a result, there

has been increased interest in using technologies such as struvite precipitation that allow for reuse of phosphorus that would otherwise be lost to the ocean (Daigger, 2008), thereby increasing the environmental sustainability of the sidestream treatment process.

Multiple struvite precipitation process have been developed and commercialized. In North America, a process using a fluidized-bed reactor for struvite precipitation (marketed under the commercial name Ostara®) has shown significant promise and has been demonstrated to be technically and commercially viable at multiple full-scale facilities (Baur, 2008).

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Chapter 10

Structured Process Models for Nutrient Removal

(continued)

1.0 USE OF MODELS IN PROCESS ENGINEERING

In the past decade, mathematical modeling has found its place in the standard engineering toolkit used in process design and optimization of nutrient removal systems. As more stringent nutrient discharge limitations are placed on treatment plants, the complexity of the processes used continues to increase. New processes are being developed and implemented in addition to familiar and well-understood standard configurations for nitrification, denitrification, and biological and chemical phosphorus removal. In the liquid line, innovative processes such as various fixed film systems are being implemented. In the solids line, new sludge treatment and sidestream processes dealing separately with high concentration, high temperature liquors are emerging. With decreasing effluent limits and increasing system complexity, plant-wide models that consider interactions and all important mass flows within the wastewater treatment plant (WWTP) rapidly are becoming a necessity. A mathematical model considering the whole plant will not replace expert knowledge and the requirement to thoroughly

understand key and more subtle characteristics of proposed unit process and their interactions. It does help to consistently track interlinked mass flows, to calculate conversion rates in unit processes, and to estimate likely performance for effluent quality, sludge production, oxygen and chemical demand, and other key indicators.

The objective of this chapter is to provide information on the various models and modeling methodologies available for plant-wide process design. The models and examples are focused on municipal wastewater, but the principles and methods (with the exception of default parameters) are also applicable for industrial wastewater processes, frequently with only small modifications.

1.1 A Note on Notation

The importance of a well-designed, logical, and flexible notation system cannot be overstated. A good notation system will help formulate and describe concepts, promote understanding through easy readability, and allow development of new research ideas.

There are two symbol systems used in North America. The first is the International Water Association's (IWA) notation, which originally was developed for activated sludge modeling. The principle of the notation is based on a description of filterability and degradability of organic and inorganic components in mathematical models, denoted by S and X. The subscript identifies the specific component, for example,

- Soluble components: S (S_U, inert [unbiodegradable] soluble organics);
- Particulate components: X (X_U, inert [unbiodegradable] particulate organics); and
- Slowly degradable substrate, denoted by X_S, is partially soluble.

The second system is the South African (SA) notation, which comes from the early activated sludge models developed at the University of Cape Town (UCT). The naming principle of variables is as follows:

- Chemical oxygen demand (COD): S;
- Volatile suspended solids: X;
- Nitrogen: N; and
- Phosphorus: P.

The subscript identifies the biodegradability of the specific component.

1.2 Principles of Notation Used in This Chapter

In this chapter, a consistent version of the IWA notation (filterability and degradability) will be used in accordance with a recently proposed framework (Corominas et al., 2010).

The principle is that the first capital letter identifies the filterability (particle size) of the component:

- *S* soluble (<1.2 or 0.45 μm);
- *C* colloidal (sample filtered through 1.2-μm filter, then flocculated); and
- *X* particulate (not passing 1.2-μm filters).

Total concentration is denoted by *T* (which is the sum of *S*, *X*, and *C* [$T = S + X + C$ mg/L]). All these letters appear in first position and may be joined if appropriate. The most typical example is slowly biodegradable substrate, which includes both particulate and nonparticulate (colloidal) material. The symbol for this component following this logic is XC_B.

The subscript in the symbols identifies the type of material, in as short a form as possible, but the component must be easily recognizable. For example, *ANO* for ammonia nitrifying organisms; *B,N* for biodegradable nitrogen; *U,P* for unbiodegradable phosphorus; CH_3OH for methanol. The letter N, P, S, O, H should be reserved for the respective chemical elements; E is endogenous residue. Subscripts can include a comma to clarify meaning, for example, sample source is from the influent ($S_{B,Inf}$).

Other major symbols and abbreviations frequently used in practice are *M* for mass (kg); *F* for mass rate (kg/d); *Q* for flow (m^3/d); *V* for volume (m^3). Common acronyms include COD; biochemical oxygen demand (BOD); volatile suspended solids (VSS); fixed suspended solids; total suspended solids (TSS); dry solids; and total solids.

1.3 What Is the Difference Between Empirical, Mechanistic, and Structured Models?

Empirical (experience-based) models express relationships between key measured variables such as solids residence time (SRT), sludge production, effluent quality, oxygen demand, and others. Because of the complex nature of underlying processes and the different, often incompatible units of variables that can be readily measured by standard analytical methods (VSS, BOD, TSS, etc.), empirical models typically are not mass-balance-based. They are often expressed in correlations or in graphical format as nomograms or charts that are easy to use. Empirical models and the knowledge they contain remain important in engineering work, even with the detailed mechanistic models available today.

An example of an empirical "model" is the SRT-sludge production relationship as shown in Figure 10.1. The plot shows the mass of solids produced per unit BOD_5

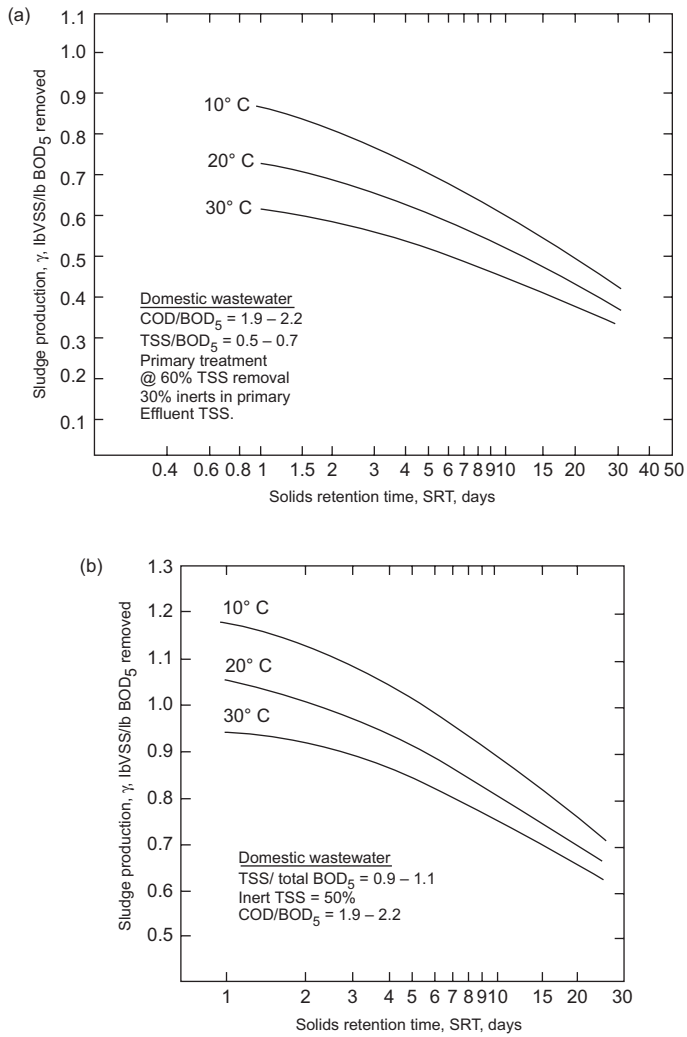


FIGURE 10.1 Net sludge production versus solids retention time and temperature (a) with primary treatment and (b) without primary treatment (lb/lb = kg/kg) (BOD = biochemical oxygen demand; COD = chemical oxygen demand; TSS = total suspended solids; and VSS = volatile suspended solids) (Water Environment Federation et al., 2009).

(five-day BOD) removed at a typical plant plotted versus SRT (in semi-logarithmic scale).

Mechanistic or structured models, on the other hand, are based on mass balances performed on a consistent set of basic components (called state variables in mathematical modeling) that are sometimes not directly measurable (e.g., active heterotrophic biomass). Mass balances in these models can be expressed in two different ways:

(1) In steady state for each component as shown in eq 10.1. Steady-state mechanistic models can only be used to calculate stable conditions, for example monthly averages. In this case there is no mass accumulation or loss over time in the system.

$$0 = \text{Input (kg/d)} - \text{Output (kg/d)} +/- \text{Reaction rate (kg/d)} \quad (10.1)$$

Where,

Reaction rate = production or loss of the component considered because of chemical or biological reactions.

(2) Dynamic models, on the other hand, express the mass change in time, and thus can be used for calculation of dynamic events, such as diurnal variation, storms, peak oxygen demand or similar.

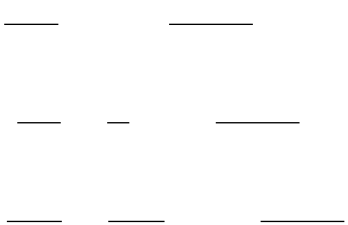
$$\text{Mass change (kg/d)} = \text{Input (kg/d)} - \text{Output (kg/d)} +/- \text{Reaction rate (kg/d)} \quad (10.2)$$

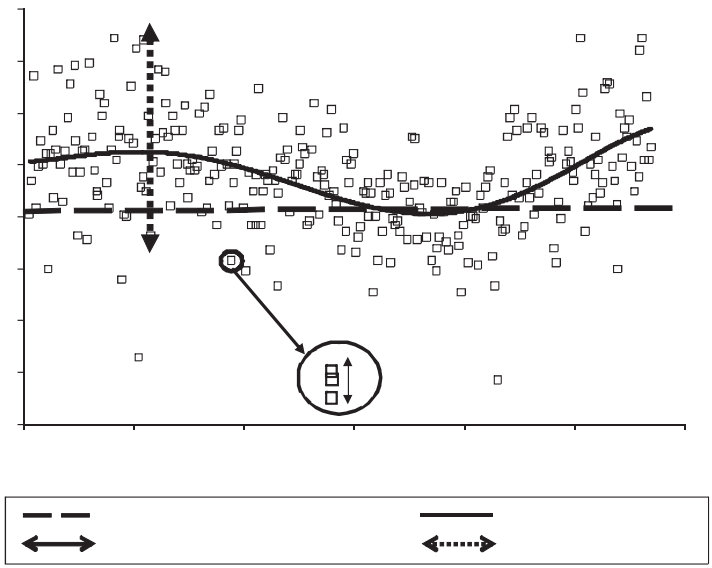
The focus of this chapter is mechanistic, structured models that are used for the calculation of plant-wide nutrient removal performance and mass balances, typically implemented in simulation software.

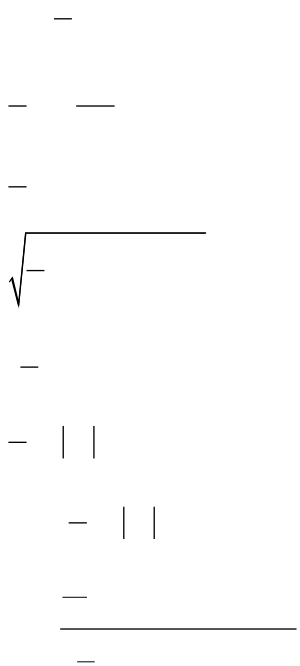
2.0 BACKGROUND ON STRUCTURED MODELS

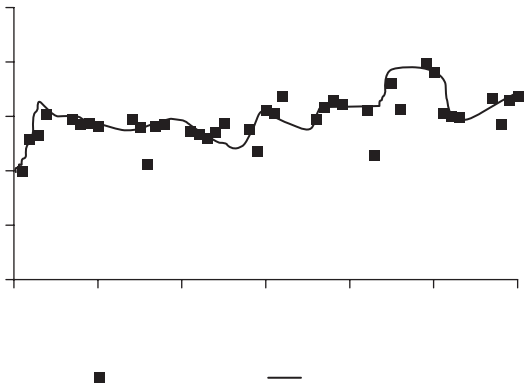
Herbert (1958) presented the first mathematical description of incorporating the endogenous respiration concept in an activated sludge model. Herbert studied the characteristics of pure cultures grown on soluble synthetic substrates in chemostats; that is, flow-through reactors without recycle, where the HRT equals the SRT. It was noted that the observed biomass yield decreases as the organism retention time increases. Herbert, accepting Monod's concept of constant cell yield, proposed that the most probable explanation for the reduction in specific yield with increasing organism retention time is that, in addition to the anabolic metabolism of the organisms (conversion of substrate to cell mass), the organisms also have a constant specific endogenous

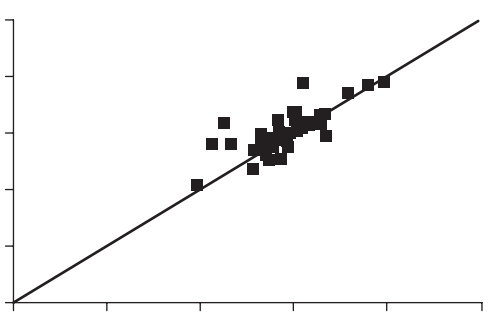
$$\frac{dX}{dt} = \mu \cdot X - b \cdot X$$

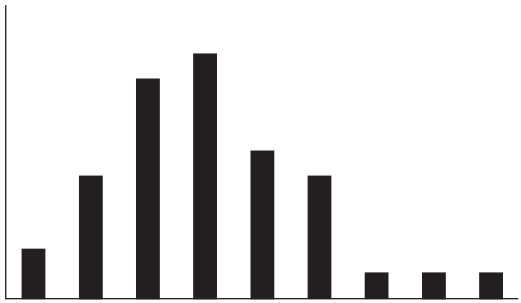


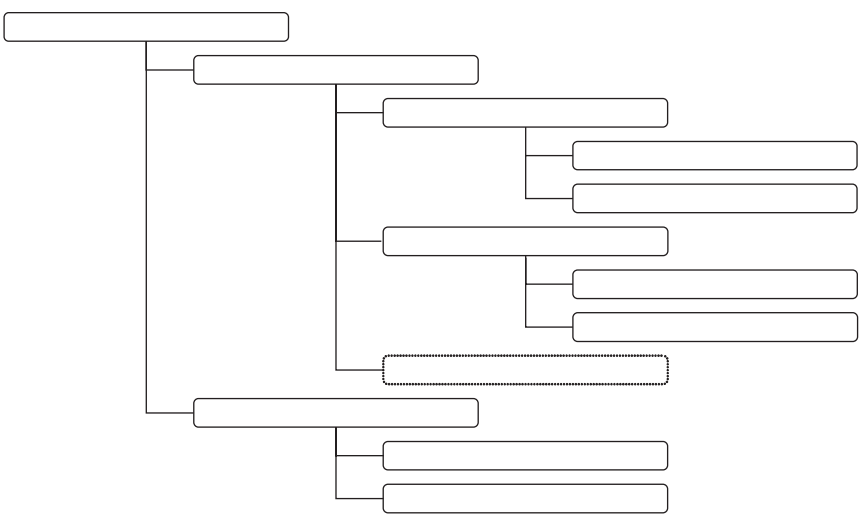


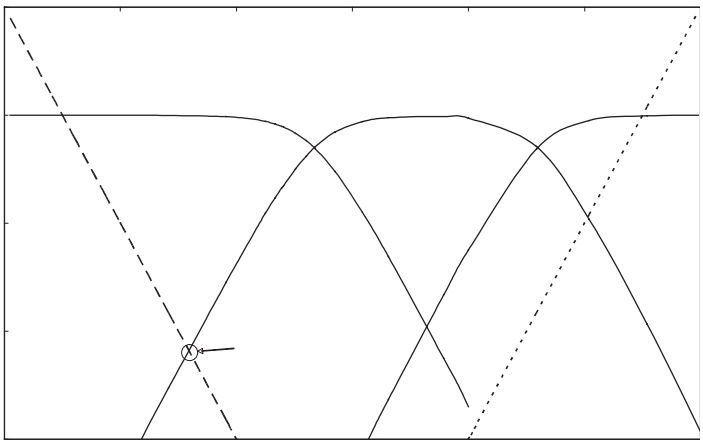


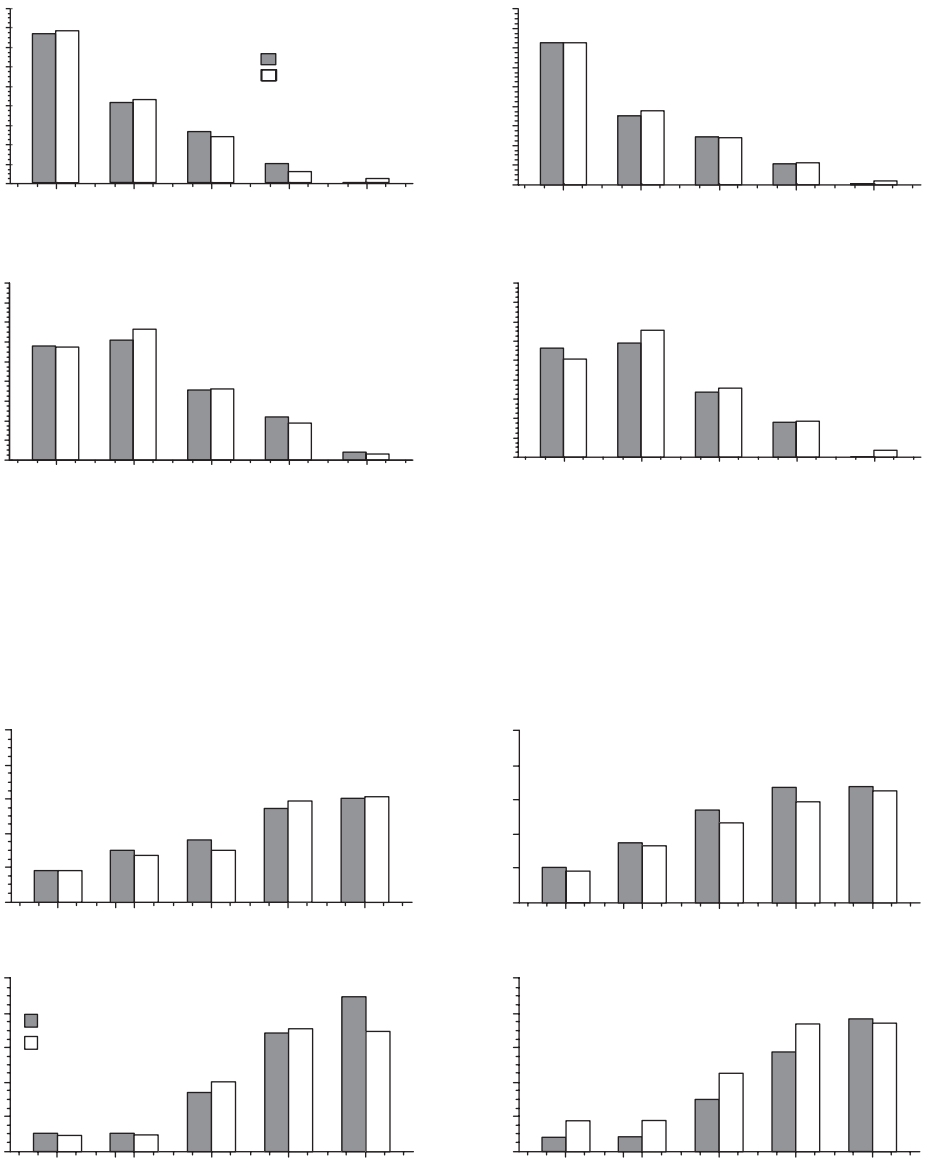


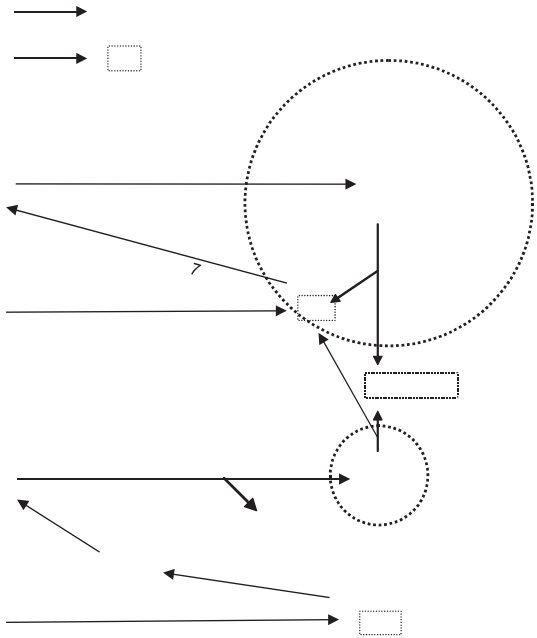


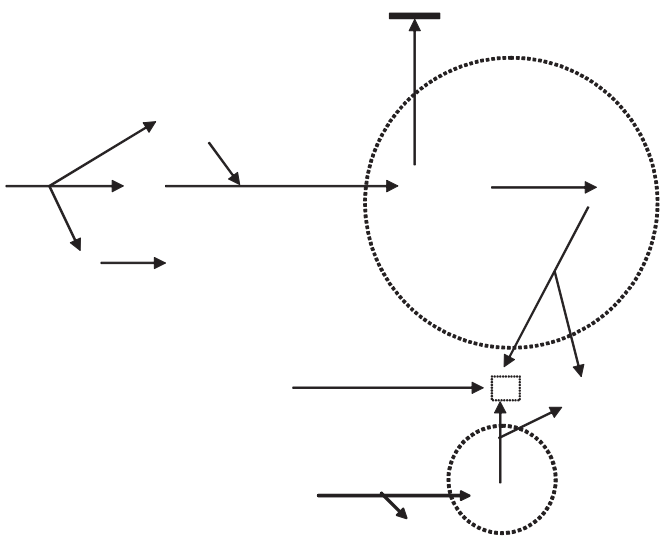


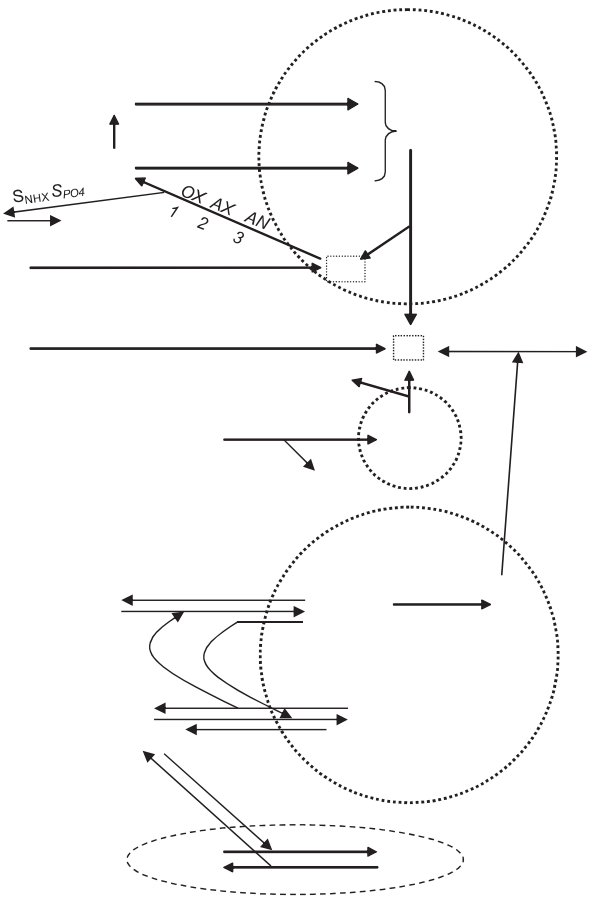


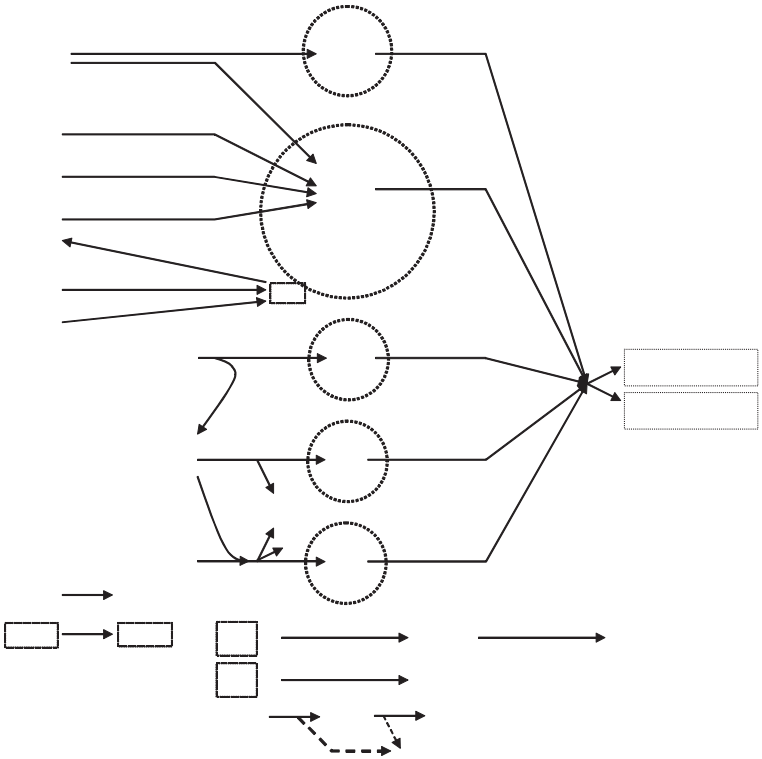


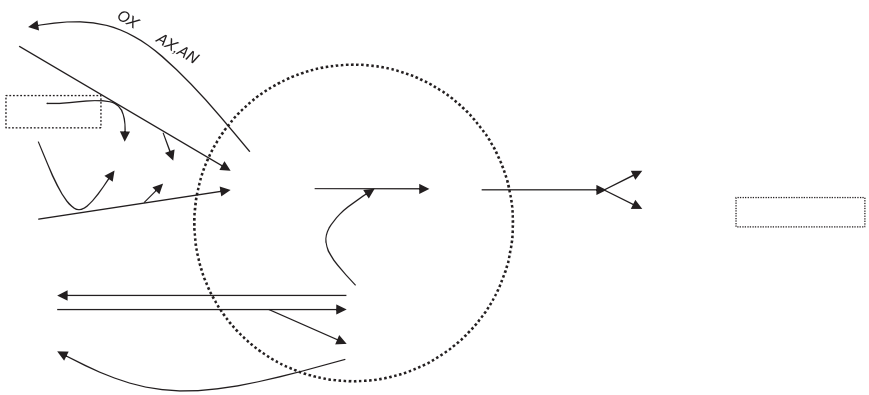







S_{NHX} S_{PO4}
OX AX AN
1 2 3

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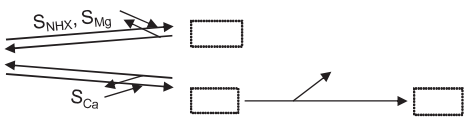
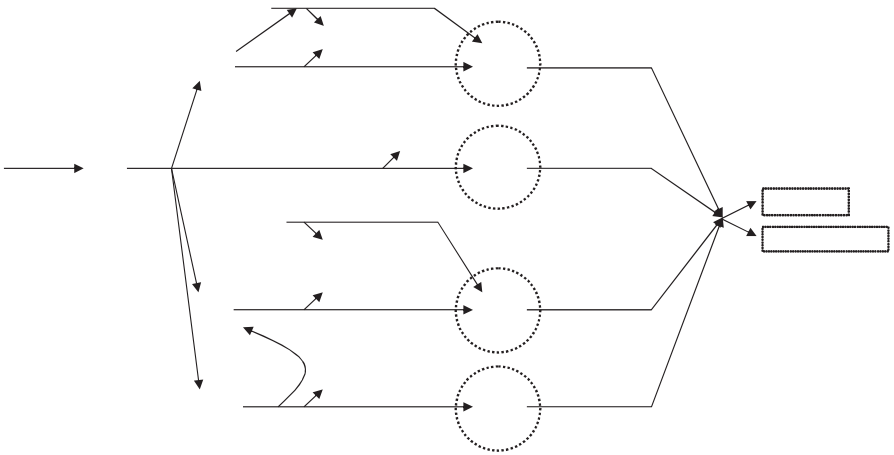

S_{NHX}, S_{Mg}
S_{Ca}



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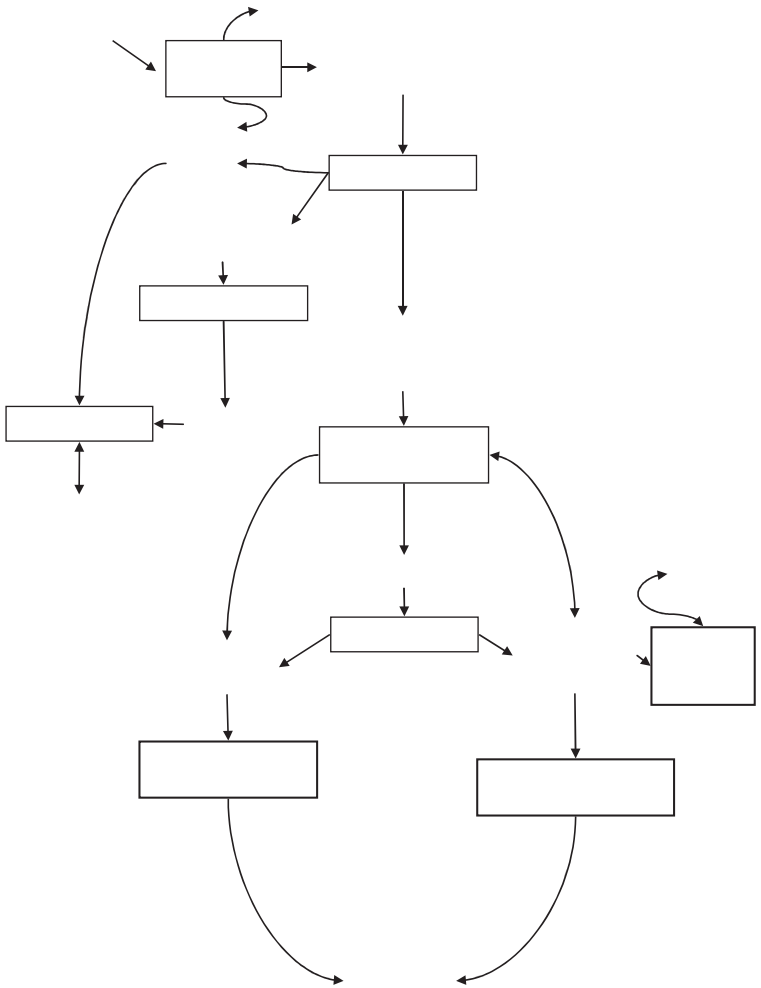
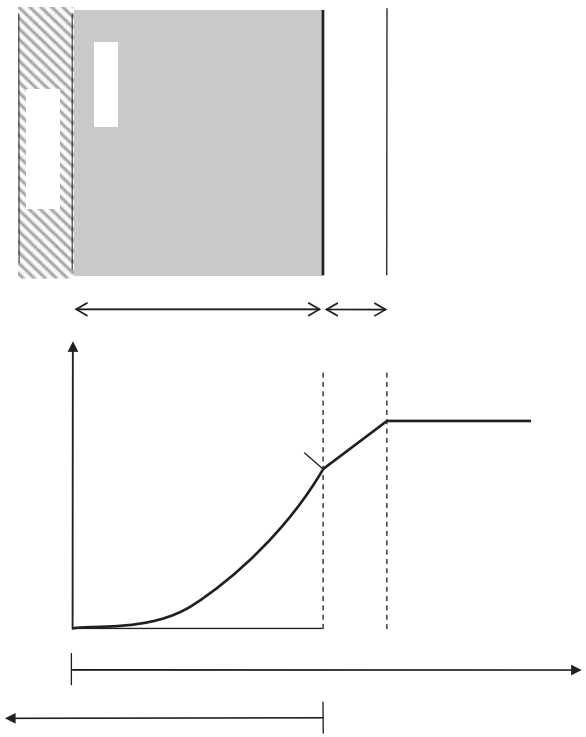
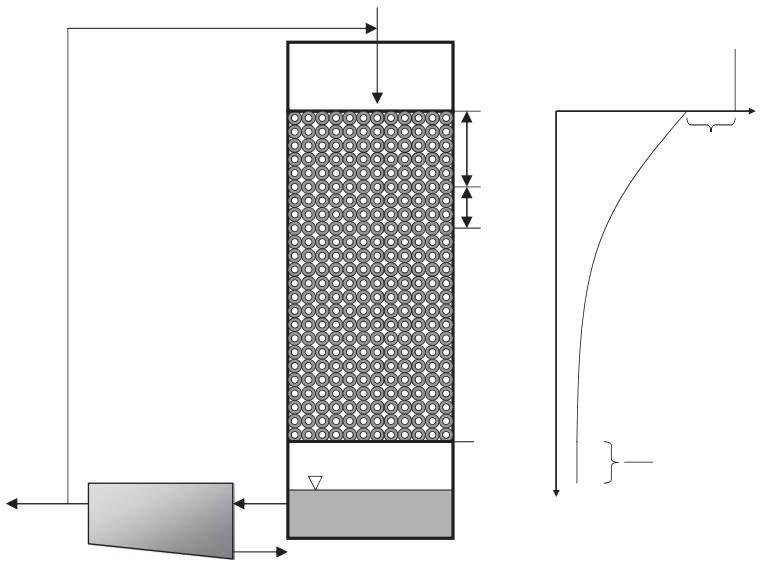
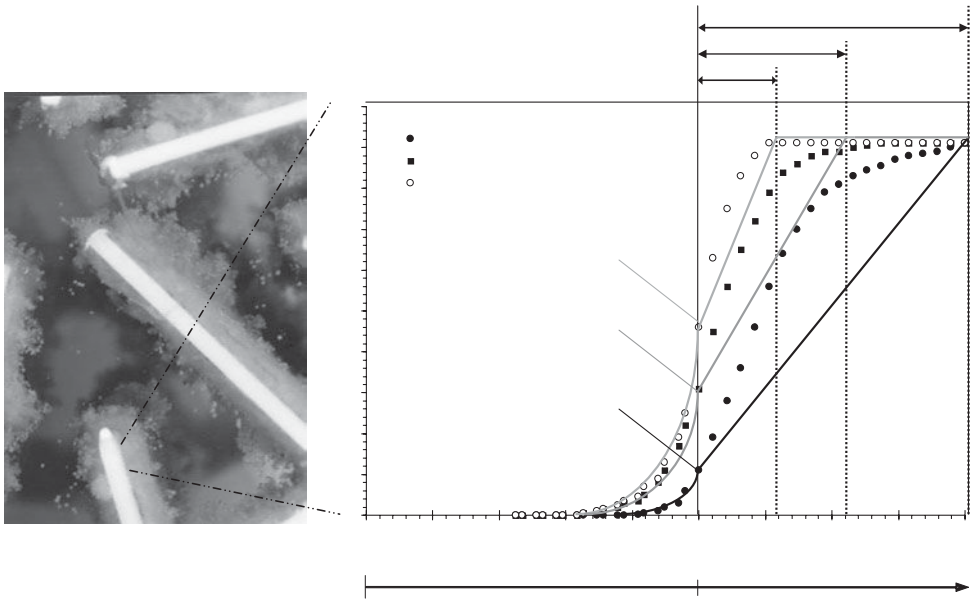
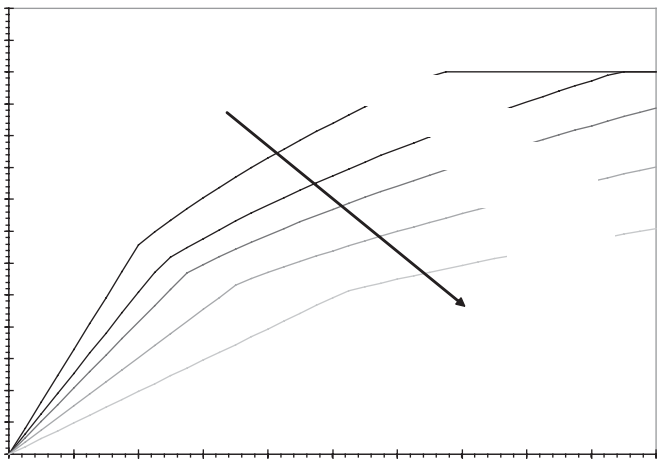
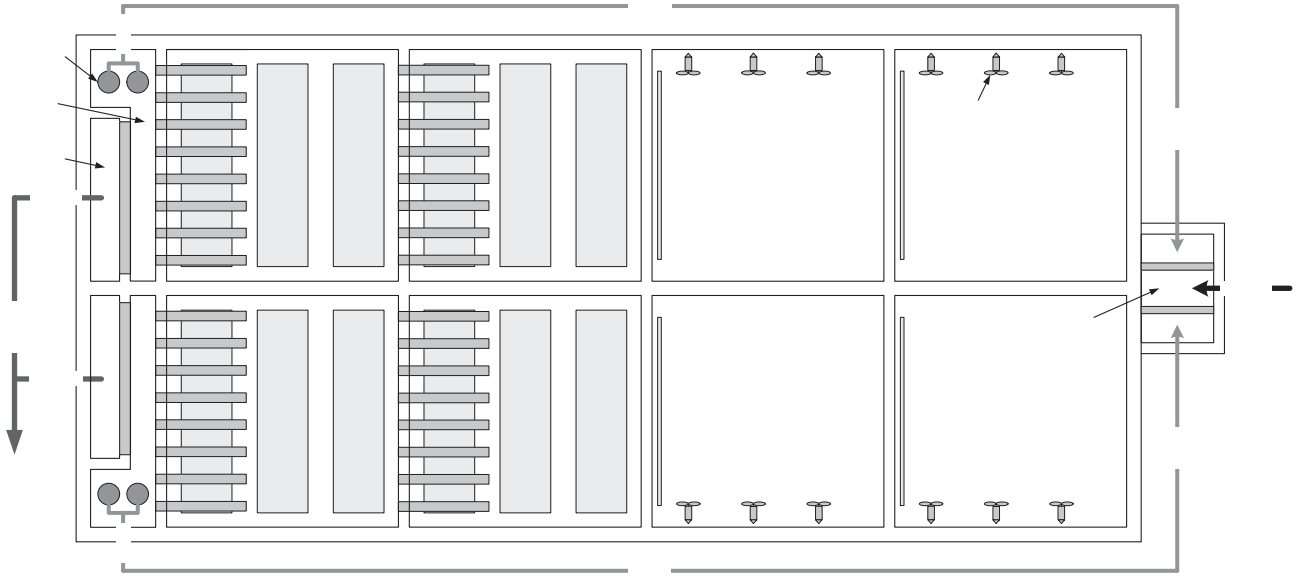


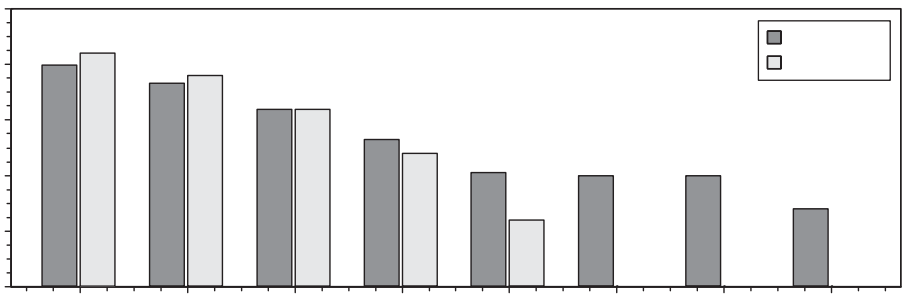


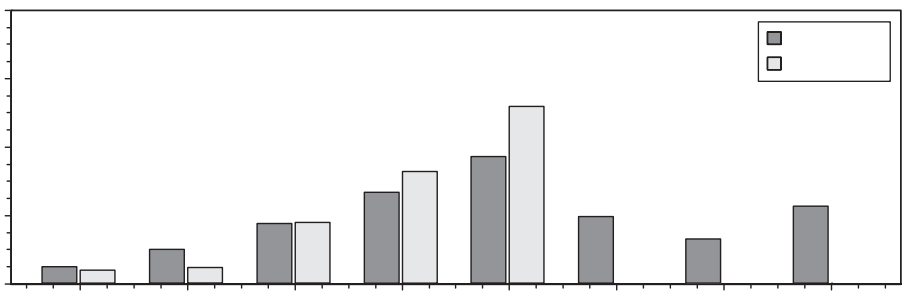


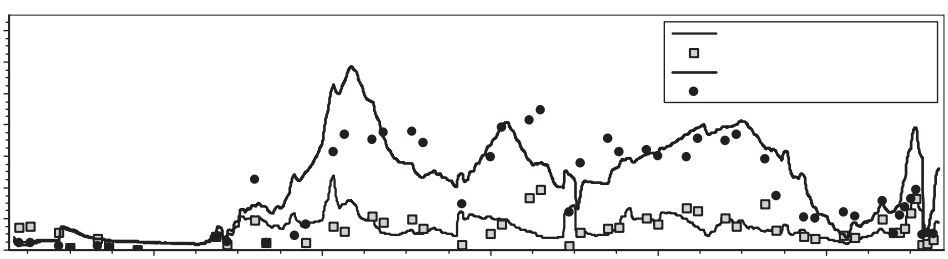


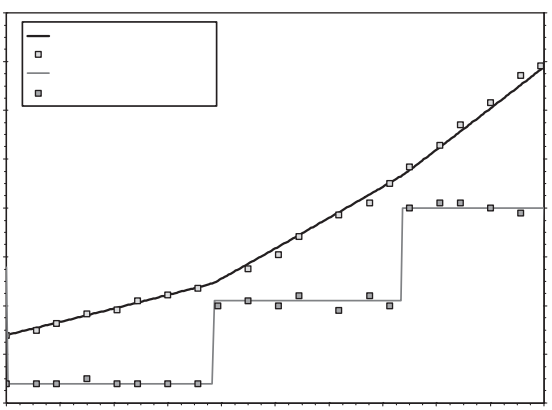


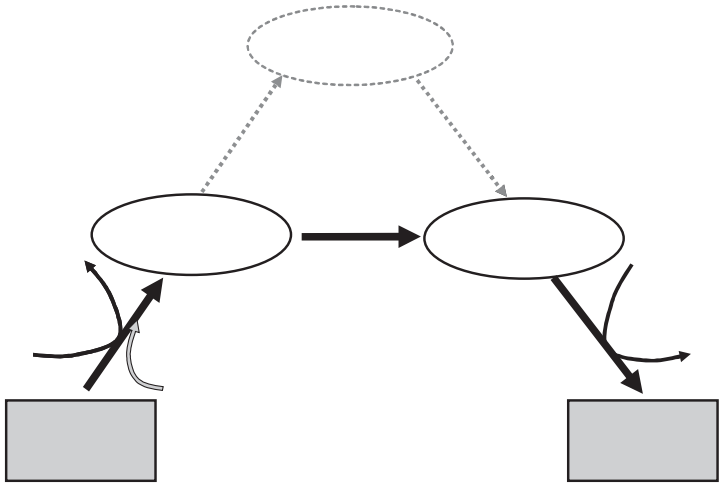


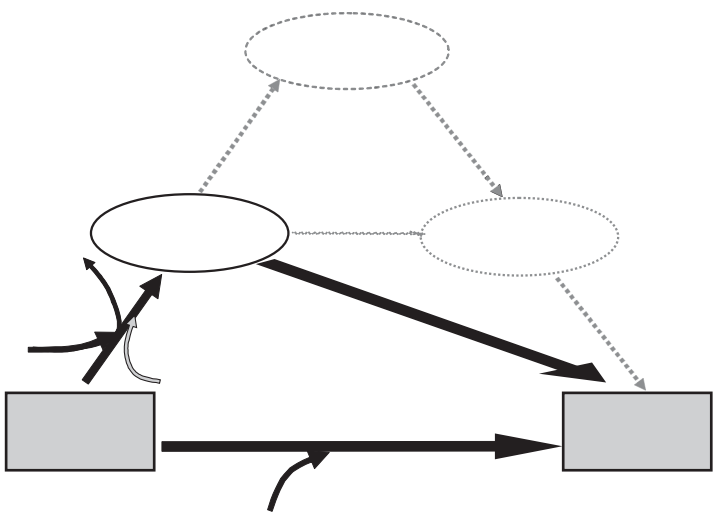


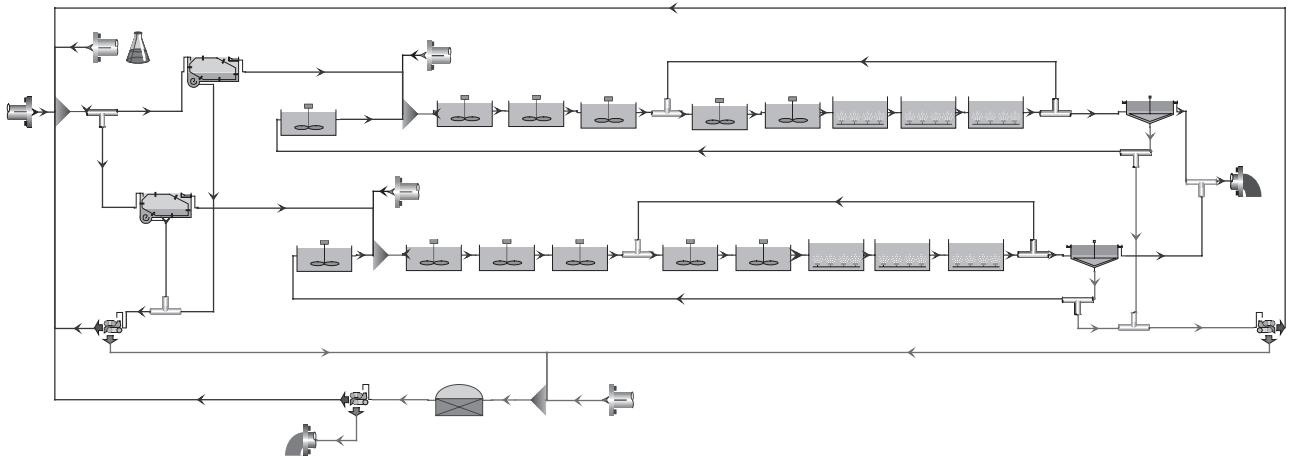


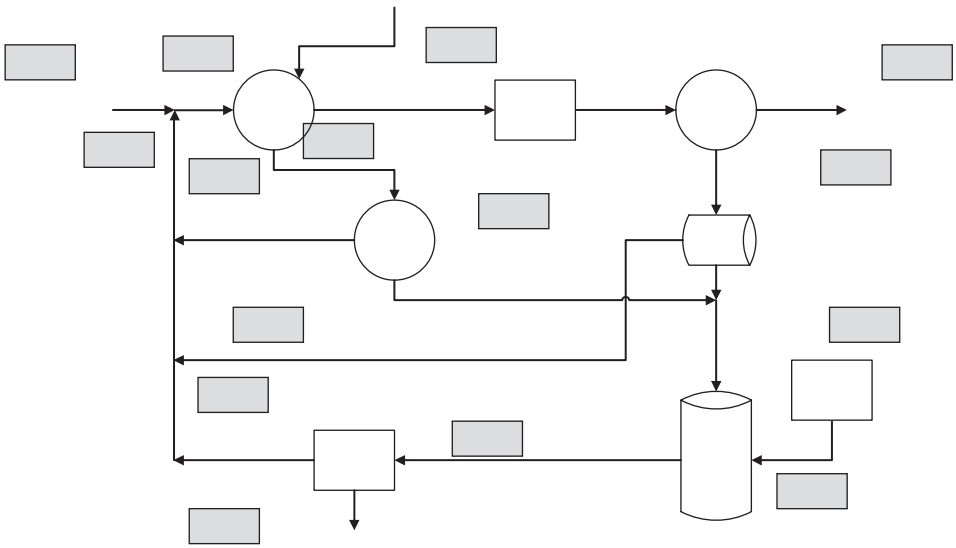


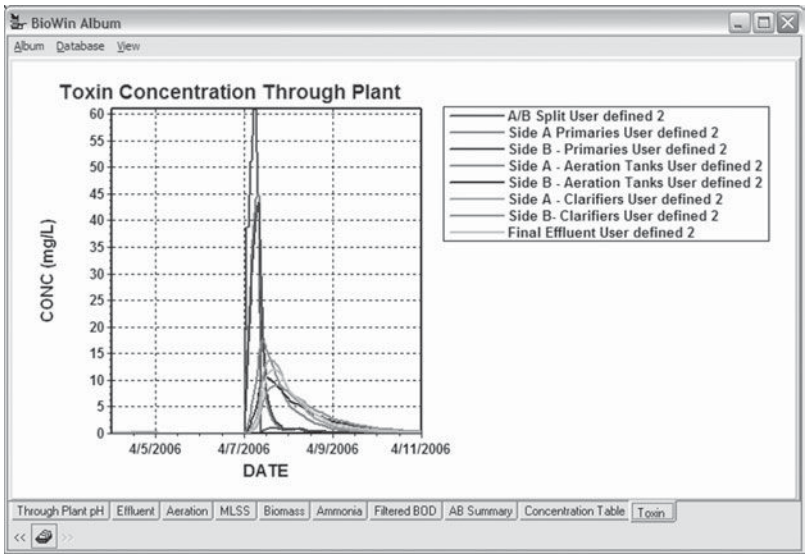


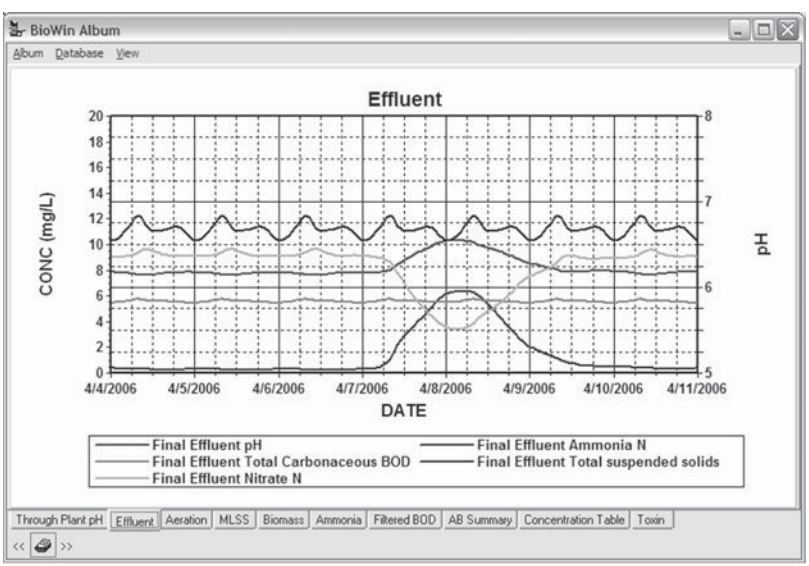









BioWin Album
Album Database View
Toxin Concentration Through Plant
CONC (mg/L)
DATE
4/5/2006
4/7/2006
4/9/2006
4/11/2006
A/B Split User defined 2
Side A Primaries User defined 2
Side B - Primaries User defined 2
Side A - Aeration Tanks User defined 2
Side B - Aeration Tanks User defined 2
Side A - Clarifiers User defined 2
Side B- Clarifiers User defined 2
Final Effluent User defined 2
Through Plant pH
Effluent
Aeration
MLSS
Biomass
Ammonia
Filtered BOD
AB Summary
Concentration Table
Toxin


BioWin Album
Album Database View
Effluent
CONC (mg/L)
pH
DATE
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4/5/2006
4/6/2006
4/7/2006
4/8/2006
4/9/2006
4/10/2006
4/11/2006
Final Effluent pH
Final Effluent Ammonia N
Final Effluent Total Carbonaceous BOD
Final Effluent Total suspended solids
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Through Plant pH
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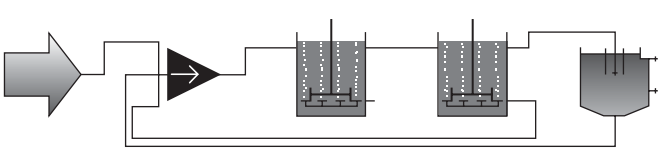
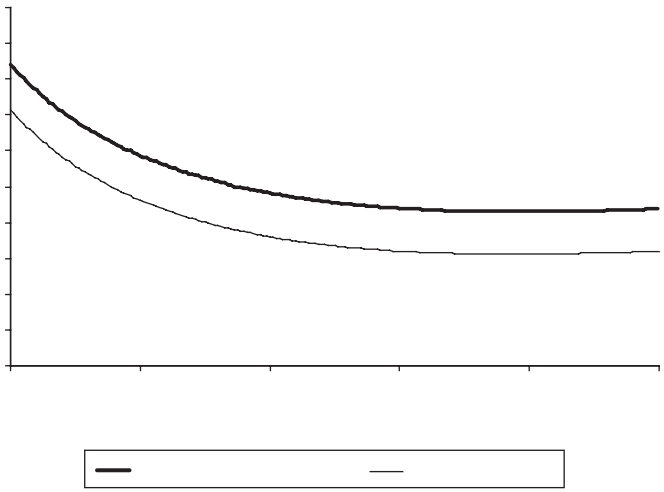
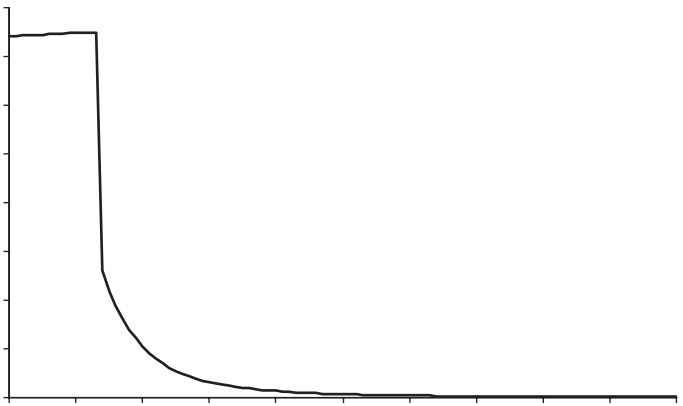
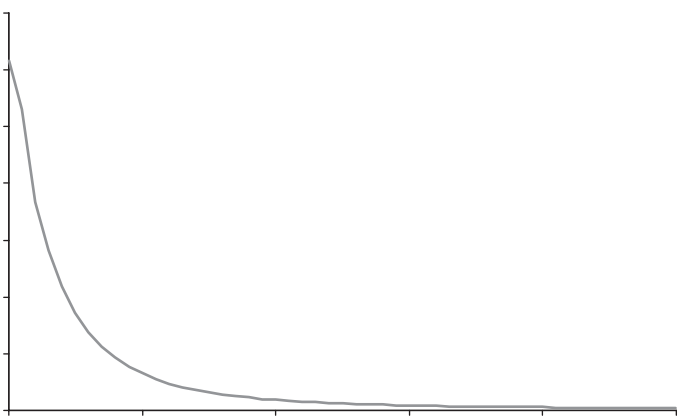
MLSS
Biomass
Ammonia
Filtered BOD
AB Summary
Concentration Table
Toxin









Different options are available for implementing process control within a WWTP. Process control may involve one or all of the following approaches:

- Process design. One of the most effective methods of control is to attenuate disturbances by incorporating appropriate plant design features. An example is the inclusion of equalization tanks to balance influent and return stream flow and concentration variations.
- Fixed operating strategies. These strategies typically involve using constant or proportional pumping rates and flow distributions (e.g., constant or proportional RAS and internal recycle flows, constant WAS flow, fixed step feed distribution). The settings used could be based on experience or taken from modeling studies.
- Feedback control. Feedback control systems use measured process output variables (controlled variables) to make automatic adjustments to process input variables (manipulated variables) using a control algorithm.
- Model-based control. Model-based systems use a process model to assist in the calculation of their control actions. This can range from simple, model-based control calculations (e.g., waste rate calculated from SRT calculation based on average values) to feedforward/feedback control to complex model-based controllers.

Control systems can be manual in which operators observe the plant and implement control actions manually, or they can be automatic in which control loops use feedback or model-based control. Automatic control systems typically consist of local regulatory control loops that are managed by a SCADA system.

4.7.2 Feedback Control

A diagram of a typical feedback control system or loop is shown in Figure 10.35 (Marlin, 2000). As shown, a feedback control system uses outputs from the system, typically measured values, to determine values for inputs to the system so that desired values for the controlled variables can be achieved.

Basic feedback control algorithms include on/off, proportional-integral-derivative (PID), and cascade.

On/off control is a form of feedback control that is used in a variety of applications. For example, household heating and cooling systems operate using on/off control. Intermittent aeration systems, level controllers, and some pumping controls may use on/off control.

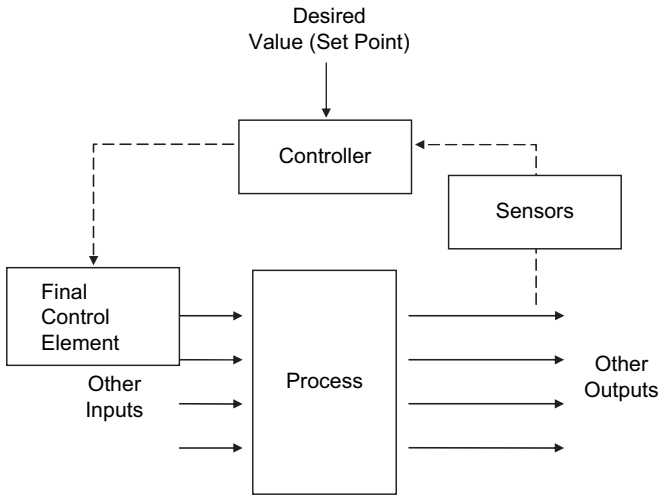


FIGURE 10.35 Typical structure of a feedback control system (adapted from Marlin, 2000).

The PID controllers are used widely in WWTP applications because of their simplicity and good performance for basic single-loop control applications. In continuous form, the PID controller algorithm with built-in derivative kick protection is given by:

$$MV(t) = K_c \cdot \left(E(t) + \frac{1}{T_I} \int_0^t E(\tau) d\tau - T_D \cdot \frac{dCV(t)}{dt} \right) + I \tag{10.48}$$

Where,

MV = manipulated variable;
CV = controlled variable;
E = controller error (setpoint = CV);
K_c = proportional gain, a controller tuning constant;
T_I = integral time, a controller tuning constant;
T_D = derivative time, a controller tuning constant;
I = initialization constant; and
t = time.

Derivative kick protection involves using the rate of change in the controlled variable instead of the setpoint error. This prevents large jumps from occurring in the manipulated variable as the result of setpoint changes.

The proportional gain, K_c, integral time, T_I, and derivative time, T_D, are controller tuning constants. The controller must be tuned for each specific application, and the tuning may need to be changed over time if the process being controlled is significantly nonlinear. The initial tuning constants can be determined using tuning rules or correlations and then fine-tuned using process simulation and plant tests (Ciancone and Marlin, 1992; Rivera et al., 1986; Ziegler and Nichols, 1942). Some simulators offer auto-tuning modules that determine tuning parameters by running step tests using the process model and then calculating the tuning constants based on tuning correlations.

The individual modes of the PID controller can be used individually or in pairs; common combinations include proportional-only and proportional-integral control, in addition to full PID control. As the majority of PID controllers are now implemented using computers, the discrete form of the PID algorithm is used more frequently than its continuous form. The discrete form is the version typically implemented in WWTP simulation platforms.

The velocity form of the digital PID equation is recommended because it has built-in protection against rest windup as long as the controller tracks past values of the manipulated variable that are actually implemented (Marlin, 2000). Reset windup occurs when a persistent, nonzero setpoint error results in a large value of the integral mode of the PID, forcing the control action to "saturate" (i.e., to maintain the manipulated variable at its minimum or maximum value). Even when the setpoint error returns to zero, the control action remains saturated. When using the velocity form, the control action can return to within the control range after one sampling period.

In the velocity form (eqs 10.49 and 10.50), the change in the control action is calculated at each control interval as:

$$\Delta MV_N = K_c \left(E_N - E_{N-1} + \frac{\Delta t}{T_I} E_N - \frac{T_d}{\Delta t} \left(CV_N - 2CV_{N-1} + CV_{N-2} \right) \right) \tag{10.49}$$

$$MV_N = MV_{N-1} + \Delta MV_N \tag{10.50}$$

Where,

' MV_N = change in the manipulated variable at control interval N;
CV_N = controlled variable at control interval N;
E_N = controller error at control interval N; and
' t = controller execution interval.

Bounds on the manipulated variable values and on the rate of change frequently are used to reflect limitations because of physical equipment or safety.

Cascade control is a special case of feedback control where two feedback controllers are used. The output of the primary controller, or master, serves as the setpoint for the secondary controller, or slave. It is used to improve upon the performance of a single-loop controller in cases where disturbances and nonlinearities affect the secondary-loop manipulated variable and where the secondary-loop dynamics are much faster than the primary-loop dynamics. An example would be in dissolved oxygen control where the primary dissolved oxygen controller sends an airflow rate setpoint to a flow-rate controller manipulating a valve (Olsson and Newell, 1999).

Most WWTP simulation platforms provide the capability of implementing and testing basic feedback controllers. These controllers may be included as part of the unit process setup menus for common control loops such as dissolved oxygen and SRT control or may be configurable using separate controller modules. Table 10.11 provides a list of feedback control loops that are typically preconfigured or can be created easily within a WWTP simulator.

Table 10.11 Typical feedback control loops modeled in wastewater treatment plant simulators.

Unit process	Controlled variable	Manipulated variables
Influent	Influent flow	Pumping rates, flow split fractions, bypass flowrate
Primary treatment or gravity thickening	Sludge depth	Sludge pumping rate
Chemical addition	Orthophosphate concentration	Metal salt addition rate
Activated sludge	Dissolved oxygen in aeration tanks or basins	Airflow
	Solids retention time or mixed liquor suspended solids (MLSS)	Waste activated sludge flowrate
	MLSS	Step feed flowrates
	Sludge depth in secondary clarifiers	Return activated sludge flowrate
	Effluent total nitrogen or nitrates	Internal recycle rate and/or carbon addition
Gravity belt thickening	Solids capture	Polymer flowrate

4.7.3 Controller Interaction

When implementing numerous feedback loops within a plant, it is important to consider potential interactions between the controllers. The concern is that the actions of one controller may influence controlled variables in other loops. Interaction is especially important when two control loops have similar response times. There are a wide range of response times found within a WWTP and this can be beneficial for plant control. For example, dissolved oxygen controllers operate on a time-scale of minutes to hours and SRT controllers work on a scale of days to weeks, which minimizes the interaction between the two control systems.

Controller interactions can be studied using relative gain array techniques (Shinskey, 1988) or using process simulation. In control systems with low dimensionality (i.e., small number of control loops), a technique known as decoupling can be used to minimize interactions (Marlin, 2000). Multivariable model-based controllers are better suited for systems with many manipulated and controlled variables.

4.7.4 Model-Based Control

The most common example of model-based control is feedforward control. In feedforward control, an input disturbance is measured, and the controller adjusts the manipulated variable to compensate for the disturbance before the controlled variable deviates from its setpoint. Feedforward control depends on models for the disturbance and the process. These models are typically first order with dead-time models derived from plant tests or process modeling. Derivation of the discrete feedforward controller equation involves the use of z-transforms.

Feedforward control is typically combined with feedback control to retain the beneficial properties of feedback. Feedforward/feedback control is considered when feedback control alone is unsatisfactory, and a feedforward variable exists that indicates the occurrence of an important disturbance.

Ratio control is a simple form of feedforward control. An example is the ratio control of RAS rate to the influent flow rate, which acts as a disturbance to the activated sludge process. Other examples of feedforward control include using the influent flow as a feedforward variable in a dissolved oxygen control system, or using online respirometry to provide feedforward information on toxicity or biodegradable influent COD (Olsson and Newell, 1999).

Model-based control also can involve using mass balances or simple models to calculate necessary control actions given other measured variables. A simple example

is the use of the definition for SRT to calculate the required WAS flow for an activated sludge process. The steady-state SRT definition can be rearranged to solve for the average waste flow rate given the desired SRT and averaged values of the MLSS and WAS TSS. This expression could be simplified further to hydraulic wasting using a mass balance around the clarifier that ignores effluent solids (Brewer et al., 1995).

Optimal feedback control is a form of model-based control that calculates control actions that optimize a performance criterion (objective function) subject to constraints (process model). It is well suited to multivariate problems because it calculates optimal control actions that account for process interactions. Linear quadratic control is a specific form of optimal control that uses a quadratic objective function, J, that is constrained by a linear process model expressed in the form of deviations from an operating point or setpoint as shown in eqs 10.51 and 10.52:

$$J = \int_0^t \left(\underline{x}^T Q \underline{x} + \underline{u}^T R \underline{u} \right) dt \tag{10.51}$$

subject to

$$\frac{d\underline{x}}{dt} = A\underline{x} + B\underline{u} \tag{10.52}$$

Where,

$\underline{x}$ = vector of state variables expressed as deviations from their setpoints;
$\underline{u}$ = vector of control actions;
A, B, C = Jacobian matrices; and
Q, R = weighting or tuning matrices.

The objective function is a weighted sum of squares of process states (in deviations) and inputs (manipulated variable actions).

The linear quadratic controllers can be configured for single-input single-output (SISO) and multiple-input multiple-output (MIMO) control problems. The use of the model helps eliminate interaction that can be a problem with multiple SISO control loops.

Different forms of linear quadratic controllers exist depending on the selected objective function and control horizon. Traditional linear quadratic controllers use an infinite or long control horizon and their control actions are equivalent to a multivariable proportional controller. Integral action can be added by using the change in the control actions in the objective function or by using a nonstationary disturbance model as part of the model equations.

Dynamic matrix control (DMC) uses a step-response model for the process and disturbances instead of state space models and is considered a model-predictive controller (Cutler and Ramaker, 1979). The DMC can be viewed as a special case of linear quadratic control with a finite prediction horizon. It calculates several future adjustments to the manipulated variables to minimize setpoint errors based on the predicted model response (with control) over the control horizon. The predicted setpoint error trajectory incorporates measured disturbances and forecasts unmeasured disturbances to introduce both integral and feedforward action into the controller. Constraints on the manipulated variables can be incorporated into the DMC structure (e.g., quadratic dynamic matrix control, or QDMC).

Optimal model-based controllers have not been used extensively in WWTPs, because most of the control loops can be handled by PID controllers. Their use is best for certain specific control loops or in supervisory control systems that calculate optimal setpoints for lower-level regulatory controllers. Some potential applications of optimal model-based control include control of effluent ammonia and nitrate by manipulating external carbon addition, internal recycle rate, and dissolved oxygen setpoint and the control of effluent PO_4-P concentration by manipulating acetate addition (Olsson and Newell, 1999). In the future, model-based controllers may become more important as regulatory concerns force plants to achieve high levels of nutrient removal while operating near constraints. Some WWTP simulators allow interfacing with control design software such as the MATLAB® Control System Toolbox. For example, a linear quadratic controller could be designed in MATLAB® and then used to calculate control actions during simulations.

4.7.5 Modeling of Sensors and Actuators

When modeling a control system for design, it can be useful to include models of the sensors and actuators to understand how their dynamics can affect the system. Sensors and actuators add delays and filtering to the dynamic response. Sensors also are subject to measurement noise, drift, recalibration and cleaning, and failures. These factors need to be accounted for when implementing a control system. Sensors or controllers typically incorporate filtering and basic fault detection or validity checks that can be incorporated into models (Schraa et al., 2005).

Sensors often are modeled as first-order processes with delay. See Rieger et al. (2003) for a discussion of models for WWTP-related sensors and Stephanopoulos (1984) for a discussion of models for sensors and actuators in the process industries. See Vanrolleghem and Lee (2003) for a summary of the sensors available for WWTPs.

4.7.6 Controller Performance Assessment

The performance of control systems can be analyzed using performance measures such as integral error, decay ratio, rise time, and settling time (Stephanopoulos, 1984). In addition, more comprehensive analyses can be performed using techniques such as frequency response, autocorrelation analysis, and dynamic simulation (Box and Jenkins, 1976; Stephanopoulos, 1984).

Dynamic simulation is the most comprehensive approach because it allows for the use of nonlinear models, can consider a wide range of input-forcing functions such as diurnal flow and concentration patterns, and can track all important plant variables throughout the transient response. Most simulators have the flexibility to allow performance measures such as integral error, decay ratios, and rise time to be incorporated to simulations using user-defined programming code.

Frequency response techniques are applicable for linear models and are useful in analyzing the capability of a control system for rejecting disturbances at different frequencies. Most feedback control systems have a frequency response as shown in Figure 10.36. In Figure 10.36, the amplitude ratio (absolute value of CV/absolute value of disturbance) is plotted versus frequency. This type of plot displays the ability of the control system to reduce the amplitude of disturbances across a frequency range. As shown, the control system can reject disturbances at low frequencies because of its feedback action. High-frequency disturbances are attenuated by the filtering effect of the process. There is a resonant peak at intermediate frequencies where the control system cannot reject disturbances and may actually amplify them. Therefore, the response speed of the process being controlled and the attenuation provided by the plant provide limits on the capabilities of the control system.

A practical example in a WWTP is an automatic SRT feedback controller. Diurnal variations in influent flow are too fast to be rejected by the control system because the time constant of the activated sludge process in response to wasting changes is typically two to three SRTs. Therefore, only the process can attenuate these disturbances through equalization tanks and holdups in other unit processes.

Autocorrelation analysis involves the study of the patterns in the autocorrelations of the setpoint errors over time. These patterns can help identify poorly tuned controllers, sensor problems, unusual disturbances, and model mismatch problems in model-based controllers. Autocorrelation analysis typically is used on actual performance data from the control system but could also be used with simulated results.

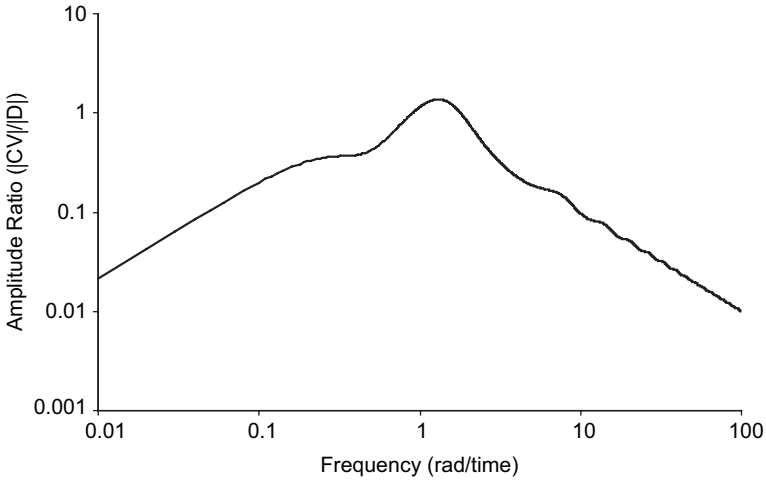


FIGURE 10.36 Closed-loop frequency response of a typical proportional-integral-derivative feedback control system.

4.7.7 Practical Issues

There are several practical issues that must be considered when implementing a process control system (Marlin, 2000):

- Correct selection of sensor and actuator ranges, which is essential for good control;
- Processing of input signals or data, which may involve basic validity checks, filtering, and fault detection;
- Selection of setpoint limits to prevent unreasonable values especially in cascade control systems;
- Provisions for controller initialization, especially when controlling variables inferred through model calculations; and
- Providing limits on the manipulated variables and/or their rate of change.

Process simulation provides a means of determining the best settings and algorithms for handling the above issues before the controller is implemented in the plant.

4.7.8 Application Example

As an example, consider the example plant shown in Figure 10.31, without the anoxic tank. Influent conditions and operating conditions are identical except that the SRT is maintained at 8 days with an MLSS and MLVSS of 1900 and 1700 mg/L, respectively.

The plant is modeled in GPS-X. The user can specify the controller algorithm (P, PI, or PID), sampling (or execution) interval, dissolved oxygen setpoint, and tuning parameters. The PI feedback controller controls the simulated dissolved oxygen by adjusting the airflow. In reality, the dissolved oxygen controller would often adjust the setpoint of an airflow controller manipulating an airflow control valve, and a pressure controller would be used to maintain a specified pressure in the air distribution header.

Dynamic simulations were conducted for one day using manual (fixed airflow) and automatic control. The influent flow was varied according to a diurnal pattern. The fixed airflow rate was selected to ensure dissolved oxygen of 2 mg O_2/L at the maximum influent flow. The dissolved oxygen setpoint for automatic control was set at 2 mg O_2/L. In Figure 10.37, the modeled dissolved oxygen concentration is shown for the manual and automatic control cases. Figure 10.38 displays the modeled airflow for both cases. As shown, the airflow rate is lower for the automatic control case. In this way, modeling could be used to determine airflow and, therefore, energy savings with different control strategies and to determine an optimal control strategy. The model can calculate the total airflow consumption, which can help with comparing alternative strategies. In this example, the automatic control case used 16% less total volume of air than for a fixed airflow.

Another control strategy that can be explored using a WWTP simulator is to have a cascade control system where an ammonia controller (based on ammonia nitrogen measurements in the activated sludge tank) manipulates the setpoint of a dissolved oxygen controller or an SRT controller. Figure 10.39 compares the effluent ammonia nitrogen simulation results for the following cases: fixed airflow, dissolved oxygen control with a setpoint of 2 mg O_2/L, and ammonia control with an ammonia nitrogen setpoint of 1 mg N/L. As shown, the ammonia controller provides the best performance because it better determines the airflow required to meet nitrification demand. The improved performance comes at the expense of increased airflows during periods of peak demand as compared with the other two control strategies (see Figure 10.40). Total airflow required is similar for the fixed flow and ammonia control cases. This example is conceptual and may not be practical because of the difficulty

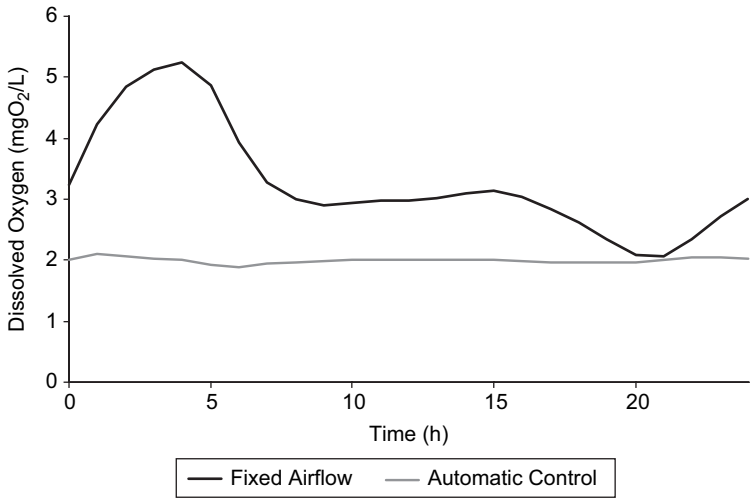


FIGURE 10.37 Modeled dissolved oxygen concentrations with manual (fixed airflow) and automatic control.

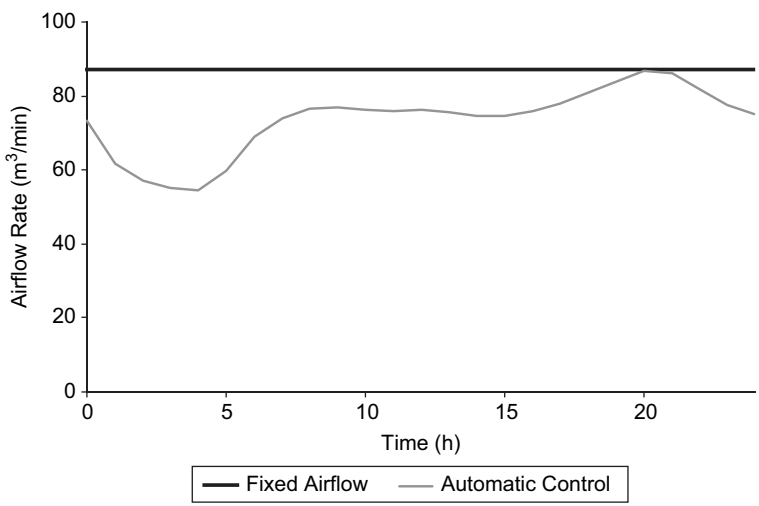


FIGURE 10.38 Modeled airflow rates with manual (fixed airflow) and automatic control.

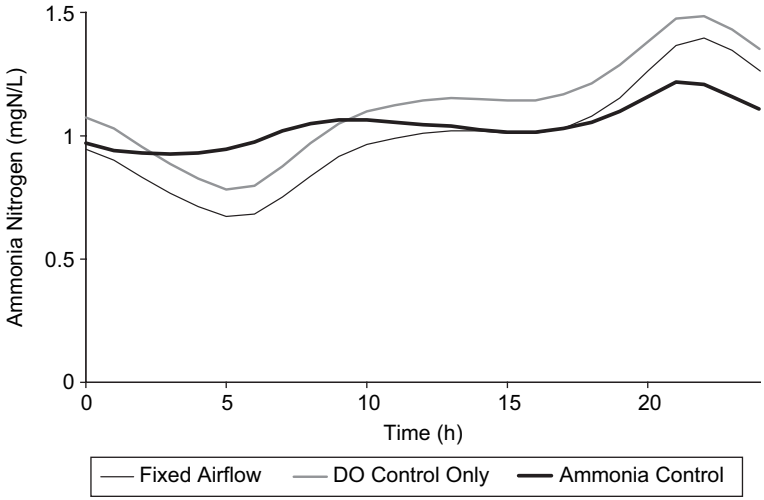


FIGURE 10.39 Modeled effluent ammonia nitrogen with manual control, dissolved oxygen (DO) control, and ammonia control.

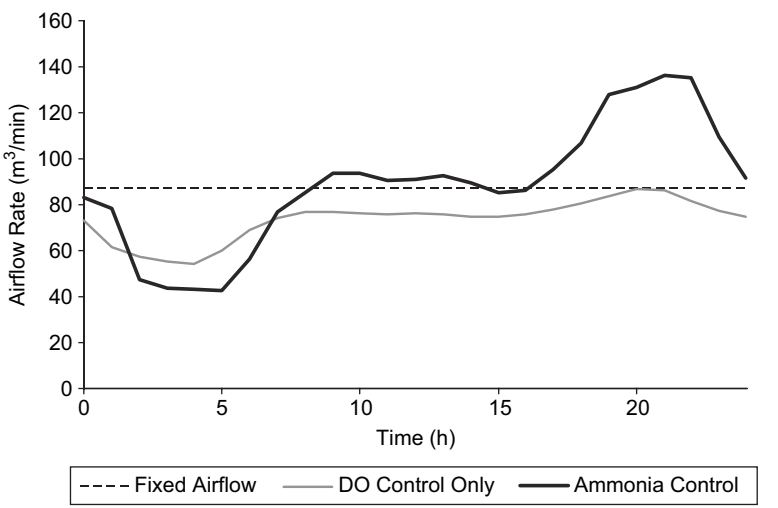


FIGURE 10.40 Modeled airflow rates with manual control, dissolved oxygen (DO) control, and ammonia control.

with measuring ammonia to a high degree of accuracy. A plant model alternatively could be used as a soft sensor to estimate the effluent ammonia for the purposes of control.

If a WWTP simulator is being used for control design, the user can experiment with controller tuning and can add more details to the control system model such as sensor dynamics, transportation delays, and stochastic disturbances which will make the simulations as realistic as possible.

4.8 Online Modeling

Online modeling systems collect plant data in real time and use these data in WWTP models to assist with plant analysis, control, and optimization. The objectives of online modeling as outlined by Takács et al. (1998) may include

- Reduction in duration and frequency of water quality effluent excursions;
- Ability to cope with unusual plant operating conditions;
- Reduction in energy costs;
- Deferred capital expenditures because of optimal use of existing facilities; and
- Reduction in the overall pollutant loadings to receiving water bodies.

Online modeling systems can range from monitoring systems for single process units to comprehensive monitoring, control, and optimization systems for entire WWTPs. The basic structure of an online modeling system is outlined below:

(1) Data validation—basic signal processing;
(2) Model updating—data reconciliation, parameter estimation and tracking, fault detection and diagnosis;
(3) Model-based analysis—troubleshooting, forecasting, and optimization; and
(4) Results validation—determine if results to be implemented in plant are reasonable and should be sent to the process control system.

These steps may overlap because certain tasks may be performed simultaneously. For example, data reconciliation and parameter estimation can be performed simultaneously. Other steps may be omitted depending on the objectives of the system. For example, optimization may not be performed or the optimized results may be provided to the SCADA but only implemented if desired by the operators.

To date, few full-scale implementations of online modeling have been reported in the literature. One early example is the Integrated Computer Control System (IC^2S) developed by Takács et al. (1998). The IC^2S system included several building blocks: a dynamic WWTP simulator (GPS-X); data filtering and fault detection algorithms; an autocalibration tool; off-line analysis and forecasting modules; a control design module; and a process optimizer. Other examples of online modeling systems are given by Jumar and Tschepetzki (2002).

In addition to online modeling, other systems have been developed to promote use of models by onsite staff. Examples from the literature include operator training systems and plant-specific simulators or decision support tools (Amerlinck and Printemps, 2004; Fonseca et al., 2003; Schraa et al., 2008). These systems provide operations personnel with simulation tools for troubleshooting, training, and conducting "what-if" studies. The objective is to create user-friendly simulation models with predefined input parameters, output graphs, and scenarios, with interface images that are similar to existing plant diagrams or SCADA screens. The simulation framework typically allows for use of online data in the model for forecasting plant performance.

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Chapter 11

Troubleshooting for Full-Scale Nutrient Removal Facilities

(continued)

1.0 OVERVIEW

This chapter focuses on the fundamental principles and concepts that a process designer should consider to troubleshoot design and to optimize performance of a biological nutrient removal (BNR) facility. Many of the principles mentioned in this chapter have been discussed in greater detail in earlier chapters, but a certain level of overlap is necessary for an effective discussion on troubleshooting. Nitrification, denitrification, and phosphorus removal principles often are discussed together because of their interrelationships. This chapter is organized into four sections. The first section covers important elements of a process assessment when troubleshooting a BNR facility. This includes a troubleshooting matrix in Section 2.6 that summarizes potential causes and remedial steps for several of the most common performance problems experienced at nutrient removal facilities. The second section focuses on physical aspects, such as plant hydraulics and mechanical equipment, that can contribute to operational and performance problems. The third and fourth sections discuss troubleshooting for chemical phosphorus removal and tertiary denitrification attached growth processes, respectively.

The reader can reference *Biological Nutrient Removal Operation in Wastewater Treatment Plants* for a comprehensive troubleshooting guide developed for operators to systematically identify the cause and effect for their performance challenges (Water Environment Federation [WEF], 2005). This chapter is written to introduce the fundamental principles behind many of the challenges experienced at nutrient removal facilities, using examples and case studies where possible to emphasize a point.

2.0 PROCESS ASSESSMENT

One of the first activities when troubleshooting a BNR facility is to conduct a thorough process assessment to identify the design and operational issues that may be contributing to the problems being experienced. The process assessment should include a review of influent wastewater characteristics, key operating parameters, and several microbiology and kinetic factors that may be influencing plant performance. This section discusses the key points in each of these areas.

2.1 Wastewater Characterization

Influent wastewater characteristics significantly influence the operation and performance of a BNR facility. It is important to understand site-specific influent nitrogen and phosphorus speciation and the quantity and quality of carbon to support BNR. Although these issues are discussed in other chapters, they are examined here from the perspective of assessing the performance of a BNR facility.

2.1.1 Sampling

In many cases, sampling plans are developed primarily for meeting regulatory reporting requirements and documenting plant performance, rather than for gathering data for troubleshooting and optimizing plant operations. Consequently, it may be necessary to adapt the sampling program to obtain data that can be helpful in identifying operating problems or inefficiencies.

Process modeling using simulator packages, such as BioWin or GPS-X, are not only powerful tools in design but also for troubleshooting plant operations and performance. The sampling program must be designed to consider specific process and basin configuration and overall performance requirements. Sampling protocol should be reviewed to ensure that sample location, collection frequency, sample type, and analytical procedures are appropriate for collecting accurate data that will help guide the operation and will document the performance of each unit process. To ensure that representative samples are being collected, sampling lines should be located at points of high energy, mid-depth, and away from basin corners where there may be stratification of solids and other pollutants.

Most influent parameters are measured on a time- or flow-composite basis collected over a 24-hour period. Diurnal variations in mass loading, however, can have severe impacts on BNR plants, especially when treatment objectives include at or near-limits of technology (LOT) discharge limits. The LOT is defined as the lowest levels of phosphorus and nitrogen species that could be achieved without excessive cost or additional treatment steps. Typically, this is total nitrogen (TN) and phosphorus effluent concentrations of less than 3 and 0.3 mg/L, respectively. When a

facility must meet LOT, collecting diurnal information on both weekdays and weekends can be helpful to pinpoint performance problems. Whole-plant mass balance process modeling can be effective in troubleshooting BNR performance because it can identify inconsistencies between actual operating data and model predictions. These inconsistencies can provide valuable insight to the root cause of a performance problem. To assist in the calibration of a whole-plant mass balance model, the sampling plan should include collection of nitrogen, phosphorus, and chemical oxygen demand (COD) concentrations at intermediate points in the plant. Although five-day biochemical oxygen demand (BOD_5) values also could be helpful, process simulation models typically use COD as the basis for their calculations. This is because the relationship between BOD_5 and the ultimate BOD (BODu) varies from one plant to the next and the addition of inhibitors in the BOD_5 test to prevent nitrification may affect the carbonaceous BOD_5 determination. Plant sidestreams, such as decant from aerobic or anaerobic digesters and thickening and dewatering processes, can contribute significantly to the phosphorus and nitrogen loads that must be taken into account when assessing nutrient removal efficiency and plant performance.

Sampling and analysis of sludge streams are necessary to define accurately the sludge production and to validate the calibration of a process model. Most problems arise from inaccurate hydraulic measurements of return streams. One effective strategy used to evaluate the accuracy of sludge production data is to see whether it is possible to close an inert solids mass balance around the plant (i.e., the difference between the total suspended solids [TSS] and volatile suspended solids [VSS]). This works because inert material is not affected by biological or chemical reactions when no chemicals of consequence are added to the process. One exception to this rule that must be accounted for is that inert phosphates do accumulate in the sludge of a biological phosphorus removal process. Developing an inert solids balance can also help pinpoint problems related to sampling locations, analytical procedures, or flow metering that result in inaccurate sludge data collection. A phosphorus balance throughout the plant could also be used to validate data accuracy because phosphorus is not destroyed by biological treatment and chemical reactions taking place in a BNR plant. Consequently, the difference between the total influent and effluent phosphorus mass must be equal to the phosphorus mass in the sludge. Characterization of the carbonaceous material in terms of COD is preferred over BOD_5 or total organic carbon (TOC) because COD is a more consistent basis for quantification of sludge production, oxygen demand, and mass balances (Water Environment Research Foundation [WERF], 2003). The sampling plan should include analysis of the COD, soluble COD after filtering through a 0.45 micron paper or membrane filter, and flocculated filtered

COD (ffCOD) for the plant influent, primary effluent, and secondary effluent. The difference between the ffCOD of the primary effluent and that of the final effluent of a long solids retention time (SRT) activated sludge process is the biodegradable soluble COD, which is related closely to the readily biodegradable COD (rbCOD). Developing a total COD, BOD_5, and VSS mass balance around the primary clarifiers is useful in verifying influent COD fractions or for estimating the fractions when sufficient data is not available. When measuring soluble COD and BOD_5, it is important to document the type of filter used because it affects the definition of soluble organic content.

Influent total Kjeldahl nitrogen (TKN) and NH_3-N values are required because these nitrogen species contribute significantly to system oxygen demand and alkalinity and pH balance. Influent TKN concentrations can be 50% higher than typical in arid regions, making it more difficult and costly to meet a relatively moderate effluent total nitrogen concentration based limit of approximately 8 mg/L. An effluent total nitrogen target of 8 mg/L typically can be met with a two-stage nitrogen removal configuration. The two-stage process, however, relies on dilution between the influent and the internal mixed liquor recycle (MLR) and the return activated sludge (RAS) to meet the desired effluent total nitrogen concentration. This makes it much more challenging to meet total nitrogen of 8 mg/L when the influent TKN concentration is relatively high. For example, it is not theoretically possible to achieve an effluent total nitrogen concentration of 8 mg/L in a two-stage process if the influent TKN concentration is greater than 45 mg/L and the internal MLR rate is limited to four times the plant influent flow, even when there is adequate carbon to support full denitrification in the anoxic zone. Table 11.1 summarizes the theoretically achievable effluent total nitrogen concentrations for a two-stage process. It is based on a range of influent TKN concentrations and operational assumptions including: an internal MLR of four times the influent, no internal simultaneous nitrification and denitrification (SND) in the aeration basin, complete hydrolyses of the organic nitrogen to ammonia, a synthesis nitrogen uptake based on BOD/TKN of 4.5, an effluent ammonia–nitrogen concentration of 0.2 mg/L, and an effluent recalcitrant dissolved organic nitrogen (rDON) concentration equal to 3% of the influent TKN.

The theoretical effluent total nitrogen values are only possible if adequate carbon is available to achieve complete denitrification of the nitrate in the return streams to the anoxic zone. Increasing the internal MLR more than five times the influent flow is typically not helpful and could actually reduce performance because of carbon limitations and the effects of dissolved oxygen in the recycle. The level of SND can also vary significantly from plant to plant, depending on the basin configuration, mean cell residence time, and type of aeration system, which can significantly affect the

Table 11.1 Theoretical minimum effluent total nitrogen for two-stage nitrogen removal (courtesy of Black & Veatch).

Influent TKN, mg/L	25	30	35	40	45	50
Internal recycle rate, %Q	400	400	400	400	400	400
Effluent NO_3-N, mg/L	3.7	4.5	5.2	6.0	6.7	7.5
Effluent NH_3-N, mg/L	0.2	0.2	0.2	0.2	0.2	0.2
Effluent RDON, mg/L	0.75	0.9	1.05	1.2	1.35	1.5
Effluent total nitrogen, mg/L	4.7	5.6	6.5	7.4	8.3	9.2

TKN = total Kjeldahl nitrogen; RAS = return activated sludge; and rDON = recalcitrant dissolved organic nitrogen.

level of nitrogen removal. Point-source aeration, such as slow-speed surface aeration, imparts a degree of SND that can decrease effluent total nitrogen values.

Influent NO_3-N and NO_2-N should be checked occasionally because although they are typically insignificant in municipal wastewater, they have been observed at several plants in concentrations that have created performance problems. For example, the Eagle's Point BNR plant in Minnesota suffered from too much NO_3-N in the influent. Design information for the Eagle's Point facility stated an influent volatile fatty acid (VFA) concentration of 40 ± 8 mg/L, which did not include influent NO_3-N measurements. During plant commissioning, analytical results indicated that the primary effluent NO_3-N concentration ranged from 1 to 5 mg/L, while influent VFAs were less than 5 mg/L (Figure 11.1). At times, nitrate passed through the primary settling tanks to the point where the nitrate load to the anaerobic zone was too high for efficient biological phosphorus removal given the limited supply of influent VFA. Primary sludge fermentation was later provided to generate additional VFAs to enhance biological phosphorus removal and to compensate for the nitrate in the plant influent. Nitrate typically is not present in domestic wastewater, especially when VFAs exceed 20 mg/L, because VFA will not form in wastewater containing nitrates. If nitrate were observed in domestic wastewater, then variability in concentration would be similar to other domestic pollutants and would not vary significantly from day to day. This was not the case at the Eagle's Point facility, which experienced a high variability in influent nitrate, which suggested a periodic discharge of nitrate into the sewer either from an industrial source or addition of nitrate for odor control. Adding nitrates to the sewer for odor control in Henderson, Nevada, changed the influent wastewater characteristics significantly.

There are a few important considerations when monitoring for nitrate. Nitrate will be reduced in the collection system, so it can be assumed that the nitrate load

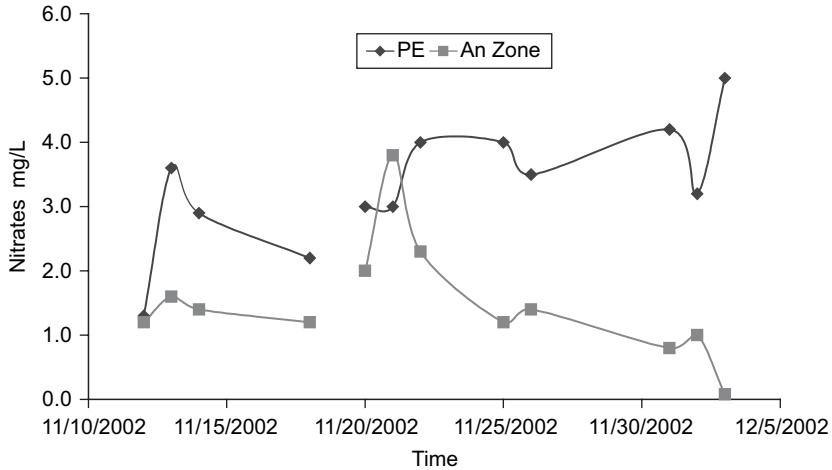

FIGURE 11.1 Nitrates in primary effluent and in the anaerobic zone (courtesy of Black & Veatch).

that entered the collection system was higher than that being measured at the plant. Therefore, nitrate loading could vary during the course of a year, as the rate of nitrate reduction in the collections system swings with wastewater temperature. Nitrate may also be reduced in a composite or grab sample before being analyzed, so samples should be filtered immediately or fixed to obtain accurate nitrate data. Further guidelines for various sampling methods and selection of representative locations are discussed in Chapter 12 of *Biological Nutrient Removal (BNR) Operation in Wastewater Treatment Plants* (WEF, 2005).

2.1.2 Phosphorus Speciation

Common forms of phosphorus found in domestic wastewater include orthophosphate, polyphosphate, and organic phosphate, which are combined as total phosphorus (TP). The orthophosphate is the simplest form of soluble phosphorus available to microorganisms for uptake and synthesis. Phosphorus in wastewater can be classified as soluble and insoluble, organic and inorganic, biodegradable and unbiodegradable, and reactive and nonreactive. As effluent phosphorus limits become more stringent, fine suspended colloidal organic or particulate matter becomes more important because this material is not removed by biological reactions, sedimentation, or possibly even sand filtration unless it is well flocculated. Reactive phosphorus, which consists mostly of orthophosphate, refers to the phosphate that is detected by the colorimetric test or ion chromatography without preliminary hydrolysis or digestion (WEF, 2005).

Permit limits typically apply to total phosphorus. To evaluate process performance, however, it is necessary to differentiate between total, soluble, and orthophosphate. Some industrial discharges include soluble forms of phosphorus that do not register as orthophosphate and are nonreactive; this phosphorus fraction cannot be removed biologically or chemically. For most domestic waste treatment applications, it is reasonable to measure only the influent total phosphorus because the nonreactive soluble phosphorus fraction is typically very low and nearly all influent phosphorus will hydrolyze to orthophosphate before it reaches the aerobic zone. All orthophosphate is available for cell growth or luxury uptake. The plant influent total phosphorus to VFA ratio or total phosphorus to biodegradable COD (rbCOD) ratio is often used to determine if the wastewater characteristics are favorable for biological phosphorus removal. These relationships are further discussed in Section 2.1.4.

2.1.3 Nitrogen Speciation

Although some regions in North America are introducing only nitrogen limits, other regions are establishing low total nitrogen and total inorganic nitrogen (TIN) discharge limits. Total nitrogen is the sum of TKN plus nitrate/nitrite nitrogen. The TIN is defined as the sum of ammonia nitrogen plus nitrate/nitrite nitrogen. Analysis for TKN uses a chemical digestion process to free ammonia from soluble and suspended organic material. The difference between the ammonia concentration before and after the digestion process is the organic nitrogen. When troubleshooting plant performance, it is necessary to know the fraction of organic nitrogen because alkalinity will be gained when organic nitrogen is hydrolyzed. This is in contrast with conversion of ammonia to nitrate, which consumes alkalinity at the ratios shown in Table 11.2.

Table 11.2 Effect of unit processes on alkalinity (courtesy of Black & Veatch).

Process	Alkalinity change, mg/L	Per mg/L of
Nitrification	–7.1	Ammonia-nitrogen oxidized
Denitrification	+3.6	Nitrate-nitrogen reduced
Breakpoint chlorination	–1.4	Chlorine added
Dechlorination	–2.4	Sulfur dioxide added
Phosphorus removal	–5.6	Aluminum added
Phosphorus removal	–2.7	Iron added

Additional analyses are needed to further break down TKN into different components. This level of nitrogen speciation is necessary for advanced process modeling to separately track these nitrogen species through the wastewater treatment plant (WWTP). Even if advanced modeling is not used, long-term process control must consider the various nitrogen species for permit compliance.

Of the nitrogen species, the most important form for predicting what effluent total nitrogen concentration can be achieved with traditional biological and filtration technologies is unbiodegradable soluble organic nitrogen, which is often referred to as the refractory dissolved organic nitrogen (rDON). The rDON remaining when the effluent ammonia is low cannot be further reduced unless sophisticated physical/chemical methods are used. Ammonia concentration consistently can be reduced to less than 0.2 mg/L provided there are no mechanical failures or toxic interferences. To reliably comply with a 3 mg/L total nitrogen limit, it is necessary to define the rDON concentration such that treatment targets can be established for ammonia and nitrate. If ammonia can be reduced to less than 0.20 mg/L, then a reasonable nitrate target to ensure reliable compliance would be one-half of the remainder once the rDON and ammonia is subtracted from the 3.0 mg/L discharge limit. The typical range for rDON is 0.5 to 1.5 mg/L, but it can be higher depending on the industrial contribution. If a given wastewater has an rDON concentration of 1 mg/L and it is possible to effectively reduce ammonia to less than 0.2 mg/L, then the nitrate treatment target should be 50% of the remainder (3.0 – 0.2 – 1.0 = 1.8) or 0.9 mg/L. This results in a total nitrogen treatment target of 2.1 mg/L to maintain a reasonable buffer to ensure compliance. As the rDON concentration rises, the nitrate margin is diminished, and consideration should be given to physical/chemical methods such as chemical coagulation plus membrane filtration or ion exchange.

The rDON is a composite refractory material with a composition that is mostly unknown, and ranges from labile to very recalcitrant portions. Some of the labile fraction is bioavailable to algae in the presence of bacteria and may be oxidizable through chlorination. Chlorination is not a desired removal strategy, however, because the high chlorine dose required could result in the formation of trihalomethanes and other chlorination byproducts. Only biological tests can determine the rDON. Plant operational data often can be used to approximate the rDON concentration, however, by measuring the TKN when the plant is achieving complete nitrification and the effluent ammonia concentration is low. A batch test with long aeration time can also be used to reduce ammonia to a very low concentration. To accurately determine effluent soluble organic nitrogen, a flocculated and filtered test similar to the ffCOD

test should be used to eliminate any colloidal particulate nitrogen that may remain in filtered samples. The difference between filtered rDON and flocculated and filtered TKN is the colloidal organic nitrogen that will pass through filters.

The concentration of rDON largely is affected by the industrial discharges to the plant, but some rDON may form as a result of the biological mechanisms in the activated sludge process. Food and textile industries are contributors of rDON. For example, the influent rDON concentration at Cumberland, Maryland, averages 0.75 mg/L without the industrial loadings. This increases to an average of 3.24 mg/L with the industrial loadings, which makes it impossible to achieve the effluent total nitrogen limit of 3.0 mg/L. The plant manager has several choices when high rDON concentrations are being experienced from high industrial discharges, including

- Pretreatment of the industrial flow to reduce rDON to acceptable levels;
- Determining how much of the filtered TKN is rDON using the flocculating and filtering method to determine if postchemical treatment and filtration can reduce the effluent TKN; and
- Negotiating with the regulatory authorities for a variance or for standards based on TIN once the true rDON is determined.

2.1.4 Quantity and Quality of Carbon

Organic carbon compounds (expressed as COD) need to be present in the influent to achieve both denitrification and biological phosphorus removal. A minimum ratio of COD/TN of approximately 9/1 is required in the influent for reliable gentrification. A COD/TP of approximately 40/1 is required for biological phosphorus removal. Some substrates having the same COD, however, are much more readily biodegradable than others, as illustrated in Figure 11.2. The initial rapid rate results from the fraction of the COD that is readily biodegradable. As wastewater becomes more septic, acid fermentation will produce more rbCOD, and the denitrification rates will continue to increase. The second denitrification rate represents the adsorbed COD that slowly hydrolyzes, and the third rate is the endogenous denitrification rate experienced when the organic substrate is fully removed. Fermentation of primary sludge to produce rbCOD or the addition of carbon supplements such as methanol, ethanol, sugars, or molasses may be required to get the desired effluent nitrate concentration.

In biological phosphorus removal plants, phosphorus-accumulating organisms (PAOs) present in domestic wastewater must uptake short-chain VFA, mainly acetic

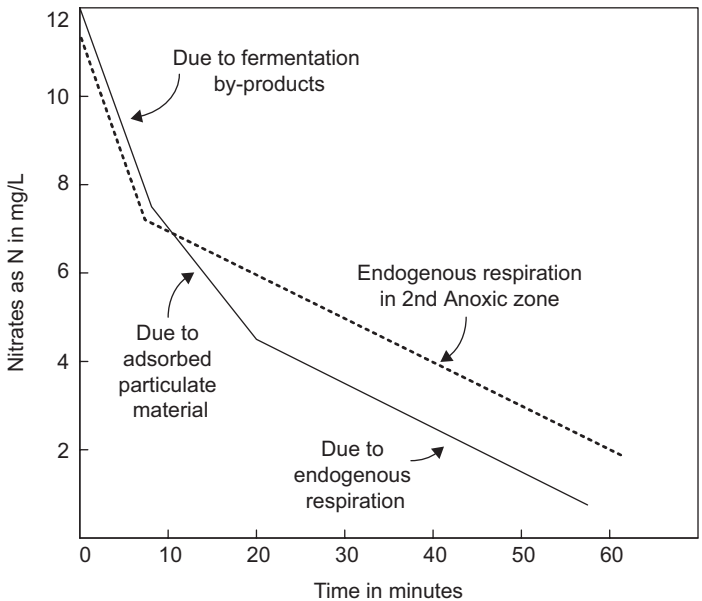

FIGURE 11.2 Denitrification rates for domestic wastewater.

and propionic acids, under anaerobic conditions. The VFA in the wastewater can be generated in several ways:

- Fermentation of soluble and particulate COD in sewer systems;
- Fermentation of particulate matter in primary clarifiers or gravity thickeners;
- Fermentation of mainly rbCOD in the anaerobic zone; and
- Fermentation of some of the mixed liquor or RAS.

The intricate reactions taking place in the WWTP are well represented by mathematical models, which form the basis of simulator programs such as BioWin and GPS-X. The characteristics of wastewater showing the fraction of COD that is rbCOD and the fraction of the rbCOD that is VFA must be determined, as well as the reduction of the various constituents during pretreatment.

When the required conditions are met and there is sufficient rbCOD in the feed to the plant, biological phosphorus removal is extremely reliable and predictable. Operators, however, need to be able to determine what the problem may be

when phosphorus removal is erratic. The minimum VFA/P for reliable phosphorus removal is quoted in the literature as ranging from 3 to 20; however, because of fermentation, a portion of the rbCOD in the anaerobic zone will increase the available VFA. The VFA content of the feed by itself is not sufficient to determine the success of biological phosphorus removal. The VFA formed in the anaerobic zone is also taken up by the PAOs as fast as it is formed, which makes it difficult to determine the actual accumulative VFA (influent and that formed in the anaerobic zone) available to the PAOs. The rbCOD/P by itself is also not a reliable indicator for assessing the viability of biological phosphorus removal because only a portion of this material is fermented in the anaerobic zone. When assessing the viability of biological phosphorus removal, it is necessary to look at both the VFA and the rbCOD in the influent and that produced in the process. Figure 11.3 shows a plot of the rbCOD/P against the fraction of the influent rbCOD that is VFA. The line in the plot was produced from the BioWin process simulator and represents the minimum ratios required for reliable phosphorus removal. If the fraction of the rbCOD that is VFA is 0.2, then a minimum of 14 g rbCOD will be required for each gram of total phosphorus in the influent for reliable phosphorus removal.

Figure 11.3 also shows several points that represent the carbon-to-phosphorus relationships for several plants that have removed phosphorus reliably. One exception is the Eagle's Point plant before and after implementation of primary sludge fermentation. The additional VFA generated by primary sludge fermentation resulted in reliable phosphorus removal, but the plant occasionally experienced significant nitrate loads that disrupted performance.

The relationships shown on Figure 11.3 provide guidance as to whether wastewater characteristics are favorable for biological phosphorus removal. Reliable phosphorus removal is possible if wastewater characteristics represent a point well above the line. If wastewater characteristics represent a point well below the line, then optimization measures must start by dealing with the unfavorable carbon-to-phosphorus ratio by providing VFA supplementation. In practice, the fraction of rbCOD that is VFA ranges from 0.15 to 0.2 for normal domestic wastewater, so the rbCOD-to-phosphorus ratio must typically exceed 16 for reliable biological phosphorus removal, as illustrated on Figure 11.3.

Measurement of VFA must be done by a specialized laboratory because the titration method is not accurate at the typical domestic wastewater VFA concentrations. The concentration of VFA in domestic wastewater could vary from 5 to 80 mg/L. The titration method typically is used for testing VFA concentration, ranging from 500 to

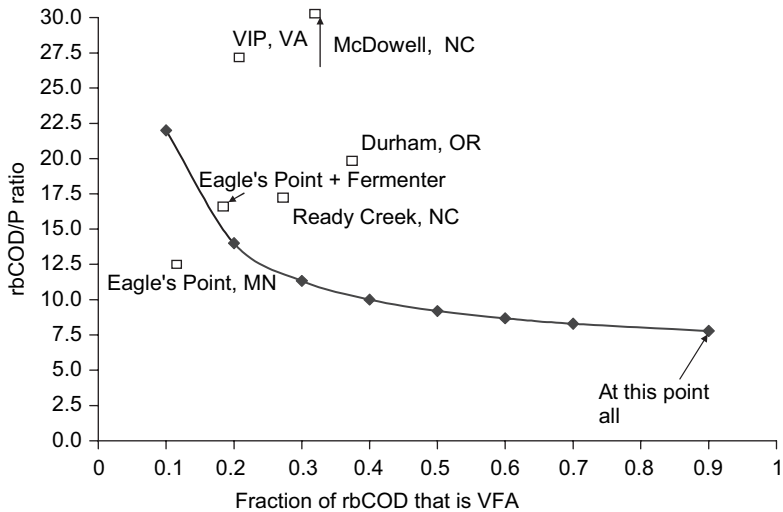

FIGURE 11.3 Line indicating minimum requirements for biological phosphorus removal (rbCOD = recalcitrant dissolved organic nitrogen and VFA = volatile fatty acid).

1500 mg/L in an anaerobic digester. If the VFA values are outside typical wastewater range, then split samples should be sent to various laboratories to determine accuracy and reliability. The most reliable method for measuring the rbCOD is to conduct oxygen uptake rate (OUR) tests. A batch of mixed liquor spiked with influent wastewater is monitored to measure the first rapid uptake of oxygen, or nitrates in place of oxygen, to develop a curve similar to that shown on Figure 11.2. The OUR curve will show the demand associated with the rbCOD and the slowly biodegradable COD. The rbCOD can also be approximated by the truly soluble degradable COD by using the ffCOD that can be performed by most plant laboratories. If the activated sludge process has a long SRT of greater than 10 days, then rbCOD can be estimated by subtracting the effluent ffCOD from the influent ffCOD.

2.1.5 Volatile Fatty Acid Preservation

Many biological phosphorus removal facilities will encounter periods when lack of VFA in the feed is limiting the performance of the process. The rate of VFA generation in the collection system is highly dependent on the residence time and the temperature of the wastewater. In addition, management practices can adversely affect VFA

formation in the collection system. Collection system management should be an integral part of any nutrient removal strategy. Hydrogen sulfide and VFA are produced under anaerobic conditions in the collection system. Many hydrogen sulfide removal or control strategies can also affect the production or survival of VFA in the collection system.

Chlorine used for odor control will oxidize hydrogen sulfides, but as a strong oxidant it will also react with easily oxidizable material such as rbCOD or VFA. Chlorine used for odor and corrosion control may also interfere with the natural fermentation process in the sewer, thus having a detrimental effect on VFA generation and the performance of biological phosphorus removal. Similarly, hydrogen peroxide is a strong oxidant that will also oxidize readably biodegradable compounds or reduce the production of VFA. Nitrate compounds typically are used for odor and corrosion control in a collection system. This practice is equivalent to adding dissolved oxygen because fermentation is eliminated until septic conditions are reestablished. In addition, microbes in the wastewater use nitrate to oxidize readily biodegradable carbon that is required for BNR. The blow-down of oxidants from chemical scrubbers used for gaseous hydrogen sulfide treatment will also inhibit fermentation if discharged to a collection system.

When biological phosphorus removal suddenly deteriorates, a review of the odor and corrosion control practices at the plant and collection system should be conducted to determine if changes have been made that could be affecting the rbCOD or VFA generation. Sulfide control using oxidants in the collection system may result in the need for costly carbon or VFA supplementation to enhance nutrient removal at the WWTP. Using iron salts for odor control may be a better choice because sulfides would precipitate with the iron without detrimentally affecting carbon or VFA production. The cost of collection system odor control and carbon supplementation should be considered and alternatives investigated to achieve the most economical solution.

Preservation of VFA also must be considered at the plant to increase efficiency of biological phosphorus removal. The hydraulic design and plant operations, which are discussed in Section 3.0, should minimize the transfer of oxygen to the wastewater ahead of the anaerobic zone. It is also important to accomplish denitrification of the RAS through endogenous respiration in a preanoxic zone, as occurs in the West Bank Process. This can also be accomplished by using carbon remaining after the anaerobic zone that is recycled back to a preanoxic zone, as occurs in the Modified Johannesburg Process.

2.2 Operating Parameters for Troubleshooting

2.2.1 Solids Retention Time

The SRT is a measure of the average time that the mixed liquor solids are retained in the system before being removed either in the waste activated sludge (WAS) or in the plant effluent. Ninety-five percent of the mixed liquor suspended solids (MLSS) is contributed by the COD and TSS load; ammonia and nitrite oxidizers typically account for less than 5% of the solids. Thus, doubling the ammonia load to the plant will only result in a fractional increase in the MLSS, but a doubling of the COD load will double the solids production for the same SRT. The design SRT is determined by the need to keep the slow-growing nitrifiers from being washed out and should be at least the inverse of the growth rate of the nitrifiers. For example, if the net growth rate of the nitrifiers is 0.2 per day, then the SRT should exceed five days (1/0.2 = 5).

In addition, the total nitrogen feed to the plant varies considerably during the day, and there should be enough nitrifying organisms to convert the highest concentration of total nitrogen in the influent, which requires a higher SRT than the minimum steady-state, average SRT. Daily variation can be modeled to establish the required minimum SRT. For BNR plants, the optimum oxic SRT needed to maintain complete nitrification under all operating conditions will be dictated by the nitrifier growth rate, which is dependent on the dissolved oxygen concentration, temperature, pH, and potentially inhibitory substances in the wastewater.

When chlorine is used for disinfection, a high variation in effluent nitrite can result in erratic chlorine demand because of the disinfection process going in and out of breakpoint chlorination during the course of the day. A high variability in chlorine demand can be a sign of nitrite breakthrough and incomplete nitrification, resulting from operating at a too short SRT, too high or low of pH, or too low dissolved oxygen concentration to maintain complete nitrification. Many operational parameters should be considered when selecting the targeted SRT for preventing nitrite breakthrough: plant influent flow and load variability, wastewater temperature, dissolved oxygen concentration, and alkalinity and pH of the wastewater.

When plants are designed and operated for carbonaceous BOD_5 removal only, the SRT should be as low as possible to avoid nitrification. When the mixed liquor temperature exceeds 24°C, however, it is almost impossible to avoid nitrification at any reasonable SRT. For example, attempts were made to operate the 23rd Avenue plant in Phoenix, Arizona, at a low SRT to avoid nitrification. This significantly reduced the oxygen transfer efficiency of the aeration system, however, because of

a depressed alpha factor (α-factor). To resolve this operational challenge, an anoxic zone was created near the inlet end and an internal recycle from the aeration zone back to the anoxic zone was provided so that the process achieved both nitrification and denitrification. These modifications reduced overall aeration energy requirements because of the oxygen recovered through denitrification and an increased alpha-factor (Albertson and Hendricks, 1992; Groves et al., 1992).

There are several advantages of operating a plant near the lowest SRT for complete nitrification:

- Energy savings by not aerating the activated sludge unnecessarily;
- Discouragement of growth of glycogen accumulating organisms (GAOs);
- Less phosphorus release in the oxic zone because of reduced endogenous respiration; and
- Reduced potential for bulking sludge and scum formation because of lower oxygen demand, higher F/M, and less potential for the accumulation of filamentous bacteria.

The optimum SRT of a membrane bioreactor (MBR) process is often above the minimum required for complete nitrification because a higher SRT allows for improved membrane permeability and reduced potential for membrane fouling. The performance of an MBR process can be affected by higher sludge volume index (SVI) of the mixed liquor that can be experienced with a longer SRT. Because of the high MLSS, the diluted SVI test must be performed in place of the simple SVI test, or a comparison should be based on stirred SVI at 3.5 g/L. A correlation between SVI and permeability has been observed with better permeability at lower SVI values.

The MBR process can experience scum and foam formation from excessive SRTs. Selective wastage of scum and mixed liquor can keep both the SRT and the scum in check (see Section 3.8).

In all domestic WWTPs there is a pronounced peak of influent TKN in the mornings and occasional smaller peaks in the evening. The magnitude of these peaks will typically depend on the size of the plant service area, thus larger plants will typically experience lower influent TKN diurnal peaks than smaller facilities. Facilities that experience higher influent TKN diurnal peaks will also experience higher diurnal peaks in effluent ammonia when the plant is operated at or near the minimum SRT that prevents washout of the nitrifiers. Unless a plant operates

at an excessively long SRT (extended aeration), the influent TKN diurnal peaks can result in diurnal spikes in the effluent ammonia even when the average effluent ammonia concentration remains low. Monitoring diurnal variations in effluent ammonia concentrations can be an effective strategy to determine whether the SRT of the process is close to the optimum for reliable and efficient performance. If the SRT is too long, then no significant increase will be observed in the diurnal peak effluent ammonia concentrations. When the SRT is near optimum, the diurnal peak effluent ammonia concentration can be observed as high as 2.0 mg/L but the short duration peak will not significantly contribute to the daily average concentration. The effluent ammonia diurnal peaks will be more sensitive to changes in the SRT than the daily average concentrations. Therefore, under ideal conditions of pH and dissolved oxygen, the magnitude and duration of diurnal peaks in the effluent ammonia can serve as a good indication of whether the process is operating near its desirable SRT. Observing this peak is also one of the advantages of having online ammonia monitoring, which allows for efficient operations while managing the risk of permit violations.

Online instrumentation can be used to better monitor diurnal peaks in effluent ammonia to help optimize the SRT of the process. When an operator relies on composite samples for control, collecting discrete samples to understand the diurnal pattern is an effective strategy to evaluate how well the plant is performing and if the SRT is at or near the optimum duration. It should be noted, however, that an increase in the diurnal peak effluent ammonia concentration could also indicate lack of oxygen or toxic interference.

Figure 11.4 illustrates how diurnal variations in flow and loading can have a drastic effect on plant effluent ammonia (as predicted by the GPS-X process simulation model), especially when the facility is operating near the washout SRT for the nitrifying bacteria. The upper line in Figure 11.4 represents the predicted peak effluent ammonia concentration and the lower line is the predicted minimum concentration. As the SRT increases, the effluent ammonia concentration tapers off and the differential between average, peak, and minimum is further reduced. As the SRT is reduced, but still not near the washout SRT (seven-day SRT on Figure 11.4), the average effluent ammonia is predicted to increase to 1.0 mg/L along with an appreciable increase in the diurnal peak. When operating close to the washout SRT, effluent ammonia will become unpredictable as the plant experiences significant ammonia bleed through to the effluent.

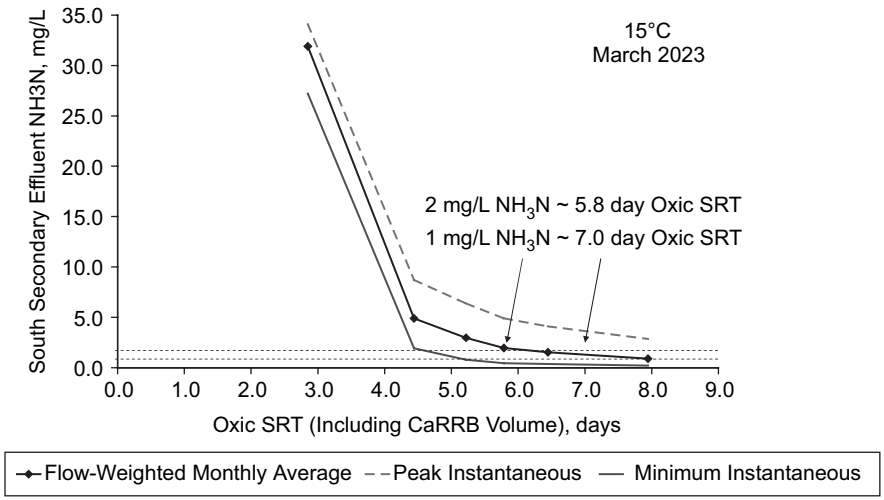

FIGURE 11.4 Predicted effluent ammonia versus oxic solids retention time (SRT) (courtesy of Black & Veatch).

The traditional method for calculating the aerobic SRT (days) is to divide the mass of solids under aeration by the mass of solids wasted each day from the process. This can be written as:

$$\text{SRT}, \theta = V \times C_m/(dV \times C_u) \tag{11.1}$$

Where,

V = volume of aeration tank, m^3;
C_m = concentration of the mixed liquor, g/m^3;
dV = volume of RAS wasted, m^3/d;
C_u = concentration of clarifier underflow, g/m^3; and
θ = SRT in days.

When wasting mixed liquor directly to a settling tank or a dissolved air flotation (DAF) thickener, the value of C_m and C_u is the same and the SRT equation will become:

$$\text{SRT}, \theta = V \times C_m/(dV \times C_m) = V/dV$$

The SRT can thus be determined by dividing the flowrate into the volume of the aeration basin. Because the volume of the basin is constant, the SRT is determined

directly from the wastage rate of the mixed liquor. The mixed liquor will find its equilibrium, which will depend on the BOD or COD load to the plant. An additional advantage of mixed-liquor wasting is that surface scum can be removed along with the wasted sludge. This wasting strategy is referred to as selective wastage and has been applied to many plants, especially when wasting to DAF thickeners where the size of the thickener typically is determined by the solids loading rate.

When wasting clarifier underflow there can be significant variability in the day-to-day determination of the MLSS, the clarifier underflow concentration, wasted scum, and the WAS pumping rate, although it is logical that under normal operating conditions, the SRT cannot change rapidly. For meaningful results, the SRT should be calculated based on a four-to-five-day average for each parameter. Online metering of solids concentrations should not be used directly for automatic control of the WAS rate because it can lead to wide swings in the WAS rate. At least a three-day rolling average of the metered parameters should be used to set or reset the WAS rate.

For better accuracy, effluent solids can be included in the SRT calculation as solids wasted from the process. Although effluent TSS concentration is usually not significant, it can be when calculating the SRT of a high-rate process that operates at a relatively short SRT of only a few days. Another limitation of aerobic SRT calculations is that they typically do not include the total inventory of solids in the process such as solids in unaerated zones and in the final clarifier sludge blanket. When secondary clarifiers are operated with a sludge blanket exceeding 300 mm (1 ft), it is possible to have 25% to 30% of the total solids inventory in the clarifiers. These solids must be considered when adjusting wasting rates to recover from a plant upset condition or when performing a mass balance around the plant.

The required anoxic SRT will depend on the type of carbon substrate available to support denitrification (see Section 2.1.4). When operating at a longer than optimum SRT for nitrification (which is temperature related), there is a greater potential for low food-to-microorganism (F/M) filamentous bulking and foaming. A longer SRT also will increase the overall oxygen demand of the process because of additional endogenous respiration and increase clarifier solids loading rates from the higher than necessary MLSS concentration.

Maintaining a longer than necessary SRT also can affect the performance of biological phosphorus removal. An extended aeration stage results in more endogenous respiration (cell breakdown and oxidation) that releases phosphorus. In addition, a longer SRT will yield less sludge containing phosphorus-storing biomass and hence less phosphorus removal (Kobylinski et al., 2008).

2.2.2 *Mixed Liquor Recycle*

The rate of MLR controls the mass of nitrate being returned from the aerobic zone to the anoxic zone. Unfortunately, the MLR also returns dissolved oxygen to the anoxic zone. Consequently, the dissolved oxygen concentration at the point in which mixed liquor is pumped from the aerobic zone should be maintained as low as possible for optimum performance.

The overall percentage of denitrification will increase as the rate of MLR increases up to a certain point depending on the available carbon to support denitrification and the amount of oxygen being returned to the anoxic zone with the MLR. For ideal performance, the MLR rate should be controlled to the point where the nitrate in the last of two or three anoxic cells operating in series is nearly depleted. The optimum recycle rate will thus depend on the availability of carbon in the feed to the anoxic zone, the anoxic retention time, and the denitrification rate. If the MLR is too high, then it can cause excessive dissolved oxygen to be returned to the anoxic zone and actually result in less nitrate removal than that experienced at a lower MLR rate. Incomplete denitrification in the anoxic zone also favors the growth of *Microthrix parvicella* (Casey et al., 1993).

When the MLR rate is too low, nitrates will be fully depleted in the anoxic zone, creating conditions favorable for fermentation, secondary release of phosphorus, and the growth of nocardia foam in the aeration basin. For practical purposes, MLR rates up to four to six times the influent flow typically can improve denitrification if the dissolved oxygen in the recycle is maintained at less than 1.0 mg/L. Higher MLR rates, or higher dissolved oxygen concentrations, can often result in lower levels of denitrification, as shown on Figure 11.5.

When the anoxic zone has at least three distinct cells, nitrate profiling through the anoxic zone is a good strategy to determine if the rate of MLR is optimized. If there is only one anoxic zone, then it is more difficult and the MLR should be varied and the removal of nitrates closely monitored. The MLR rate should be increased until nitrate is nearly depleted. The maximum denitrification efficiency in a completely mixed anoxic zone is when the nitrate concentration of the mixed liquor is above 1 mg/L, which is above the nitrate half-saturation concentration value for denitrification. This is not a simple operation because the nitrate concentration in the anoxic zone of a completely mixed tank typically will be low even with the diurnal ammonia load variation to the plant. Variable control of the MLR pumps is preferred and, although it is difficult to automate based on the daily nitrate profile, the MLR rates can be preset to operate at varying rates depending on the time of day. It is preferable

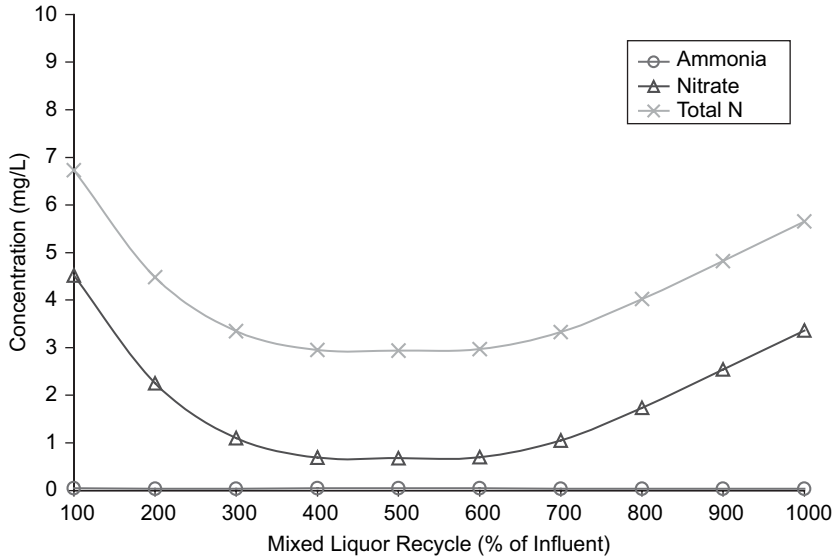

Figure 11.5 Effect of mixed liquor recycle (MLR) rate on plant effluent nitrogen from a computer analysis for a four-stage Bardenpho plant in Florida (courtesy of Black & Veatch).

to have a series of anoxic zones, which would allow the operator to study the nitrate profile through them. The nitrate profile should be developed on a mass basis rather than on concentration because primary effluent and RAS flow will dilute the nitrate concentration of the MLR flow.

It is difficult to reduce the dissolved oxygen at the point from which mixed liquor is recycled because the aeration system for most plants is designed to a minimum air flow to maintain mixing at all times. This may result in dissolved oxygen concentrations in excess of 5 mg/L, which is counterproductive. In this situation, it may be necessary to evaluate the effects of operating below the recommended minimum airflow for mixing or to provide mechanical mixing to augment the mixing energy. This allows the airflow to be reduced as necessary to operate at the desired dissolved oxygen concentration of 1.0 mg/L at the point of MLR.

2.2.3 Return Activated Sludge

The rate of RAS should be controlled to ensure the clarifier sludge blanket is maintained at less than 300 mm (1 ft). The theoretical optimum RAS flow rate can be

calculated based on a solids mass balance around the final clarifier considering the plant flow, MLSS, and RAS concentrations. The RAS concentration will be influenced significantly by the SVI of the MLSS. If it is assumed that the effluent TSS is negligible, then the mass balance results in the following formula for calculating the theoretical RAS flow rate:

$$Q_{RAS}/Q = \text{MLSS}/(C_{RAS} - \text{MLSS}) \quad (11.2)$$

Where,

Q = plant flow, m^3/d;
Q_{RAS} = RAS rate of return, m^3/d;
C_{RAS} = TSS concentration of the RAS, g/m^3; and
MLSS = mixed liquor concentration, g/m^3.

RAS flow rates calculated from the above formula are theoretical values, so operational adjustments may be necessary to compensate for nonideal conditions in the clarifier. Sludge blanket depth and effluent turbidity should be monitored to optimize fully the RAS pumping rate. Variable speed pumps dedicated to each clarifier are preferred to fully control the removal of sludge from each clarifier, rather than relying on hydraulics to obtain equal sludge draw-off with a RAS suction manifold system. When the RAS concentration in one clarifier becomes marginally higher than in another clarifier connected with a common sludge draw-off manifold, the thinner sludge will have less resistance, and the pumps will draw significantly more RAS from this clarifier. The pumps also may favor the clarifier with the shortest suction line or the one with the lowest headloss. Individual pumps that discharge into a common manifold with high headloss should also be avoided. The pumps used for RAS typically have flat hydraulic curves and a slight change of pressure in the manifold that could influence the actual discharge from the pumps connected to the manifold. The number of pumps in operation will affect the sludge removal rate from any one clarifier in plants that have a common delivery pipe for several pumps. Switching one pump on or off will change the rates of recycle from other pumps, which requires constant readjustment to maintain a reasonably balanced withdrawal of sludge from all clarifiers. With dedicated RAS pumps for each clarifier, it may be necessary to experiment with the RAS pumping rate to determine which rate provides the best sludge blanket depth control. Overpumping of RAS actually can reduce the amount of sludge removed from the clarifier because of reduced RAS concentration resulting from "rat-holing" and thinner liquid being sucked through the sludge blanket.

This problem can be diagnosed by comparing the clarifier sludge blanket and RAS concentrations. Tracer studies also may be used to warn against short-circuiting.

A lower RAS rate may allow the sludge blanket to further concentrate and return greater sludge mass to the aeration basin. Using state point analysis (SPA) is helpful for optimizing clarifier performance by finding the optimum RAS pumping rate. Zone settling tests to obtain plant-specific correlation between SVI and the Vesilind constants for settling are helpful to calibrate the SPA to be specific to the MLSS at the facility.

Up to a point, lower RAS pumping rates are advantageous for biological phosphorus because lower pumping rates will reduce the mass of nitrates returned to the preanoxic or anaerobic zones, thus preserving the available VFA and rbCOD for the PAOs. Lower RAS pumping rates also reduce the solids loading rate on the final clarifier, which can be helpful when a plant is losing solids to the effluent during an upset condition. Lower RAS rates, however, may lead to denitrification and rising sludge and secondary release of phosphorus if the sludge retention time in the clarifier becomes too long. The RAS recycle rate should be adjusted to maintain a RAS orthophosphate concentration of no more than 1 to 2 mg/L.

When phosphorus removal is not a consideration but nitrogen removal is required, higher RAS pumping rates effectively can increase the level of denitrification in plants that are lacking MLR pumping capacity. A high level of nitrogen removal can be accomplished in plants not designed with a formal anoxic zone or MLR pumps by turning down aeration at the inlet side of the basin to create an informal anoxic area. In these situations, a high rate of RAS flow will increase the return of nitrates to the anoxic area, which will increase the potential for nitrogen removal. In plants with slow-speed surface aerators, turning down the first one or two aerators has been used to reduce total nitrogen by as much as 90% (Randall et al., 1992). This strategy can also be used in plug-flow plants with fine bubble aeration if the length-to-width ratio exceeds approximately 8:1. This could lead, however, to excessive filamentous growth. Therefore, careful monitoring and control should be practiced to limit the risk of bulking sludge.

2.2.4 Dissolved Oxygen

As noted previously, it is widely accepted and understood that good dissolved oxygen control is a desirable feature for all activated sludge systems and is especially important for BNR plants. Dissolved oxygen in the aerobic zones should be continuously monitored to ensure sufficient oxygen is provided during all flow and loading

conditions. Dissolved oxygen in excess of 2 mg/L is essential in the first oxic zone following the anaerobic or anoxic zones to enhance biological phosphorus uptake by PAOs and guard against growth of *Microthrix parvicella*. The ideal aeration basin layout for good dissolved oxygen control is semi-plug flow partitioned into at least three zones. The partitions do not need to be watertight to create isolated zones, but the aeration systems should be tapered to allow the aeration system to match the oxygen demand along the length of the aeration basin while maintaining target dissolved oxygen concentrations.

Phosphorus uptake is highly dependent on the residual dissolved oxygen in the first oxic zone of the process, as discussed in Chapter 8. Orthophosphate can be reduced to a level as low as 0.1 mg/L when sufficient oxygen is supplied in the first oxic zone of the BNR process and all other conditions for biological phosphorus removal are met. The aeration system supporting the first zone should be designed to operate at a dissolved oxygen concentration higher than 2.0 mg/L, while meeting the high synthesis and nitrogenous demands experienced at this point in the process. If the plant has a completely mixed aeration tank, then phosphorus removal efficiency may be increased by partitioning the tank to cost-effectively maintain a high dissolved oxygen in the first oxic cell.

Low residual dissolved oxygen also decreases the efficiency of BOD_5 removal and growth rate of the nitrifying bacteria (Figure 11.6). Note the rapid reduction in the rate when the dissolved oxygen decreases below 2 mg/L. Partitioning of the aeration tank allows for optimum dissolved oxygen control at various points in the process. As previously mentioned, the dissolved oxygen in the first oxic zone should be 2.0 mg/L or greater to enhance phosphorus uptake, and lower than 1.0 mg/L at the point of MLR to avoid excessive recycle of dissolved oxygen to the anoxic zone. A small (nominal HRT of 20–30 minutes) deoxidation zone located before the MLR pumps can also be considered to reduce further the residual dissolved oxygen concentration. Too much dissolved oxygen introduced to the anoxic and anaerobic zones can inhibit both denitrification and biological phosphorus removal, as discussed in previous sections. Sufficient dissolved oxygen also must be maintained in the effluent of the bioreactor to avoid problems associated with denitrification and secondary release of phosphorus in the sludge blanket of the final clarifiers. A small partitioned zone following the MLR pumps is desirable to increase the dissolved oxygen again before the mixed liquor passes to the final clarifiers.

For completely mixed systems, it is possible to control the airflow with one dissolved oxygen probe strategically located to provide an accurate average reading.

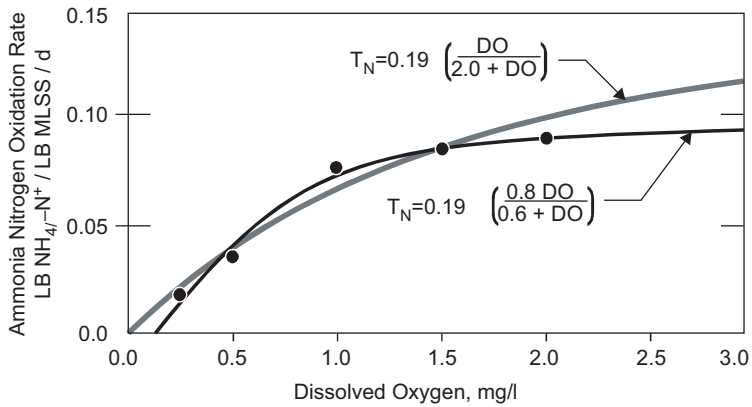

FIGURE 11.6 Dissolved oxygen versus nitrification rate graph.

Reactors with length-to-width ratios as low as 4:1, however, can encounter significant oxygen demand gradients, especially when partitioned. As a result, tapered aeration systems and multiple dissolved oxygen control grids should be considered. In true plug-flow systems, each pass will have a different oxygen demand, with the air demand in the last pass often lower than the air required for mixing. For these configurations, more sophisticated control systems are recommended. It is ideal to provide a common header system equipped with multiple control valves to regulate the airflow to each pass based on dedicated dissolved oxygen probes. When instrumentation and control equipment are limited, it is possible to control the aeration system with one strategically placed dissolved oxygen probe provided that the air distribution to each of the aeration grids can be manually controlled to avoid under- or overaeration.

The dissolved oxygen concentration at the end of an aeration basin near the MLR pumps should be maintained preferably at less than 1 mg/L to minimize the amount of oxygen pumped back to the anoxic zone. Because nitrification will be complete, the OUR at the end of an aeration basin is associated primarily with endogenous respiration. The recommended minimum airflow rates for mixing may make it difficult to maintain low dissolved oxygen concentrations. Many operators have ignored recommended minimum airflow rates for mixing and control the dissolved oxygen at the desired low concentration with mostly positive results. A mechanically mixed deoxygenation zone should be considered if problems related to lack of mixing energy are experienced.

2.2.5 *Alkalinity and pH*

Alkalinity and pH are closely related. Chemically, pH is defined as the negative log of the molar concentration of hydrogen ions. It is an inverse relationship because the concentration of hydrogen ions increases as the pH is lowered. Domestic wastewater pH can vary from a low of 5.5 to a high of 9.0, but typically it is between 6.0 and 8.0 in activated sludge and other biological treatment systems. The pH is important for two reasons: (1) permit compliance and (2) process performance. Low influent alkalinity to buffer the pH value will inhibit nitrifying bacteria as the pH drops below 7.0 (see Figure 11.7). By the time the pH is lowered to 6.0, the rate of nitrification is near zero.

Table 11.1 shows the effects of various processes on wastewater alkalinity. Hydrolyzation of 1 mg/L of organic nitrogen to ammonia will produce +3.6 mg/L of alkalinity. For this reason, it is essential to know the concentration of organic N in the influent or primary effluent. Nitrification of 1 mg/L of ammonia results in a loss of 7.1 mg/L of alkalinity, and 3.6 mg/L alkalinity is recovered through denitrification. When influent alkalinity is low, nitrification may suppress pH to the point where it is not possible to achieve complete nitrification. Creating anoxic zones at the inlet to denitrify the RAS flow may recover enough alkalinity to allow the process to achieve full nitrification. When nitrification volume is limited, addition of alkalinity to control the mixed liquor pH, especially during the cold months, will enhance the growth rate of nitrifying bacteria and possibly allow reliable nitrification at a shorter SRT.

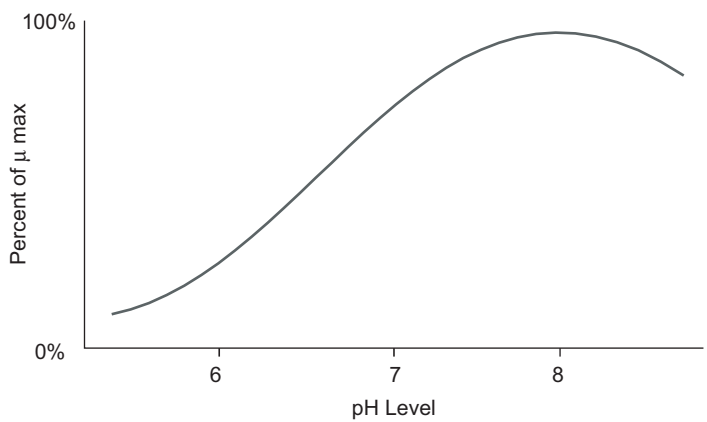

Figure 11.7 The pH versus nitrifier growth rate.

Chemical precipitation of phosphorus with aluminum or iron is effective over a wide pH range; but to precipitate phosphorus with lime, the pH must be raised above 8.5.

When testing alkalinity to determine if it is adequate to support nitrification, it is important to collect the sample at the aeration basin inlet rather than at some point internal to the process. In the anaerobic zone of a biological phosphorus removal process, the phosphorus stored in the microbes is released, and orthophosphate can be three to four times higher than the influent orthophosphate concentration. Therefore, alkalinity samples collected at the end of the anaerobic zone will have artificially high readings because of the high orthophosphate. The phosphate alkalinity, however, will be removed immediately in the first oxic zone, so it will not be available to control the pH for nitrification. Sampling for alkalinity in the anoxic zone can also produce higher readings because of elevated orthophosphate, but not to the extent experienced in the anaerobic zone. The high MLR and RAS rates also will dilute the influent to the anoxic zone, which will further confuse the alkalinity reading if it is taken in the anoxic zone.

A second concern with sampling for alkalinity is the fermentation that occurs in a primary clarifier, whether it is incidental or intentional to generate additional VFA to support biological phosphorus removal. Organic acids generated by fermentation will create alkalinity, but in a form that is not available or usable for nitrification. Organic acids such as acetic, propionic, and butyric acids are weak acids with *pKa* values in the 4.5 to 5 range. This means that these organic acids count as alkalinity. Acetic acid could contribute as much as 0.8 mg of $CaCO_3$ per mg of acetic acid, so influent containing 40 mg/L of acetic acid could have as much as 32 mg/L of alkalinity as $CaCO_3$. These organic acids, however, will be consumed rapidly in the anoxic or aerobic zones of the process through biological oxidation and will have no alkalinity benefit for nitrification.

When chemical phosphorus precipitation is used in the activated sludge process, iron or aluminum salts in excess of stoichiometric requirements will react to form a hydroxide precipitate. This excess chemical dose typically is required to reduce orthophosphate concentration to levels less than 1.0 mg/L. Alkalinity consumption is 2.3 mg of $CaCO_3$ per mg of iron precipitated as $Fe(OH)_3$ and 5.6 mg $CaCO_3$ per mg of aluminum precipitated as $Al(OH)_3$. When performing an alkalinity balance, the loss of alkalinity through chemical precipitation of phosphorus must be taken into account to ensure that sufficient alkalinity is available for nitrification and to maintain an acceptable effluent pH to meet the discharge permit. Effluent alkalinity should be maintained above 80 mg/L as $CaCO_3$, but preferably above 100 mg/L to

ensure that the pH will not adversely affect the nitrification rate. When incomplete nitrification is observed in a high-rate plant, there is an option to add alkalinity to increase the nitrification rate. This may only be necessary in winter when the nitrification rates are reduced by the low temperature. The alternative will be to increase the size of the aeration basin or switch anoxic zones to aeration zones.

When alkalinity supplementation is needed, it is best to add the chemical directly into the aeration basins. Adding supplemental alkalinity to the plant influent can create problems and may be ineffective. When adding alkalinity, it is possible to shift the pH to above 8.4, at which point calcium hardness will begin to precipitate and form scale. Because carbonate alkalinity in the pH range of 7.4 to 8.4 provides little buffering capacity, the shift in this range occurs rapidly. Calcium scale can constrict the inner diameter of the pipes, causing additional headloss and a reduction in flow capacity. If alkalinity supplementation is provided in front of primary clarifiers, then softening reactions and scale formation will occur but the calcium carbonate and added alkalinity will be removed with the primary sludge. In essence, the alkalinity added can be precipitated and removed from the system with the primary sludge. To avoid problems when adding supplementary alkalinity at the influent or at a flow-distribution structure, a titration curve should be developed to determine if the pH will be increased to the point where precipitation of calcium carbonate will occur. Adding alkalinity in the aeration basin can produce a localized calcium carbonate precipitate. As nitrification consumes alkalinity, however, calcium carbonate will dissolve and once again be available as alkalinity.

2.3 Microbiology and Kinetics

2.3.1 Nitrification

Many plants are plagued by inhibition of the nitrifying organisms, which can manifest in several ways. Often when retrofitting a high-rate plant for nitrification, performance challenges can be experienced when no apparent problems were observed before the retrofit. It is not that there were no toxic materials in the influent before the retrofit but rather that the inhibition did not manifest itself as a problem until nitrification was required. Sometimes, such events are not picked up during pilot testing because the toxic discharge can be infrequent and it could have been missed during the pilot study.

If there are gradual increases in effluent ammonia during an otherwise steady period, and the dissolved oxygen and MLSS concentrations have not significantly

changed, then it is likely that the plant is experiencing nitrification inhibition because of a toxic substance in the influent. Either a heavy metal such as nickel, zinc, or chrome, or any of a long list of organic compounds could be causing inhibition. When inhibition occurs frequently, it is good policy to keep individual daily samples of the mixed liquor for a few weeks, continuously adding new ones and discarding old ones. Heavy metals will accumulate in the sludge, and when an upset occurs, it is possible to analyze the sludge to help identify and locate the offending industry. If there is a gradual increase in effluent ammonia caused by lack of aeration, the effluent ammonia should be reduced shortly after adequate air is supplied to maintain a good dissolved oxygen residual.

Comparative nitrification inhibition tests also can be conducted to help detect inhibitory industrial discharges. Conducting tests on samples collected before and after the discharge point of several different catchments in the collection system is a cost-effective way to isolate the point of discharge.

Surveillance of the influent wastewater also should be practiced when troubleshooting a plant plagued with nitrification inhibition. At the Windhoek, Namibia, plant, where effluent is reclaimed for potable reuse, the effluent ammonia increased from near 0 to 30 mg/L in days. The operators noticed and recorded that on the Sunday morning preceding the event the influent had an abnormal "yellowish, greenish tint" which was unusual for the domestic-only wastewater. There was a chrome plating industry in the service area, but it was not supposed to be connected to the sewer system. After a warning (vehemently denied) no such incident reoccurred in more than 20 years. This shows that the power of sharing such observations with industry cannot be underestimated.

Under normal conditions, nitrite oxidizing bacteria (NOB) grow faster than ammonia oxidizing bacteria (AOB), and, consequently, there is no accumulation of nitrites. The NOBs, however, are more sensitive to toxins, high and low pH, and low dissolved oxygen environments, which means that accumulation of nitrites indicates an operating problem. When nitrites are observed, it is advisable to determine if pH and dissolved oxygen are normal, and then to look for low-level toxins that might affect the NOB more than the AOB. If pH is low, then denitrification should be introduced or increased to regain alkalinity and, if necessary, supplemental alkalinity should be provided to restore complete nitrification.

Other factors that have a profound effect on the rate of nitrification are temperature, dissolved oxygen, and pH and alkalinity. Poor hydraulic design also can lead to short-circuiting and breakthrough of ammonia to the effluent. Hydraulic problems

are not always obvious and must be closely investigated to identify areas that are creating performance challenges.

2.3.2 Denitrification

There is movement in some regions of the United States and other parts of the world toward effluent total nitrogen limits of 3 mg/L. In long SRT plants, the ammonia can be reduced to less than 0.2 mg/L and the rDON concentration can vary from 0.6 to more than 2 mg/L depending on the type of industrial waste being discharged to the plant. Therefore, it may be necessary to reduce effluent nitrate to less than 1.0 mg/L to reliably meet a total nitrogen discharge limit of 3.0 mg/L (also see discussion in Section 2.1.3).

The Modified Ludzak-Ettinger (MLE) nitrogen removal process configuration typically can remove approximately 85% of the nitrogen in domestic wastewaters that have adequate carbon to support this level of denitrification. If the carbon (as COD)-to-nitrogen ratio in the plant influent is greater than 9, then there should be adequate carbon for denitrification; but the type of carbon or COD also is important. rbCOD is needed for a rapid rate of denitrification. The ffCOD tests can be conducted to determine the soluble degradable COD, which can be equated to the rbCOD concentration of the influent wastewater. If rbCOD is in short supply, then carbon supplementation by sludge fermentation or chemical addition should be considered. Methanol, ethanol, sugar, acetic acid, or short-chain, high-COD industrial waste products are all viable supplemental carbon sources. Fermentation of primary sludge will produce rbCOD that can be used effectively to increase denitrification rates and overall nitrogen removal. Primary sludge contains proportionally more carbon than ammonia, and the fermentate will have a favorable C/N. The fermentate, however, also will contain some ammonia, so it should be used only in the first anoxic zone of a two-stage process and not in a second anoxic zone of a four-stage process or a tertiary attached growth system designed for denitrification.

To achieve more than 85% total nitrogen reduction, a second anoxic zone is required, or further denitrification must take place on a tertiary treatment attached growth system such as denitrifying sand filters or a moving bed bioreactor process. A carbon source free of nitrogen compounds should be used in a second anoxic zone or tertiary denitrification process.

The second anoxic zone of the Bardenpho process relies on endogenous respiration for denitrification. Endogenous denitrification rates are sensitive to wastewater temperature, so the rates are reasonable in warmer climates like in Florida, but adding

carbon in the second anoxic zone should be considered in colder climates to enhance the denitrification rate. Although methanol is a pure, low-cost carbon supplement that has a relatively low solids yield, it is consumed only by special, slow-growing methylotrophic bacteria whose growth declines sharply with temperature. At a minimum wastewater temperature of approximately 10°C, the second anoxic zone SRT must be increased to above three days to prevent washout of the methylotrophic bacteria and loss of denitrification. Maintaining a three-day SRT in a second anoxic zone could result in an HRT of greater than four hours, which becomes an unreasonable volume for many facilities. When confronted with this problem, other carbon sources such as acetate, ethanol, and sugar should be considered. These carbon sources can be used by ordinary denitrifying organisms that can maintain higher denitrification rates at colder temperatures. In this way, it is possible to achieve the desired level of denitrification in a reasonable second anoxic zone volume. It is possible, however, to use methanol in cold climates for tertiary denitrification using deep bed filters or an anoxic moving bed bioreactor (MBBR) process. The slow growth rate of the methylotrophic bacteria is less pronounced for attached growth systems because the organisms cannot be washed out.

Adding attached-growth media (floating or stationary) to a second anoxic zone also would allow for continued use of methanol in cold climates. This is because the slow-growing methylotrophic bacteria would develop in the biofilm, significantly reducing the retention time required to achieve the desired level of denitrification. The use of attached-growth media in the second anoxic zone, with sieves to retain the media, is also an effective strategy for an MBR process that must achieve low-effluent nitrogen. Because there is no thickening of the return sludge in an MBR process, a sludge return rate exceeding four times the forward flow from the membrane zone to the aerobic zone is required. This high return rate reduces the retention time in the second anoxic zone and brings more dissolved oxygen from the aeration zone into the anoxic zone, making denitrification with methanol to low levels near impossible at mixed liquor temperatures below 12°C.

When troubleshooting a plant that is experiencing denitrification problems, it may be helpful to run denitrification rate tests (see WERF, 2003). Measuring denitrification rates in situ by adding nitrates to a sample of the mixed liquor is fraught with difficulties. When samples of mixed liquor from the end of the aeration basin of a BNR plant are mixed with samples of the influent and RAS in the same proportion as in the full-scale plant, three distinct rates will be observed as shown on Figure 11.2. The first denitrification rate is the result of rbCOD removal, the second rate results from hydrolysis

of the adsorbed particulate matter, and the third represents endogenous denitrification. If rates are measured early in the morning, then the first rate will be significantly lower than at midday because of the lower concentration of rbCOD. When measuring rates in samples taken from the anoxic basin, the rbCOD would have been used up and only two rates will be observed—a faster rate and one for endogenous respiration when the substrate is depleted. If the anoxic zones are oversized, then some fermentation may occur after the nitrates are depleted. This can result in an artificially high denitrification rate when nitrate is spiked to a batch test for that zone. With multiple anoxic zones, it is best to look at the profiles of nitrates through the basins or to rely on online monitoring. In most cases, operators simply look at comparative rates in batch tests from day to day at the same hour to compare performance.

Denitrification rates will vary from plant to plant and also can vary from one external substrate to another. Most bacterial populations that denitrify can use almost any carbon source but methanol. Some other monocarbon compounds require specific organisms that feed off these substrates. A specific organism must be cultivated to break down the methanol while using the nitrate as an electron acceptor. As a result, the bacterial mass must be acclimated to the methanol feed before an attempt is made to measure the denitrification rate.

With the emphasis on achieving very low effluent concentrations of both nitrogen and phosphorus, it should be stressed that denitrifying organisms need phosphorus to grow. When using tertiary attached-growth denitrification systems, there must be sufficient phosphorus to sustain the growth of the denitrifying organisms. This may require a final phosphorus precipitation step to achieve effluent phosphorus levels of less than 0.02 mg/L. There are indications that the attached growth denitrifying organisms can use chemically bound phosphorus in sand filters, but there seems to be more difficulties in using chemically bound phosphorus in suspended media systems such as the MBBR process.

There appears to be a conflict between carbon needed for phosphorus removal and for denitrification in a plant with an anaerobic zone for phosphorus removal. The PAOs will soak up the VFA in the influent. Although some of the PAO can use nitrate instead of oxygen, the rate of denitrification is much slower. There are reports, however, that contradict this (van Huyssteen et al., 1990). Process simulator models predict that when the readily biodegradable carbon supply is insufficient for both biological phosphorus removal and denitrification, the denitrification rate will suffer. This can lead to use of chemical addition for phosphorus removal, reserving the rbCOD for denitrification.

Redox meters for measuring the oxidation/reduction states of mixed liquor are used for detecting when the anoxic zone is running out of nitrate. There is no absolute meter reading at which the nitrate will disappear, but when there is a sudden drop in the readings, the mixed liquor is going into the fermentation mode. The oxidation reduction potential (ORP) probes and control logic exist that can detect this change and provide early indication of a potential denitrification problem.

2.3.3 Biological Phosphorus Removal

PAOs can only take up acetic and propionic acid in the anaerobic zone. In the anaerobic zone, fermentation of some of the rbCOD to VFA is essential to the process. Although some higher-carbon VFAs may be present, the literature typically refers to these two acids when using the acronym VFA. Phosphorus removal has been remarkably reliable, provided that sufficient rbCOD or VFA is available, competing organisms are kept under control, and there is sufficient dissolved oxygen in the aeration basin.

2.3.3.1 Competing Organisms

Organisms that compete with PAOs are those that deplete VFA. Heterotrophic bacteria using oxygen or nitrates as electron acceptors will proliferate and rapidly consume the available VFA, which is why it is necessary to provide an anaerobic zone with no dissolved oxygen or nitrates in the influent. In such an environment, the PAOs have the opportunity to take up the VFA before it is consumed by the ordinary heterotrophic bacteria. The term "anaerobic" is used here to distinguish this from the anoxic zone, which also has no oxygen supply but to which nitrates are fed for denitrification. Some fermentation of rbCOD to VFA takes place in the anaerobic zone, but there is little to no methane formation and little sulfide production. Therefore, odors emitted from an anaerobic zone of a biological phosphorus removal process may be less compared with the first section of an aeration basin.

GAOs also can compete with PAOs in the anaerobic zone. Under normal operating conditions, PAOs will outgrow the GAOs. The following conditions have been observed to favor GAO proliferation over PAOs and thus should be avoided or minimized as much as possible to optimize biological phosphorus removal (see Section 4.10, Chapter 8 for additional discussion of GAOs):

- The pH is too low;
- The SRT is longer than necessary;

- Wastewater temperature is too high;
- Acetic acid only is fed to the plant in place of a mixture of acetic and propionic acid;
- Glucose is fed to the anaerobic zone; and
- Unaerated zones are too long.

The amount of VFA in the influent is often not sufficient to sustain reliable phosphorus removal. In these cases, VFA augmentation is necessary. A portion of the rbCOD in the influent will be fermented to VFA in the anaerobic zone. It is important, however, to preserve as much VFA as possible to support biological phosphorus removal and to reduce VFA augmentation requirements. When nitrates enter the anaerobic zone, they serve as electron acceptors for organisms that can consume VFA and impair fermentation of the rbCOD. Even when oxygen and nitrates are totally excluded from the anaerobic zone and conditions do not favor the growth of GAOs, fermentation of rbCOD in the anaerobic zone may not be sufficient and supplemental VFA may be required. The VFA can be added in the form of acetate or can be obtained by fermentation of primary sludge, MLSS, or a readily biodegradable substrate such as sugar or molasses. It is, therefore, important to know both the rbCOD and the VFA concentration in the influent. Figure 11.3 can be referenced to benchmark if there is sufficient VFA and rbCOD in the wastewater to support a good growth of PAOs and to achieve reliable biological phosphorus removal.

2.3.3.2 Inhibition of Phosphorus-Accumulating Organisms

Inhibition of PAOs is very rare. In fact, PAOs are not inhibited by chemical addition to the final clarifiers for polishing of phosphorus from the final effluent. In one instance, however, pickle liquor added to the aeration basin did inhibit biological phosphorus removal, but this probably was because of impurities in the liquor. Urea has been shown to inhibit PAOs. While treating abattoir effluent in Kwazulu-Natal, South Africa, the feed to the plant contained more than sufficient VFA, but there was no observed release or uptake of phosphorus even when additional VFAs were provided (Randall et al., 1992). Biological phosphorus removal was possible only after the waste streams from the animal pens were excluded. Another example of observed urea inhibition was at a tobacco processing plant near Richmond, Virginia. The tobacco waste was rich in phosphorus but devoid of nitrogen. When urea was added to the feed as a source of nitrogen, no phosphorus removal was observed.

Biological phosphorus removal recovered immediately, however, when the urea was added in the aeration basin rather than in the feed.

2.3.3.3 Secondary Release of Phosphorus

The success of biological phosphorus removal depends on PAOs releasing phosphorus in the anaerobic zone to supply energy for the uptake and storage of VFA. The energy they gain from releasing phosphorus is used to take up VFA and store it as an intermediate byproduct. Figure 11.8 illustrates a typical release of phosphorus in the anaerobic zone. Secondary release of phosphorus is the phenomenon whereby PAOs release phosphorus without taking up VFA. Under anaerobic conditions without VFA, PAOs release phosphorus for maintenance energy because they are obligatory aerobes and otherwise would die off. Because no energy is taken up in the form of food during this release, there is no stored food to supply energy for the uptake of phosphorus upon subsequent aeration. Figure 11.8 shows secondary release of phosphorus in the second anoxic zone. The nitrates formed in the aeration basin were removed completely in this unique plant through a process of SND in the aeration basins. With no nitrates in the second anoxic zone, secondary release of phosphorus was experienced in the second anoxic zone and the released phosphorus was not entirely taken up in the reaeration zone.

Secondary release of phosphorus has been experienced under the following conditions, which should be avoided to optimize biological phosphorus removal:

- In the anaerobic zone, if it is too large and the VFAs are depleted early in the available retention time;

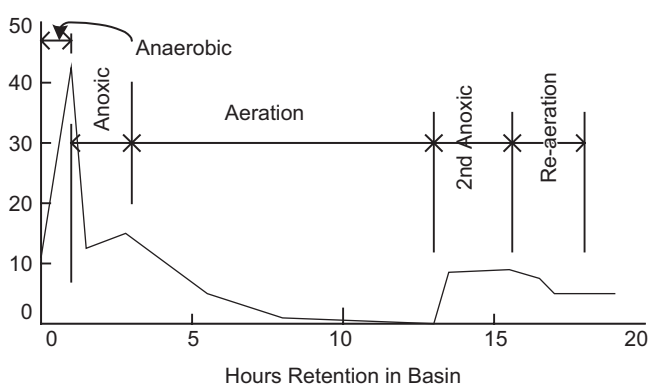

FIGURE 11.8 Secondary phosphorus release in second anoxic zone.

- In the main anoxic zone, if it runs out of nitrates, creating anaerobic conditions with no available VFA;
- In the second anoxic zone, where nitrates are fully depleted (see Figure 11.8); and
- In the sludge blankets of final clarifiers when the RAS rate is too low and sludge is not removed fast enough.

2.3.4 Analyzing Orthophosphorus Profiles through a Biological Nutrient Removal Plant

A simple batch test can provide valuable information for diagnosing potential performance problems for a biological phosphorus removal plant. The bench test looks at the release of orthophosphate to mimic what is occurring in the anaerobic zone of the process. The test is initiated by combining the anaerobic zone influent, RAS, and supplemental VFA in a vessel in the same proportion as that being introduced to the anaerobic zone in the plant. The vessel is mixed without introducing air, and orthophosphate samples are taken every 5 to 10 minutes and plotted to determine the time profile. Ideally, there will be a rapid rate of release followed by a slower rate as shown on Figure 11.9. The rapid rate is primary release associated with the uptake of VFA; the lower rate is secondary release that occurs without the uptake of VFA. The point of inflection is the ideal retention time for the anaerobic zone, so that secondary phosphorus release is avoided.

Biological phosphorus removal is not possible without prior release of phosphorus in an anaerobic zone. A more rapid rate of release and the higher overall release would appear to indicate better phosphorus removal kinetics. A WERF study (2005), *Factors Influencing the Reliability of Enhanced Biological Phosphorus Removal*, however, found that there was no direct correlation between phosphorus release and uptake. The release of phosphorus can result in phosphorus concentration in the anaerobic zone from two to four times the influent concentration and still result in good phosphorus uptake in the aeration basin. This could be because of more fermentation taking place in the anaerobic zone of one plant than in another plant. Once a plant operator has established the necessary release curve for obtaining good phosphorus uptake, occasional testing to monitor the health of the system is good practice.

If the orthophosphate concentration in the anaerobic zone is dropping, then it may be an indication that the system needs more VFA or rbCOD. It also may be an indicator of too much dissolved oxygen or nitrate entering the anaerobic zone with

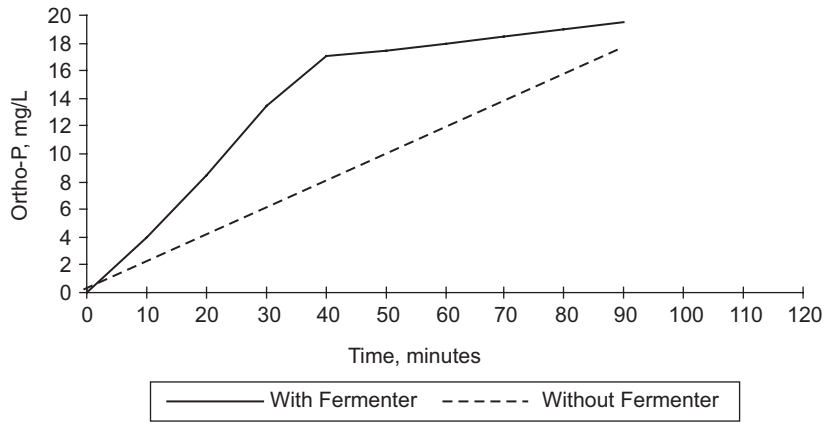

FIGURE 11.9 Release of phosphorus in a batch reactor when adding influent.

the RAS flow. Once the anaerobic zone orthophosphate concentration returns to normal level, BPR also should return to normal performance.

There are two phenomena currently thought to obstruct successful BPR. The first is excess secondary phosphorus release, and the second is dominance of GAOs over PAOs (Barnard, 1984). Knowledge of these phenomena and good design and operational practices can lead to successful BPR.

Developing nitrogen and phosphorus profiles through the zones of a BNR plant often can reveal why the facility is performing well or why it is underperforming. Scruggs et al. (2005) studied the profiles of three plants in the same city, one performing well and the other two with erratic or consistently poor biological phosphorus removal. The problems inhibiting performance at the two poorly performing facilities were not well known at the time of the study. It was expected, however, that GAO dominance would demonstrate a phosphorus release and uptake trend similar to that shown by Saunders et al. (2002) on Figure 11.10. Although acetate, glycogen, and polyhydroxyalkanoates typically are not measured at WWTPs, phosphorus concentrations are tracked through a plant when effluent nutrients are of concern. Phosphorus data were available at each of the plants included in this study.

2.3.4.1 Plant A

Plant A received mostly domestic wastewater, but the VFA content was being enhanced by activated primaries. The plant consisted of a three-stage Phoredox

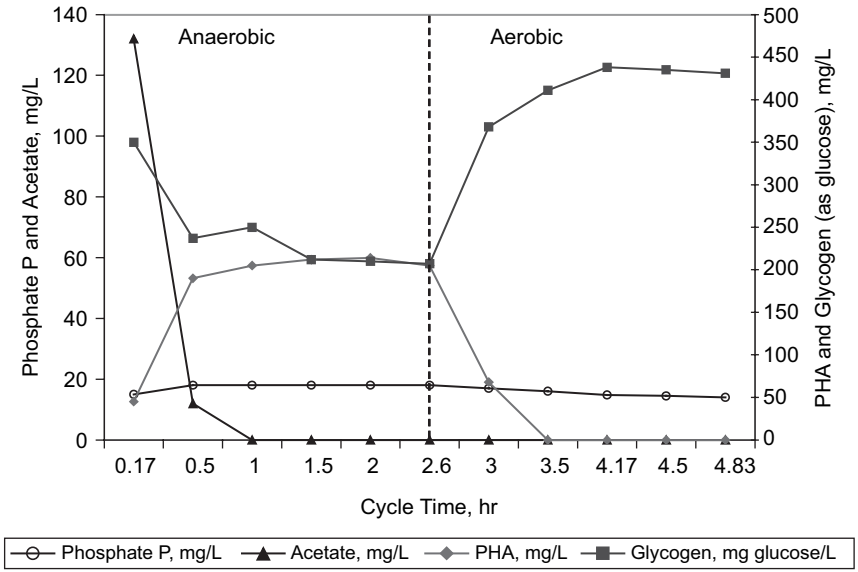

FIGURE 11.10 Typical behavior of a glycogen accumulating organism–dominated sludge through anaerobic and aerobic stages (PHA = polyhydroxyalkanoates) (Saunders et al., 2002).

system (similar to A2O), with slow-speed surface aerators in approximately two-thirds of the plant. The remaining third was unaerated and comprised the anaerobic zone at approximately 9% of the volume and the anoxic zone at approximately 21% of the volume. The graph on Figure 11.11 shows a typical profile of nitrogen and phosphorus species through Plant A, averaged over one month of operation.

Total phosphorus in the influent was approximately 7.5 mg/L. The phosphorus released in the anaerobic zone (13 mg/L) appeared to be much less than what would be expected. The original pilot work that led to development of the Bardenpho process was performed at this facility; phosphorus release averaged 32 mg/L. At this plant, the RAS rates of individual tanks were controlled hydraulically through gate setting and the RAS conveyed to screw pump stations. There were problems with controlling the RAS rate, and the actual rate of return could not be measured.

A mass balance of ammonia around the anaerobic zone was performed to estimate the RAS flow rate by comparing the sum of the mass of ammonia in the influent and RAS with that present in the anaerobic zone. Development of the mass balance

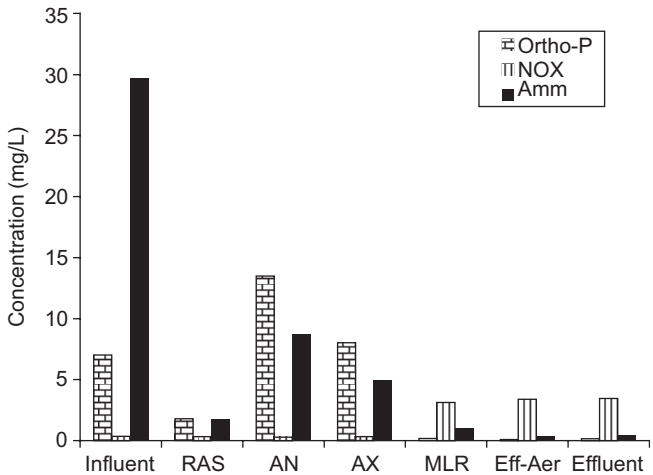

FIGURE 11.11 Profiles of orthophosphorus, nitrate nitrogen, and ammonia—Plant A (AN = anaerobic; AX = anoxic; Eff-Aer = effluent aeration; MLR = mixed liquor recycle; and RAS = return activated sludge).

was based on the assumption that in the anaerobic zone, only particulate matter was adsorbed and little hydrolysis of organic nitrogen occurred so the mass of ammonia entering the anaerobic basin had to equal the mass leaving it. In this case, the RAS rate was estimated to be at least 2.8 times the average flow. The above assumption about hydrolysis in the anaerobic zone likely is not correct, but if ammonia is released, then the true RAS recycle rate will be even higher. The approximated RAS flow rate was then used to perform a phosphorus mass balance around the anaerobic zone. Although a mass balance of total phosphorus (including that in sludge) around the anaerobic zone would be more accurate, existing information was used.

The finding from the phosphorus mass balance was a release equal to 3.9 times the mass in the combined influent and RAS. The phosphorus released was thus not immediately apparent from the profiles because of dilution by the high RAS rate. The high RAS rate was detrimental because some nitrates may be recycled, and the retention time of the anaerobic zone is shortened.

Because there was cell growth in the anoxic zone, the same type of mass balance strategy could not be used to estimate the internal MLR rate. Plant staff estimated the MLR to be approximately three times the plant average flowrate. Using this estimate,

a mass balance around the anoxic zone indicated virtually no release or uptake of phosphorus. Therefore, the very low effluent phosphorus concentration was the result of efficient phosphorus uptake in the aerobic zone.

There was sufficient primary phosphorus release and lack of significant secondary phosphorus release. The high RAS rate did not influence the phosphorus removal because of ample influent VFA. The growth of GAOs was not suspected or measured, but GAO interference did not affect plant performance.

2.3.4.2 Plant B

Plant B treated a population equivalent of 1 million. Although much of this was contributed by domestic sources, a population equivalency of approximately 200 000 came from a brewery and approximately 30 000 from a slaughterhouse. The main outfall sewer passed through a long inverted siphon of approximately 3 km, resulting in septic plant influent. Because of the expected fermentation in the siphon, onsite fermentation was not included in the design because excellent phosphorus removal was expected and initially experienced.

The plant was a three-stage Phoredox with the anaerobic, anoxic, and aerobic volumes set at 11%, 22%, and 67% of the total reactor volume, respectively. The RAS rate was controlled as in Plant A. Mixed liquor could be recycled from the aeration zone to the anoxic zone at rates varying from two to six times the average flow (Q), depending on the number of mixed liquor pumps running. The SRT in the plant was maintained between 16 and 18 days while operating at a minimum temperature of approximately 16°C because of inadequate treatment capacity to waste sludge at the rate necessary to lower the SRT.

Figure 11.12 shows a profile of orthophosphate, ammonia, and nitrate nitrogen for Plant B. From this concentration profile, the primary phosphorus release in the anaerobic zone seemed relatively low. With sufficient VFA in the influent, this could be interpreted as a sign of GAO interference.

The RAS pumping rate was estimated by applying the same principles and assumptions as used in the analysis of Plant A with respect to the ammonia mass balance around the anaerobic zone. The RAS rate was estimated to be at least three times the average plant flow. Based on the mass balance around the anaerobic zone, the phosphorus release was at least three times the mass of the combined influent to the anaerobic zone. Although the phosphorus release was not as high as that observed in Plant A, it is adequate to anticipate good BPR performance.

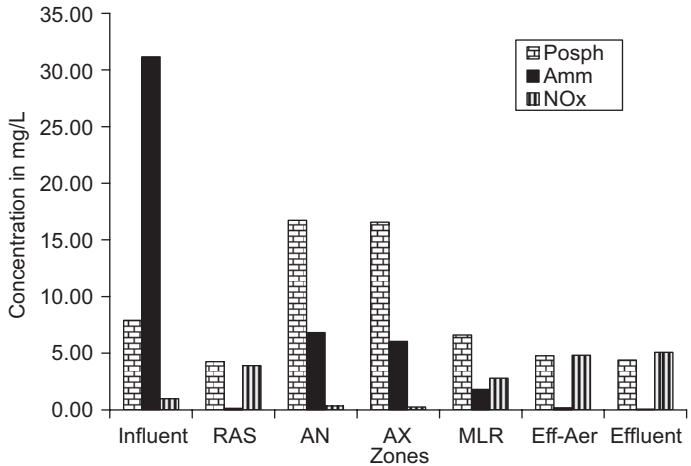

FIGURE 11.12 Profile of orthophosphorus, ammonia, and nitrate nitrogen—Plant B (AN = anaerobic; AX = anoxic; Eff-Aer = effluent aeration; MLR = mixed liquor recycle; and RAS = return activated sludge).

Although only one of the three MLR pumps could be operated it was assumed that the MLR rate was approximately two times the plant average flow. The flow out of the anoxic zone was approximated and used in a mass balance around the anoxic zone to determine whether there was phosphorus release in the anoxic zone. The mass balance results indicated significant secondary release of phosphorus in the anoxic zone. This was attributed to complete nitrate removal in the first section of that zone because of inadequate pumping of MLR.

In the case of Plant B, the apparent lack of phosphorus release in the anaerobic zone was because of an excessively high RAS recycle rate and not GAO. The main problem was secondary release in the anoxic zone. Inadequate MLR or high RAS rate, or both, which returned excessive nitrates to the anaerobic zone and reduced retention time, were probable causes of the poor BPR performance.

2.3.4.3 Plant C

Plant C is a BNR facility that treats about 22 ML/d of primarily domestic waste. Prefermentation is included in the process train to ensure sufficient VFA in the anaerobic zone influent. There are two mirror-image trains at Plant C: Train #2 and Train #3. Because performance is similar in both trains, only Train #2 will be discussed here.

The volume of each train is divided as follows: 7% anaerobic, 21.5% anoxic, and 71.5% oxic. The process schematic was similar to that of Plant B, except that the anoxic volume was divided into three equally sized cells, and the oxic portion was split into several equally sized cells. The graph on Figure 11.13 shows a typical profile of nitrogen and phosphorus species through Plant C, which indicates this plant was performing well.

By applying the same methodology used for the analysis of Plant A and Plant B, the RAS recycle ratio was estimated to be about 1.4 × Q ML/d, where Q is the average flowrate. The phosphorus content of the influent was 4.1 mg/L and that of the RAS was 2.2 mg/L. Thus, the phosphorus load to the anaerobic zone was 4.1 × Q + 2.2 × 1.4 × Q = 7.2 × Q kg/d, and the soluble phosphorus leaving the anaerobic zone was 14.1 × 2.4 × Q = 33.8 × Q kg/d. This indicates a mass phosphorus release of almost 4.7 times the total mass of combined influent phosphorus.

The MLR rate was approximately 3Q ML/d, so the flow exiting the first anoxic zone would be 5.4 ML/d, and the mass of phosphorus from that zone was 5.4 × Q × 4.4 = 23.8 × Q kg/d. This shows a phosphorus uptake through the first anoxic zone of (33.8 – 23.8) × Q = 10 × Q kg/d, indicating anoxic uptake. The mass of phosphorus

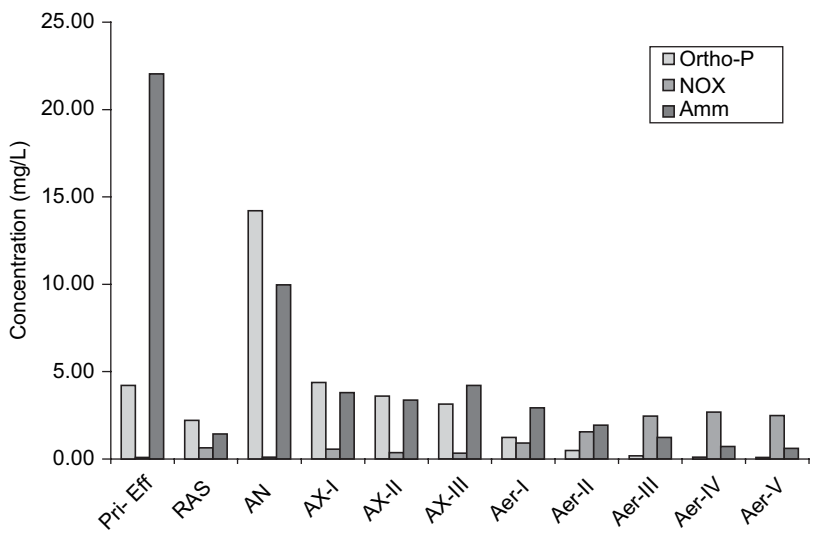

Figure 11.13 Profile of orthophosphorus, ammonia, and nitrate nitrogen—Plant C (RAS = return activated sludge).

leaving the second and third anoxic zones is 18.9 kg/d and 16.7 kg/d, respectively, demonstrating that further anoxic phosphorus uptake occurred in these zones. Clearly, the MLR rate was adequate, and sufficient nitrate was available in the anoxic zones to encourage phosphorus uptake instead of release. This plant was had excellent BPR performance with an average effluent phosphorus concentration of less than 0.2 mg/L, which also can be attributed to the continued uptake and lack of phosphorus release in the oxic zones. Although the effluent phosphorus concentration was low, the phosphorus concentration of the RAS was 2.2 mg/L, indicating some secondary release in the sludge blanket.

In summary, the following observations were made in developing and using nitrogen and phosphorus profiles through the plants to help troubleshoot BPR performance:

- Plant A performed well but had a low phosphorus concentration in the anaerobic zone, indicating an apparent low release of phosphorus. A mass balance showed that the RAS rate was excessive and that the mass of phosphorus release was more than three times the influent mass. Despite the excessive RAS rate, good phosphorus removal was observed probably because of sufficient VFA in the feed.
- Plant B similarly had an RAS rate in excess of three times the influent flow. A too low MLR from the aeration zone, however, resulted in secondary phosphorus release in the anoxic zone and poor BPR performance, despite sufficient VFA in the feed.
- Plant C had a more typical RAS rate and showed good release of phosphorus in the anaerobic zone and some uptake of phosphorus in the anoxic zone. There was enough VFA in the influent and excellent BPR performance was experienced.

Barnard and Fothergill (1998) reported an incidence in which effluent orthophosphate content in a five-stage plant deteriorated from less than 0.1 mg/L to approximately 1.5 mg/L. After examining the profiles, it was found that the orthophosphate concentration in the RAS was 10 mg/L compared with approximately 12 mg/L in the influent. The RAS rate was increased from 0.6Q to 0.8Q, and the RAS orthophosphate concentration reduced to approximately 1.0 mg/L. As a result of adjusting the RAS rate, the initial good BPR performance of the plant was recovered.

The presence of GAOs can be established through studies with fluorescent in situ hybridization (FISH) tests. The GAOs do not appear to be a problem until they

dominate the PAOs, at which point they will interfere with BPR. Typically, at neutral pH values and shorter SRTs, PAOs will dominate. The McDowell plant in Charlotte, North Carolina, operates at a high COD/P because of the addition of a sugar waste to the anaerobic zone. Despite of a high population of GAOs, the plant consistently achieves an effluent total phosphorus concentration of approximately 0.1 mg/L (WERF, 2005). It would appear that the GAOs consume the VFA remaining after the PAOs have used their share of the VFA. There is some evidence, however, that at high temperatures, GAOs may have an advantage as demonstrated at several facilities.

Profiles through BNR plants can be difficult to interpret because the true uptake and release of phosphorus might be influenced by recycling of RAS or mixed liquor. When the actual recycle rates are known, a mass balance through the plant will reveal the true state of release and uptake. Where the actual flows are not known, it is often possible to approximate them by using the available data and developing mass balances around the various zones in the process. Because phosphorus is not destroyed in the biological process, mass balances easily can be developed by evaluating the total phosphorus profile.

2.3.5 Bulking, Foam, and Scum

Foaming and scum accumulation can challenge BNR plants. It can affect effluent quality and create problems with maintenance, safety and health, and odors. Although any activated sludge process can experience these problems, they may be more problematic at BNR plants because of the additional partitioning of the reactor. When bulking occurs in the activated-sludge process, the mixed liquor flocs do not settle or compact well in the final clarifiers. This may result in high secondary clarifier sludge blankets that can lead to a significant loss of MLSS to the effluent. In some instances, the latticework formed by the filamentous organisms can trap solids and produce a clear effluent when the clarifiers are underloaded but may quickly result in washout during high flows. Bulking sludge is typically the result of excessive growth of filamentous organisms. Growth of slimy bacteria such as zooglea or fungi can also cause bulking, but this is not common in BNR plants. Foam and scum caused by nondegradable surfactants or filamentous organisms can accumulate on the surfaces of BNR basins or secondary clarifiers. It can be a light-color, frothy foam or a dense, darker foam.

One of the first steps in troubleshooting a bulking or foaming problem is to perform a microscopic examination of the mixed liquor to determine the presence or absence of various microorganisms and to evaluate the floc structure. It is important

to recognize the significant groups of microorganisms in the mixed liquor, such as filamentous bacteria, protozoa, and rotifers, and the effect each has on the system (WEF, 2005). A phase-contrast microscope with magnification up to 1000 times is recommended for viewing the structure of filamentous bacteria and other microorganisms (Jenkins et al., 2004). Detailed information on microscopic evaluation/identification of the activated sludge characteristics, levels, and types of filamentous organisms is presented in the *Manual on the Causes and Control of Activated Sludge Bulking, Foaming, and Other Solids Separation Problems* (Jenkins et al., 2004).

Incidences of foaming and bulking are not well understood, and although it is possible to identify the organisms responsible, it is not always easy to design and operate to avoid related problems. Wastewater characteristics, process design parameters, and operating conditions significantly can affect growth of filamentous bacteria. The following discussion touches on a number of key factors that should be considered when troubleshooting a plant that is having filamentous foaming or bulking problems. Additional information on this topic is presented in Chapter 7 of the *Biological Nutrient Removal (BNR) Operation in Wastewater Treatment Plants* (WEF, 2005).

There are several causes of filamentous foaming or bulking problems:

- Low dissolved oxygen concentration;
- Low F/M (loading) conditions;
- Hydrogen sulfide and septic conditions;
- Micronutrient deficiency (e.g., Fe);
- Toxic conditions; and
- Low or high pH.

Filamentous bulking or foaming problems encountered in the treatment of ordinary domestic wastewater are usually the result of low dissolved oxygen concentration and/or low F/M conditions. Low F/M bulking is common in completely mixed aeration tanks when there is a high concentration of rbCOD in the influent. This problem can be solved by using selectors consisting of a partitioned section of the aeration basin where a high COD/MLVSS of between six and eight can be maintained. Alternatively, an anaerobic selector can be used. With biological phosphorus removal, the anaerobic zone serves as a selector. Casey et al. (1993) also proposed that the formation of nitrous oxides during incomplete nitrification or denitrification encourages the growth of *Microthrix parvicella*, which is a filamentous organism that

is not affected by selectors. To overcome the formation of nitrous oxides, it is necessary to achieve complete nitrification in the aeration section and complete denitrification in the anoxic zones. There are several causes of incomplete nitrification:

- Too short a mean cell residence time for the wastewater temperature, resulting in washout of the nitrifying bacteria;
- Inadequate dissolved oxygen concentration;
- Depressed pH because of inadequate alkalinity; and
- Nitrification inhibition, as discussed further below.

There are also several causes of incomplete denitrification:

- Carbon limitations;
- Inadequate hydraulic retention time or mean cell residence time in the anoxic zone;
- Excessive MLR rate;
- Dissolved oxygen concentration is too high at the point of MLR; and
- Insufficient mixing in the anoxic zone or too much mixing energy, which can entrain air.

To comply with requirements for both complete nitrification and denitrification to reduce the potential for the proliferation of *M. parvicella*, the dissolved oxygen concentration should be high at the front-end of the aeration basin and low at the point of MLR. If the dissolved oxygen at the end of the aeration basin is high, then excessive dissolved oxygen is recycled to the anoxic zone. The additional oxygen reduces the efficiency of denitrification, and the presence of some dissolved oxygen at low concentration in the anoxic zone encourages the growth of nitrifiers in a stressed environment thus increasing the potential for nitrous oxide formation. Design standards and operating protocols often call for high mixing energy at all points in the aeration basin, which can lead to excessively high dissolved oxygen concentrations at the point of MLR. Typically, reducing the mixing energy at the end of the aeration basin to less than the traditional design standards will do little harm. Airflow rates at the end of an aeration basin can be reduced to maintain a target dissolved oxygen concentration of less than 1.0 mg/L. This will minimize the mass of oxygen transferred back to the anoxic zone with the MLR pumps. Another option is to use coarse bubble aeration at the end of the aeration tank to transfer less oxygen while providing better

mixing properties. Operators can experiment by turning aeration down toward the end of the aeration basin to achieve the goal of less than 1 mg/L dissolved oxygen concentration.

Incomplete denitrification often can be controlled by manipulating the MLR rate to the point where there is only slight bleed-through of nitrate from the end of the anoxic zone to the aerobic zone. If the MLR rate is too high, then significant amounts of nitrate will break through the anoxic zone. Incomplete denitrification can lead to formation of nitrous oxides and encourage growth of *M. parvicella.*

Using anaerobic selectors is an effective strategy to overcome low F/M conditions that can lead to filamentous bulking or foaming by certain organisms that thrive in this environment. Anaerobic selectors, however, will not effectively control *M. parvicella*. The objective of a selector is to provide a high substrate concentration environment, especially in the form of rbCOD to favor the growth of floc-forming organisms over filamentous bacteria that are more efficient at low substrate concentrations. A selector is a partitioned zone at the influent end of the bioreactor with a volume that will result in a loading rate F/M of approximately 6 to 8 kg COD/kg MLVSS·d. The selector can be operated under aerobic, anoxic, or anaerobic conditions. Anaerobic selectors have been reported to be more effective in controlling filamentous organisms. In BNR plants, it is preferred that the aeration basin be split into at least three zones to allow for a higher dissolved oxygen in the first zone and a lower dissolved oxygen in the last zone.

In BNR plants, the anaerobic zone allows PAOs to take up rbCOD, which allows them to compete with the low F/M filamentous bacteria that can cause bulking. The PAOs are exceptionally good floc formers, and the higher phosphorus content of these organisms helps to further compact the MLSS. Anaerobic selector zones are included for this purpose even where phosphorus removal is not required.

Although selectors can provide excellent control of bulking, other strategies such as adding chlorine and peroxide to the RAS may be used as a temporary control measure or as a backup for plants designed with selectors. Chlorinating the RAS is an effective strategy to control filamentous bulking, but care must be taken not to overchlorinate and impair the floc-formers or harm the nitrifying organisms. Chlorine also will oxidize VFA, which is needed for phosphorus removal. Detailed discussion on proper chlorination for filamentous bulking control can be found in Chapter 7 of *Biological Nutrient Removal (BNR) Operation in Wastewater Treatment Plants* (WEF, 2005).

Spraying a high-concentrate chlorine solution (0.5–1.0%) on the surface of an aeration basin also has been used to control nocardia foam (WEF, 2005). When used

to control foam, chlorination is not always effective in eliminating filamentous bacteria because they often are shielded by thick layers of foam.

Several types of filamentous bacteria proliferate in hydrogen sulfide and reduced substrates in septic wastewater. Control measures include prechlorination of the wastewater to control their growth (Kobylinski et al., 2008). High doses of chlorine-inhibited biological phosphorus removal in the Subiaco (MLE) plant in Perth, Western Australia, where chlorine was added to the primary influent for odor control. Biological phosphorus removal was restored by eliminating the chlorine feed and covering of the tanks to allow for removal and treatment of odorous gases.

Plants treating industrial wastewater or a combination of industrial and municipal wastewaters can encounter problems that result in filamentous bulking such as of nutrient deficiency, inhibition, and abnormal pH values. Nutrient deficiency seldom is found in plants treating only municipal wastewater. Plants receiving wastewater with low nutrient concentrations or low (or high) pH must have provisions for adding nutrients and adjusting the pH. As a rule of thumb, influent wastewater containing a mass ratio of 100:5:1 in BOD_5:N:P is considered to have a sufficient nutrient balance. Appendix A of WEF's *Biological Nutrient Removal (BNR) Operation in Wastewater Treatment Plants* (2005) presents detailed procedures for calculating the amount of nutrient to be added.

2.4 Instrumentation and Controls

Online instrumentation can provide invaluable information for troubleshooting the performance of a BNR facility. Using online instrumentation for control also can significantly improve operating stability and prevent problems from occurring in the first place. When treating to very low nitrogen and phosphorus concentrations, there is less room for error, and any deviation from what is typical must be detected and corrected immediately.

2.4.1 Instrument Selection and Implementation

In wastewater treatment applications—particularly for control or troubleshooting—it is more important for the instrument to produce repeatable results and trends than absolutely accurate measurements.

To ensure confidence in readings, regular calibration and validation of the instruments are essential. This requires either a rigorous program of manual cleaning and calibration or more sophisticated automated cleaning, calibration, and validation. It is important to consider the cost of owning and maintaining instrumentation. If the

information produced by an instrument has value, then it will be worth the investment to provide good cleaning and calibration to ensure reliable, consistent information. In recent years, the focus of online instrumentation has moved more toward in-situ probes and analyzers, which are simpler and less costly to install and maintain. Some of these instruments may not be as accurate as the more complex analyzers that require significant sample preparation. They do produce repeatable and reliable data, however, that can be effectively used to establish trends that can help with troubleshooting. Winkler et al. (2004) provide a good comparison of in-situ technologies and make a strong case for using ion selective electrodes (ISEs) for nutrient monitoring.

2.4.2 Data Presentation

Online instruments instantaneously track the hour-by-hour or even minute-by-minute changes in the plant throughout each day. Two aspects of online data presentation are worth noting.

First, even the most relevant and useful data need to be presented in a usable format and not hidden away in the supervisory control and data acquisition (SCADA) system. Many SCADA systems include screens that are designed to show current data readings or, at best, readings for the past few hours. They often are not designed, however, to track changes and patterns over longer periods.

Second, it typically is most useful to check the patterns and trends in the data rather than looking at current values alone. This is most easily done by plotting a full 24 hours of data and perhaps overlaying data from the previous 24 hours (or the same 24 hours for the previous week). Thus the operator can look for any unusual patterns. It is also useful to plot longer-term data to see if values are drifting from typical ranges. More sophisticated statistical techniques or expert systems also can be used. Figure 11.14 provides an example of a seven-day output from oxygen demand monitoring for two separate treatment trains overlaid on the same graph. From this single graph the operator can see that: (1) there is a distinct diurnal pattern in the loads to each of the trains; (2) there is a distinct weekly pattern with lower loads during the weekend; and (3) oxygen demand for all trains is almost identical, indicating that they are evenly loaded.

2.4.3 Use of Online Monitoring Data for Troubleshooting

The increasing requirements for lower effluent concentration of phosphorus and nitrogen will make online monitoring essential. Operators must be able to diagnose a problem before it gets out of hand.

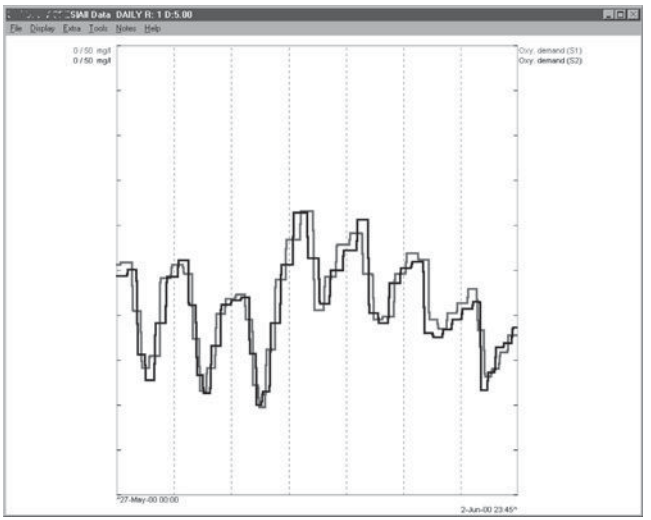

FIGURE 11.14 Example of a seven-day trend of oxygen demand for two separate treatment trains showing the two trains have identical loads (courtesy of Black & Veatch).

2.4.3.1 Flow

Plant flows, particularly influent flows, have a significant effect on process performance. When a process upset is suspected, the first and most basic things to check are the influent and recycle flows to make sure they have not changed significantly from their usual patterns. Sudden changes in these flows can be detrimental to BNR plant performance. Online flow monitoring can be used to protect the BNR process from sudden changes. Most notably, online flow measurements can be used to identify storm flow conditions and to allow steps to be taken to mitigate the effects. Unsynchronized influent pumps can cause great fluctuations in the flow pattern, which can negatively affect BNR performance. This information, therefore, can be used to control the pumps or to change pump sizes to allow better adaptation to the flow pattern.

Smaller plants have more flow and load variation than larger plants. When treating to high effluent quality, flow and load equalization should be considered for coping with high variations that would otherwise require sophisticated control equipment.

2.4.3.2 Dissolved Oxygen

A BNR process functions best when the dissolved oxygen in the oxic zones is maintained within a relatively narrow range. If the dissolved oxygen drops below approximately 1.5 mg/L near the inlet to the first oxic zone, then nitrification and phosphorus uptake are inhibited and favorable conditions are created for the proliferation of filamentous bacteria. If dissolved oxygen is too high, especially near the point of MLR, excess oxygen may be returned to anoxic and anaerobic zones, inhibiting denitrification or phosphorus release. Online dissolved oxygen measurement is required for BNR facilities. Daily variations in plant flows and loads will result in significant swings in oxygen demand, which, in turn, affect dissolved oxygen concentrations. To ensure a good, robust BNR operation, good automated dissolved oxygen control is essential. All dissolved oxygen probes used for control should be regularly cleaned and calibrated. Figure 11.15 shows a typical four-day dissolved oxygen profile for an aeration zone with no dissolved oxygen control. It indicates unacceptable variations in dissolved oxygen concentration that will, in most cases, result in poor BNR performance.

Online dissolved oxygen measurement coupled with airflow measurement also can be used to detect problems with an aeration system, such as fouling of diffusers. If dissolved oxygen levels are decreasing over weeks and months or if airflows must be increased to maintain concentrations, then diffusers may be fouled.

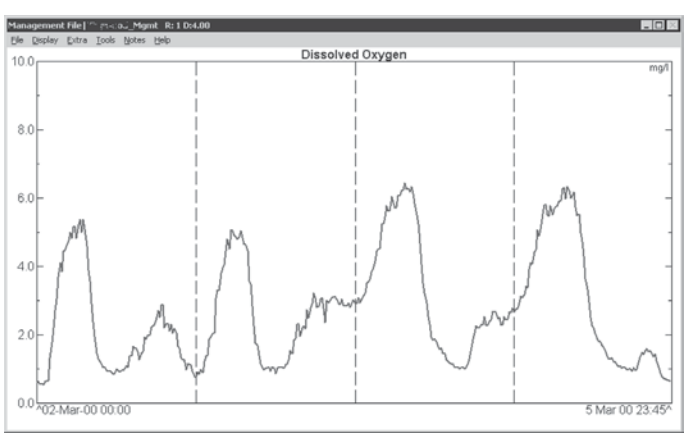

FIGURE 11.15 Typical four-day dissolved oxygen plot for an aeration zone with no automated control (courtesy of Black & Veatch).

When this happens, the dissolved oxygen probes should be cleaned and calibrated to ensure that the aberration was not caused by fouling of the probes. Increasing MLSS concentrations in the plant also may produce a similar dissolved oxygen residual and airflow trends because of the effect of MLSS on the α-factor. A sudden increase in dissolved oxygen levels (or a sudden drop in the air supply required for an automated control system) is a clear indication that the OUR of the mixed liquor has dropped. A sudden drop in OUR may indicate a drop in the influent ammonia or BOD_5 load or, more seriously, a drop in the nitrifier activity because of inhibition.

2.4.3.3 Mixed Liquor Suspended Solids

Efficient BNR also depends on adequate and stable mean cell residence time. Online MLSS probes can be used to monitor trends in MLSS concentrations to make sure they do not drift too high or low. The probes also show that MLSS concentrations can vary significantly through each day. Having an online measurement rather than relying on a grab sample taken at a particular time of the day gives the operator a better measurement of the true daily average MLSS concentration. If MLSS probes are installed on multiple treatment trains, then they can also be used to identify problems with influent and RAS flow distribution between trains or for potential mixing issues in a basin.

2.4.3.4 Sludge Blanket Measurement

Sludge blankets that are rising because of poor settling, high influent flows, low RAS flows, or a combination of these also can serve as a warning. If the blankets rise too high relative to the depth of the clarifier, there is danger that significant amounts of solids will be carried over into the secondary effluent, which significantly can increase effluent nitrogen and phosphorus concentrations. In addition to monitoring the blanket, some analyzers also give a reading of the profile of solids through the clarifier depth, which can be used to monitor the more diffuse solids above the sludge blanket. Figure 11.16 provides an example of two consecutive days of diurnal output of an online sludge blanket probe that can monitor both the thick sludge layer (labeled "RAS layer") and the flocculation settling layer (labeled "pin floc"). The diurnal variation is similar on both days. An important consideration in monitoring the sludge blanket level is the retention time of solids in the clarifier. A deeper blanket increases retention time of solids in the clarifier, which increases the potential for gentrification. In extreme cases, this may cause sludge to float and can lead to secondary release of phosphorus if the sludge blanket becomes anaerobic.

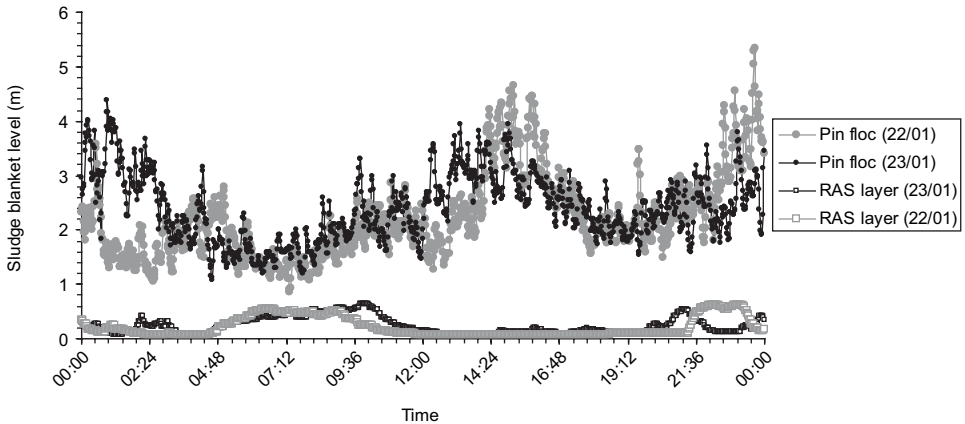

FIGURE 11.16 Example output for a sludge blanket probe. Overlay of two days of diurnal profiles for return activated sludge (RAS) layer and "pin floc" layer (courtesy of W2W Alliance).

2.4.4 pH and Oxidation Reduction Potential

Nitrification consumes alkalinity and roughly half of the amount consumed is recovered through denitrification. In a plant with adequate background alkalinity, pH values vary only slightly through the process and over time. A significant shift of pH from normal values can be an indication of problems with nitrification and denitrification and possibly insufficient alkalinity. Monitoring the pH also can show the effect that chemicals such as ferric chloride or organic acids are having on the plant. If the chemicals are overdosed, then pH values may shift significantly, serving as an early warning of the problem.

Measurement of ORP in the anoxic and anaerobic zones indicates the degree to which the zones are anoxic or anaerobic, which provides valuable information for making operational changes (usually recycle flow rates) to ensure optimum environments for BNR performance. The ORP measures all ionic species in the water and cannot be used to make fine adjustments based on subtle changes. It should be used only to make significant changes based on the order-of-magnitude shifts in its readings. Figure 11.17 shows a typical 24-hour profile of ORP for a sequential batch reactor (SBR) in Daniel Island, South Carolina. Increasing ORP occurs during the aeration cycle; gradual decreasing occurs when the air is turned off and the basin becomes anoxic during settling and decanting. There is also a characteristic shoulder drop

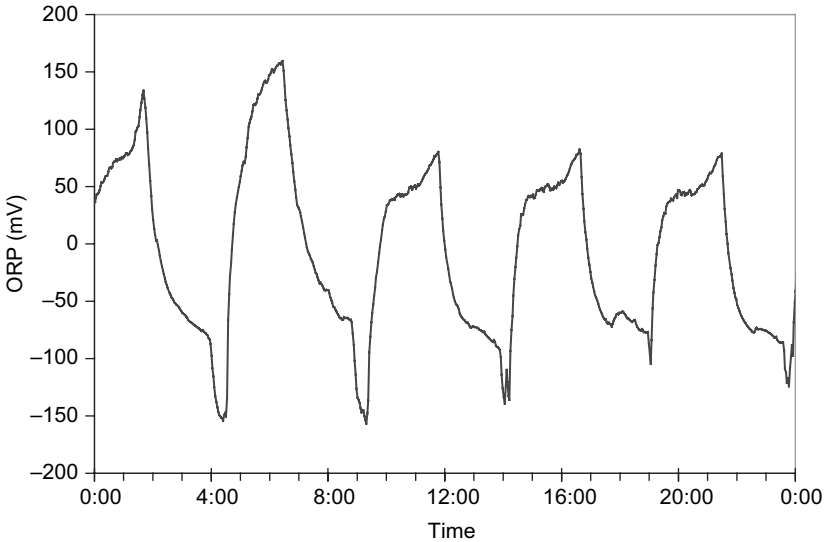

FIGURE 11.17 Typical oxidation reduction potential (ORP) profile for the Daniel Island, South Carolina, sequencing batch reactor (courtesy of Charleston Water System, South Carolina).

during the initial filling of some cycles, which may be indicative of the SBR becoming anaerobic for brief periods, which is desirable for ensuring good SVIs.

Aeration control with dissolved oxygen probes in channel systems is problematic because of relatively small changes in dissolved oxygen required for optimizing SND. The ORP measurements are used in channels systems to indicate when the mixed liquor is depleted of nitrates, indicated by a sudden drop in the ORP, at which point aeration could be increased. When an ORP meter is used at the end of the anoxic zone, it will also show when the nitrates run out and when to increase the MLR rate.

The pH and ORP along with other basic measurements such as turbidity, conductivity, and temperature in the plant influent also may be used to give an indication of an unexpected industrial or other toxic discharge.

Increasingly sophisticated analyzers are available to measure nutrients directly in the process. Analyzers can be used for ammonia, nitrate, nitrite, and phosphate through the treatment process. Many of these analyzers are expensive to purchase

and maintain, but provide invaluable information on the dynamic variations in nutrient concentrations through the process that can be used to troubleshoot performance. For example, a nitrate analyzer in an anoxic zone can indicate whether or not denitrification is complete; a phosphate analyzer monitoring the anaerobic zone can show phosphorus release; and an ammonia analyzer in the aeration zone can monitor if nitrification is complete. Figure 11.18 shows the seven-day output from an online nitrate analyzer that was monitoring an activated sludge treatment plant with MLR. For the first three days of monitoring, the MLR was shut off, but it was returned to service on the fourth day. It can be seen that the nitrate concentrations decreased steadily over the subsequent days.

Online instrumentation and nutrient analyzers also can be used to develop profiles through a BNR process that can be extremely helpful in isolating a potential performance problem as discussed earlier.

2.5 Process Modeling for Troubleshooting

As user-friendly modeling software packages have made process models easier to run, more and more utilities are using them to troubleshooting plant performance.

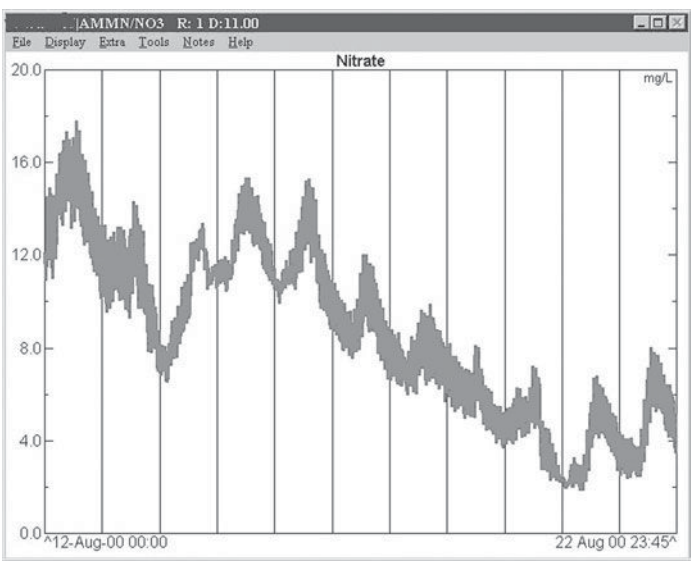

FIGURE 11.18 Example output for an online nitrate analyzer monitoring the effect of turning on the mixed liquor recycle (Watts et al., 2000).

There are two myths about process models that need to be dispelled: (1) they are too complicated for operating staff to use; and (2) the process model is always right. Sound judgment can never be replaced by simulation models. It is simple to construct and run a model, but knowing which parameters should be adjusted and how the results should be interpreted and used is a matter of experience and know-how that must be taught to all who use process models.

Process models are powerful, useful tools for design and for evaluation and troubleshooting of an existing facility. Once calibrated to the specific plant, the models could be used to predict the effect of making operational changes before implementation in the real plant. Process models do not have built-in safety factors; designers must apply their own safety factors and good judgment in determining how aggressively a plant should be designed. Also, process models cannot be used to model filaments and bulking issues; however, they are able to predict conditions that favor filamentous growth and can lead to bulking.

2.5.1 Using Models to Understand and Troubleshoot Plant Performance

A plant-wide mass balance approach to process modeling is important when troubleshooting a nutrient removal facility. A plant-wide approach can assist in understanding how the various loads move through the plant and how they affect the various processes. This is particularly useful for complex plants with numerous unit processes and significant recycles. The model can be used to see the interactions of different processes in the plant. It is especially helpful in quantifying the effects of sludge processing and the resulting nutrient sidestream loads on primary and secondary treatment processes. A plant-wide model also can be used to fill in gaps where sufficient operating data or information for a process unit is not available. The plant-wide mass balance model typically is operated as a steady-state model (i.e., assumes constant flows and loads) but it can also be used for dynamic response testing. Figure 11.19 shows an example of a plant-wide mass balance that can be used to assess the interactions between different parts of the plant and to track loads throughout the plant. There is one input stream and two outputs. Solids lost to gas such as CO_2 are accounted for in the models. The daily mass of inert solids in the influent must equal the sum of mass of the inert solids in the two effluent streams, taking into consideration that phosphorus taken up in cells or precipitated with metal salts will add inert solids. A more accurate way to calibrate plant-wide mass balances is to do a total phosphorus balance, which should close.

Once a plant-wide mass balance model is established, it can be used to predict plant performance to generate profiles of nutrients and other pollutants in the facility,

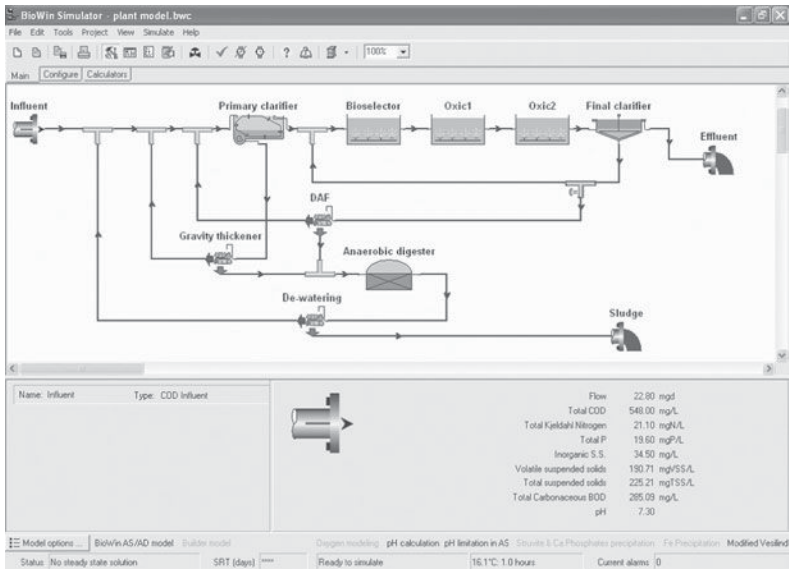

FIGURE 11.19 Plant-wide mass balance (courtesy of Black & Veatch).

and to investigate operational adjustments to optimize performance. These capabilities make the model a powerful tool for helping to identify design or operational factors that may be limiting efficiency.

2.5.2 *Dynamic Modeling*

The ability to run dynamic simulations is a powerful and insightful feature of modeling programs when troubleshooting a BNR facility where process parameters change with time. For example, a steady-state simulation at a near-critical SRT may predict effluent ammonia down to 1 or 2 mg/L. A dynamic simulation at the same SRT may show washout of the nitrifying bacteria and a much higher breakthrough of ammonia as a result of excessive peak flows. The main disadvantage of dynamic modeling is that it requires considerably more data, particularly for the influent flow and load profiles. If models are used in conjunction with online instrumentation, however, then much of the information can be obtained from the SCADA system.

Dynamic response testing can be used to determine how the process will respond to storm events, shock loads, or toxic incidents. It can also be used to test such things as sludge processing schedules. For example, Figure 11.20 shows the

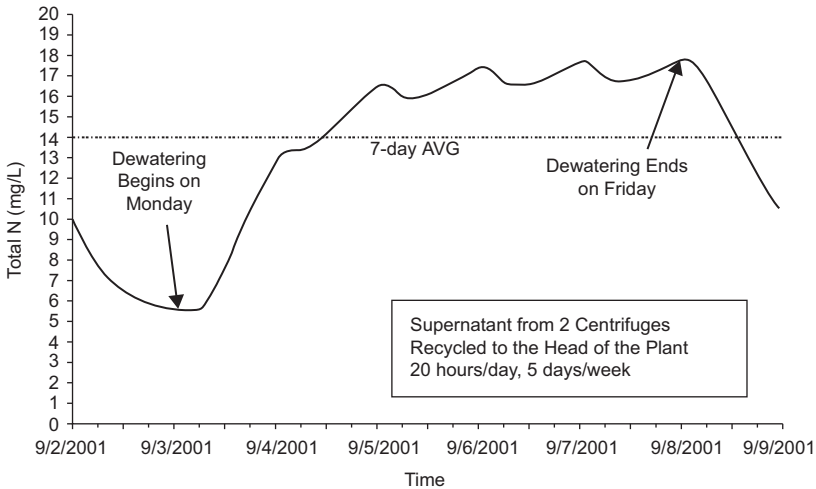

FIGURE 11.20 A plot showing the dynamic response of a model over a seven-day period with sludge dewatering occurring only five days per week (courtesy of Black & Veatch).

diurnal effluent total nitrogen concentrations for a plant, with supernatant from the centrifuges returned to the head of the plant. The centrifuges were operated for 20 hours a day, 5 days a week. On Mondays, when dewatering began, there was a sharp increase in effluent total nitrogen, and the concentrations continued to increase each day until Friday, when the work week ended and dewatering stopped. The small dips in the curve correspond to the four hours per day when the centrifuges were shut down during the week. When a single centrifuge was operated daily, the average effluent total nitrogen concentration decreased to 11 mg/L. This plant was having trouble meeting its nitrogen limit because of low influent carbon load to support denitrification and high nitrate loads in the centrate returned to the head of the plant from the solids handling facilities. As a result of this study, the centrifuges are now operated continuously, 24 hours a day, 7 days a week, and methanol is being used to provide additional carbon for denitrification. The plant has been in compliance with the effluent nitrogen limits since these changes were made.

2.5.3 Sensitivity Analysis

Once a baseline model has been constructed and calibrated, various process modifications or operational adjustments can be tested in the model to help troubleshoot

or optimize a BNR facility. The model can be used to simulate the effects of changing operating parameters, allowing engineers and operators to test the change in the model before making the change in the plant. The model can be used to run several different scenarios. It can be used to assess the potential effects on plant operation from storm flows, increasing or decreasing MLR or RAS or from adding supplemental carbon, taking tanks out of service, or adding a new waste stream or sidestream equalization or treatment. There is a significant advantage to being able to test a proposed change before implementing it in the plant.

When conducting sensitivity analyses, the model is operated repeatedly while keeping all parameters the same except for the one parameter of interest, which is adjusted over a defined range. Outputs from the model are plotted to show how sensitive the model is to changes in the parameter of interest. Figure 11.21 shows the results of sensitivity analysis conducted to predict the effluent ammonia concentrations when operating a plant at 10°C over a range of SRTs. The analysis was conducted using two different sets of nitrification kinetic parameters: the "default" kinetics for the process simulator being used in the analysis and the "Dold Kinetics"

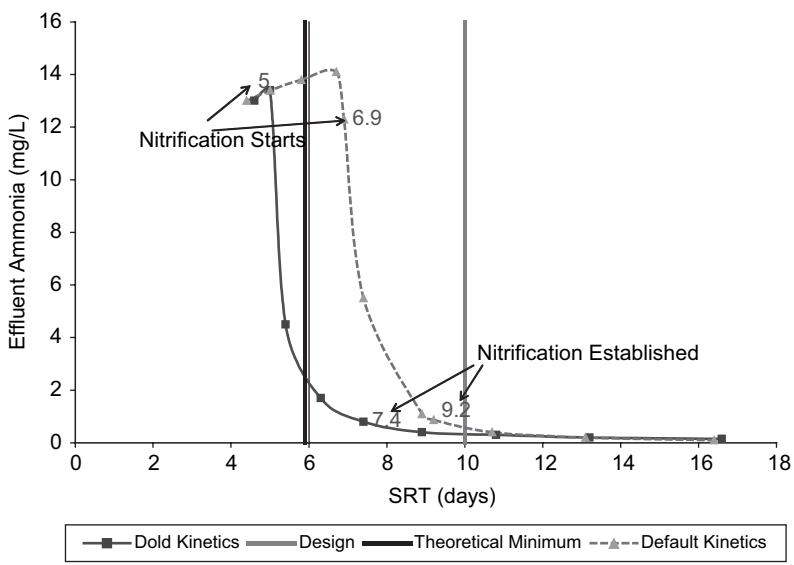

Figure 11.21 Sensitivity analysis showing the effect of solids retention time (SRT) on effluent ammonia (courtesy of Black & Veatch).

as suggested in WERF's *Methods for Wastewater Characterization in Activated Sludge Modeling* (2003). The curves for both sets of kinetics have similar shapes—with high effluent ammonia concentrations predicted at low SRTs, an initial steep drop in effluent ammonia as the SRT increases, and gradually flattening slope at higher SRTs. The sensitivity analysis provides an estimate of the SRT range at which nitrification could be lost, depending on site-specific nitrification rates. Nitrification rate tests could be conducted to further calibrate the process model to predict more accurately the minimum SRT to maintain reliable nitrification.

2.5.4 Wet Weather

Simulation software can be used to model a wet weather event to understand and evaluate the effect of wet weather flows on plant processes and effluent quality, which can offer valuable insight when troubleshooting a BNR plant that must meet limit of technology (LOT) discharge limits. Figure 11.22 is an example output from a BioWin model showing how a wet weather event may affect plant performance. The

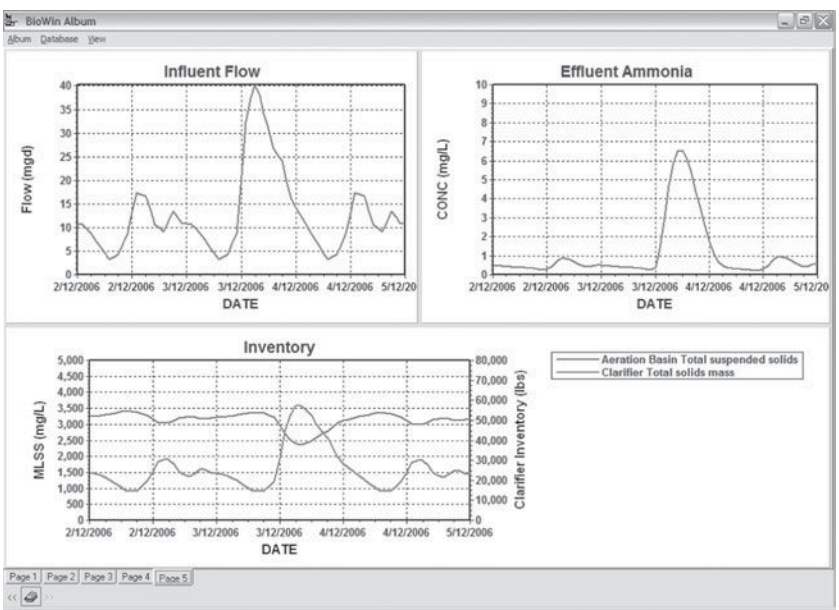

Figure 11.22 Example output of the effect of a storm on plant effluent ammonia and solids inventory (MLSS = mixed liquor suspended solids) (courtesy of Black & Veatch).

simulation was conducted for three consecutive days during which a storm occurred on the second day, as depicted by the top left graph. The storm's potential effect on the effluent ammonia concentration is plotted in the top right graph. The lower graph shows how the high storm flows might push more solids inventory into the secondary clarifiers, causing the MLSS to drop significantly. The next step after running such a simulation could be to model various strategies to lessen the effects of the storm, such as using a storm equalization tank or shifting the plant to a step-feed mode of operation to keep the inventory in the aeration basins and prevent it from overloading the clarifiers. This example demonstrates one way in which the process model can be used to understand the dynamic nature of a WWTP.

Figures 11.23 and 11.24 illustrate other examples of how a process model can be used to investigate the effects of mitigating problems that are hindering plant performance. Figure 11.23 illustrates the predicted benefit of providing plant influent flow equalization, investigating various size equalization basins. Figure 11.24 shows the effluent total nitrogen predicted by the process model of diverting the storm flow to a high-rate clarification (HRC) process for physical/chemical treatment and blending it back with the mainstream flow after secondary treatment. All flows greater than 95 ML/d (25 mgd) were diverted to an HRC process. The secondary effluent was further treated with denitrification filters. The goal was to keep the total effluent nitrogen load below 658 kg/d (1450 ppd).

2.6 Process Assessment Troubleshooting Matrix

This section includes a troubleshooting matrix (Table 11.3) that captures the fundamental principles and process underpinnings . Table 11.3 identifies several performance problems that typically are observed at BNR facilities and outlines possible contributing factors and remedial steps. Contributing factors and remedial steps have been organized in the matrix based on the sections of this chapter for reference.

3.0 HYDRAULIC AND MECHANICAL EQUIPMENT ASSESSMENT

The performance of BNR plants can be impaired by oversights in the hydraulic and mechanical equipment designs. This section identifies areas where process engineers should work closely with civil and mechanical designers to optimize design to avoid operational and performance problems. Several examples are included to

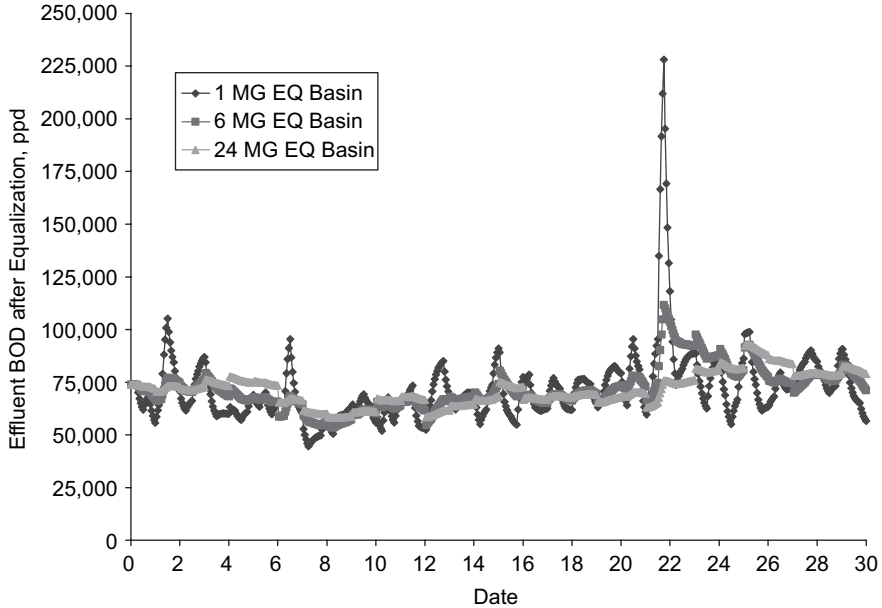

FIGURE 11.23 Effects of basin size on flow-through equalization basin effluents (BOD = biochemical oxygen demand) (courtesy of Black & Veatch).

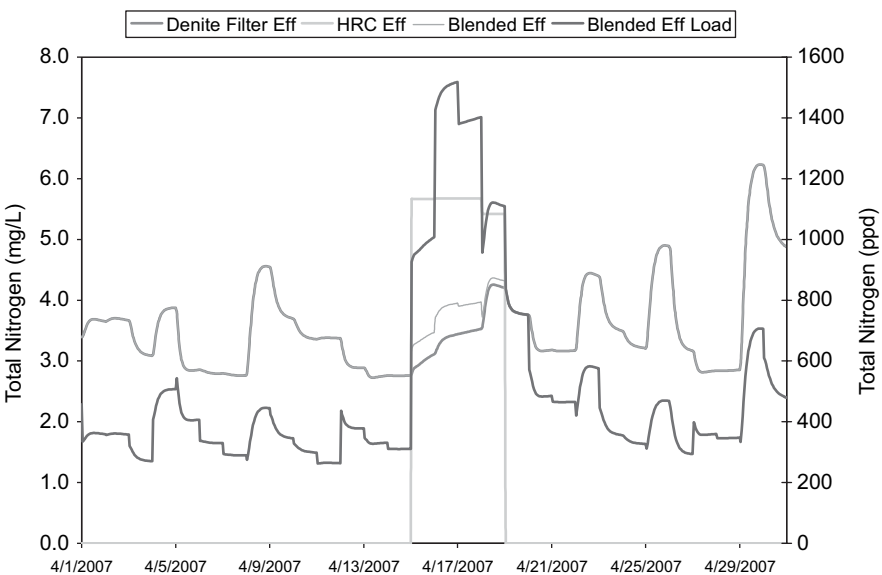

FIGURE 11.24 Model output showing blended effluent total nitrogen from denitrification filters and high rate clarification (HRC) (courtesy of Black & Veatch).

TABLE 11.3 Biological nutrient removal (BNR) process assessment troubleshooting matrix.

	Possible contributing factors and remedial steps				
Commonly observed BNR problems	**Section 2.1[a] Wastewater characterization**	**Section 2.2[a] Operational parameters**	**Section 2.3[a] Microbiology/ kinetics**	**Section 2.4[a] Instrumentation and control**	**Section 2.5[a] Process modeling**
High effluent ammonia or excessive effluent ammonia peaks	• Excessive diurnal load variation • High sidestream ammonia load • Equalize sidestream	• Low DO, maintain 2.0 mg/L at front end, 1.0 mg/L at end of aeration basin • Low SRT, increase if below theoretical washout for wastewater temperature plus a reasonable safety factor • Low pH, check alkalinity	• Nitrification inhibition • Consider inhibition and rate testing • Low temperature	• Clean and calibrate instrumentation • Evaluate diurnal patterns • Check DO • Check pH	• Use diurnal modeling to predict effluent ammonia at plant operating condition • SRT sensitivity analysis • Full-plant mass balance to account for sidestreams
High effluent nitrates	• Carbon-to-nitrogen ratio is low • rbCOD fraction is low • High influent TKN making it difficult for anoxic/aerobic process to achieve low nitrate	• Increase C/N and rbCOD fraction by fermentation or chemical supplementation • High DO in MLR, reduce tail end DO to <1.0 mg/L • Anoxic SRT too low, increase MLSS if possible • MLR too high or too low for optimum performance	• Competition for carbon with PAOs • Low anoxic SRT or HRT, check denitrification rates	• Clean and calibrate instrumentation • Evaluate diurnal patterns • Check and control DO at MLR to <1.0 mg/L	• Investigate benefit of deoxygenation (De-Ox) zone at MLR pumps • Anoxic zone volume sensitivity analysis • MLR sensitivity analysis
	• Check theoretical minimum effluent nitrate given plant operating condition	• Poor mixing of internal recycle streams leading to short-circuiting[b]	• Low temperature • Incorporate deox zone before MLR	• Use nitrate probe/ analyzer or ORP to optimize MLR pumping	• Use diurnal modeling to predict effluent nitrate at plant operating condition

		• Hydraulic drops are entraining too much air[b]	• Overmixing of anoxic zone, entraining DO[b]		
High effluent nitrites	• Postanoxic zone carbon-to-nitrogen ratio too low for complete denitrification	• Incomplete nitrification • Low pH, check alkalinity • High DO in MLR • Low aerobic SRT • Low DO in aerobic zone • Increase C/N ratio in postanoxic zone by carbon augmentation • MLR too high for complete denitrification	• Inhibition • AOB growth exceed that of NOB; latter more sensitive to abnormal conditions	• Clean and calibrate instrumentation • Distinguish between nitrates and nitrites • Check and control DO at MLR to <1.0 mg/L; and >2.0 mg/L in rest of basin • Use nitrate probe/analyzer or ORP to optimize MLR pumping	• Perform similar sensitivity analyses as outlined above for high ammonia and nitrates, but also trend nitrite
High effluent organic nitrogen	• High rDON fraction • Industrial waste	• rDON is not biodegradable; little can be done to reduce this fraction • Longer SRT may help reduce some rDON in some cases • Source control—check industrial loadings • Optimize final clarifiers performance to reduce particulate organic nitrogen fraction	• rDON can cause some growth of algae in receiving water in presence of bacteria • Up to 25% of rDON may be available for algae growth • Some rDON can be removed by flocculants	• SRT control • Sludge blanket density meter to help optimize performance of clarifier	
High effluent total phosphorus	• Low COD/P • Low rbCOD/P • Low VFA/P	ncrease VFA/P ratio by fermentation products or chemical supplementation	Insufficient phosphorus release in anaerobic zone (see below)	Monitor release and uptake of phosphorus	• Model influent carbon fractions • RAS sensitivity analysis

(*continued*)

TABLE 11.3 Continued

	Possible contributing factors and remedial steps				
Commonly observed BNR problems	**Section 2.1[a] Wastewater characterization**	**Section 2.2[a] Operational parameters**	**Section 2.3[a] Microbiology/ kinetics**	**Section 2.4[a] Instrumentation and control**	**Section 2.5[a] Process modeling**
	• Compare with graph in Figure 11.3 (rbCOD/P versus VFA/ rbCOD) • Check for nitrates or DO in plant influent	IHigh nitrate in RAS (see high nitrate in effluent problem above) RAS rate is too high bringing back excessive nitrate and reducing preanoxic zone and anaerobic zone HRT Addition of chemicals for phosphorus precipitation SRT is too long High effluent TSS	GAO competition (see below) Inhibition from urea Secondary release of phosphorus (see below)	Check nitrates and DO in feed and RAS	• Full-plant mass balance to account for sidestreams • SRT sensitivity analysis
Glycogen accumulating organisms	• High influent glucose content • VFA mostly acetic acid • Low pH • High temperature	Low pH, consider alkalinity supplementation Excess capacity in service, SRT is too long; consider taking aeration basin offline Long unaerated zones Feeding glucose waste for denitrification, consider other carbon source Reduce SRT at high temperature >28°C	Domination by tetrad-shaped GAO bacteria	pH monitoring and control	• GAO are not modeled by most process simulators
Inadequate release of phosphorus in anaerobic zone	• Insufficient VFA and/or rbCOD	• Increase VFA/P by fermentation or chemical supplementation	• Lack of PAO • Possible GAO domination	• Online phosphorus profiles	• Full-plant mass balance to account for sidestreams

	• Check for nitrates or DO in plant influent • See also above, as GAO dominance will affect phosphorus release	• Ferment small portion of mixed liquor from anaerobic zone and return • High nitrate in RAS (see high nitrate in effluent problem above) • RAS rate is too high bringing back excessive nitrate and reducing preanoxic and anaerobic HRT • Avoid chlorination of influent	• Anaerobic HRT is too short • Consider retrofit to Johannesburg process for RAS denite to reduce nitrate and preserve VFA		• rbCOD and VFA sensitivity analysis
Inadequate phosphorus uptake in aerobic zone, and good release in anaerobic zone	• rbCOD/P[b]	• Low DO in aeration zone, target >2.0 mg/L in first aerobic zone • Secondary release resulting in excessive phosphorus for uptake (see below for secondary release)	• Conditions do not favor growth of PAO	• Online phosphorus profiles	• Model to compare predicted with actual profiles
Secondary release of phosphorus		• Anaerobic retention too long for available VFA and rbCOD • Anoxic retention too long • Too little nitrate to second anoxic zone, going anaerobic and releasing phosphorus • FC sludge blanket is too deep, going anaerobic and releasing phosphorus	• PAO release phosphorus in the absence of VFA • No stored VFA energy for take up of phosphorus upon reaeration	• Profile of phosphorus release in the anaerobic zone, anoxic zone, and in RAS	• Model to compare predicted with actual profiles
Poor settling sludge	• High VFA content	• High PC and FC sludge blankets resulting in excessive VFA formation	• Incomplete nitrification or denitrification,	• Monitor DO at inlet of aeration basin • Monitor DO in MLR	• Full-plant mass balance diurnal modeling investigating peak aeration demands

(*continued*)

TABLE 11.3 Continued

	Possible contributing factors and remedial steps				
Commonly observed BNR problems	**Section 2.1[a] Wastewater characterization**	**Section 2.2[a] Operational parameters**	**Section 2.3[a] Microbiology/ kinetics**	**Section 2.4[a] instrumentation and control**	**Section 2.5[a] Process modeling**
	• Nutrient deficiency • Low pH and alkalinity	• Excessive SRT • Low DO environments in aeration basin • MLR is too low, anoxic zone goes anaerobic and generates excessive VFA • Excessive DO in MLR feeding low DO filaments in anoxic zone	generating N_2O and favoring *Microthrix parvicella* and Type 0092 • High VFA content, feeding *Thiothrix*, and O21N filaments	• Monitor nitrates at end of anoxic zones • ORP profile through anoxic and anaerobic zones	• Use models to determine optimum recycle rates for RAS and MLR • SRT sensitivity analysis
Excessive scum/foam	High influent oil and fats	Surface blockage[b] No positive drop from anoxic to aeration[b] In plant recycle of scum, exacerbating build up of scum Overly long SRT Selective wastage from the surface of the aeration basin[b] Consider full radius scum skimmers on final clarifiers[b] Consider surface sprays to break up scum[b]	Start up foam Nocardia forms *M. parvicella* (see poor settling sludge above)	Monitor SRT Monitor DO Monitor pH	SRT sensitivity analysis tracking level of nitrification to determine if operating condition favors *M. parvicella*

[a]Reader can review these sections for additional discussion.

[b]Refer to Section 3.0.

AOB = ammonia oxidizing bacteria; COD = chemical oxygen demand; DO = dissolved oxygen; FC = final clarifier; GAO = glycogen accumulating organisms; HRT = hydraulic retention time; MLR = mixed liquor recycle; MLSS = mixed liquor suspended solids; NOB = nitrite oxidizing bacteria; ORP = oxidation reduction potential; PAOs = phosphorus accumulating organisms; PC = primary clarifier; RAS = return activated sludge; rbCOD = readily biodegradable COD; rDON = recalcitrant dissolved organic nitrogen; SRT = solids retention time; TKN = total Kjeldahl nitrogen; and VFA = volatile fatty acid.

demonstrate how hydraulic designs or mechanical equipment, or both, have affected plant performance, which will be helpful in identifying similar or related problems when troubleshooting a BNR facility.

3.1 Overaeration of Influent

Overaeration of the plant influent adds oxygen that interferes with the development of the true anoxic or anaerobic environment needed for BNR. Adding oxygen at this point in the process also causes loss of the short-chain VFAs necessary for enhanced biological phosphorus removal (EBPR). Loss of even a small fraction of VFA can be detrimental because many BNR plants experience periods when VFA is the limiting factor controlling performance.

Grit removal should be accomplished using methods that do not rely on aeration. Screw pumps should not be used to convey plant influent, primary effluent, or RAS flow. The hydraulic drop or free fall over a primary effluent weir into effluent launders should be limited; the free fall and splash as the flow hits the bottom of the concrete launder can result in significant oxygen transfer. It is also important to limit headloss or hydraulic drop from the primary sedimentation basins to the first unaerated zone of the BNR process. It helps to estimate how much oxygen can be transferred through a hydraulic drop. For every 300 mm (12 in.) of drop, approximately 1 mg/L of oxygen is transferred up to a dissolved oxygen concentration of 3 mg/L.

Hydraulic designs should be considered that provide for primary effluent weirs to be submerged only during periods of peak flow to reduce the hydraulic drop and thus air entrainment during average- and low-flow periods. A side benefit of a tighter hydraulic design is the overall savings in plant pumping head, which could significantly reduce the overall pumping energy requirements. Designers should recognize that flooding primary clarifier effluent launders during peak flows will not be detrimental to plant performance.

In existing plants, or where it is necessary to drop the flow from the primary clarifiers to a lower elevation, a mechanical device can be installed to keep the liquid level in the effluent launders just below the water level in the primary tank to minimize aeration. For example, at the Kelowna plant in British Columbia, Canada, feed contained insufficient VFA, and fermentation of the primary sludge would have been required to augment the VFA. Therefore, minimizing aeration of the influent was critically important to preserving the VFA for BPR. The rectangular primary tanks caused a considerable amount of white water in the effluent launders, and the primary effluent dropped about 1 m (3 ft) into the feed channel of the anaerobic zones.

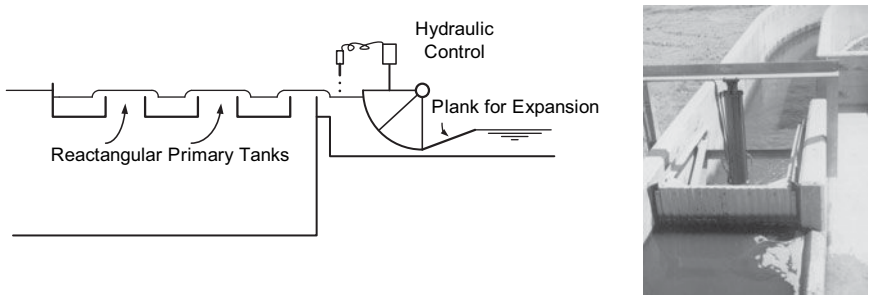

FIGURE 11.25 Control gate at Kelowna, British Columbia, Canada, plant (courtesy of Black & Veatch).

This condition resulted in too much aeration that hindered the performance of the BNR process, and created an odor problem. A gate was installed in the feed channel to control the liquid level in the effluent channels to less than 25 mm (1 in.) below the effluent weirs at all flowrates. The gate was controlled to allow flow to pass without drowning the primary tanks. The downstream end of the gate was equipped with a plank, with one end of it attached to the gate and the other end left free floating. This device allowed expansion of the supercritical flow under the gate to normal flow without creating a hydraulic jump as shown on Figure 11.25.

At the Tembisa plant near Johannesburg, South Africa, the plant was constructed so that the existing trickling filter effluent could be returned to the BNR process. A new activated primary tank was installed to provide additional VFA to support EBPR. The hydraulic fall between the grit channels and the new activated primary tank was 18 m (55 ft), which created the potential for air entrainment and transfer of oxygen to the BNR process influent within the process feed pipe. The solution was a pinch valve in the feed pipe, which was controlled from the intake at the discharge of the grit chambers, as shown on Figure 11.26. The pinch valve discharged into a box with a chimney to equalize the pressure but not to overaerate the influent.

Screw pumps can transfer considerable oxygen as the water is agitated and lifted by the screw and then dropped into a channel. Screw pumps were used widely in the 1970s and 1980s because of their energy efficiency and ability to automatically handle a wide range of flows. Many of these plants are now being upgraded for BNR, and replacement of the screw pumps should be considered to avoid overaeration of the pumped flow.

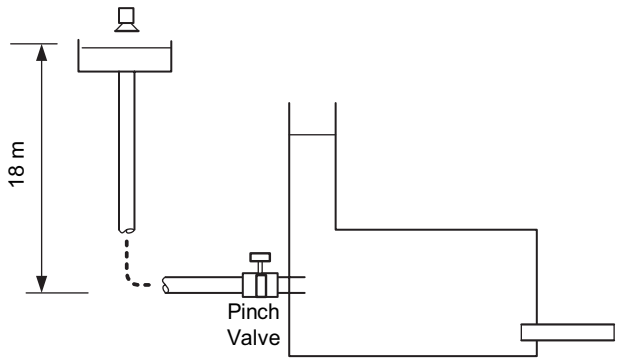

FIGURE 11.26 Pinch valve for breaking energy without aeration (courtesy of Black & Veatch).

3.2 Flow Distribution

Accurate distribution of flow to various process units should not be overlooked when optimizing or troubleshooting a BNR facility, especially when targeting LOT discharge requirements. Uniform mass loadings and HRTs can have a much greater effect on the performance of a BNR facility than a plant designed for straight secondary treatment.

Accurate distribution of flow to final clarifiers is necessary to optimize fully plant capacity and performance. A small difference in flow distribution of 15% will reduce the plant's overall capacity by 15% because the final clarifier receiving the highest flow will be the first to fail. For flow restriction strategies to be successful, it is necessary to implement a fully automated measurement and control/throttling system to balance the flow split to clarifiers for all plant flow conditions. Manual adjustment of valves to control the distribution of flow is not an effective strategy because the valves will require continuous adjustment to maintain an acceptable balance given the typical diurnal flow variations experienced at WWTPs.

The most overlooked factor in the design of flow distribution structures is the effect of momentum of the incoming flow that leads to inequalities of flow through the gates or over the weirs. A CFD analysis can be used to determine the effect of corrective measures for existing flow distribution structures and to optimize design of new structures.

3.3 Intensive Mixing of Influent and Recycle Streams

Streams of different densities do not mix easily. As a result, short-circuiting can be experienced when two or more process streams are introduced to a reactor if there is insufficient mixing. The potential for short-circuiting also can increase as the sidewater depth of the reactor increases. An example of this is when RAS, primary effluent, and MLR are discharged to an unaerated zone. Provisions must be made to ensure proper mixing of the incoming streams because the momentum and density currents may carry the streams in different directions. The result of poor mixing is that the influent substrate or nitrate will not be available to the bacteria for much of the retention time in the unaerated zone, which can greatly reduce the nutrient removal efficiency of the process. Much depends on how the flow streams are brought together into the zone and the applied mixing energy in that zone. Common design criteria for mixing energy range from 4 W/m^3 (0.15 hp/1000 cu ft) to 20 W/m^3 (0.75 hp/1000 cu ft). Slow-speed vertical mixers are up to three times more efficient than high-speed submersible mixers, which has been ignored when specifying mixing energy requirements for an unaerated BNR zones. The design of slow-speed vertical mixers at an applied mixing energy of greater than 13 W/m^3 (0.5 hp/1000 cu ft) has resulted in excessive dissolved oxygen entrainment and has hindered the performance of some BNR facilities.

Intensive mixing of the influent streams in specially designed chimneys will help avoid short-circuiting and enhance performance. The mixing energy created by flow momentum in the chimney provides thorough mixing of two or more influent streams before they are discharged at the floor of the basin into the unaerated zone. Use of influent chimneys allows for lower mechanical mixing energy in the unaerated zone and ensures intense contact of the bacteria with the influent substrate.

The effects of poor mixing and short-circuiting were observed in the Bushkoppie plant in Johannesburg, South Africa, where the RAS and primary effluent flows were discharged to the surface of the tank. In addition, there was an 800-mm (2.7 ft) drop from the channels to the anaerobic zone that entrained air. These poor hydraulic conditions resulted in unreliable phosphorus removal. The remedy to this problem was to construct an influent chimney to provide good mixing of the two influent streams and to discharge the combined flow at the bottom of the tank. The chimney was designed to discharge approximately 95% of the flow through openings at the bottom. The remainder was allowed to overflow to the surface when flow exceeded average design flow to prevent accumulation of scum. Figure 11.27 shows a section through the chimney and a picture of the completed structure. Elimination of

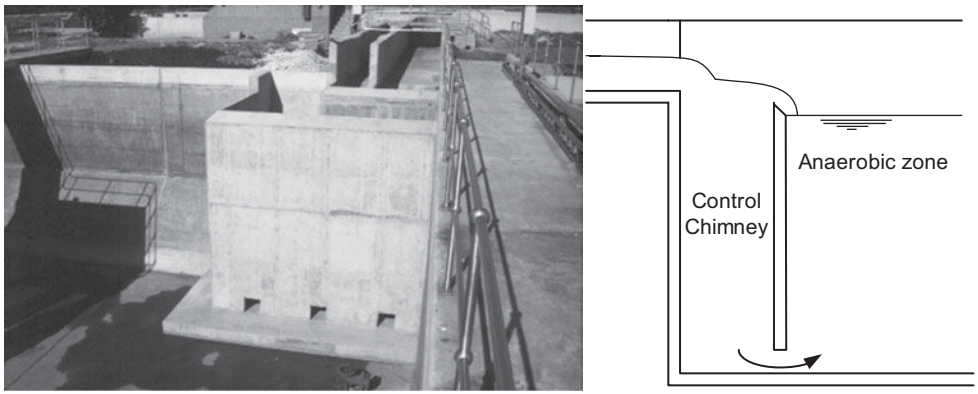

Figure 11.27 Example of a "chimney" for intimate mixing of influent streams (courtesy of Black & Veatch).

the short-circuiting and intensive mixing of the incoming stream resulted in more reliable phosphorus removal.

3.4 Momentum and Density Gradients

The effect of momentum and density gradient created by introducing two or more streams into a bioreactor can lead to severe short-circuiting problems. Below are two examples observed in various plants created by improper introduction of flow streams into a bioreactor. Review of these examples should be helpful in troubleshooting similar challenges.

3.4.1 Pelham, South Carolina

The Pelham WWTP in South Carolina consisted of three parallel unfolded carrousels, one of which is shown on Figure 11.28. The feed was not mixed with the RAS before it entered the aeration basin. The RAS entered the basin near the floor and the primary effluent entered about 2.5 m (8 ft) below the surface at the point shown on Figure 11.28. The operators noted that when the aerator near the entry point for the feed was turned off, ammonia appeared in the effluent. This did not occur when the other aerator was turned off and the near aerator was operating. The short-circuiting was because of the density gradient created in the channel when the aerator near the feed point was turned off. The momentum of the influent, which contained little TSS, would carry it up and over the more concentrated MLSS far into the tank

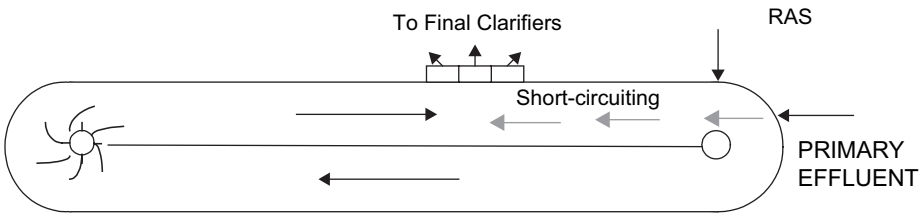

FIGURE 11.28 Short-circuiting in the Pelham, South Carolina, carrousel plant (courtesy of Black & Veatch).

while rising to the surface. This resulted in significant short-circuiting to the effluent. The remedy for this problem was to install a baffle at the inlet pipe to redirect the momentum of the influent. A mixing chimney also was provided to better mix the influent and RAS streams and to introduce the combined flow at the bottom of the basin.

3.4.2 New York, New York

Thirteen of the 14 step-feed plants owned by New York City are being converted to step-feed denitrification by installing baffles to form anoxic zones at each feed point, as shown on Figure 11.29a. A portion of the primary effluent is introduced at each anoxic zone, as shown on Figure 11.29b. When troubleshooting the performance of one plant, it was found that the openings to convey the mixed liquor from one pass to the next was on the floor and carrying air bubbles into the anoxic zone of the following pass. The momentum of the primary treated influent carried it deep into the anoxic zone without much mixing. Consequently, dissolved oxygen was observed in one-third of the anoxic zone. The solution to this challenge was to place a small deoxygenation zone at the end of the aerated pass with a downflow operation to prevent bubbles from being swept into the anoxic zone. Baffles were also added to break the momentum of the influent flow and to use that energy for instantaneous mixing of the influent with the mixed liquor. In retrofitting tanks that are configured poorly for mixing, a simple baffle can go a long way to improve mixing and prevent short-circuiting by breaking the momentum of the incoming streams.

3.5 Anaerobic/Anoxic Zone Mixing Intensity

The mixing intensity applied to an anoxic or anaerobic zone drastically can affect BNR performance. As described above, inadequate mixing can result in short-circuiting

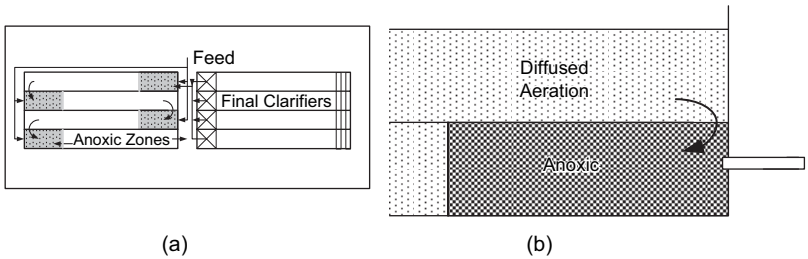

FIGURE 11.29 Momentum from influent to anoxic zones, New York City (courtesy of Black & Veatch).

and poor performance, and too much mixing energy can lead to excessive surface agitation and oxygen entrainment. Both submersible high-speed mixers and slow-speed vertical mixers can be used effectively, but the mixing efficiency of the latter is much higher than that of high-speed submersible units. With a slower rotational speed, a larger, more efficient impeller can be used to transfer the same amount of mixing at much lower energy input. Operating at rotational velocities of less than 25 rpm, as opposed to approximately 600 rpm with a submersible mixer, results in less slippage and reduced energy transfer of heat to the water. The energy input for mixing can be reduced to 5 W/m^3 (0.2 hp/1000 cu ft) or less when slow-speed vertical mixers are used in conjunction with influent chimneys to provide good initial mixing of the influent streams. There is a tendency to specify the energy input regardless of the type of mixer used, which can result in ove-mixing, vortexes, and aeration. For example, vertical mixers operating at 20 W/m^3 (0.75 hp/1000 cu ft) will form vortexes that entrain too much air for efficient nutrient removal. Vertical baffles also may be used with vertical slow-speed mixers to avoid surface vortexes. Submersible mixers typically are less expensive to install because they do not require an access bridge.

3.6 Mixing Energy in Aeration Basins

Drury et al. (2005) and others have shown that efficient biological phosphorus removal requires a semi-plug flow arrangement with high dissolved oxygen concentrations near the inlet to the aeration basin. This is also required for controlling the growth of *M. parvicella*. Where possible, the first section of the aeration zone should

be large enough to ensure an OUR that can be met reliably under all load conditions with the supplied aeration system. The OUR limit for fine-bubble diffused aeration, as calculated based on actual oxygen requirement, typically is considered to be approximately 120 mg/L·h. Typically, the ammonia–nitrogen is depleted ahead of the last aerated zone, which results in a much lower oxygen demand at this point. In most plants, the aeration system has been designed to supply enough air to the last section to maintain the "mixing energy requirements," or a minimum airflow requirement for ceramic diffusers. These minimum airflow rates may result in dissolved oxygen concentrations in excess of 5.0 mg/L at the point where mixed liquor is recycled to the anoxic zone, thus reducing nutrient removal efficiency of the plant.

There are numerous examples of plants being operated successfully with the airflow at the end of a plug-flow reactor below the accepted minimum for mixing energy. The Padre Dam plant near San Diego, California, is operated with no concern for the mixing energy, but only for dissolved-oxygen control to limit the conveyance of oxygen to the anoxic zones. Plant performance has been excellent, operating well below typical minimum airflow rates for mixing. Other methods to deal with overaerating is to provide mixers in the last part of the aeration tank or to switch to coarse bubble diffusers that impart more energy for mixing and less dissolved oxygen transfer. Another solution is to "burp" the plant by controlled short periods of high aeration twice per day to resuspend solids that may have settled at the reduced airflow necessary to maintain the desired low dissolved oxygen concentration at the end of the aeration basin.

3.7 Scum Control

It is important to avoid back-mixing from aerated to unaerated zones while ensuring that scum is not trapped but moves freely through the BNR reactor. Back-mixing of flow from aerated to unaerated zones not only transfers undesired oxygen to these zones but also increases the potential for excessive scum and foam formation. Baffle walls or other barriers prevent scum from passing from one zone to the next, further aggravating the problem. Excessive foaming has been observed in many plants that experience back-mixing of oxygen.

The high turbulence induced by the surface aerators resulted in the rise of air bubbles on the upstream side of the scum baffle that also served as a walkway support. In this low dissolved oxygen environment, scum started to grow and eventually filled the basin as shown on the sketch. A weir was added on top of the partition wall between the anoxic and aerobic zone to reduce the liquid level by approximately 50 mm (2 in.).

This hydraulic drop induced adequate energy on the downstream side of the partition wall to break up the scum, entrain it in the MLSS, and pass it under the walkway. The hydraulic drop also prevented back-mixing of oxygen. The scum disappeared.

Baffle walls that extend above the liquid level are problematic because they not only trap scum but provide a surface area for foam-forming bacteria to attach and grow. When possible, baffles and chimney walls should be installed just below the liquid surface to ensure that foam can migrate freely through the BNR zones and to eliminate surface attached growth where slime growth tends to start. If a meandering flow pattern is used in an anaerobic or anoxic zone to prevent short-circuiting, then intermediate baffle walls should be submerged. In this situation, the last baffle wall separating the aerobic zone from the unaerated zone should extend above the liquid surface or at least create adequate headloss to avoid back-mixing. When the hydraulics will not allow for a slight drop, the velocity of the mixed liquor passing from the anoxic to oxic zone should exceed 300 mm/s (1 ft/sec) at all times.

If elevations are properly established, then 95% of the flow will follow the meandering path submerged baffle walls, with only a small fraction of the flow passing over the baffle walls to carry scum through the unaerated zones.

At JEA's Southwest Water Reclamation Facility (WRF) in Jacksonville, Florida, partitions are just below the surface, creating a meandering flow. There is a drop of approximately 50 mm (2 in.) from the anoxic to the aerobic zone.

Baffles separating aerated and unaerated zones should not have both top and bottom openings because this would encourage the flow from the unaerated zone to pass under the baffle while lighter aerated mixed liquor passes back over the baffle to the anoxic zone. Small openings of not more than 200 mm by 200 mm (8 in. by 8 in.) should be provided at the bottom of a baffle wall for drainage.

Ideally, the flow over the submerged weir separating an unaerated zone from an aerated zone should have a minimum velocity of approximately 0.6 m/s (2 ft/sec) under maximum flow conditions, and there should be no back-mixing at the minimum plant flow. If the overflow weir is too long, then the weir could become uneven and allow a rotational flow that can carry air bubbles back to the anoxic or anaerobic zone. For long weirs, it may be necessary to use an adjustable weir plate that can be set during commissioning to achieve uniform discharge. Downward-opening weir gates or adjustable, hinged weirs also can be used to provide flexible level control for basins designed to accommodate wide flow ranges associated with recycle rates.

3.8 Selective Wasting

Despite precautions and design efforts to pass scum effectively though a plant, it will continue to form and accumulate on the surface of some BNR processes. Selective wasting of surface scum and mixed liquor is an effective way to mitigate operational and performance problems associated with excessive scum formation. Figure 11.30 illustrates how scum can be removed from the surface and wasted from the process with the mixed liquor. The float ensures a sufficient drop and turbulence to entrain the scum for effective removal with mixed liquor. The flow adjusts automatically to the liquid level and to the rate of withdrawal. The size of the float will determine the drop and amount of turbulence. Because the liquid level in the tank is determined by the overflow weir to the final clarifiers, the actual size of the float is not critical. An alternative would be to use a motorized tilting weir controlled by an automated level control. If this waste is pumped to a DAF unit, then flow could be continuous and could be metered to determine automatically the SRT of the system. A similar system was first installed at the Kelowna plant in British Columbia, Canada, and has an operating history of approximately 15 years.

Selective wasting of mixed liquor and scum is gaining favor and can be retrofitted to existing plants, especially when problems with foam and scum are occurring. By wasting mixed liquor instead of RAS, the operator can set volumetrically the sludge wasting rate for a predetermined SRT. For example, wasting one-tenth of the volume of the aeration zone per day in the form of mixed liquor will result in a 10-day SRT. It is necessary to consider the additional volume of WAS and the additional hydraulic

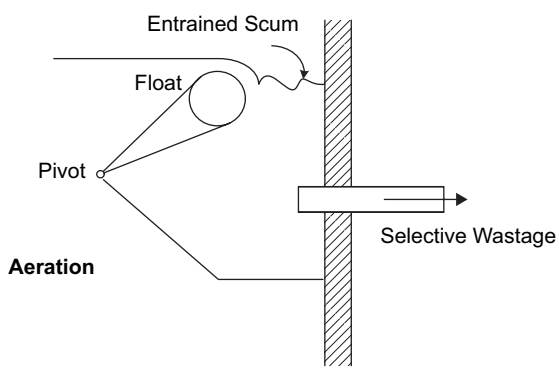

FIGURE 11.30 Selective wasting of scum and mixed liquor (courtesy of Black & Veatch).

load on the WAS thickening process before implementing selective wasting. There are some thickening processes, however, such as DAF that are designed based on the solid load limitation even at a feed solids concentration as low as 0.4%. Selective wasting significantly reduces the concern of overloading the thickening process. An additional advantage of DAF thickening is that it removes scum very efficiently. Other mechanical thickening equipment may be overloaded quickly if not designed for the thinner feed solids concentrations associated with selective wasting.

3.9 Final Clarifiers

Final clarifiers that support BNR processes should be designed and operated to provide high solids capture. This is because the effluent solids contain significant nitrogen and phosphorus that contribute to effluent total nutrient concentrations. With well-designed and operated final clarifiers that are able to maintain effluent TSS to less than 8 mg/L, it may be possible without filtration to achieve an effluent total phosphorus concentration of less than 0.5 mg/L, if the orthophosphate concentration is reduced to less than 0.1 mg/L.

The design and operational factors that should be considered when a clarifier is not performing optimally include

- Poor sludge settling characteristics;
- Uneven flow distribution;
- Dissipation of inlet energy;
- Good flocculation at inlet;
- Sludge retention time in clarifier;
- Optimum RAS pumping rate;
- Effluent launder baffling; and
- Surface scum removal.

Care must be taken to avoid high turbulence and breakup of the flocs. Energy dissipation inside the floc well and flocculation is important to produce a clear final effluent. The clarifier inlet must be designed to dissipate energy while reducing the water fall effect of the higher-density MLSS flow entering the clarifier.

Final clarifiers that support BNR processes must be designed and operated to minimize SRT to avoid secondary release of phosphorus in the sludge blanket. The clarifiers should be designed and operated for rapid sludge removal to prevent

secondary release of phosphorus while avoiding excessive disturbance of the sludge blanket. For circular clarifiers, suction lift or ToBro-type sludge collection systems are attractive options, especially for clarifiers in excess of 30 m (100 ft). These systems remove sludge quickly and do not rely on scrapers to transfer sludge to a center hopper. Centrally scraped circular final clarifiers that are designed for rapid conveyance of sludge to a center sludge hopper have been used successfully in many BNR plants, especially those equipped with deep spiral blade scrapers. Scraping mechanisms must be designed and installed to operate with a clearance of less than 25 mm (1 in.) between the floor and the bottom of the scraper to avoid gas development and "popping" of leftover sludge as the thin sludge layer becomes anoxic or anaerobic. The rotational speed of the scraper mechanism and the depth of the blades should be evaluated to confirm they can transport the sludge to the center of the clarifier in a timely manner (Randall et al., 1992). The scraping mechanisms can be provided with variable-speed drives to optimize the speed of sludge transport to the center sludge hopper to ensure a low sludge blanket. Sludge scrappers have been reported to operate efficiently with tip speeds ranging from 3.0 to 8.0 m/min (10 to 27 ft/min), depending on diameter of the clarifier and scraper design. Variable-speed drives on the scrapers give the operator some flexibility to adjust and find the optimum tip speed for a given clarifier.

One of the main issues for BNR clarifiers is to prevent short-circuiting of either the liquid or the solids. Ideally the RAS nitrate and phosphorus concentration should be low. If there is rat-holing in the sludge blanket, and some sludge short-circuits from the inlet to the RAS, there may be high nitrate in the RAS because the retention time was not adequate for the nitrates in the sludge to be reduced. Short-circuiting by rat-holing also increases the retention time of the sludge further out in the tank to the point where it can start to release phosphorus. This then will increase both the effluent and RAS phosphorus concentration. The following activities can be used to evaluate and ameliorate short-circuiting and rat-holing in final clarifiers:

- Measuring the sludge blanket depth and concentration in various places from the center to the perimeter to determine if there is accumulation in the outer section of the clarifier.
- With spiral scrapers, measuring the sludge blanket in various sections of the tank. If the blanket is too high, then the rotational speed of the scrapers should be increased.
- Installing a horizontal baffle over the sludge withdrawal point to prevent rat-holing.

- Retrofitting to provide more scrapers in a ring around the center column to ensure that there is always some movement over the intake.

For rectangular clarifiers, the inlet must be designed for good flocculation and for mixed liquor discharge near the floor when the sludge is scraped in the direction of flow. The ideal rectangular final clarifier configuration for BNR is the Gould Type II, which provides sludge removal halfway through the length of the tank. For rapid removal of sludge, scrapers of at least 300-mm (1-ft) deep traveling at 1.8 m/min but equipped with variable-speed drives are recommended (Randall et al., 1992). With counterflow scrapers and RAS withdrawal at the inlet side, there is a great chance of short-circuiting of sludge. The location of sludge withdrawal and the energy dissipation inlet should be designed to avoid such conditions. In some cases, this clarifier configuration may have to be down-rated for BNR plants. In addition, CFD studies may be required to optimize these clarifiers for BNR plants.

The rate of RAS return should be controlled carefully to minimize SRT in the clarifiers and to reduce the volume of nitrate-rich RAS flow returned to the BNR zones. When the returning rate is too low, secondary phosphorus release may occur as the sludge blanket turns anaerobic, which will make it difficult to achieve low effluent orthophosphate concentrations. If the RAS rate is too high, then too much nitrate is recycled to the anaerobic zone, or the RAS denitrification zone, which may be detrimental to biological phosphorus removal. In addition, the higher RAS rate reduces retention time in the anaerobic zone. When a low-effluent total nitrogen is not required, processes such as the Johannesburg (JHB) or the Modified University of Cape Town (MUCT) are used to reduce the nitrates before the RAS enters the anaerobic zone. Too high of an RAS rate can be detrimental to biological phosphorus removal if the plant is not designed to achieve a high level of nitrogen removal. The RAS nitrate concentration at these facilities could be as high as 10 mg/L.

The Vereeniging plant in South Africa is one example of biological phosphorus removal being hindered by not operating at the optimum RAS pumping rate (Randall et al., 1992). This facility was biologically removing phosphorus from 11 mg/L in the influent to less than 0.1 mg/L in the effluent. Performance deteriorated, however, to the point that the effluent orthophosphate concentration was increased to 1.5 mg/L. As a first attempt to resolve this problem, plant operators reduced the RAS flow rate to decrease the mass of nitrates being recycled to the anaerobic zone. Reducing the RAS pumping rate, however, extended the SRT in the final clarifiers, which increased the orthophosphorus concentration in the RAS to 10 mg/L, further

hampering biological phosphorus removal. The problem ultimately was resolved by identifying that the secondary release in the final clarifier sludge blanket was causing the performance problem, rather than excessive RAS pumping. The problem was resolved quickly by increasing the RAS above the rate being used at the time when the plant performance deteriorated. Within days, the effluent orthophosphate concentration was again reduced to less than 0.1 mg/L.

Effluent launder baffles (McKinney baffles or similar) should be used to redirect velocity currents that can result in loss of solids over the effluent weir. Foam and scum also can contribute significantly to effluent suspended solids. Provisions must be made for efficient removal of scum from the final clarifier surface using full-radius scum removal mechanisms or longer scum beaches for central drive clarifiers. Common problems with peripheral drive clarifiers include a beach that is too steep; a scum baffle that is too shallow; and a scum trough too high above the liquid surface, which makes it difficult to remove. The Tai Po WWTP in Hong Kong, China, is an example of a plant that struggled with scum removal in the final clarifiers. At this facility, scum was forced up a steep slope on the beach toward the scum hopper. This resulted in scum being pushed under the scum baffle and out to the effluent while very little was moved up the slope to the hopper. For this WWTP, it would have been better to remove the scum baffles because growth accelerated with accumulation on the surface of the clarifiers.

In some plants, scum collected on the clarifiers is returned with the RAS to the aeration basins. This should be avoided because it accelerates growth and accumulation in the system.

If necessary, operating strategies, such as adding polymer to enhance flocculation, can be considered to maintain high solid capture during peak flow events. Tertiary filters are used to capture the solids lost in the final clarifiers, especially when low effluent total phosphorus is required. Solids captured in the tertiary filters, however, can lead to secondary release of phosphorus if anaerobic conditions develop in the filter bed. In these cases, a low concentration of metal salts can be added to tie up the phosphorus released from the captured floc.

4.0 CHEMICAL PHOSPHORUS REMOVAL IN ACTIVATED SLUDGE SYSTEMS

Chemical addition for phosphorus removal can take place at several points in the main process stream. Chemicals can be added to the primary influent, to the activated

sludge in the aeration basin, to the mixed liquor before settling, and to the influent of a tertiary process for phosphorus precipitation. Chemicals also are used in the solids handling process to prevent phosphorus from returning to the main plant.

The objective of chemical phosphorus removal is to convert soluble phosphorus to a precipitate that can be removed through clarification or filtration. There are five overriding factors that affect chemical precipitation of phosphorus: (1) chemical dose, (2) chemical reaction time, (3) method of mixing and coagulation, (4) timing for adding polymers, and (5) species of remaining phosphorus compounds in the effluent. When adding chemical in the primary tanks, phosphorus is removed with the primary sludge by direct precipitation of the soluble phosphorus and coagulation and precipitation of particulate phosphorus. In some cases, ferrous salts are added to the influent for odor control. For actual phosphorus removal in the primary tanks, alum or a ferric salt may be added. Ferrous salts also may be added directly to the aeration basin where they will be oxidized to the ferric form that binds with the phosphorus. Alum, ferric, or PAC typically is added to the effluent of the aeration basin just before clarification and at a turbulent location; some reaction time should be allowed before polymer is added. When adding chemicals to a tertiary removal stage, the chemicals should be added into a rapid-mix tank followed by coagulation and flocculation with polymer. A one-to-one molar dose is required to attain a residual orthophosphate concentration of 1.0 mg/L. Reducing this concentration to less than 1.0 mg/L will require a higher molar dose of either iron or aluminum.

Attempts to achieve effluent phosphorus concentration of less than about 0.1 mg/L by adding chemicals to the biological process will become counterproductive. When trying to achieve very low effluent phosphorus concentrations, chemicals should be added to a tertiary stage, and the required chemical-to-phosphorus molar ratio will increase significantly. Figures 11.31 and 11.32 show the correlation between molar chemical dose and the resulting effluent orthophosphate concentration, based on data from several chemical phosphorus removal plants. When it is necessary to reduce the effluent phosphorus concentration to less than 1.0 mg/L, the excess iron and aluminum will precipitate as a hydroxide solid, thus producing more chemical sludge and increasing the consumption of alkalinity. The alkalinity consumption can be significant and must be taken into account when assessing supplemental alkalinity requirements for a BNR facility.

When polymer is used to improve chemical phosphorus precipitation, the polymer and coagulant should not be added together at the same location. It takes a few minutes for a chemical phosphorus precipitate to form; formation of the hydroxide

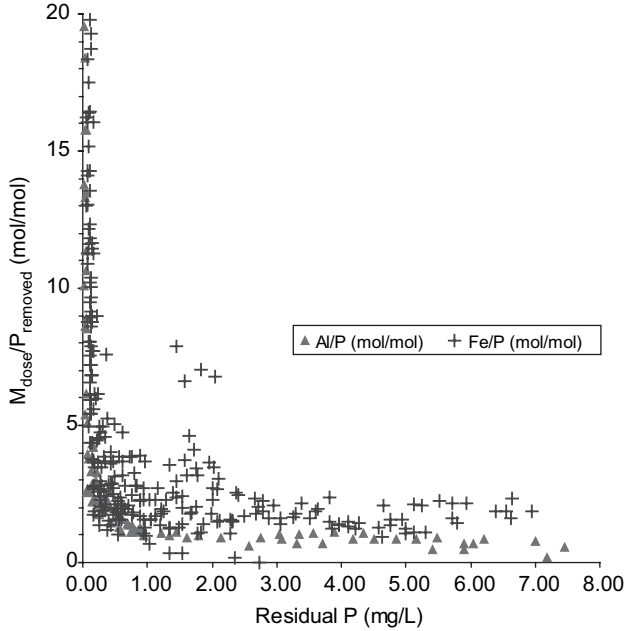

FIGURE 11.31 Molar doses for precipitation of phosphorus using iron and aluminum (courtesy of Black & Veatch).

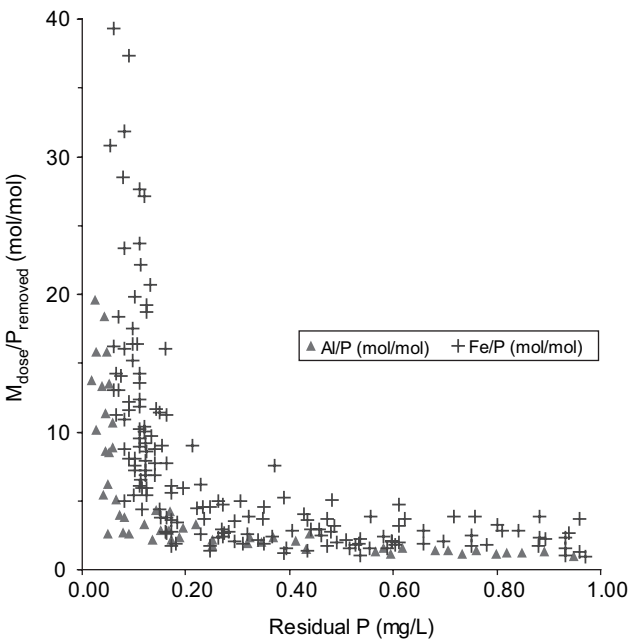

FIGURE 11.32 Molar doses for precipitation of phosphorus to less than 1 mg/L using iron and aluminum (courtesy of Black & Veatch).

product is relatively fast. Phosphorus precipitation is a two-step process in which some of the soluble iron or aluminum reacts with phosphorus to form a precipitate, and the remainder of the iron or aluminum forms the hydroxide solid. If the phosphorus is not completely removed at first contact, it will continue to react with the metal hydroxide until it reaches equilibrium. Polymer creates an interference with this reaction because it coats the surface of the particle and prevents further reaction of the orthophosphate with the hydroxide solids. If sufficient chemical is added to precipitate phosphorus, but the results are poor, then it may be possible to enhance performance by moving the iron or aluminum feed point farther upstream to extend the reaction time by several minutes before polymer is added. Intensive mixing at the point of chemical addition also can enhance performance, because the additional agitation will minimize the formation of iron or aluminum hydroxides.

When using iron salts in a primary clarifier, the iron initially will react with the sulfide in the influent to form an iron sulfide precipitate because it is less soluble in water than iron phosphate. For this reason, a ferrous salt is preferred to control sulfides. Ferrous phosphate compounds that are soluble will form after the sulfide is precipitated. It is for this reason that ferric or aluminum salts are added to the primary sedimentation tanks for phosphorus removal and coagulation of suspended and colloidal solids. Recent findings suggest that soluble ferrous phosphate compounds passing to the aeration basin will be oxidized to the ferric form and will then precipitate as ferric phosphate. The additional iron demand for sulfide removal must be taken into account when estimating the required dose of iron salt to achieve a desired effluent orthophosphate concentration.

Sulfide will not interfere when alum is used to precipitate phosphorus. For this reason, it is sometimes stated that aluminum is more efficient in precipitating phosphorus than iron, but jar tests should be conducted to compare the actual dose requirements. Local chemical costs and availability also should be considered when selecting the coagulant for phosphorus precipitation.

A higher molar dose is required to achieve an effluent phosphorus concentration of less than 1.0 mg/L. This higher chemical dose results in the formation of more hydroxide solids and, consequently, more sludge. If iron or aluminum is added to an activated sludge process (aeration basin or final clarifiers), the generated chemical solids will accumulate in the MLSS and reduce the effective mean cell residence time of the process. Accumulation of chemical solids in the MLSS can be determined by conducting batch tests to define the molar ratio of Fe:P required to reduce phosphorus to the desired level. Figures 11.31 and 11.32 also can be used to approximate

the required Fe:P based on data collected at other municipal WWTPs. For example, as indicated on Figure 11.33, a Fe:P molar ratio of approximately 1.5 is required to achieve a residual phosphorus concentration of 0.5 mg/L. From this information, it is possible to calculate the mass of the $FePO_4$ precipitate for a given plant influent flow and phosphorus concentration, and the remaining iron will precipitate as $Fe(OH)_3$. In this simplified example, 1.0 of the molar mass will precipitate as $FePO_4$, and the remaining 0.5 will precipitate as $Fe(OH)_3$. The total daily chemical solids production is the sum of the two precipitates, and the total mass of metal salts in the mixed liquor can be calculated by the product of the total daily chemical solids production and the SRT of the process.

Precipitating of most of the soluble and some particulate phosphorus in the primary clarifiers reduces the accumulation of inert chemical solids in the activated sludge process. The activated sludge process needs phosphorus as a nutrient. Because some particulate phosphorus remains after chemical precipitation in the primary tanks, however, there is little chance of removing so much of it that it can interfere with the biological process. It is possible, however, to chemically remove too much phosphorus in the primary clarifier if the downstream biological processes are designed for high-level denitrification with carbon supplementation. In industrial processes, removal of too much phosphorus may cause low nutrient conditions that may lead to the proliferation of filaments. Tertiary processes, such as denitrifying sand filters or BAF units for nitrification and denitrification, also will require some phosphorus to support the growth of the denitrifying bacteria. It is fortuitous that in denitrifying filters, the chemically bound phosphorus that is trapped in the media can serve as a source of phosphorus for denitrification (deBarbadillo et al., 2006).

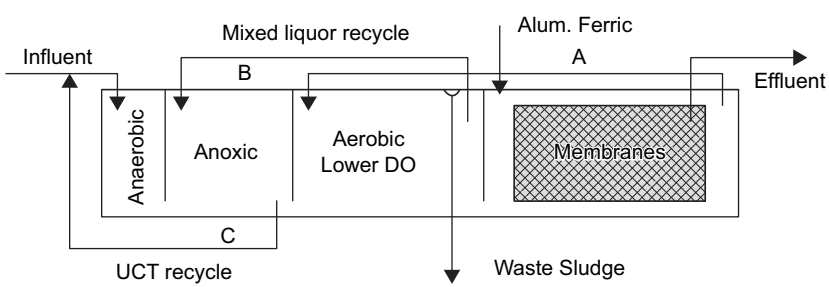

FIGURE 11.33 Membrane bioreactor (MBR) process for nitrogen and phosphorus removal (DO = dissolved oxygen and UCT = University of Cape Town).

Chemical precipitation of phosphorus will consume alkalinity and lower the pH, which can reduce the nitrification efficiency in the activated sludge process by lowering the growth rate of the nitrifying bacteria. Plants that have to achieve a low effluent phosphorus concentration may have to add a significant amount of excess iron or aluminum (beyond stoichiometric requirements) that will consume a large amount of alkalinity. This loss of alkalinity must be taken into account, and supplemental alkalinity may be required to avoid pH depression. Ferrous iron (Fe^{++}) does not form a hydroxide precipitate at neutral pH. As a result, when ferrous is used for phosphorus removal, it must be added directly to the activated sludge process where it is oxidized to the ferric (Fe^{+++}) form. Excess ferrous iron added at the final clarifier inlet will remain soluble and can interfere with disinfection by creating additional chlorine demand and by discoloring the effluent. The soluble ferrous iron also absorbs UV energy, making less energy available for disinfection, which will result in higher effluent bacterial counts. Ferrous iron will also foul the quartz sleeves of a UV disinfection system.

Addition of chemicals to the activated sludge process can remove total phosphorus to between 0.1 and 0.15 mg/L after filtration. For lower effluent concentrations, chemical phosphorus removal is provided in a tertiary process. The effluent pH, however, must still be monitored to maintain compliance with the discharge permit because alkalinity will be consumed by the added chemical. It is also easier to monitor and control a tertiary process because nutrient analyzers are more accurate and reliable and require less maintenance in this application. One potential concern when using ferric chloride in a tertiary process is the small amount of ferrous iron in the purchased product that will pass through to the plant effluent and interfere with the disinfection process. The specification for the ferric iron product should limit the acceptable amount of ferrous iron it contains as byproduct or contaminant. The use of an industrial recycling product should be evaluated carefully before using it in a tertiary system.

5.0 MEMBRANE BIOREACTORS

An increasing number of BNR plants use membranes for liquid/solids separation. The advantage is that effluent solids virtually are all retained and will not contribute to nutrient concentrations in the effluent. MBR plants are designed for nitrogen removal because of the need for higher SRTs to reduce membrane fouling. In addition, denitrification is desirable to recover energy and alkalinity, especially when

chemicals are used for phosphorus removal. Typically, MBR plants are configured for moderate levels of nitrogen removal but can also be optimized to meet stringent nitrogen limits. In this sense, the MBR operates similar to the MLE process with the final clarifiers being replaced by a membrane for solids/liquid separation. The absence of final clarifiers allows operation at elevated mixed liquor concentrations of between 8 and 10 g/L. Because of the high dissolved oxygen concentration in the membrane reactor, which results from the scour air needed to reduce solids accumulation on the membranes, the RAS (A-recycle in Figure 11.33) is recycled back to the inlet end of the aeration basin where oxygen demand is high. The dissolved oxygen is then reduced toward the end of the aeration basin at the point of the mixed liquor (B-recycle) to the anoxic zone. The mixed liquor concentration is reduced with each recycle from the highest concentration in the membrane reactor followed by the aeration zone, then the anoxic zone. The recycle from the membrane to the aerobic reactor typically is set at approximately four times the plant average flow. The recycle rate to the anoxic zone will depend on the effluent total nitrogen requirements.

Biological phosphorus removal can be achieved by incorporating the UCT recycle (C-recycle) from the end of the anoxic zones to an anaerobic zone where it is mixed with the influent. In this case, the mixed liquor b-recycle should be controlled to ensure that the nitrate concentration at the end of the anoxic zone is less than 1 mg/L to reduce recycling of nitrates to the anaerobic zone. The C-recycle also should be variable for optimal phosphorus removal, but typically is operated at a flow rate equal to the plant average flow. Just as for conventional BNR, VFA could be added to the anaerobic zone for improved phosphorus removal. An upflow fermenter using raw screened wastewater also can be used for generation of VFA. In this case, all the sludge and liquid will be passed to the anaerobic zone.

Scum accumulation may be a problem in MBRs. Surface wasting of mixed liquor and scum can be considered to help mitigate the problem. Surface wasting to a DAF thickener can ensure trouble-free operation with the added advantage of volumetric SRT control.

The MLE-type configuration can only reduce the nitrogen to approximately 8 to 10 mg/L, depending on influent concentration. For nitrogen reduction to less than 3 mg/L, a second anoxic zone as in the Bardenpho plant is required between the aeration and membrane reactors. A carbon compound such as methanol could be added to reduce the nitrates to less than 1 mg/L. Because of the long retention time of the mixed liquor in the membrane basin, a slight increase in nitrates can be experienced because of endogenous respiration. With the higher SRT, the effluent ammonia

should be very low. If the nitrates in the second anoxic zone can be reduced to less than 1 mg/L, then it will be possible to achieve high levels of nitrogen reduction. Depending on the concentration of the residual rDON—which typically is less than 1 mg/L but can range from 0.5 to more than 2 mg/L—it would be possible consistently to reduce total nitrogen to less than 3 mg/L. A TIN concentration of less than 2 mg/L is achievable.

Because of the high RAS recycle rate, the actual retention time in the second anoxic zone can be quite low (10 min). Short-circuiting should be avoided and good mixing between the mixed liquor from the aeration zone and the carbon feed is essential. Some form of rapid mixing is required, preferably with a discharge to the bottom of the anoxic zone. The second anoxic zone should preferably be plug flow or should include partitions.

When using methanol, the anoxic retention time should be sufficient to avoid washout of the slow growing, temperature-sensitive methylotrophes. An operational option is to add some methanol to the first anoxic zone to increase the overall anoxic retention time for the growth of methylotrophes. If there are nitrates in the mixed liquor at the end of the first anoxic zone at a b-recycle of three times the plant average flow, then it would be advantageous to add methanol to the first anoxic zone over trying to remove all the nitrates in the second anoxic zone. This concern does not apply to the use of other carbon sources containing two or more carbon atoms.

Phosphorus removal to very low levels is possible in an MBR process with the addition of chemicals directly to the membrane zone, either as a polishing step or as the main means of phosphorus removal. Good filtration of the colloidal and particulate phosphorus can produce effluent total phosphorus concentrations of less than 0.05 mg/L. The lower the required effluent phosphorus, the higher the required chemical dose and the greater the competition between the mechanisms of biological and chemical phosphorus removal. This occurs because more of the metal hydroxide will be returned to the aeration basin where it will bind with the free phosphorus. This will deprive the PAOs of phosphorus to store for release and uptake of VFA in the anaerobic zone, which will slowly lead to washout of the PAOs.

6.0 DENITRIFICATION FILTERS

This section summarizes potential performance challenges and corrective actions for tertiary denitrification filters along with possible corrective actions.

6.1 Excess Backwashing

Excess backwashing of filters is an issue in terms of both operating costs (power use) and filter performance. In static-bed denitrification filters, nitrate removal performance in a filter cell that has just been backwashed may be somewhat reduced as a result of less biomass in that filter. If the filter is being backwashed too frequently, then it may be difficult to maintain enough biomass for adequate denitrification. Backwashing frequency can be reduced by increasing the time between backwashes. If the filter is frequently backwashed because of too much headloss from TSS accumulation, then final clarifier performance should be enhanced for TSS capture efficiency. This can be accomplished by operating at optimum conditions with respect to dissolved oxygen, F/M, and SRT to generate good sludge settling characteristics. This will ensure accurate flow splits to all clarifiers and low final clarifier sludge blankets. Numerous clarifier enhancements are possible if operational adjustments do not improve performance. Coagulants such as ferric chloride and alum can be used to enhance final clarifier solids capture efficiency. In the case of moving bed filters, it may be necessary to reduce the bed turnover rate if denitrifying biomass is not being maintained in the filters.

6.2 Gas (Nitrogen) Accumulation

In static-bed denitrification filters, nitrogen gas needs to escape in a direction counter to the flow and accumulation of gas bubbles within the media increases the headloss through the filters. This increase in headloss is controlled by periodic nitrogen release cycles. The nitrogen release cycle typically is initiated based on the water level in the filters. In moving bed filters, gas accumulation does not occur because the sand (and nitrogen gas bubbles) is drawn continuously through the airlift. If the filter bed turnover rate is lowered to reduce the wasting of biomass from the filter to enhance denitrification, however, the additional headloss may be experienced from nitrogen gas accumulation.

6.3 Solids Breakthrough

Solids breakthrough to the filter effluent may be an indication of filter overloading or problems with the underdrain. For static bed filters, this may be an indication that backwashing frequency should be increased. For moving bed filters, it may be necessary to increase the bed turnover rate. The airlift pump also should be inspected for plugging and to verify that it is pumping at the desired rate.

6.4 Nitrate/Nitrite Breakthrough

There are three causes of excess nitrate and nitrite in the filter effluent:

(1) The filter is in a startup mode, where biomass is still being developed; or it is being backwashed too frequently, which results in the loss of too much biomass.
(2) Inadequate carbon is being added to support full denitrification.
(3) The filter influent wastewater may contain insufficient phosphorus to support denitrification.

If the filter is in startup mode, or in a period of transition (e.g., if influent nitrogen loads to the plant increase, causing nitrate loading to the filters to increase), then it is likely just a matter of time until the biomass develops and stable operation is achieved. During startup and transition periods, backwashing frequency may be reduced to avoid overwasting of biomass, and carbon dosing should be checked frequently.

If the filter is not receiving adequate carbon (methanol) for complete denitrification, then elevated levels of nitrate and nitrite levels in the effluent may occur. It may be necessary to increase the chemical dosing slightly to meet actual process requirements. Elevated dissolved oxygen concentrations as high as 5 or 6 mg/L are not unusual in high-quality secondary effluent entering a denitrification filter, which increases the chemical demands. In this situation, it may be possible to avoid aeration by installing a device to allow for headloss without excessive aeration. Denitrification filters should not be operated "halfway." If denitrification filters are operated to achieve partial denitrification, then nitrate is converted preferentially to nitrite, and nitrite to nitrogen-gas conversion is limited based on the remaining carbon. Other process upsets, such as significant changes in load or temperature, also can lead to elevated effluent nitrite levels. Based on this, the nitrite-to-nitrogen-gas step appears to be more sensitive than the nitrate-to-nitrite step.

This results in failure to meet nitrogen limits and increases chlorine demand in the downstream chlorine disinfection facilities. If it is not necessary for the filter to completely remove the nitrate, then it is more reliable to denitrify fully a portion of the flow that is then blended with the remaining secondary effluent flow to achieve the desired effluent total nitrogen concentration.

If the filter is not undergoing a startup or transition period and is receiving sufficient chemical for denitrification but is still experiencing significant nitrate or nitrite breakthrough, then the process may be phosphorus-limited. If the available phosphorus is insufficient for denitrification, phosphoric acid can be dosed carefully to the filter influent.

6.5 Phosphorus Management

Plants that must meet stringent effluent total phosphorus limits in addition to operating a tertiary denitrification process should monitor closely phosphorus, nitrate, and nitrite concentrations in the filter influent and effluent to ensure that sufficient phosphorus is available for denitrification. When the available phosphorus is critically low, growth of slimy organisms that can block the filters may be encouraged. Therefore, careful management of the phosphorus concentration is required, especially when treating to low phosphorus concentrations.

The denitrification process consists of biological oxidation of the influent COD (in most cases methanol) using nitrate and nitrite as the electron acceptor. The COD is used for cell growth and respiration, and a specific amount of phosphorus is required. The literature suggests that 0.022 g of total phosphorus is required per gram biomass COD. For example, using a filter influent NO_3-N concentration of 6 mg/L, a methanol dosage ratio of 3 g per gram NO_3-N and a corresponding COD-to-methanol ratio of 1.5, the rbCOD would be 27 mg/L. The biological yield coefficient for denitrification using methanol is estimated at 0.4 g biomass COD per gram COD oxidized (Copp and Dold, 1998). Applying this yield coefficient, and the biomass phosphorus requirement to the influent COD of 27 mg/L, results in a phosphorus requirement of 0.24 mg/L for denitrification. This can be expressed as 0.009 g of phosphorus per gram COD removed or 0.04 g of phosphorus per gram NO_x-N removed. Therefore, the level at which phosphorus becomes limiting depends on the amount of nitrate to be denitrified in the filters.

Data from the H.L. Mooney WWTP, Occoquan, Virginia; Truckee Meadows WRF, Reno Nevada; and the Hagerstown, Maryland, pilot suggests that the threshold for phosphorus limitation on denitrification occurs at a filter influent OP/NO_x-N of approximately 0.01. At ratios of 0.02 and higher, denitrification does not appear to be affected even though this is below the estimated requirement of 0.04 OP/NO_x-N. This difference may be made up in part by release of phosphorus from secondary

effluent solids captured in the filters, phosphorus release from any PAOs, and decay of denitrifying biomass.

Phosphorus release in the filters from PAOs may help denitrification but potentially can negatively affect the ability of the plant to meet very low total phosphorus limits without having an additional chemical precipitation step.

It is estimated that denitrification filters can be operated successfully to meet effluent total nitrogen limits of 3 mg/L while meeting total phosphorus limits as low as 0.15 to 0.2 mg/L. If necessary, chemical polishing of phosphorus can be performed simultaneously by adding a metal salt to the filter influent wastewater. If there is a need to reach lower effluent total phosphorus limits, the advantages and disadvantages of this and other options such as postchemical treatment and membrane filtration merit serious consideration.

6.6 Carbon Breakthrough

Elevated BOD_5 levels in the effluent may be the result of excess methanol. The effluent soluble BOD_5 (or COD) concentrations should be compared with the concentrations in the secondary effluent to confirm that the upstream activated sludge process is operating as intended. If the soluble BOD_5 is increasing across the filters, then the methanol dose is too high and should be decreased to match the level of denitrification occurring in the filter. The methanol dose should be mixed properly to minimize potential for short-circuiting through the filter.

6.7 Operation during Peak Flow Events

Operation during peak flow events can be challenging because of the greater hydraulic throughput and the resulting increases in headloss through the filters. Depending on the operation of the secondary clarifiers upstream, the plant may also experience high solids loadings to the filters during such peak flow, which will increase backwashing frequency. Although it is possible to continue denitrification during peak wet weather flow events, it can become difficult to manage denitrification while handling additional loadings. If the effluent nitrogen limit is enforced on quarterly or annual average basis, then it typically is not necessary to fully denitrify during peak wet weather events. In this situation, peak flows greater than a certain level can be bypassed around the filter complex to reduce load to the filter. Alternatively, methanol dosing can be discontinued during peak wet weather events.

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Chapter 12

Aquatic Natural Treatment Systems

(continued)

1.0 AQUATIC NATURAL TREATMENT SYSTEM DESCRIPTIONS

Aquatic natural treatment system describes engineered systems that look like aquatic ecosystems found in nature, such as ponds and wetlands, but are used for achieving a pollutant removal goal treating a municipal, industrial, or agricultural wastewater. Land-based or terrestrial systems, such as slow rate and rapid infiltration land treatment, are not discussed but information on the nutrient removal capacities of these systems can be found in several sources (WEF, 2010). Aquatic natural treatment systems are characteristically low in operation and maintenance costs but relatively high in land requirements, resulting in their greater use in rural environments. The description and discussion of wetlands in this manual will focus on constructed wetlands and not on wetlands that created or restored for wildlife habitat.

Aquatic natural treatment systems have been used for treating a wide variety of wastewaters. Treatment performance of these systems, however, can vary significantly depending on wastewater characteristics and environmental conditions.

1.1 PONDS AND LAGOONS

The terms, "ponds" and "lagoons," are often used interchangeably to describe natural systems typically dominated by free-floating algae and bacteria in relatively deep basins lacking submerged or emergent aquatic plants. The manual does not distinguish between the two, although "pond" most often is used for systems treating

stormwater and domestic wastewaters, and "lagoons" typically are associated with agricultural or industrial wastewaters. There are several ways to classify ponds and lagoons: by type of water or wastewater treated, degree of pretreatment, organic loading rates, whether mechanical energy is used for mixing or aeration, and duration and frequency of discharge (Water Environment Federation [WEF], 2010). Ponds and lagoons are used in all types of climates and for a variety of waters and wastewaters with varying degrees of mechanical energy inputs and process control. At one extreme, aerated ponds look and act like complex activated sludge systems with sophisticated controls. Systems that look like activated sludge systems are not discussed in this section. At the other extreme, many pond systems function with only gravity flow inputs and outputs without any process control, sometimes not even flow measurement. The less the system is "engineered" and controlled, however, the more complex the important removal mechanisms are and the more difficult it is to predict treatment capacity. Table 12.1 summarizes the range of pond and lagoon systems. Ponds and lagoons typically are not associated with high degrees of nitrogen and phosphorus removal but are capable of achieving high nutrient removal levels under certain circumstances.

1.2 Floating and Submerged Aquatic Plant Systems

Floating aquatic plant (FAP) treatment systems are engineered systems that treat domestic and industrial wastewater and stormwater. They are designed to achieve specific treatment and water quality objectives. The primary plant species used include duckweed *(Lemna minor)* and water hyacinth *(Eicchornia crassipes)*. Submerged aquatic plants such as waterweed, water milfoil, and water cress, often present in

Table 12.1 Typical pond and lagoon system loadings (adapted from Metcalf and Eddy, 2003, and Water Environment Federation, 2010).

System	Surface organic loading rate kg/ha·d (lb BOD_5/d/ac)	Hydraulic detention time (days)
Nonaerated facultative pond	28–56 (25–50)	>45
Partial-mix aerated facultative lagoon	224–560 (200–500)	4–10
Partial-mix aerobic lagoon	336–728 (300–650)	3–6
Complete-mix aerobic lagoon with solids recycling	1120–8970 (1000–8000)	0.25–2.0

BOD_5 = five-day biochemical oxygen demand.

aquatic systems, typically are not used; for this reason, discussion of them is limited in this chapter.

Duckweed systems typically are used for algae removal from oxidation pond effluents, enhanced settling, or nutrient removal following secondary treatment. Duckweed systems have been used across a wider geographic area than water hyacinths because of their greater temperature tolerance. Duckweed occurs naturally in open areas within some treatment wetlands and can be factored into a treatment process.

Although water hyacinths have been used in various experimental and full-scale systems for treating wastewater, their historic use for secondary treatment has expanded to include polishing of secondary effluent and treatment of stormwater. The use of water hyacinths has been limited to warm-weather regions because of their sensitivity to freezing conditions. They can also be used in greenhouses in cold climates.

Periphyton is a complex assemblage of algae, fungi, bacteria, protozoa, zooplankton, and other invertebrates attached to submerged substrates in a wide range of aquatic ecosystems. Periphyton treatment systems sometimes are grouped with submerged aquatic vegetation (SAV) and categorized as nonemergent wetland systems (Kadlec and Wallace, 2009). Periphyton systems rely on the intrinsic rapid growth of algal and bacteria ubiquitous in the aquatic environment to assimilate nutrients, metals, or other pollutants into biomass for subsequent harvest (Bays et al., 2001; Vymazal, 1988). Engineered systems containing attached algae, or periphyton, or SAV are a new category of natural treatment system, sometimes called "non-emergent treatment systems" that can be configured as either active or passive systems. Similar to floating aquatic macrophytes in their development, engineered periphyton or SAV systems are growing in use as a natural polishing system.

1.3 Free Water Surface Constructed Wetland Systems

Free water surface (FWS) wetland treatment systems are shallow constructed basins, typically marshes, that are densely vegetated by a variety of rooted emergent plant species such as bulrush and cattails. The FWS wetland substrates are composed of flooded organic or mineral soils. Although individual sites may vary considerably in response to the type of effluent treated, FWS wetlands designed for effluent treatment have average water depths that are typically less than 0.50 m (1.5 ft) with hydraulic loading rates averaging 0.60 cm/d (1.5 in./d). In FWS wetlands, the emergent plants take up nutrients in the effluent and provide a substrate for the growth of microbial

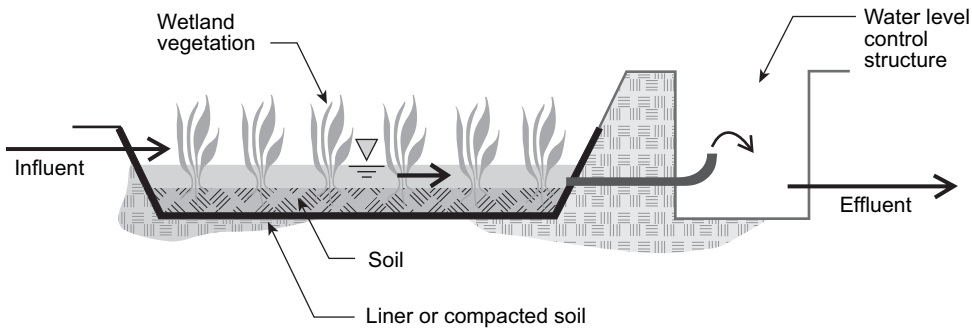

FIGURE 12.1 Free water surface constructed wetlands (Water Environment Federation, 2010).

populations that assimilate constituents in the wastewater through uptake, transformation, and sedimentation processes. Above the sediment–water interface, aerobic conditions predominate, while below the interface, anaerobic processes occur. This creates environments suitable for growth of microbes specializing in the transformation and assimilation of pollutants and long-term accumulation of elements in plant biomass and wetland soil.

Among all types of wetland treatment systems, FWS wetlands offer the most potential for creating the ancillary benefits of wildlife habitat and public recreational uses such as birdwatching and nature study. Alternating zones of deep water and shallow, emergent marsh interspersed with habitat islands, can create optimal habitat for waterfowl, wading birds, and other species valued for their ecological and recreational value.

Treatment cells are designed for site-specific conditions allowing easy and efficient management of the system. Constructed wetlands may be used in all climates, but potential limitations such as reduced microbial activity and ice formation in colder climates need to be considered in the design. FWS wetlands typically are used for tertiary treatment applications (Water Environment Research Foundation [WERF], 2006). A typical wastewater treatment train including an FWS wetland is shown in Figure 12.1.

Subsurface flow constructed wetlands (SSF) are a type of constructed wetland that contain a bed of media, such as crushed rock, small stones, gravel, sand, or soil,

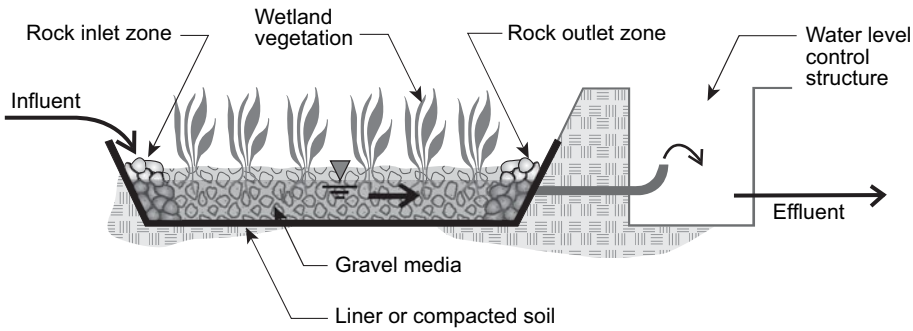

FIGURE 12.2 Schematic of subsurface flow constructed wetlands (Water Environment Federation, 2010).

that has been planted with aquatic plants (see Figure 12.2). These systems also are known as vegetated submerged bed systems and sometimes as rock-reed or reed-bed systems. It is appropriate to think of SSF systems as attached growth systems because bacteria attached to media and roots provide the vast majority of the biological activity. They typically are used for relatively small systems with flows less than 200 m^3/d because of the cost of the media. In most SSF systems, wastewater flows horizontally through the media, although there are also vertical flow SSF systems. When properly designed and operated, wastewater stays beneath the surface of the media. The primary advantages of SSF systems over other types of aquatic natural treatment systems are the greater surface area for attached bacteria to grow and the lack of standing water, which prevents mosquito breeding and human contact with wastewater. These systems, however, have reduced habitant value compared with other aquatic natural treatment systems. In addition, because of oxygen transfer limitations in the system, they can generate odor when loaded too heavily.

Pollutant removal in SSF systems is significantly limited by low oxygen input and lack of oxygen for aerobic biological conversion. Several researchers have investigated ways to improve the treatment performance of SSF systems (Behrends et al., 1996; George et al., 2000; Young et al., 2000). Typical modifications involve either unsaturated vertical flow or some type of cyclic filling and draining of the system to improve the oxygen input to wastewater. These systems have been defined as alternative SSF systems (U.S. Environmental Protection Agency [U.S. EPA], 2000). The

potential improvement in performance with alternative SSF systems is offset to some degree by a more complex and expensive operating system.

The SSF wetland also can be classified by the type of influent wastewater and the treatment goal. There are four categories of influent wastewater: (1) septic tank and primary sedimentation effluents, (2) pond and lagoon effluents, (3) secondary effluents such as trickling filter and activated sludge effluents, and (4) all others, including stormwater and landfill leachates. Typical treatment goals for SSF systems are: (1) biochemical oxygen demand (BOD) and total suspended solids (TSS) removal to secondary standards (30 mg/L BOD/30 mg/L TSS); (2) ammonia removal; (3) total nitrogen removal (nitrification/denitrification); and (4) denitrification of a nitrified wastewater. Another method to classify SSF systems is by the wetland plant species used, but there is insufficient data to support such a classification. The most common SSF systems in the United States treat septic tank and lagoon effluents primarily for BOD and TSS removal. In Europe, SSF systems typically are used to treat septic tank effluents, although they have also been used extensively in England for polishing activated sludge, trickling filter, and RBC effluents and treating combined sewer bypass flows (Cooper, 1990; Green and Upton, 1994).

1.4 Combination Systems

There are numerous examples of using aquatic natural treatment systems in combination to achieve a treatment goal more efficiently and economically than using a single system. One of the more common combinations is the use of a pond followed by a constructed wetland. The pond allows algae growth to provide oxygen for the bacterial oxidation of organic matter and ammonia nitrogen, and the wetland systems can remove algae and nitrate. Another option is to design FWS wetlands to incorporate the advantages of the pond, known as a wetland combination.

2.0 MAIN COMPONENTS OF AQUATIC NATURAL TREATMENT SYSTEMS

2.1 Hydrology and Hydraulics

The hydrology and hydraulics of aquatic natural treatment systems are very important factors in system design and treatment performance. Typically, models for predicting the performance of aquatic natural treatment systems are based on the

hydraulic retention time and a reactor-based model of the movement of water within the system. The hydrology of these systems can vary significantly depending on the climate of a specific geographic location and time of year. Hydrology significantly can affect hydraulic retention time of a system. For example, retention ponds, which are designed to store and evaporate all of the influent flow with no effluent discharge, may be practical in certain areas of the United States. Even moderate rainfall inputs and evapotranspiration losses, however, significantly can change the effluent quality and the actual hydraulic retention times in wetland systems compared to their design values. Models of hydraulic movement can vary between an ideal plug flow and a single complete-mix reactor. The pollutant removal performance of plug-flow and complete-mix reactors will vary significantly for many reactions modeled in these systems; therefore, it is important to use the reactor model that best describes the water movement.

The hydrology of an aquatic natural treatment system is defined mathematically using a water balance:

$$\frac{dV_W}{dt} = Q_i - Q_e + P \times A_C + I \times A_I + ET \times A_W \tag{12.1}$$

Where,

V_W = water volume or storage in the pond or wetland, m^3;
t = time, days;
Q_i = influent wastewater flow rate, m^3/d;
Q_e = effluent wastewater flow rate, m^3/d;
P = precipitation including snow and ice melt, m/d;
A_C = catchment surface area, m^2;
I = infiltration to groundwater, m/d;
A_I = infiltration area, m^2;
ET = evapotranspiration, sum of evaporation and transpiration, m/d; and
A_W = water surface area, m^2.

The theoretical hydraulic retention is defined as the total water volume of the system divided by the flow into the system. When the effluent flow is significantly different than the influent flow, an average of the in and out flows is used to estimate the theoretical hydraulic retention time (HRT). The total water volume is determined by multiplying the total system volume at a specified water level by the porosity (or void fraction) of the system. The void fraction can be as low as 0.35 for SSF systems and as high as 0.95 for FWS wetlands. It is impossible to generalize

the hydrology of aquatic natural treatment systems without making simplifying assumptions. Often, a worst-case scenario for treatment performance is assumed. For some aquatic natural treatment systems with large water depths, such as systems with relatively small surface area to volume ratios, the effects of areal hydrologic parameters (precipitation, infiltration, and evapotranspiration) on treatment performance can be relatively small because of minor effects on total water volume. In most systems, infiltration to groundwater is low and assumed to be zero. For shallow systems, the effects of areal hydrologic parameters on treatment performance can be difficult to quantify and predict. For example, precipitation in constructed wetlands will dilute pollutants in the system, which seemingly improves performance, but it also decreases the hydraulic retention time hurting pollutant removal performance.

Water conveyance in aquatic natural treatment systems is typically hydraulically complex and often varies in both space and time. Most mechanically mixed ponds are modeled as complete mix reactors even when the mixing energy is not sufficient to fully mix the pond. Most wetlands are considered and often modeled as plug-flow reactors even though there is considerable evidence that there is often significant dispersion and short-circuiting in wetlands (see Figure 12.3) (U.S. EPA, 2000). This is an important factor because plug-flow reactors theoretically perform better than complete-mix reactors for many reactions. However, assuming ideal plug-flow conditions in the design process is not conservative and can lead to gross underdesign. It is more conservative to model the system as a series of two to four complete-mix reactors in most cases. Some systems, such as SSFs, are prone to high levels of short-circuiting, which results in a significant reduction in the theoretical hydraulic retention time (40–80% less for SSFs) (U.S. EPA, 2000). Tracer studies can help in defining the hydraulics of a system after it is constructed. Unless the study is repeated after steady state is reached, however, it may not be representative of the system. The simplest model that can provide a reasonable fit to the tracer curves typically is a series of equal-volume, complete-mix reactors. A more realistic model is probably a plug-flow reactor with dispersion, but it is difficult to couple reactions to this type of model (U.S. EPA, 2000).

2.2 Vegetation

One of the main distinguishing factors of aquatic natural treatment systems is the vegetation of the system. There are several good references describing the vegetation

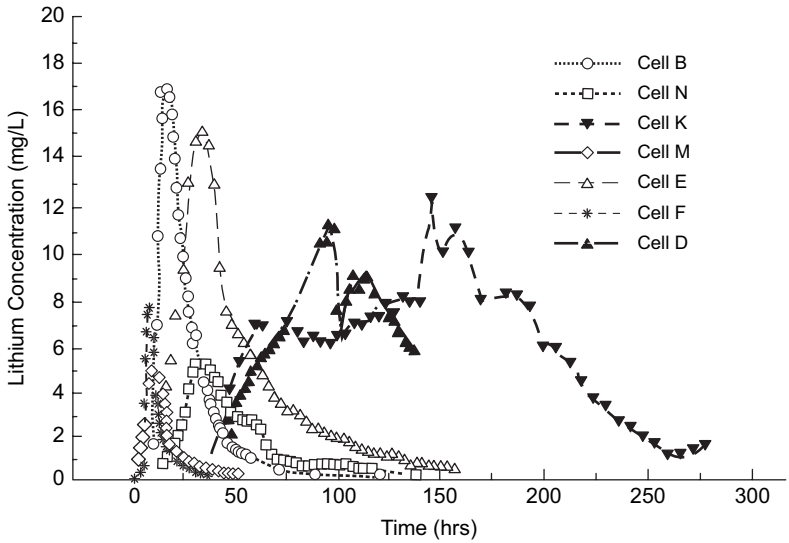

FIGURE 12.3 Lithium chloride tracer studies in a VSB system (George et al., 2000).

of aquatic natural treatment systems (Kadlec and Knight, 1996; U.S. EPA, 2000). The vegetation of these systems varies. The function of vegetation also varies and includes removing pollutants, providing habitat for microorganisms and higher life forms, and creating aesthetics. The importance of vegetation in aquatic natural treatment systems in pollutant removal performance varies depending on the system. FAP systems rely heavily on the vegetation for pollutant removal, whereas ponds and lagoons typically do not have any significant aquatic vegetation.

Aquatic vegetation can be classified in many ways. One of the simpler and more useful classification methods is by the location of the roots, shoots, and leaves in the substrate or soil and water column. Submerged aquatic plants, such as hydrilla, are rooted in the soil or substrate, and their shoots and leaves are submerged in the water column. FAPs, such as water hyacinths and duckweed, have leaves that emerge out of the water column, shoots that extend both in and out of the water, and roots that grow only in the water. Emergent aquatic plants, such as bulrush and cattails, have leaves that are in the atmosphere above the water, shoots that extend

through the water column, and roots in the soil or substrate. Table 12.2 provides a summary of the plants typically used in aquatic natural treatment systems.

Aquatic plants facilitate nutrient pollutant removal in three major ways:

(1) They can be both a sink and a source of nutrients via plant uptake, storage, and release.
(2) Plant surfaces in the water are substrate for attached microorganisms that convert nitrogen from one form to another.
(3) They can serve as both a source and a sink of oxygen.

Table 12.2 Plant types, characteristics, and functions in ponds, lagoons, floating aquatic plant systems, and free water surface constructed wetlands (adapted from U.S. Environmental Protection Agency, 2000).

Plant type	General characteristics and examples	Function in treatment process	Function or importance for habitat
Free-floating aquatic	Roots or root-like structures suspended from floating leaves. Will move with water currents if not restricted by barriers. Water hyacinth (*Eichhornia crassipes*), common duckweed (*Lemna*)	Primary purposes are nutrient uptake and shading to retard algal growth. Some provide structure for microbial attachment and releasing oxygen to the water column during daylight hours. Dense floating mats limit oxygen diffusion from the atmosphere	Limit oxygen supply for fish, some species provide food and shelter for some animals
Rooted floated aquatic	Typically have floating leaves, but may have submerged leaves. Rooted in bottom stratum. Water lily (*Nymphea*), Pennywort (*Hydrocotyle*)	Primary purposes are providing structure for microbial attachment and releasing oxygen to the water column during daylight hours. Dense floating mats limit oxygen diffusion from the atmosphere	Limit oxygen supply for fish. Some species provide food and shelter for some animals
Submerged aquatic	Typically totally submerged; may have floating leaves. Rooted in bottom stratum. Pondweed (*Potamogeton*), water weed (*Elodea*)	Primary purposes are providing structure for microbial attachment and releasing oxygen to the water column during daylight hours	Provide food and shelter for some animals, especially fish

(*continued*)

TABLE 12.2 Continued

Plant type	General characteristics and examples	Function in treatment process	Function or importance for habitat
Emergent herbaceous aquatic	Rooted in bottom stratum. Tolerate flooded or saturated soil conditions. Cattail (*Typha*), bulrush (*Scirpus*), common reed (*Phragmites*)	Primary purposes are providing structure to induce flocculation and sedimentation for microbial attachment. Secondary purposes are shading to retard algal growth, windbreak to promote quiescent conditions for settling. Most common plants in vegetated submerged bed systems where plant roots provide structure for microbial attachment and release oxygen to the water column	Provide food and shelter for some animals. Plants provide aesthetic beauty for humans
Emergent woody shrubs and trees	Rooted in bottom stratum. Tolerate flooded or saturated soil conditions. Dogwood (*Cornus*), holly (*Ilex*), maple (*Acer*), willow (*Salix*)	Treatment function is not defined	Provide food and shelter for some animals, especially birds. Plants provide aesthetic beauty for humans

Submerged aquatic plants provide oxygen to the water column during photosynthesis; and in some cases, plant roots can provide oxygen to organisms growing on the roots in the water column. Plants also can represent an oxygen sink because of plant respiration, periodic release of organic matter from roots, and microbial breakdown of dead plant material.

One of the main differences between FWS and SSF systems is the location of the emergent aquatic plant roots relative to the water or wastewater. In SSFs, the roots are in contact with at least some of the water or wastewater being treated; in FWS, it is assumed that virtually none of the water or wastewater being treated is in direct contact with the roots. Oxygen input via root oxygenation can be important for low-load systems, but the amount of oxygen input will vary with season in most cases.

2.3 Soil and Substrate

Soil is the biologically active upper zones of the earth's surface and has significant levels of organic matter and inorganic matter from parent rocks. The term, substrate, has multiple meanings in the context of waste treatment. It is most often used to describe the limiting nutrient for microbial growth. It is also used, however, to describe relatively inert materials onto which bacteria attach themselves in fixed-film processes. In FAP and FWS wetland systems, plant shoots and roots are an organic-based substrate for fixed-film bacteria and other microorganisms. Substrate can also be used to describe the support material (media) into which rooted plants grow in vegetated submerged bed systems. In SSF systems, the media (typically rock) is both a substrate for emergent aquatic plants and attached microorganisms. Furthermore, the plant roots in SSF systems also provide a substrate for attached microorganisms. Although plant materials are important substrate surfaces on which microorganisms grow, the subsequent use of "substrate" in this chapter will be reserved for the mineral substrates, mostly the media in SSF systems.

Both soil and substrates vary significantly in their chemical and physical properties. The physical properties of soil and substrate, such as water and air conductivities, are dominated by the sizes of the materials that compose it. The chemical characteristics of soil, such as cation exchange capacity and phosphorus adsorption capacity, are dominated by the presence of clay minerals and organic matter. Natural wetland soils are relatively high in organic matter from accumulation of dead plant material because of the reduced aerobic microbial activity in the flooded conditions of wetlands compared with nonflooded soils.

The basins of most aquatic natural treatment systems typically are constructed of soils having low hydraulic conductivities or impermeable liners to protect against groundwater pollution. If a liner is used for a wetland system, then soil or substrate must be placed on top to allow the aquatic plants to root. Soil typically is used for FWS systems with liners. A much coarser media, typically rock, is used as the substrate in vegetated submerged beds.

The role of soil and substrate in pollutant removal in aquatic natural treatment systems is fairly limited. In ponds and lagoons, FAP systems, and FWS wetland systems with soil bottoms, the ratio of the surface area of soil to the volume of water is low, and the organic matter in the wastewater or dead plant material and algae quickly overlies the soil, reducing its importance. In vegetated submerged bed systems, the media surface area to water volume ratio is much higher, and the media

can be a significant sink for phosphorus for at least a short time. Eventually, the phosphorus adsorption capacity of the media will be saturated, and phosphorus will no longer be absorbed. The size of the media in SSF systems is important because of the potential for hydraulic clogging and subsequent surface flow caused by the accumulation of organic matter in the pores of the media. Larger media is desirable, but the media size must be small enough to allow for the planting and establishment of the plants.

3.0 NUTRIENT ENTRAPMENT, CONVERSION, STORAGE, AND REMOVAL MECHANISMS

Because of the complexity of the systems and processes, it is useful to discuss the different removal mechanisms separately when describing nutrient removal in natural aquatic treatment systems. A distinction must also be made between short-term nutrient removal from the water flowing into and out of the systems versus long-term net nutrient removal from the system that occurs either by transport of nitrogen to the atmosphere or plant harvesting and by removal of sludge, sediment, or detritus. Nutrient entrapment is used here to describe the physical removal of particulate and dissolved organic matter and the initial removal of dissolved mineral nutrients from the water by several mechanisms. Natural aquatic treatment systems often have large sinks of stored nutrients, and nutrient removal from the water can vary greatly with the seasons. It is even possible in some systems that effluent total nitrogen or phosphorus, or both, exceed influent levels for short periods. Finally, nutrient removal capacity of a system is highly dependent on influent water quality. For example, systems treating a primary or septic tank effluent will need to be larger than systems treating secondary effluent for significant nitrification to occur.

3.1 Nutrient Entrapment

An important first step for nutrient removal in aquatic natural treatment systems is entrapment (physical separation from the water) of nitrogen and phosphorus in the forms of dissolved and particulate organic matter and dissolved mineral nutrients. Particulate matter entrapment mechanisms include discrete and flocculant settling, filtration and interception, and resuspension (Kadlec and Knight, 1996; U.S. EPA, 2000). Mechanisms for the entrapment of dissolved organic and mineral nutrients include adsorption onto organic and inorganic matter, and plant and microbial uptake and

release (Kadlec and Knight, 1996; U.S. EPA, 2000). Many of these mechanisms are mass transport limited to some degree.

3.2 Nutrient Species Conversions

Nitrogen and phosphorus species conversions are described in detail in earlier sections of this manual. Nitrification, denitrification, combined nitrification–denitrification, and anaerobic ammonium oxidation (anammox) are all possible in the proper circumstances in natural aquatic treatment systems. Phosphorus conversions are also important in the removal of phosphorus in these systems.

The primary difference between most engineered systems and natural aquatic treatment systems is the relative importance of both short- and long-term storage of nitrogen and phosphorus in the biomass of the system. Natural aquatic treatment systems often have large sinks for the storage of nitrogen and phosphorus in the forms of rapidly decaying and slowly decaying biomass compared to the nutrient inputs. Nutrient conversions associated with biomass changes and the buildup of slowly decaying biomass are important.

Natural aquatic treatment systems typically have a significant amount of the system's active biomass in the form of plants and algae, which are relatively high in cellulose content. Cellulose is the primary parent component of the slowly decaying biomass that accumulates in these systems. Another important factor in the accumulation of slowly decaying biomass is the oxygen status in the storage zone; aerobic conditions greatly speed up the decay of biomass. Most of the slowly decaying biomass is stored in the anaerobic benthic zones of ponds, lagoons, and FWS wetlands. There are several sources describing the conversion processes associated with the buildup of slowly decaying biomass (Kadlec and Knight, 1996; U.S. EPA, 2000).

3.3 Nutrient Storage

Nutrients can be stored for relatively short periods (months) in the active biomass of natural aquatic treatment systems. This short-term storage can be significant in terms of the nutrient loading to the system and seasonal removal from the water, but unless the active biomass is harvested before it dies and begins decomposing, it cannot be considered an important mechanism in net nutrient removal.

3.3.1 Long-Term Storage in Slowly Decaying Biomass

Accumulation of slowly decaying biomass is the major mechanism for the long-term storage of nitrogen and phosphorus in natural aquatic treatment systems. The rate of

accumulation will vary significantly depending on the systems. Unfortunately, there are not good estimates of the accumulation rates of slowly decaying biomass in most systems. The accumulation of slowly decaying biomass in SSF systems is expected to be significantly less than in other wetland systems because the plant shoot and leaf matter above the media are aerobically decomposed.

3.3.2 Storage on Soil and Substrate

The soil bottoms and side slopes in most aquatic natural treatment systems have some capacity for adsorbing both ammonium and phosphates. This capacity typically is small compared with nutrient loading, however, and within a relatively short time after the system begins operation, the capacity is either saturated or the soil is isolated by an accumulation of biomass. The media typically used in SSF systems often have significant adsorption capacity that can remove and store nutrients for a much longer period. Even in SSF systems, however, the capacity is eventually exhausted. Small-scale and relatively short-term tests have been conducted in SSF systems with media chosen for its capacity to store phosphorus.

3.4 Nutrient Removal by Plant Harvesting and Removal of Slowly Decaying Biomass

It is possible to estimate the potential for nutrient removal by plant harvesting in many systems. Several researchers have documented the rates of nutrient uptake by plants in natural aquatic treatment systems (Kadlec and Knight, 1996; Reed et al., 1995). Plant harvesting is seldom practiced in most systems, however, most likely because of the difficulties associated with harvesting, processing, and disposing of the biomass. Plant harvesting is practiced most frequently in FAP and SSF systems, most likely because of the relative ease of harvesting compared with other systems. Whole-plant harvesting is practiced in FAP systems; harvesting in SSF systems is limited to the shoot and leaf plant matter above the media.

The removal of slowly decaying biomass from natural aquatic treatment systems is also a problem for many systems, especially wetland systems. This is most easily accomplished in pond and lagoon systems by one of two methods: (1) the pond or lagoon is dredged, the biomass is dewatered on land nearby, and the dewatered solids are hauled away for disposal or beneficial reuse; or (2) the pond or lagoon is drained and the solids are dewatered in situ and hauled away. These operations are relatively expensive and take place infrequently. Removal of slowly decaying biomass in FWS wetlands is more easily accomplished than in vegetated submerged

bed systems, where it is virtually impossible to accomplish without removing and replacing all the media. Removal of slowly decaying biomass is not documented in the literature, but in FWS systems the process would most likely be accomplished by draining, in situ dewatering, and hauling off of the biomass. The removal of plant roots during the process likely would require replanting of wetland plants.

3.5 Nutrient Removal by Gaseous Transport

Several forms of aqueous nitrogen are relatively volatile and potentially can be removed or added to aquatic natural treatment systems by gaseous transport. The nitrogen species that are most likely to be lost, however, are nitrogen gas (N_2), nitrous oxide (N_2O), and unionized ammonia (NH_3). It is also possible that small amounts of oxidized nitrogen (primarily NO_2 in the form of HNO_3) and ammonia from the atmosphere can be added to an aquatic natural treatment system with precipitation as opposed to direct gaseous transport to the water in the system. These inputs are so small, however, that they typically are ignored in aquatic natural treatment systems. Two of the nitrogen species, N_2 and N_2O, are potential products of biological denitrification of oxidized nitrogen present in aquatic natural treatment systems. The loss of aqueous unionized ammonia from a system by gaseous transport to the atmosphere is called ammonia volatilization. Phosphorus typically does not exist in volatile forms in aquatic natural treatment systems, so it cannot be lost or gained by gaseous transport mechanisms.

In considering the gaseous transport of nitrogen species out of an aquatic natural treatment system, it is necessary to consider the role of mixing. Apparent gas transfer coefficients are likely to be dependent on several factors, including air temperature and wind speed directly over the water surface and degree of mixing in the water.

3.5.1 Gaseous Loss of Nitrogen Gas Following Denitrification

Microbial conversion of nitrate and nitrite to aqueous nitrogen gas is covered in detail in other sections of this manual. It is typically assumed that once aqueous nitrogen gas is formed, it is stable and will not further react to form other nitrogen species. So the rate at which aqueous nitrogen gas is transported to the atmosphere is not an issue. For N_2O, it is often assumed that only an insignificant amount is generated in the denitrification process and is lost as a gas. No one has measured the potential for N_2O release from aquatic natural treatment systems. Mass transport does not appear to limit the removal of nitrogen once oxidized nitrogen has been converted to either nitrogen or nitrous oxide gases via biological denitrification.

3.5.2 *Ammonia Volatilization*

Ammonia (in the forms of unionized ammonia and ammonium ion) is often a major fraction of the nitrogen present in aquatic natural treatment systems and of its loss via gaseous transport can be significant in an overall nitrogen balance for some systems. There are several factors that control the rate of ammonia volatilization, including pH, temperature, and degree of mixing in the water and the atmosphere above the water surface. The governing equation, which is based on two-film theory, for ammonia volatilization is:

$$J_{NH_3} = K_L (C^*_{NH_3} - C_{NH_3}) = K_G (P^*_{NH_3} - P_{NH_3}) \quad (12.2)$$

Where,

J_{NH_3} = flux of ammonia out of the water, g NH_3-N/m^2·h;
K_L = liquid mass transfer coefficient, m/h;
$C^*_{NH_3}$ = mass concentration of aqueous unionized ammonia in equilibrium with the bulk atmospheric concentration of gaseous ammonia, g NH_3-N/m^3;
C_{NH_3} = mass concentration of aqueous unionized ammonia, g NH_3-N/m^3
K_G = gas mass transfer coefficient, g NH_3-N/m^2·atm/h;
$P^*_{NH_3}$ = partial pressure of ammonia in equilibrium with the bulk liquid concentration of aqueous unionized ammonia, atm; and
P_{NH_3} = partial pressure of ammonia in the atmosphere, atm.

The governing equation must be properly applied in a mass balance to an appropriate control volume to get a working model for ammonia volatilization from a system. It typically is assumed that the bulk atmospheric concentration of ammonia is zero. The assumptions made on the size of the control volume and the other conditions are important in generating a representative model. The overall rate of ammonia volatilization from a system that is based on the relative loss of ammonia from the water will be highly dependent on the gas/water interfacial area. Shallow systems should have larger rates of ammonia loss per unit volume of water than deeper systems, and diffused aeration should significantly increase ammonia volatilization per unit volume of water.

The pH of the water controls the equilibrium between unionized ammonia and ammonium. Higher pH results in more ammonia in the unionized form and higher rates of ammonia volatilization. At 25°C and pH 9.3, 50% of the total ammonia is in the unionized form. At pH 7.3, only 0.5% is in the volatile, unionized form.

The mass transfer coefficients, K_L or K_G, are dependent on the values of the liquid and gas diffusivity and the thickness of either the air stagnant boundary layer,

the water stagnant boundary layer, or both, depending on the relative solubility of the gas, which is defined by Henry's law. Ammonia is a highly soluble gas, and the thickness of the gas boundary layer is the controlling factor for the mass transfer coefficient. Therefore, the mixing conditions in the air column directly above the water column control ammonia volatilization if no mechanical energy is added to increase the water surface area in contact with the atmosphere. One group of researchers has found that the mass transfer coefficient is linearly related to wind speed for systems having a relatively quiescent water surface (Freney et al., 1985).

Temperature has a direct effect on both the air and water diffusivities of ammonia. The mass transfer coefficient will increase with increasing water and air temperature. Although air temperature should be more important than water temperature for ammonia volatilization because of the greater dependence on air diffusivity as a controlling factor, the air temperature in the mass transfer zone may be controlled by the water temperature.

The relative importance of ammonia volatilization on the overall nitrogen removal from a system will depend on several factors including rates of ammonia conversion in the system, relative gas transfer conditions in the system, pH, air temperature, and overall hydraulic retention time. Despite the relatively high gas transfer conditions in an activated sludge system, ammonia volatilization is not recognized as a significant factor.

4.0 NUTRIENT REMOVAL CAPACITY AND DESIGN CONSIDERATIONS

From the previous discussion, it should be clear that nutrient removal capacity will vary significantly in aquatic natural treatment systems. Most of these systems are not designed or operated specifically for nutrient removal. Also, nutrient removal in these systems is often highly seasonal. The database for defining nitrogen and phosphorus removal rates in systems operating at steady state is much smaller than that for new systems, which may provide unsustainable removal during startup. In addition, removal capacity of one system treating one type of wastewater does not predict removal capacity of that same system treating a different wastewater. Pollutant loading and pollutant entrapment, conversion, storage, and removal mechanisms operating in the system must be considered. Designers are advised to visit several similar systems to their planned system if nutrient removal is an important requirement.

4.1 Ponds and Lagoons

Sufficient information does not exist on the nutrient removal capacity of ponds and lagoons, except for those treating domestic wastewaters. The main mechanisms for total nitrogen removal in ponds and lagoons treating domestic wastewaters are storage in slowly decaying biomass (dead algae) accumulated in benthic zones and ammonia volatilization, although nitrification and nitrification–denitrification also have been identified as potentially important, especially in mechanically aerated systems. One recent study using ^{15}N-labeled ammonia found that storage in benthic sludge was the major removal mechanism for unaerated ponds (Camargo Valero and Mara, 2007). Two similar models (developed using the same database) for estimating nitrogen removal from unaerated ponds are the only models found that used more than one system in model development (Reed et al., 1995; WEF, 2010). The key values in the models are water temperature, pH, and hydraulic retention time. The lowest hydraulic retention time of the systems used to generate the models was 42 days, and the ammonia removal in that system was 46%. There are ponds and lagoons achieving as great as 95% ammonia nitrogen removal. Typical removal is significantly less, however, and long retention times (months) are required for unaerated ponds to achieve significant ammonia removal. Aerated ponds can achieve significant ammonia removal with lower hydraulic retention times, depending on the level of oxygen input.

The main mechanism for total phosphorus removal (without chemical addition for precipitation) for ponds treating domestic wastewater is limited to storage in slowly decaying biomass (dead algae) accumulated in benthic zones, although phosphorus precipitation at algae-induced high pH also has been identified. No models exist for predicting phosphorus removal from ponds and lagoons. Phosphorus removal is typically less than 50% in most ponds and lagoons.

The design practices for maximizing nutrient removal in ponds and lagoons include using multiple basins in series to better capture algal biomass and using a relatively deep first basin in a series for the storage of influent solids.

4.2 Floating and Submerged Aquatic Plant Systems

Nitrogen and phosphorus removal capacity considerations are discussed separately for duckweed, water hyacinth, and periphyton systems in the following sections.

4.2.1 Duckweed Systems

Nitrogen can be removed by plant uptake and harvesting, by denitrification, or by a combination of these. Optimum growth and frequent harvest are required to remove

nitrogen by plant harvest. The density of plants at the water surface depends on temperature, availability of nutrients, and frequency of harvest. The typical density on a wastewater pond might range from 1.2 to 3.6 kg/m^2 (0.25 to 0.75 lb/sq ft) (Reed et al., 1995). The optimum growth rate is approximately 0.49 kg/m^2·d (0.1 lb/sq ft·d). Annual harvest amounts range from 13 to 38 t/ha (5.9 to 17.3 ton/ac), with 22 t/ha (10 ton/ac) dry weight being typical. Assuming that the nitrogen content is 5.9% of dry matter, 108 kg/ha·mo (96 lb/ac·mo) of nitrogen can be removed (Hyde et al., 1984).

Plant harvest can result in some limited phosphorus removal. Typically, less than 1 mg/L of phosphorus can be removed from the waste stream. If wastewater phosphorus concentrations are small and removal requirements minimal, then harvesting may be suitable. If significant phosphorus removal is required, however, chemical precipitation with alum, ferric chloride, or other chemicals used in a separate treatment step may be more cost-effective (Reed et al., 1995). Phosphorus concentrations in the dry biomass of duckweed grown in wastewater may be approximately 0.6% of dry weight (Hyde et al., 1984). Using the same growth rates assumed above, approximately 11.2 kb/ha·mo (10 lb P/ac·mo) can be removed.

The design of duckweed systems is similar to that of aerated or facultative ponds. Rectangular ponds with earthen dikes typically are used. Lemna Technologies, Minneapolis, Minnesota, systems use propriety floating plastic barriers to keep the duckweed in place. The retention time for the system design depends on influent quality and effluent requirements. Pond depth can range from 1.5 to 4.5 m (5–15 ft), and retention times are typically 20 to 30 days. Korner et al. (2003) recommend depths less than 50 cm (1.6 ft). Table 12.3 summarizes typical design criteria.

Because duckweed effectively can cover and seal the pond surface, reaeration from the atmosphere is limited, and the pond water column can become anoxic. If effluent dissolved oxygen levels are specified in the discharge permit, then reaeration may be necessary.

4.2.2 Water Hyacinth Systems

Biological nitrification–denitrification is the primary mechanism for removing nitrogen. Sedimentation removes a portion of the organic nitrogen. Plant uptake and subsequent harvest is also a sink for nitrogen, but this is not an effective means of treatment. Some nitrogen is lost to ammonia volatilization. Nitrification–denitrification occurs primarily in the root zone. Thus, it is important for wastewater containing various forms of nitrogen to flow past the water hyacinth roots, where bacteria responsible for the transformation and removal of nitrogen are located. Nutrient removal data from the water hyacinth system at San Diego is shown in Table 12.4.

TABLE 12.3 Typical design criteria and expected effluent quality for duckweed systems. (Crites and Tchobanoglous, 1998; Water Environment Federation, 2010).

Parameter	Unit	Value
Design criteria		
Influent wastewater		Facultative or aerated pond effluent
BOD_5 loading rate[a]	kg/ha·d	20–30
Detention time	d	20–30
Water depth	m	1.5–4.5
Harvest schedule		Monthly for secondary treatment, weekly for nutrient removal
Expected secondary effluent quality		
BOD_5	mg/L	<30
TSS	mg/L	<30
TN	mg/L	<15
TP	mg/L	<6

[a] kg/ha·d × 0.892 = lb/d/ac.

BOD_5 = five-day biochemical oxygen demand; TN = total nitrogen; TP = total phosphorus; and TSS = total suspended solids.

TABLE 12.4 Nutrient removal performance summary for water hyacinth wastewater treatment ponds at San Diego, California (Aqua III), from October 1994 through September 1995 (Western Consortium for Public Health, 1996).

Constituent	Pond influent (mg/L)	Pond effluent (mg/L)	Reduction (%)
NH_4-N	21	9.5	55
NO_3-N	0.05	1.4	0
TKN	31	13.9	46
Phosphate	5.1	3.4	33

TKN = total Kjeldahl nitrogen.

Adsorption to wastewater solids and plant material, adsorption to organic matter in the sludge layer, and plant uptake temporally remove phosphorus from wastewater. In time, most of the adsorbed phosphorus is released back to the water column. Limited amounts of phosphorus also are removed when routine harvesting

of water hyacinth plants is practiced. Adsorption to the organic matter in the sludge layer is the other primary fate of phosphorus remaining in the system. When effluent limitations on phosphorus exist, phosphorus should be removed in a preapplication or posttreatment step because phosphorus removal in water hyacinth and other constructed wetland treatment systems is limited and often erratic.

Several factors need to be considered to optimize the performance of water hyacinth systems for nutrient removal:

- Climate—Because water hyacinths are sensitive to cold temperatures, their use is restricted to Arizona, Texas, Mississippi, Louisiana, Alabama, Georgia, Florida, and southern portions of California. Combined systems using several aquatic plants (e.g., duckweed, pennywort, and water hyacinth) may be suitable for locations with greater climatic variations.
- Pretreatment—The minimum level of pretreatment should be primary treatment, short retention time aerated ponds with settling, or the equivalent. When effluent limitations on phosphorus exist, phosphorus should be removed in a pre- or postapplication treatment step because phosphorus removal in aquatic treatment systems is limited and inconsistent. Nitrogen removal is limited similarly unless special design approaches are used, either through pretreatment or within the facility itself.
- Water depth—In nonaerated water hyacinth systems, water depth is important for controlling vertical mixing in the pond so that the wastewater being treated contacts the plant roots, which offer ideal settling conditions and contain most of the bacteria that accomplish biological treatment. In aerated water hyacinth systems, greater liquid depths can be used because the aeration devices also serve as airlift pumps that create a circulation flow in the pond. The added oxygen in aerated systems allows organic loading rates four times greater than those in nonaerated systems. Typical operating depths for nonaerated and aerated water hyacinth systems vary from 0.45 to 0.75 m (1.5–2.5 ft) and 0.1.2 to 1.4 m (4–4.5 ft), respectively.
- Growth rate—water hyacinth can grow rapidly and ranks eighth among the world's top 10 weeds for growth rate. The growth of water hyacinth is influenced by: (1) efficiency of the plant to use solar energy, (2) nutrient composition of the water, (3) cultivation methods, and (4) environmental factors (Stephenson et al., 1980).

- Harvest—The need to harvest plants depends on water quality objectives, growth rates of the plants, and the effects of predators such as weevils. Harvesting aquatic plants maintains a rapidly growing crop with a higher metabolic uptake of nutrients. For example, frequently harvesting water hyacinths (e.g., every week) is necessary to achieve enhanced nutrient removals. Significant phosphorus removal is achieved only with frequent harvesting.
- Step-feed and effluent recycle—Step-feed and effluent recycle may be important to optimize the performance of water hyacinth treatment systems.

4.2.3 Periphyton Systems

Most of the nitrogen removal (31–52%) in periphyton systems is through assimilation into algal biomass and subsequent harvesting (Kebede-Westhead et al., 2003). Measurable reductions in total nitrogen have been observed for a wide range of wastewater strengths. In municipal wastewater (Table 12.5), an average inflow total nitrogen of 18.7 mg/L was reduced by 42% to 10.8 mg/L (Craggs et al., 1995). For treatment of water from a eutrophic lake in Florida, periphyton raceways reduced labile inorganic nitrogen (NO_x + NH_4-N) from 0.122 to 0.029 mg/L, but total nitrogen showed little difference in inflow and outflow concentrations (influent total nitrogen = 1.12 mg/L, effluent total nitrogen = 1.08–1.15 mg/L) (DB Environmental Laboratories, 2000). For dairy wastewater treated by algal systems under different light and loading conditions, total nitrogen was reduced from 3.77 to 3.10 mg/L at the low end and 14.79 to 17.43 mg/L at the high end (Kebede-Westhead et al., 2003).

Periphyton can remove phosphorus from water by a combination of filtration, adsorption, assimilation, and precipitation. Most of the phosphorus removal is by assimilation into algal biomass or precipitation of inorganic phosphorus. Precipitation of soluble reactive phosphorus with inorganic elements Ca, Mg, and Al are known to occur at pH 8.9 to 9.5, depending upon water alkalinity. Several passive and active periphytic algae-based systems have reported significant phosphorus removal rates. A periphyton stormwater treatment area reduced inflow phosphorus from 0.024 to 0.015 mg/L, which corresponds to a 37% removal (CH2M HILL, 2003). The S-154 Floway reduced concentrations from 0.333 to 0.258 mg/L and achieved phosphorus removal rates of 92 g/m^2·a from an average phosphorus loading rate of 397 g/m^2·a (Hydromentia, 2005). The Patterson system achieved an average reduction of 3.1 to 1.5 mg/L (Craggs, 2001).

Table 12.5 Mean annual influent and effluent concentrations of water quality variables measured over three years at the Patterson, California, Algal Turf Scrubber (periphyton system). (Craggs, 2001).

Parameter	Influent (mg/L)	Effluent (mg/L)
TON	10	6.2
NH_4-N	5.8	2.9
NO_3-N	3.9	1.7
TP	3.1	1.5
SRP	2.2	0.9

SRP = soluble reactive phosphorus; TON = total organic nitrogen; and TP = total phosphorus.

The details of engineering the installation of a periphyton treatment system vary depending on whether the system can be characterized as active or passive. Active systems are engineered periphyton treatment floways that require a high level of operations and maintenance including byproduct harvesting and processing, distribution systems, and pulsed or surged inflow mechanisms. Active systems also have greater energy requirements. In contrast, passive periphyton treatment systems are built to require minimal operations and maintenance and are constructed to look relatively natural. They do not require pulsed or surged flows and typically are not harvested. Several factors need to be considered when using periphyton treatment systems for nutrient removal:

- Climate—Periphyton has a universal distribution and can be found in any natural aquatic water body throughout the world. Available data, however, indicate that engineered applications may be limited in cold temperate climates.
- Water depth—Pepth is an important consideration in periphyton systems because shallower depth provides more opportunity for contact between the algal mat and the water column.
- Harvest (active systems)—The largest mass of nutrients removed from the water column in a periphyton treatment system is stored in algal biomass. Harvesting in an active periphyton treatment system is important to maximize the exponential growth phase of the algae and nutrient removal.

Performed manually in pilot-scale systems, harvesting is most efficiently performed mechanically in full-scale systems. Disposal of algal biomass remains a key obstacle to greater acceptance of this technology. Algal biosolids can be mixed with hay to add carbon and reduce moisture content and then composted.

- Proprietary systems—Two companies market proprietary applications of the engineered periphyton treatment system concept. Hydromentia Inc., Ocala, Florida, and Aquafiber, Orlando, Florida. The former holds an industrial license for Algal Turf Scrubbing (ATF) and has developed expanded ATS systems that have been demonstrated at various locations in Florida (Hydromentia, 2008).

4.2.4 Free Water Surface Systems

Nutrient removal, especially removal of nitrogen and phosphorus, has always been and continues to be a major focus of research and development for FWS and other types of treatment wetlands. Efforts are underway to assess the effectiveness of treatment wetlands and to summarize information from diverse data sources into coherent and predictive descriptions of performance. One of the most comprehensive efforts to date to assess the effectiveness of treatment wetlands was the development of the North American Treatment Wetland Database (NADB) funded by the U.S. Environmental Protection Agency (U.S. EPA) (Knight et al., 1993a, 1993b). The NADB was updated in 1998 (NADB v. 2.0). Kadlec and Knight (1996) have used data from NADB v. 2.0 to calibrate wetland performance assessment models. The Water Environment Research Foundation (2006) provides summaries of small-scale wetland performance from a database representing 1640 FWS systems from across North America, all less than or equal to 6 ha in size and with less than or equal to 2000 m^3/d flow. These datasets and the models calibrated based on them provide the most current and robust techniques for estimating nutrient removal capacity and sizing wetlands.

Numerous biological-mediated transformations of nitrogen occur in FWS wetlands, including mineralization/ammonification, nitrification, and plant and microbial uptake, and denitrification (Vymazal, 2007). The low rate of oxygen transfer into water and sediment and the oxygen demand exerted by microbial and animal respiration maintain anaerobic conditions in wetland sediments. Although deeper layers

are anoxic in wetland sediments, a thin layer of oxidized soil at the soil–water interface permits oxidized forms of prevailing ions to exist.

The nitrogen removal capacity of FWS wetlands is a function of several factors, including the forms of nitrogen in the influent, areal mass loading rates, temperature, and organic loading. Degradation of organic and ammonia forms of nitrogen is typically oxygen-limited in FWS wetlands. Nitrogen removal from nitrified wastewaters is more efficient because of the prevalence of anaerobic conditions in wetlands. Denitrification is the most likely pathway for nitrate loss from wetlands. Rates of nitrate-nitrogen removal as great as 2.8 $gN/m^2 \cdot d$ have been reported from southern California wetlands (Bachand and Horne, 1999). Approximately 18 t (20 tons) of NO_3-N per month, mainly through denitrification, is removed through the 182-m^2 (450-ac) Prado Basin wetlands in Southern California (Lund et al., 2000; Reilly et al., 2000). For demonstration wetlands treating advanced secondary wastewater in Arizona, Kadlec (2008) determined that total nitrogen was reduced by approximately 60% from an inflow concentration between 6 and 8 mg/L. Speciation of the inflow was approximately 25% organic nitrogen, 25% ammonium nitrogen, and 50% nitrate nitrogen. Typical outflow concentrations were approximately 1.2 mg/L organic, 0.5 mg/L ammonium, and 0.0 to 2.5 mg/L nitrate. Other studies indicate that more than 80% of influent nitrate nitrogen maybe lost to denitrification (Crumpton et al., 1994; Moraghan, 1993).

There are seasonal and diurnal changes in an FWS wetland that affect nitrogen removal, including temperature fluctuations, daily cycles in photosynthesis, and ice formation (WERF, 2006). Table 12.6 summarizes mean removal values of total nitrogen in FWS wetlands.

Table 12.6 Mean values for total nitrogen removal in free water surface treatment wetlands.

C_{in} (mg/L)	C_{out} (mg/L)	Efficiency (%)	N	Source
14.3	8.4	41.2	85	Vymazal, 2007, 2001
16.9	11.0	34	NA[a]	Crites et al., 2006 (secondary effluent source)
19.1	8.9	53	NA	Crites et al., 2006 (primary effluent source)
9.7	4.5	53	44	Knight et al.,1993; Kadlec and Knight, 1996

[a] NA = not available.

The ultimate sink for phosphorus removed in an FWS wetland is the sediments, primarily through the accumulation of recalcitrant fractions of wetland plants (Craft and Richardson, 1993; Kadlec, 1994). Sorption, plant uptake, and precipitation are saturable sinks, whereas peat and soil accumulation of phosphorus is not saturable (Vymazal, 2007). Short-lived organisms with a rapid turnover take up and accumulate phosphorus in a short-term, partly reversible cycle, returning a fraction of the phosphorus to the sediment with a period of days to weeks (International Water Association [IWA], 2000). The annual cycle of growth and renewal in larger plants such as cattail and bulrush occurs over a longer period of months to years. Detrital accumulations from both processes contribute to the long-term storage in wetland sediments. Phosphorus in particulate matter is trapped by physical sedimentation in the wetland environment. Biological influence on water column chemistry can increase phosphorus accumulation, such as algae-driven precipitation of phosphorus with calcium.

The net accumulation of organic and inorganic sediment is approximately 1 to 10 mm/a (Kadlec and Knight, 1996; Reddy et al., 1991). Removal rates of phosphorus by sediment accretion are a function of phosphorus loading, wetland size, climate, and vegetation type (WERF, 2006). Surface flow wetlands provide sustainable removal of phosphorus but at relatively low rates (IWA, 2000). Based on a review of the literature, Vymazal (2001) suggested a mean removal rate of approximately 1 $g/m^2 \cdot a$ (Reddy et al., 2005; WERF, 2006). Crites et al. (2006) suggest that phosphorus concentrations seldom will be reduced by more than 1 to 3 mg/L in SFW systems with hydraulic retention times of 5 to 10 days. Very low loading rates may result in discharge of background concentrations, and very high loadings result in essentially no net removal (Kadlec, 1999; WERF, 2006).

As a first approximation of phosphorus removal performance in wetlands, a best-fit regression of inflow-outflow phosphorus reduction in marshes is provided by IWA (2000):

$$C_o = 0.195 q^{0.53} C_i^{0.91} \tag{12.3}$$

Where,

C_o = outflow concentration, mg/L;
C_i = inflow concentration, mg/L;
q = hydraulic application rate, cm/d;
$r^2 = 0.77$;
$N = 373$;

TABLE 12.7 Mean values for total phosphorus removal in free water surface treatment wetlands.

C_{in} (mg/L)	C_{out} (mg/L)	Efficiency (%)	N	Source
4.2	2.15	48.8	85	Vymazal, 2007, 2001
5.0	2.4	46	10	Crites et al., 2006
3.8	1.6	57	44	Knight et al., 1993; Kadlec and Knight, 1996

$0.02 < C_i < 20$ mg/L;
$0.009 < C_o < 20$ mg/L; and
$0.1 < q_{av} < 33$ cm/d.

Background levels of phosphorus are an important but variable quantity considered to range between 10 and 50 ug/L (IWA, 2000). The importance of this quantity on wetland phosphorus performance is evident only when outlet concentrations are within this range. The first-order rate constant for nonforested wetlands averages 10 m/a, and 3 m/a for forested wetlands (IWA, 2000; Kadlec and Knight, 1996).

Seasonal and temperature effects have not been shown to be significant factors in projections of annual performance. Start-up effects of sorption and biomass growth enhance phosphorus assimilation, and leaching from accumulated materials can decrease apparent assimilation (IWA, 2000). These short-term startup effects may take one to four years to disappear (Kadlec and Knight, 1996). Table 12.7 provides a summary of mean removal rates for phosphorus in FWS treatment wetlands.

Most wetlands are more autotrophic than heterotrophic, resulting in a net surplus of fixed carbonaceous material that is buried as peat or is exported downstream to the next system (Mitsch and Gosselink, 1993). This net production results in an internal release of particulate and dissolved biomass to the wetland water column, which is measured as nonzero levels of BOD, TSS, total nitrogen, and total phosphorus. Enriched wetland ecosystems such as wetlands used to treat wastewater are likely to produce higher background concentrations than oligotrophic wetlands. This is because of the larger biogeochemical cycles that result from the addition of nutrients and organic carbon. Wetland systems typically have background concentrations within the following ranges (Kadlec and Knight, 1996):

- Organic and total nitrogen: 1 to 3 mg/L;
- Ammonium-nitrogen: less than 0.1 mg/L;

Table 12.8 Background concentrations in small-scale free water surface wetlands. (Water Environment Research Foundation, 2006).

Parameter	Background concentration, C^*, 50th percentile	Background concentration, C^*, 75th percentile	Background concentration, C^*, 90th percentile
TKN	1 mg/L	2 mg/L	5 mg/L
TP	0 mg/L (nondetect)	1 mg/L	3 mg/L

(TKN = total Kjeldahl nitrogen and TP = total phosphorus.)

- Nitrate-nitrogen: less than 0.1 mg/L; and
- Total phosphorus: less than 0.1 mg/L.

These background concentrations of pollutants leaving lightly loaded constructed treatment wetlands are generated from internal processes and are not the residual pollutants contained in the treated effluent that was put into the wetland. Table 12.8 shows the range in background concentrations observed in small-scale treatment wetlands.

Several fundamentals are critical to meeting design discharge criteria for nutrients in wetland systems (Kadlec and Knight, 1996; WERF, 2006):

(1) Accurately estimating the influent flows and loads to the treatment wetland.
(2) Estimating wetland performance and the area and volume required to meet the most limiting treatment goal.
(3) Estimating the overall system water balance, including effects of evapotranspiration, infiltration, and precipitation.
(4) Controlling water flows and hydraulic efficiencies to attain levels of performance at least as high as the performance of the systems used to derive empirical rate constants.
(5) Creating and maintaining physical, chemical, and biological wetland system components necessary to achieve normal pollutant processing rates.
(6) Not removing wetland vegetation to maximize nutrient removal, which typically is not recommended because the mass removed is not significant compared with mass loading (Brix, 1994; Vymazal, 2001; WERF, 2006).

Many other issues are also important in design and operation of treatment wetlands. These include conventional civil engineering design criteria for dikes and levees, water control structures, and soil compaction and grading; mechanical design details for flow measurement devices; and architectural/landscape design details for operator and public access. There are also many construction and operation issues that are of importance in treatment wetlands. These related issues include clearing and grubbing requirements, plant selection and plant maintenance techniques, water level control, avoidance of nuisance conditions from mosquitoes, operator and public safety, and wildlife management. Several sources provide more detailed information on these aspects of treatment wetland technology (Arizona Department of Environmental Quality, 1995; IWA, 2000; Kadlec and Knight, 1996; Reed et al., 1995; U.S. EPA, 2000; WEF, 2010).

"Nutrient farming," or the use of large-scale riparian wetlands for treatment, has been proposed as a means of providing nutrient treatment for very large cities such as Chicago (WERF, 2005). Annual costs per ton of total nitrogen or total phosphorus treated would be approximately 51% to 63% less for the wetland alternative, and 76% to 78% less if surplus nutrient credits can be sold.

An important initial consideration that drives design is the extent of nitrification in the influent water. Wastewaters that are high in organic and ammonia nitrogen will be difficult to treat unless systems are lightly loaded, as these systems are typically dissolved oxygen-limited (WERF, 2006). The most important factors affecting TKN removal (organic and ammonia nitrogen) are mass loading rates, temperature, and oxygen transfer (WERF, 2006).

When dealing with fully nitrified effluents, denitrification becomes the focus, and temperature and the availability of organic carbon are the key factors (WERF, 2006). Denitrification rates are affected by the availability and quality of the carbon source, which is primarily decaying wetland vegetation. To avoid carbon limitations on denitrification rates, C:N ratios should be at least 5:1 (Baker, 1998). The availability of carbon varies by type of wetland plant. Floating plants typically have lower lignin content than emergent plants (Hume et al., 2002). Oxygen will be used preferentially by microorganisms to degrade organic matter. Therefore, the total organic load (wastewater plus internal cycling within the wetland) determines how much dissolved oxygen remains for oxidation of nitrogen (WERF, 2006).

All biological processes are slow in response to colder temperatures. Wetland plants become dormant in the fall, and production of new plant biomass stops when temperatures fall below freezing. Removal of the BOD_5, TSS, metals, and total

phosphorus is not significantly affected by the cold temperatures that exist in treatment wetlands covered by ice and snow. The vegetative cover of treatment wetlands helps to trap an insulating layer of snow that is typically deeper than actual snowfall because of retention and capture of blowing snow (Kadlec and Knight, 1996). Successful operation of an SFW has been documented under 2 m of snow in the Alps (Kadlec and Knight, 1996; Navarra, 1992). Water flowing under the ice will have temperatures a few degrees above freezing because of the insulating quality of the snow and the air gap below the ice surface and from latent heat from the earth. Although most of the microbial nitrogen transformation processes are slowed, some nitrogen reduction continues.

The potential for phosphorus removal in FWS wetlands is limited, and conservative design is imperative. To achieve low effluent concentrations, loading rates should be less than 1 kg/ha·d (WERF, 2006). There are several specific design considerations:

(1) If phosphorus levels are elevated in sediments used to construct wetlands, there may be net release of phosphorus rather than removal.
(2) Physical disturbance of accumulated sediments or draining and reflooding wetland areas may lead to phosphorus release.
(3) Because the retention of phosphorus relies on accretion of sediments, long-term system performance depends on having sufficient freeboard.
(4) Lower limits of phosphorus removal are defined by local geology.

4.2.5 Subsurface Flow Constructed Wetlands

As described in Section 1.3.1, SSF systems behave as attached-growth (or fixed-film) biological reactors. Organic nitrogen trapped within the bed will undergo ammonification. The released ammonia may be available for plant uptake depending upon the location of the plant roots. Flow below the plant roots will carry ammonium downstream. Plant uptake of nitrogen is low compared to typical nitrogen loading to SSF systems (uptake = 0.03 to 0.3 $gN/m^2 \cdot d$). Nitrogen and phosphorus removal by plant uptake will vary with time. This is because most of the removal occurs during rapid plant growth and a release or no removal is likely during senescence. Therefore, unless nutrient removal standards for an SSF system also are variable and synchronous with plant uptake and release, the presence of plants may be more harmful than helpful. Finally, it is unlikely that the nutrient removal obtained by harvesting is worth the considerable time and labor required.

Several conventional SSF systems have been designed, built, and operated to remove ammonia from wastewaters. Although some degree of ammonia removal has been achieved in several systems, removal rates have been less than predicted (George et al., 2000; WERF, 2000; Young et al., 2000). The primary mechanism of ammonia removal is nitrification, but plant uptake may also be important during the startup of an SSF system or in harvested systems. Nitrification rates slow down significantly as water temperatures approach freezing. An offsetting factor, however, is that dissolved oxygen levels increase as water temperatures drop. Ammonia removal appears to be severely oxygen-limited in conventional SSF systems because removal at colder water temperatures is often as good as or better than removal at higher temperatures. The U.S. EPA (2000) summarized an analysis of the capacity of conventional SSF systems to remove TKN from septic tank and primary effluent. The TKN removal performance was found to be poor and highly variable (Figure 12.4). The conclusion was that conventional SSF systems should not be used alone to treat septic tank and primary effluents if significant ammonia removal is

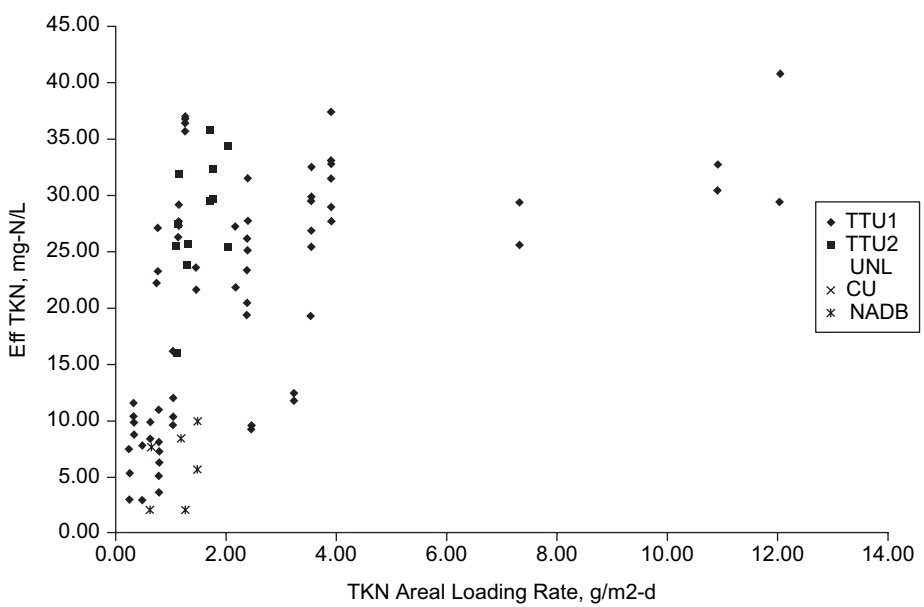

Figure 12.4 Eff TKN (mg N/L) versus TKN areal loading rate (g/m^2-d) (U.S. EPA, 2000).

consistently required. Significantly less data is available on the TKN removal of SSFs treating a pond or lagoon effluent. Two studies, however, found the TKN removal to be negligible in both systems (Batchelor and Loots, 1997; U.S. EPA, 2000). In conventional SSF systems, significant and reliable ammonia removal is achieved only at very low loading rates, often rendering the process too costly compared with other alternatives.

Alternative SSF systems likely will be more effective in ammonia removal via nitrification because of better oxygen transfer. Several alternative SSF systems already have demonstrated a higher capacity for ammonia removal than conventional SSF systems (Behrends et al., 1996; George et al., 2000; May et al., 1990). Also, unsaturated vertical flow wetlands have demonstrated significant ammonia removal capacity (Vymazal, 2007).

Although conventional SSF systems seem well suited for denitrification of a nitrified effluent, there are relatively few studies of their potential for this purpose (Gersberg et al., 1983; WERF, 2000; Stengel and Schultz-Hock, 1989). The conclusion from these studies is that conventional SSF systems treating well-oxidized secondary effluents or other carbon-limited wastewaters have inadequate carbon for rapid and complete denitrification. Conventional SSF systems, which achieve some level of nitrification treating a higher strength wastewater, such as septic tank or primary effluent, also typically achieve a high degree of denitrification of the nitrate (George et al., 2000; Young et al., 2000).

The net removal of phosphorus from SSF systems typically relies on accumulation of slowly decaying biomass and on chemical precipitation and adsorption on the media. Phosphorus loading to these systems is typically large relative to plant uptake. Reliable, sustained removal by harvesting of plants before senescence does not provide significant removal. The long-term capacity of the media for phosphorus adsorption typically is limited.

Although phosphorus is partially removed, SSF systems treating septic tank and primary effluents are not very effective or reliable for long-term phosphorus removal (Figure 12.5) (U.S. EPA, 2000). Phosphorus data shown in Figure 12.5 are from SSF systems that are relatively new, when phosphorus precipitation and absorption capacity of the media typically would be at its greatest. As is the case for nitrogen, there is considerably less available data on the phosphorus removal of SSFs treating a pond or lagoon effluent; however, one study found the phosphorus removal to be negligible (U.S. EPA, 2000).

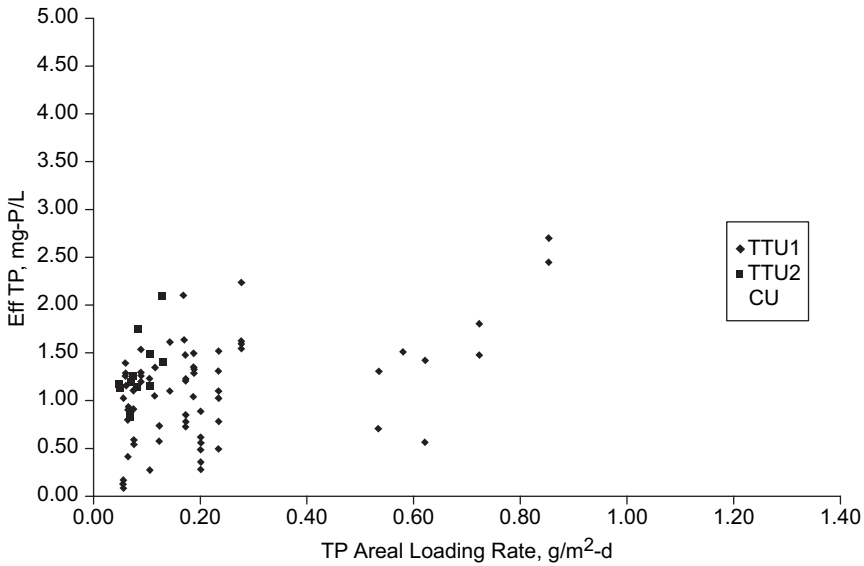

FIGURE 12.5 Eff TP (mg N/L) versus TKN Areal Loading Rate (g/m^2-d) (U.S. EPA, 2000).

Design practices for maximizing nitrogen removal in SSFs include better aeration by the use of either unsaturated vertical flow wetlands or alternating draining and filling operation.

4.2.6 Combination Systems

A sequence of treatment systems creates stages of chemical reactions and conditioning of pollutant content suitable for processing by different systems. A common design approach is to have FWS wetlands downstream from pond- or lagoon-based systems. Treatment-train approaches have been used effectively to exploit the strengths of different systems to achieve greater levels of total nitrogen removal. For example, pulsed vertical flow treatment wetlands followed by FWS wetlands achieve good nitrification and denitrification (Vymazal, 2007). For nutrient removal systems designed to achieve very low levels to protect the Everglades, treatment trains may include FWS to SAV to periphyton systems or floating aquatic vegetation to periphyton systems.

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