Non-Targeted Screening of Wastewater Organic Disinfection By-products using Low Density Polyethylene (LDPE) Passive Samplers

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DEDICATION

This thesis is dedicated to my affectionate parents and my very good friends.

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List of Abbreviations

ASM	Abraham solvation model
BCF	bioconcentration factor
BMF	biomagnification factor
BOD	biochemical oxygen demand
COD	chemical oxygen demand
DBP	disinfectant bi products
EPA	environmental protestation agency
GC×GC	comprehensive two-dimensional gas chromatography
PAA	Peracetic acid
PDBS	diffusion bag sampler
SPMD	semipermeable membrane device
SPME	solid-phase micro-extraction
THMs	Trihalomethanes
TOF-MS	time of flight - mass spectrometer
TOX	total organic halide
TWA	time-weighted average
UNEP	United Nation Environmental Program
VOCs	volatile organic compounds

ABSTRACT

Insufficient water supply and deterioration in water quality are serious concerns in various regions of the world. These problems are due to several reasons that include sustained urban development, pollution of surface and underground water, uneven water resources distribution and recurrent droughts worldwide due to global warming. Therefore, new sustainable water management models are emerging. Wastewater treatment offers treated wastewater with a quality that should be beneficial for use. To achieve this goal, wastewater treatment usually involves several steps, such as biodegradation of organic matter, precipitation of suspended solids, nutrients removal, and disinfection to inactivate or kill pathogenic microorganisms. Disinfectants produce a wide range of disinfection by-products (DBP), having health and regulatory concerns. Conventionally 'Grab Sampling' has been the preferred method for DBPs monitoring but may not be sufficient or economically feasible thus alternative techniques are needed. In this study, non targeted screening of disinfection by-products was performed by Low Density Polyethylene (LDPE) passive sampling at Membrane Bioreactor (MBR) waste water treatment plant in Islamabad. This research study consisting of two-parts i.e. computational and experimental. First part based on development of two parameter model for the estimation of Low Density Polyethylene (LDPE) to water partition coefficients. For this purpose, data sets were retrieved from literature. Then most suitable dependent variable (Kpdms) and independent variables (Kow and Kaw) was selected using AIC information criteria AKIAKE. Subsequently, Multi Linear Regression (MLR) was performed to train the model on experimental datasets while cross validation was done by using models1 via 'R' programming. Principal Component Analysis (PCA) was also executed for dimensionality analysis to check the redundancy of this model and to ascertain which variable is contributing to maximum information. In second part, being the most convenient passive sampler, LDPE was being selected and prepared. At time of deployment, four replicates field strip samples were simultaneously submerged into waste water with the help of BBQ grills and metallic gauzes, and exposed for period of 15 and 30 days from Aug 2018 to Dec 2018. After these exposure experiments, the samples were carefully retrieved, instantly wrapped in aluminum foil and carried to the lab in ice box to secure the adsorbed contaminants for further analysis. These adsorbed contaminants were extracted by ethyl acetate. Resultant samples were stored in vials for GCMS time of flight MS analysis and characterized via NIST library match. 116 DIBs were identified on the basis of library match score > 800. Results were further processed for risk and fate analysis

through modelling of EPI suite. Results of non-targeted screening of disinfection by-products have suggested that the disinfected waste water is still not safe for non-potable use and need further polishing treatment using Titanium Nanotubes (TNTs) and char.

Chapter 1

Introduction

1.1 Background

Water, being one of the most important natural resource for all of the living organisms on the planet earth, plays a very vital role in determining not only the habitat of the living organisms but also is a factor contributing to their quality of life. As water covers almost 70 percent of the earth's surface, it is considered commonly that there may not be any issue of water. However, the reality is quite the opposite as various regions on the earth surface are water scarce and some areas are vulnerable to water scarcity. Besides this, the quality of the fresh water is deteriorating day by day due to a number of factors. Considering water as a non-renewable resource and ensuring its good quality availability to public must be the need of the hour.

Throughout the history, people came to know about the water crisis of water related mortality gradually. People directly involved in chronic and fatal accidents due to water quality make an evidence of the matter. According to the UNDP report, around 50 to 100 liters of water is required on average for a person per day, an absolute of 20 liters per person per day (UNDP, 2006).

A number of factors like never ending growth in population, urbanization, socio-economic advancements, and the change in the consumption behavior and pattern, contribute to the increase in water usage by 1 percent per year since the decade of 1980s. Forecasting this global water demand, as expected to keep up surging at a homogeneous measure until 2050, the escalation in the level of water use may shoot up by 20 to 30% above the present-day amount of water use, primarily because of the upsurge demand and development in the industrial and domestic sectors. More than 2 billion humans are residents of high water stressed countries and about 4 billion humans are exposed to intensive water scarcity for a period of at least one month per year. As long as the demand for water increases and the impacts of climate changes escalates, the water stress levels will tend to increase (UN World Water Development Report,2019).

1.2 Uses of Water

Water is such an important commodity that it is used both directly and indirectly in almost every aspect of daily life. Directly water is used in drinking mainly, while taking bath, in cooking and cleaning etc. Indirectly water is used in wood processing for transforming it to paper. Also water is used in steel production for automobiles [1, 2].

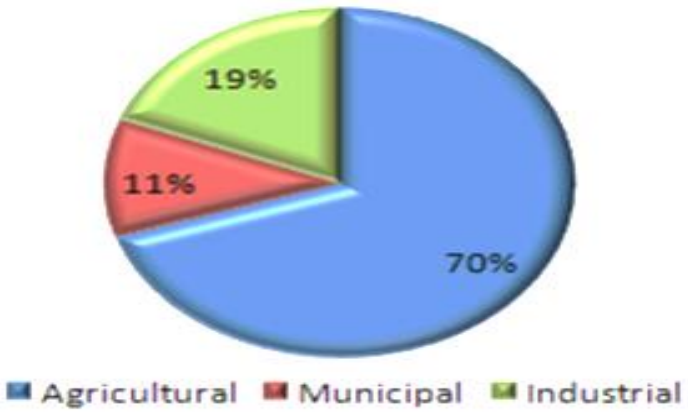


Figure 1: Global sun of water withdrawals

Water is used massively in agricultural routine, in various industrial activities, and in electricity production. Throughout the world, 70 percent of all water consumption is accommodated by agricultural activities, followed by industrial consumption which contribute to 20 percent [3]. The remaining 10 percent of water consumption is contributed by domestic activities. These figures change in developed industrialized countries where more than 50 percent water consumption is due to industrial activities. Belgium, for instance, uses 80 percent of the available water available for industry. Due to such massive usage of water, in the last 50 years the freshwater withdrawals have increased threefold.

1.2.1 Domestic Consumption: Drinking and Household Needs

The world population has been increasing rapidly in the recent past as it increased by three times in the 20^{th} century. In the same time period, the water usage for human purposes has been multiplied by six times. Humans are used water mainly for the purpose of cleaning, washing, cooking, drinking, watering food plots, and in nourishment of their pets. All of this domestic water usage accounts for mere but crucial 10 to 11 percent of the total water withdrawals [4].

High-quality water with easy access is the essential requirement of every family as they use water for drinking, body washings, food preparations, watering plants, and cleaning activities. The human body cannot function properly without a supply of an adequate amount of water. The ground statistics show only one out of five persons who does not have any access to affordable and standard safe water, where half of the human race has no access to any sanitation [5]. Waterborne diseases contribute to 3 to 4 million deaths per year out of which 2 million children deaths are because of diarrhea (World Health Organization statistics, WHO, 1996).

Therefore, the water supply should be made efficient and free from pollutants. Urbanization is one major cause of water deterioration and it reached to 38.8 percent in 2015. This urban population has been forecasted to increase up to 46.6 percent in the year 2030 and 57.5 percent in the year 2050. The water usage in urban areas is 120 liters per capita per day and 45 liters per capita per day in the rural areas (United Nations, 2015).

1.2.2 Agriculture: Food Production and forestation

A massive quantity of water is used for irrigation purposes worldwide. The largest water consumer, agriculture (practices like aquaculture, livestock, and mainly irrigation), accounts for 69 to 70 percent of annual water withdrawals globally (United Nations World Water Development Report 2019).

Asia contains almost 70 percent of the irrigated area of the world. The most important constituent of the green revolution is this irrigation which multiplies the agricultural productivity several folds. But during the irrigation processes, a heavy amount of water is used and a healthy percentage of that is lost due to poor management. Water withdrawal takes place through evaporation from reservoirs, from canals, from soils, and its incorporation into crops and transpiration by crops.

Drip irrigation can consume water up to 90 percent in irrigation where flood irrigation costs 30 to 40 percent, depending upon the relevant technologies [6]. (The rest recharges groundwater or contributes to drainage or return flows. This water can be—and often is—reused, but it has higher salt concentrations and is often contaminated with nutrients, sediments, and chemical contaminants (pesticides, herbicides) that can damage the ecosystem. Unless carefully managed, irrigated areas risk becoming waterlogged and building up salt concentrations that could eventually make the soil infertile. This process probably caused the downfall of ancient irrigation-based societies and

threatens the enormous areas brought under irrigation in recent decades. By the late 1980s an estimated 50 million hectares of the world's irrigated areas, or more than 20%, had suffered a buildup of salts in the soil.

1.2.3 Industrial or Commercial use: Industry and Commerce

Water may be used as a raw material in the industrial processes, or as cleaning agent. Water may also be used as a cooling agent, for dilution process, for washing of different mechanical parts and of raw material, for transportation process, or for boiling and cooking.

Manufacturing and other industries use water during the production process for either creating their products or cooling equipment used in creating their products. Water is also used by smelting facilities, petroleum refineries, and industries producing chemical products, food, and paper products. Large amounts of water are used mostly to produce food, paper, and chemicals.

Water is used in a huge amount during mining processes for the extraction of various materials. Water can act as cooling agent in various processes, can be used for transportation, and by the crew members for basic needs.

Mechanical energy of moving water is used for converting the energy to electrical energy through hydro-electric power plants. Similarly, water is also used for electricity generation in geothermal processes [7].

1.2.4 Water scarcity in Pakistan

Director General of Pakistan Meteorological Department (PMD) Mr. Ghulam Rasool said in a conference that **"**Pakistan will become water scarce by 2025". HE further added that without wasting more time, government should focus on new water policy that covers construction of new dams, improving water channels conditions and protecting underground water. It is estimated that 1,017 cubic meter water is available per person annually, almost near to water scarcity level(1000 cubic meter/person. According to NASA research (2003-2013), indus water basin is the second most over-stressed water channel in the world. It has maximum water exits with very low or no water addition every year.

According to the World Population Prospects 2015, currently Pakistan population is around 200 M which would jump to 244 M in 2030 and by 2100 its population expected is around 364 M. This

will further increase water demand in Pakistan and situation will be quite much drastic if water policy is not implemented [8].

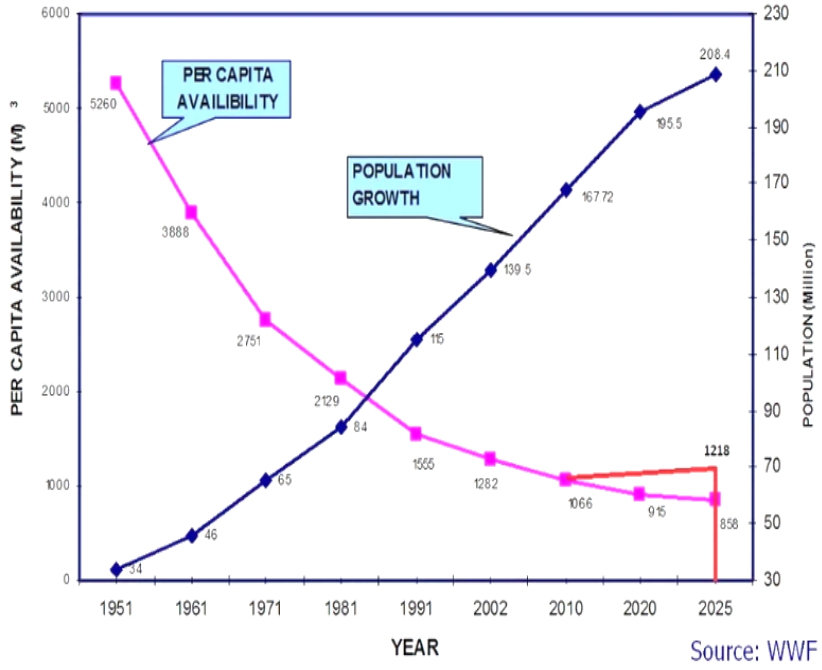


Figure 2: Projected water demand till 2025 (WHO)

By 2025, according to an IMF report in 2015, required projected water demand will 274 million acre-feet (MAF) and supply will remain stagnant at 191 MAF in Pakistan. This gap in demand and supply would further worsen the water scarcity in Pakistan will definitely push it towards a drought situation at a large scale. At the same time, irregularly changing rain patterns and poor management/maintenance of existing water resources are further deteriorating the situation. It resulted floods and droughts with uneven pattern in Pakistan. German Watch's Climate Risk Index ranked Pakistan in the list of top ten countries most affected by extreme weather events.

1.3 Water Pollution

1.3.1 Wastewater Treatment

The concept of wastewater treatment dates back thousands of years and was considered as important component of various ancient civilizations such as Indus Valleys and the Roman (Judd, 2010). Though, about in the sixteenth century, modern world wastewater treatment came about.

After that advances in wastewater treatment plant begun by introducing physiochemical and biological treatments. The twentieth century experienced the key development in this field, and the understanding of wastewater has changed since the 20th century [9].

Usually two type of treatment plants are present that is Biological and physical treatment plant[10]. Biological treatment involves use of microorganisms and biomass for the waste break down. While physical or chemical wastewater treatment involves the use of different chemical reactions along with various physical processes. The wastewater treatment plant comprises of different treatment stages and these stages are named in increasing treatment level such as preliminary is the first stage, then the primary stage in which physical waste is removed, next secondary and finally the most advance is tertiary wastewater treatment stage. In most countries prior the discharge of effluent, final stage of waste water treatment plant is disinfection that removes pathogen from effluent.

1.3.2 Disinfection by Products

Disinfection is crucial step in the wastewater treatment plant process. In this process most of pathogen are killed or inactivated and it is generally the last step before discharge of water. The utmost techniques used for disinfection are chlorination, ozone, ultraviolet (UV) radiation, peracetic acid or hydrogen peroxide and chloramines. These chemicals have highly reactive oxidizing properties that cause them to interactions with organic and/or inorganic materials naturally present in most source waters. As a result of this interaction harmful chemical compounds are formed in water called as disinfection by-products (DBP). Scientists first realized DBPs was the early on in 1970s. DBPs was first reported in drinking chlorinated water, chloroform and other trihalomethanes (THMs) by the Rook and Bellar in 1974. DBPs have adverse health effects such as carcinogenicity, miscarriage, mutagenicity, cytotoxicity and in some cases causes even birth defects.

1.4 Sampling Technologies for DBPs

For the detection of DBPs in wastewater reliable information is needed that can be used for risk assessment and can be used for making reformatory actions. For this purpose, sampling as a means of conducting environmental monitoring can be very useful. Sampling can be considered as the

most crucial phase in any analytical method and any error during sampling cannot be corrected later at any stage of analysis. It is estimated from various studies that about 70-90% of the analysis time involves sampling and sample preparation. It is therefore apparent that the maximum improvement in the analysis response time can usually be achieved by decreasing the time required to process the sample. Therefore, different studies are ongoing for the development of reliable, efficient and simple operations and equipment involved in the sampling and sample procedure [11].

International water quality monitoring programmers commonly used spot or grab sampling procedure for the determination of pollutant level in water. This technique have different disadvantage such as it is quiet costly, give the analysis of currently present contamination in water and is unable to give the result of seasonal, sporadic and tidal contamination and unable to measure concentration of dissolved contaminants accurately [12]

1.4.1 Passive Sampling

Over the past two eras, different other strategies have been sought out to solve these problems. Among them, one of the new methods that demonstrated great potential as a tool for determining the concentration of various priority pollutant in aqueous environment is the passive sampling. In this method target analytes are collected in the original or natural site without disturbing large amounts of solution. It is acknowledged now that passive sampling can perform an important role in legislative frameworks for water quality monitoring such as the European Water Framework Directive (WFD). Passive sampling will be defined in this article as any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potentials of the analyte between the two media. Net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling session is terminated by the user.

Passive sampling technique have number of advantages as compare to spot or grab sampling technology. They have potential to uptake freely-dissolved components (Cfree) of chemical present in aquatic environment and help in measuring the chemical activity of containment in trace amount [13].Furthermore, passive sampling results can be used as a measure of chemical bioaccumulation, bioavailability and ecotoxicity [14].

Different types of passive sampling devices are present on the basis of different sorbents materials for sampling a diverse range of compounds in water. Such as semipermeable membrane devices (SPMD) [15], low density polyethylene (LDPE) film, polyoxymethylene (POM) devices [16], polyurethane foam (PUF) device [17]; and polydimethylsiloxane (PDMS) fibers.

1.5 Analytic Methods for DBPs Analysis

There is a need for advance research to enhance the understanding of the nature, construction, concentration and health hazards of DBPs as their presence in water causes serious chronic health effects such as causes many waterborne diseases. For this and other related purposes analytical methodologies for monitoring water have been developed. These methodologies used for event studies of community water systems, determination of DBPs for several water treatment methods, and identification of novel species (Weinberg, 2009). In current study LDPE samples were analyzed by gas chromatography (GC) mass spectrometer (MS).

1.6 Non target screening using GCMS

Gas chromatography/mass spectrometry (GC/MS) is the most ubiquitous analytical technique for the identification and quantitation of organic substances in complex matrices. The gas chromatograph-mass spectrometer (GC-MS) is indispensable in the fields of environmental science, forensics, health care, medical and biological research, health and safety, the flavor and fragrances industry, food safety, packaging, and many others. The analytical methods for the detection and quantification of emerging contaminants are generally based on gas chromatography (GC) or liquid chromatography (LC) coupled with mass spectrometry (MS). Choosing between GC and LC is normally based on the physiochemical properties of the target analytes. For the analysis of PCPIs, it is more suitable to use GC because many of these compounds have high lipophilicity. Most of the published methods for PCPIs and related compound analyses in wastewater, surface waters and groundwater are based on GC–MS. The high resolution of GC retention allows separation of isomers and congeners; this is the case for some UV-filters that undergo isomerization under the influence of light: for example the (E)- and (Z)-isomers of 4-methylbenzylidene-camphor (4-MBC) and ethylhexyl methoxycinnamate (EHMC) can be identified and quantified.

1.7 Risk Assessment using EPI suite

The EPI (Estimation Programs Interface) Suite is a window base program design by OPPT for the screening of new chemicals that are deficient of any experimental data. This program helps in identifying physical and chemical properties such as melting point, vapor pressure etc. Chemical environmental fate can also be determined by this program such as whether the chemical absorb in atmosphere, water or soil etc. For the risk assessment of chemical, estimation of its properties is very crucial [18]

1.8 Objectives of study

1. Preparation of low-density polyethylene passive Samplers
2. Installation of samplers at water reservoirs.
3. Retrieving passive samplers from site areas.
4. Extraction of Organic pollutants
5. Analysis of Extract

Chapter 2

Review of Literature

Insufficient water supply and deterioration in water quality are a serious concern for communities, agriculture, municipalities, industry and the environment in various regions of the world. These problems are due to several reasons that include sustained urban development, pollution of surface and underground water, uneven water resources distribution and recurrent droughts worldwide due to global warming **[19]**.Therefore, a new sustainable water management model is emerging. Several approaches, such as water conservation, water reuse and water recycling, are designed to assure that current water needs are full fil without affecting future demands **[20]**.Water recycling is a comprehensive process for treating wastewater using various water treatment technologies. The rectified water can be used for different purposes such as irrigation, industrial consumptions, urban applications and water supply **[21]**. Recycling of water seems effective option for management of water resources since it does not only provide substitute water resource but also help in reducing pollution caused by release of waste water **[22]**.

2.1 Wastewater Treatment

The process in which water which is no more appropriate for use i-e waste water is converted into a form that can be used back or can be discharge into environment without causing harmful effect is called waste water treatment process. Waste water is formed by various activities such as washing, toilet, kitchen drainage, rainwater runoff etc. constituents of waste water that employ high chemical oxygen demand (COD), high biochemical oxygen demand (BOD),solids, microorganisms, nutrients like phosphorus and nitrogen, heavy metals such as iron, arsenic etc. should be removed during treatment [23].

Usually two type of treatment plants are present that is biological waste water plant and physical or chemical waste water plant. Both of them works together. Biological treatment involves use of microorganisms and biomass for the waste break down. This treatment is suitable for the wastewater of business sites and houses. While physical or chemical wastewater treatment

involves the use of different chemical reactions along with various physical processes. This treatment plants are primarily involved in the treatment of wastewater from industrial, manufacturing companies and firms. These industrial wastes contain different chemicals and toxins that can cause serious environmental hazards. The wastewater treatment plant comprises of different treatment stages and these stages are named in increasing treatment level such as preliminary is the first stage, then the primary stage in which physical waste is removed, next secondary and finally the most advance is tertiary wastewater treatment stage. In most countries prior the discharge of effluent, final stage of waste water treatment plant is disinfection that removes pathogen from effluent[24].

2.2 Disinfection of Wastewater

Various techniques such as chlorination, ozone, ultraviolet (UV), peracetic acid or hydrogen peroxide can be used for disinfection of pathogens.

In accordance to the United States Environmental Protection Agency (1998) chlorination of waste water is an effective way to remove more than 99% of pathogenic microorganisms, nevertheless this process involves a step before the water flows. It is chlorine dichlorination as it is poisonous for water inhabitants[25].Ultraviolet radiation also applied for disinfection but only efficacious in low-polluting waters to avoid lamp infestation and provide proper lighting[26]. Ozone is also used as an efficient disinfectant that requires less contact period compare to chlorine but has protection issues and is comparatively costly. Another disinfectant that has recently been proclaimed to treat sewage is Peracetic acid (PAA). It is an effective disinfectant of various pathogens that chlorine. But it can cause the regrowth of microorganisms due to its conversion into acetic acid which serve as source of carbon for these pathogen[27]. Another disinfectant which is a combination of ultraviolet light, ozone and hydrogen peroxide is peroxone their combination produces a very strong radical that is hydroxyl radical (OH) which act as a very robust disinfectant. Chlorine and ultraviolet light are mostly used disinfectant.

2.3 Disinfection By-Products Formation

Although above mentions disinfectant are very efficient in wastewater treatment plants for inhibiting and destroying pathogenic microorganisms, but they interact with other organic and inorganic substances already present in water source because of their vastly reactive oxidizing nature. That results in formation of hazardous compounds that known as disinfectant by products

(DBP). Amount or dose of DBP varies from site to site depends on different factors such as interaction time, form of disinfectant, eminence of source water and dosage used. Conditions of reactions in which it carried out also effect its concentration such pH and temperature [28].

Schematic showing the development of DBP from organic and/or inorganic and disinfectants and precursors in Figure. 2.1

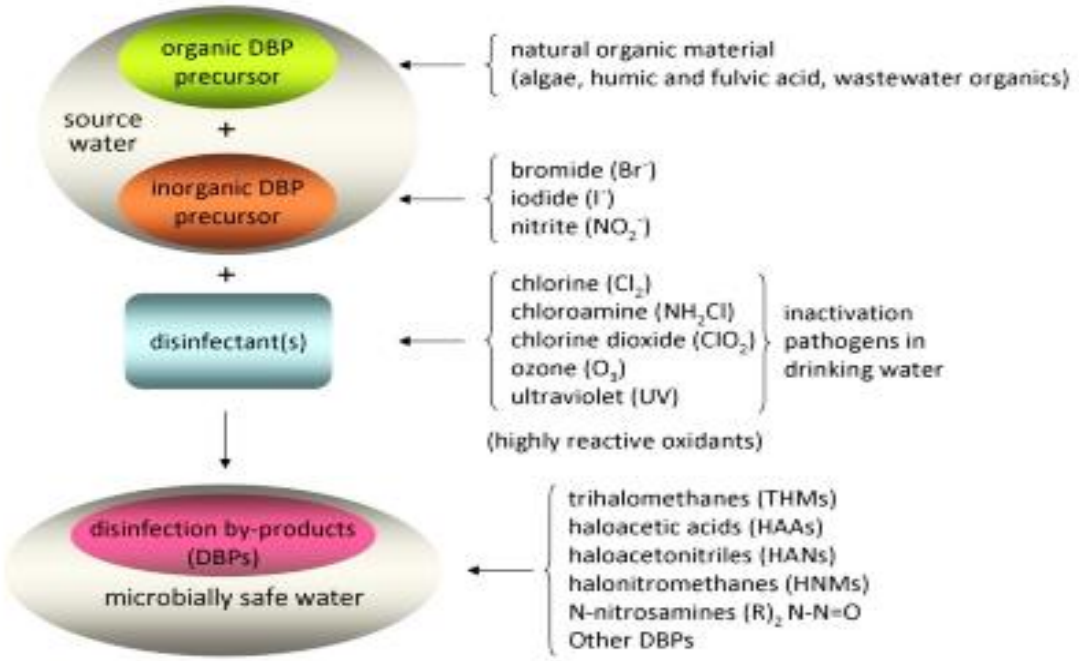


Figure 3: Schematic diagram of the formation of DBP from organic and/or inorganic and disinfectants precursors. Adopted from (Krasner, 2009)

Scientists first realized DBPs was the early on in 1970s. DBPs was first reported in drinking chlorinated water, chloroform and other trihalomethanes (THMs) by the Rook and Bellar in 1974 [29, 30]. A survey was published by the US Environmental Protection Agency (US EPA) in 1976, that displayed that drinking water commonly contain chloroform and the other THMs. Later on, U.S. National Cancer Institute in same year display a report that showed that chloroform was carcinogenic when tested on laboratory animals [31]. Also, in the later 1970 it was shown that organic substances in drinking water causes mutation as was proven by experiment on *Salmonella [32]*. All of these observations concluded that DBPs can causes carcinogenic, mutagenic and developments effects.

It is worth noting that among the more than 600 DBPs presently identified, only a few have been studied for their quantifiable and health effects. Known DBP also constitutes less than 50% of the total organic halide (TOX) during the sterilization process[33]. Hence, important parts of TOX are still not considered.

2.4 Sampling Technologies for DBPs

Sampling is a technique that can be define as a process of collecting small part of a material that can easily be transported to a laboratory that still precisely reflects the sampling environment [34]. Spot or grab sampling technique are the one of traditional techniques and among them most popular technique is point (bottle) sampling which is further analyzed by solvent extraction and by various instrumental investigation [35]. This method is well-established and effective, and in some cases, it is often problematic. This is widely recognized by the International monetary fund and International water quality legislation. The key issue of using theses traditional technologies are sample representation and completeness.

- Samples may not accurately epitomize contamination concentration because they do not show all possible water flow or contamination events.
- As during sampling small volume of water is taken which is not significant for the pollution that is present in minute quantity in such cases large volume of water is required for analysis.
- Surface water analysis is done by simply collecting sample in bottles but in case of deeper water analysis special instruments are required like peristaltic pumps or especially designed automated prompted samplers.
- Spot sampling technique give the analysis of currently present contamination in water and is unable to give the result of seasonal, sporadic and tidal contamination.
- In most cases large volume of water is require that is difficult to carry and also there are some quality control issues which need to be address.
- Also, the traditional methods like spot water sampling is unable to measure concentration of dissolved contaminants accurately[12].

Recent research studies have shown that more precise depiction of water contamination analysis can be obtained by employing latest environmental technology and water sampling tools which can consist [36].

- The high incidence of point samples outcomes in large volume samples and lower thresholds compared to traditional sampling methods.
- For better image of water contamination over time employ automatic successive sampling
- Incessant online supervising systems
- Use of biological system such as Tubificidae and Mussels for early detection of early pollutant in water [37].

2.5 Passive Sampling

Over the past two eras, different other strategies have been sought out to solve these problems. Among them, one of the new methods that demonstrated great potential as a tool for determining the concentration of various priority pollutant in aqueous environment is the passive sampling. In this method target analytes are collected in the original or natural site without disturbing large amounts of solution so provide solution to various problems listed above. Reliant on the design of the specimen, the mass of contaminants accrued from the specimen indicates the concentration at which the device is balanced or the average time the sample is displayed. Since the early 1970s such devices are accessible to monitor air quality. Later different industries used diffusion-based passive dosimeter to monitor and measure toxic chemicals in air. Afterwards the same principle was employed to monitor the pollutants in water milieu [38].

2.5.1 Principles

Passive sampling can be defined as a technique which is established on the basis of free current of analyte molecule from the sampling medium to an obtaining medium due to difference in chemical potentials of the analyte among sampling and obtaining media. The net flow of analyte molecules from one medium to another continues until steadiness in the system is attained or the sampling process ends[11].

Sampling does not require any other energy source but only the chemical potential difference between the media. Reference or receiving phase are the analytes that are captured or retained within the passive sampler in any appropriate medium. This phase can be any adsorptive, chemical reagent and solvent. The receiving phase is exhibited to the aqueous phase, but not for quantitative extraction of dissolved contaminants. Mostly the following pattern shown in figure 2.1 is followed within passive sampler for pollutant absorption or adsorption from water.

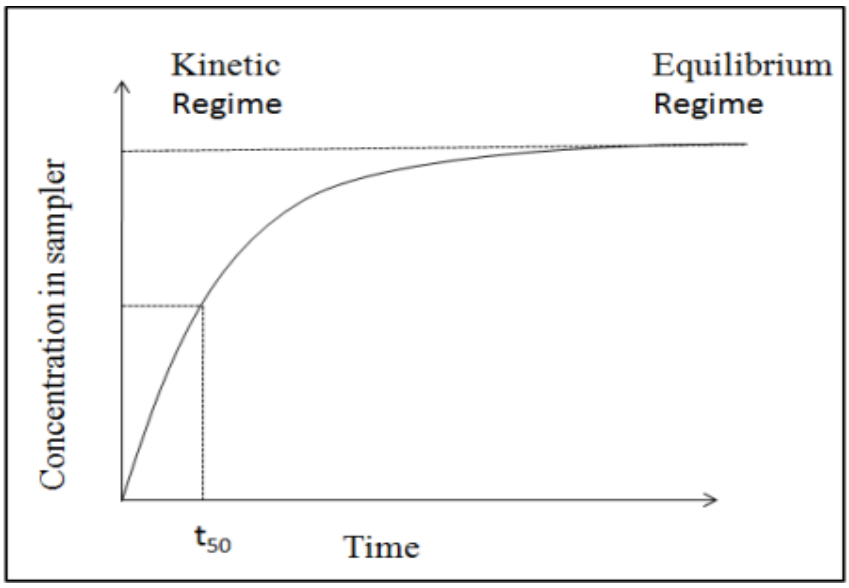


Figure 4: The general uptake in contaminant concentration over time for most

The kinetic exchange among the passive sampler and the aqueous phase can be depicted by a first-order one- compartment mathematical model as shown in equation 2.1

$$C_S(t) = C_W \frac{k_1}{k_2} (1 - e^{-k_2 t}) \qquad \text{Eqn. 2.1}$$

In above equation $C_S(t)$ is the analyte concentration in the passive sampler at exposure time t, C_W is the concentration of analyte in the water, and k1 is the uptake rate constant and k2 is the offload rate constant. In field deployment, two major accumulation schemes, kinetics or eequilibrium can be differentiated in the operation of the passive sampler [36].

2.5.2 Equilibrium-Passive Samplers

In equilibrium-passive sampling, the exposure time is long enough to allow a thermodynamic equilibrium between the aqueous and the reference phase. In such condition, equation 2.1 is reduces to:

$$C_S = C_W \frac{k_1}{k_2} = C_w \, \mathrm{K} \qquad \text{Eqn.2.2}$$

Knowing the phase water partition coefficient (K) can allow to estimate the concentration of dissolved analyte [39].

The basic prerequisite for equilibrium sampling method is to achieve a steady concentration after an acknowledged response time. The capacitance of sampler is held below the capacity of sample to avoid reduction during the extraction procedure and the response time of device requires to be briefer than any variations in the environmental medium. To monitor volatile organic compounds (VOCs) in water passive diffusion bag sampler (PDBS) has been widely used [40].

2.5.3 Kinetic Passive Samplers

By kinetic sampling, it is presumed that the mass transfer rate to the reference/receiving phase is linearly proportional to the linear ratio between the chemical activity of the contaminant in the aqueous phase and the chemical activity of the contaminant in the reference phase. At the initial stage of sampler exposure, the desorption rate of the analyte from the receiving stage to the water is insignificant and the sampler operates in a linear uptake state. In such condition, equation 2.1 is reduces to:

$C_s(t) = C_w k_1 t$ Eqn.2.3

Equation 2.3 can also be set up to an equal relationship:

$M_s(t) = C_w R_s t$ Eqn.2.4

In above equation M_s (t) is analyte mass gathered in the reference/receiving phase after an exposure time (t) where R_s in the equation is the proportionality constant i-e sampling rate, which is obtained as a product of the first order rate constant for uptake of contaminant (k1) and amount of water having the similar chemical activity as the volume of the receiving/reference phase. R_s can be taken as the amount of water free from the analyte by the passive sampler per unit of exposure time. C_w that is the time-weighted average (TWA) concentration of a contaminant in the aqueous phase can be calculated if the values of R_s (sampling rate), t (time of exposure) and M_s (t) (the mass of analyte) accumulated by the receiving phase are known [41].

Majority of equipment working in kinetic mode, value of R_s (sampling rate) does not change with C_w but water or turbulence, biofouling and temperature usually affects its value [42]. The benefit of using kinetic sampling is that they can isolate contaminants in incidents that are not normally detected by point sampling and can be applied with variable water concentrations. Kinetic

sampling can also measure the concentrations of ultra-trace but toxicologically related contaminant over prolonged periods of time.

2.5.4 Passive Sampler Design

Although there are many kinds of passive samplers, almost all passive samplers have similar design characteristics, in between the sampling medium and the receiving phase a barrier is present in all passive sampler. The function of barrier is to determine the rate of analyte molecules at which they are collected at a specified concentration. The barrier can also determine the specificity of the sampler and limit some analytes classes or sampled species. Passive sampler design can be classified in two types based on the nature of barriers (i) diffusion barrier (ii) permeation-based barrier. In both of them sampling processes is same.

Diffusion barrier sampler when exposed to water, analyte molecules are collected through diffusion that reach the receiving phase via a static layer of water comprised of precise openings in the sampler. well define. In permeation sampler analyte accumulation occur through porous or non-porous membrane [41]. The rate of analyte uptake depends on various factors such as design of sampler, analyte physicochemical properties and on various environmental factors i.e., fouling, water turbulence, temperature. The passive sampler is designed in such a way that can detect a very low level of analyte existing in the water so maximize the amount of analyte sampled. At the same time, it also confirms a quantitative relationship in the sample medium between the quality of the separated chemical and its concentration.

2.5.5 Calibration of Passive Samplers

As previously we have described the theoretical background of passive sampling in water [43, 44]. By using two different methods we can find the phase water partition coefficient (K), substance specific kinetic constants k1 and k2.

In theory, semi-empirical relationships between hydrodynamic parameters, mass-transfer coefficients and physicochemical properties chiefly diffusivities in several media can be used to calculate the kinetic parameters illustrating the analyte absorption [45]. But during exposure of the water flow around passive sampling instruments there are different complication generally in non-streamlined objects which make it difficult to calculate absorption constraints from first principles. More substance specific information is generally accessible from the literature for the K, which

depict the chemical attraction of the contaminant to the receiving media comparative to water. Through experimentally, passive sampling switch over kinetics calibration can be carried out at known exposure concentrations in the laboratory [46, 47]. In order to predict the concentration of TWA water contaminants from the levels cumulated in the passive sampler device, a number of calibration studies are required to characterize the absorption of chemicals under numerous exposure situations. The absorption kinetics of chemicals depends not only on the diffuser physicochemical properties but as well as on the sampler properties [48].

2.5.6 Environmental Factors Affecting Passive Sampling

Transportation of analytes from the surrounding medium to the passive sampling device is a many steps transport process that depends on a number of variables. Different factors such as presence of water turbulence, flow conditions, temperature, humidity rate and temperature are some of the environmental factors that affect all passive sampling devices [49].

The absorption of chemicals also relies on temperature and flow conditions. In most cases, sampling rates are low by lower the temperature and shows high rate at higher temperature. In order to avoid such variations, sampling temperature must be optimized in laboratory nearer to the actual environmental conditions. In addition, humidity and excess concentration of the pollutant or compound can also affect contaminants absorption or rotation ability of the sampler and also effect further analysis process [50]. In some case hydrophobicity can significantly change the results. Water turbulence impacts the viscosity of the unstirred water layer, which results in the formation of the diffusion limiting barrier nearby the surface of the sampler and therefore also shows impact on the mass transfer rate of the analyte. Biofouling is the formation of thick layer of microorganisms on the exposed surface of water. It can increase the thickness of the barrier and can block any water-filled pores in the membranes of passive samplers and thus decreases mass transfer rate of sampler. If membranes are made up of a biodegradable material, these colonizing organisms may impair the membrane surface [51].

2.6 Types of Passive Samplers

There are several different sorts of passive samplers are available that can be utilized to sample numerous contaminants in various environments, so choosing the right passive sampling device is critical. Different types of passive sampling devices are present on the basis of different sorbents materials. Such as semipermeable membrane devices (SPMD)[52], low density polyethylene

(LDPE) film [53] [15], polyoxymethylene (POM) devices [16], polyurethane foam (PUF) device [54] [17] and polydimethylsiloxane (PDMS) fibers [55].

2.6.1 Abraham Solvation Parameter Model

Abraham's solvation parameter model is the utmost suitable methods for analyzing and predicting partition and adsorption coefficients [56, 57]. The model is based on linear free energy relationship

$$SP = c + e.E + s.S + a.A + b.B + v.V \qquad \text{Eq.2.5}$$

SP is the dependent variable in above equation. For LDPS application, the logarithm of the solute's water-to fiber sorption coefficient, log $K_{LDPE-water}$ would be dependent variable for equation 4.5

The excess molar refractive index of solute shown by E in the above equation is (cm3mol-1) / 10; S is the polarity/dipolarity descriptor of solute; A is solute hydrogen bond acidity measure, B is hydrogen bond basicity of solute measure, V is the volume of McGowan of the solute, in units of (cm3 mol-1) / 100 [58, 59].

2.6.2 Equilibrium Partition Coefficient

A partition coefficient can be defined as concentration ration of a substance between two phases or medium at equilibrium. that is

$$K = C_1 / C_2 \text{ at equilibrium}$$

Where K is partition coefficient. C1 and C2 are concentration ratio and their units can be different depends on the type of media. Media can be of different type it can be gases such as air, can be liquids such as oil water or media can be a complex mixture such as tissue, blood. Different experimental techniques can be used to determine partition coefficient such as closed vial equilibration technique [60].

The partition coefficient has many useful applications such as it can be used for characterizing the tendency of chemicals to accumulate at specific stages, can also be used in an environmental system to determine the direction of chemical transport [61]. The partition coefficient also helpful in measuring hydrophilic and hydrophobic nature of chemical substances. Rate of mass transfer across different phases like air-water exchange, sediment-water exchange can also be calculated by partition coefficient [62].

Mobility of different chemical substances in groundwater can also be predicted by partition coefficient. The octanol-water partition coefficient (Kow) is used in the field of hydrogeology to determine the mobility dissolved hydrophobic organic substances in aquatic environment and in soil [63].

2.7 Non-Targeted Screening

In many applications such as toxicology, food safety and environment large amounts of organic contaminants are produced which are currently handled by modern analytical methods. Most of the analytical methods used up to date have focused on measuring the small number of analytes of interest, ranging from less than 100 compounds. Nevertheless, target analysis often does not give a comprehensive outline of organic pollution patterns, so there is a necessity to develop new screening methods that can detect, categorize, and even quantify large amounts of organic contaminants and residues. Non-target analysis (searching for unknowns) does not require pre-selection of any kind of compounds and has been effectively applied to the screening, identification and classification of organic pollutants in aquatic environmental [64].

2.7.1 Analytical Methodologies for Non-Targeted Screening of DBPs

There is a need for advance research to enhance the understanding of the nature, construction, concentration and health hazards of DBPs as their presence in water causes serious chronic health effects as causes many waterborne diseases. For this and other related purposes analytical methodologies for monitoring water have been developed. These methodologies used for event studies of community water systems, determination of DBPs for several water treatment methods, and identification of novel species [65].

2.7.2 Instrumental Approaches

The type of analytical method to be chosen for separation is depends on analyte properties and nature. For analytes of volatile and semi-volatile nature the best suited separation method is gas chromatography (GC). For analyte of high polarity, thermally and unstable non-volatile nature the best suited separation method is chromatography (LC). Advantages of using GC are fast separation, high resolution, ease of connection to sensitive, cheap and careful detectors selection. Up to now, predominant analytical methods for DBPS measurement are GC in conjunction with electron capture detectors (ECD), mass spectrometry (MS), electrolytic conductance detectors (ELCD) and photoionization (PID) [66]. In particular, in the discovery of DBPs in drinking water

the GC-MS method plays a key role [67]. This methodology has the advantage of confirming the ability to select soft chemical ionization (CI) in contrasted with electron ionization (EI) to decrease fragmentation, molecular tandem mass spectrometry (MS / MS) and the information of molecular weight, all these help in improving selectivity and sensitivity of analyte detection [67, 68] .

The use of liquid chromatography is often hindered by difficult operating parameters for example different analytes, expensive instrumentation, and absence of LC/MS libraries, making compound identification very disputing. Lately, highly polar hydrophilic DBPs that are hard or incredible to extract from aquatic environment, along with high molecular weight types compounds that cannot be directly detected by GC are now measured or detected by using LC/MS technology [69]. It is believed that these species are the reason for an important part of the inexplicable TOX and misplaced DBP parts.

Chapter-3

Materials & Experiment

This chapter has the details about the method followed for experimentation. A thorough process of cutting, cleaning, washing, deployment, retrieving and extraction of LDPE passive sampler are the steps involved in experimentation process.

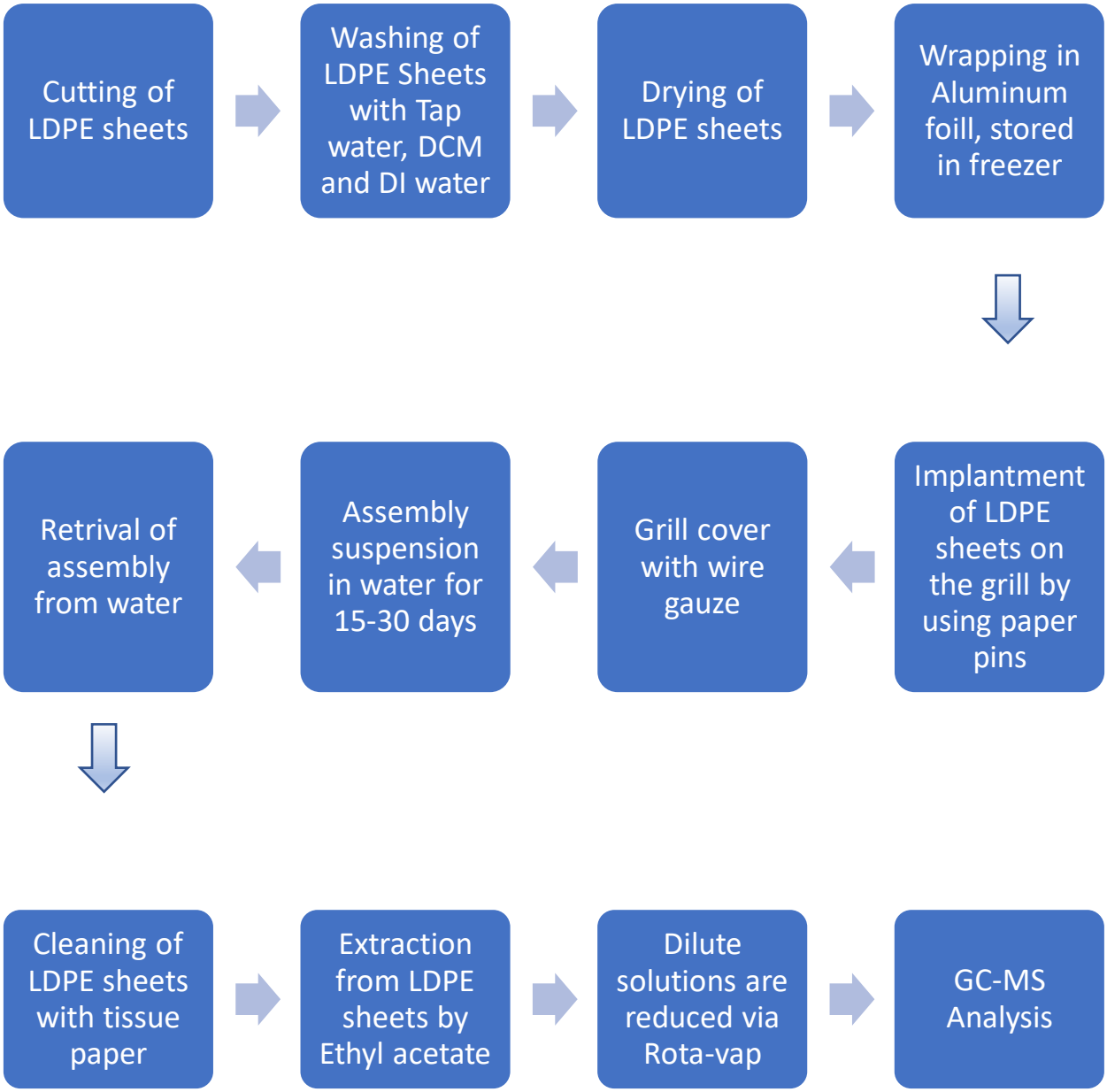
3.1 Chemicals Used:

1- Tape water
2- Dichloromethane
3- Deionize water
4- Ethyl Acetate
5- PCB-209

3.2 Equipment Used:

1- High density Polythene sheets
2- Silicon sheets
3- Aluminum foil
4- Tissue paper rolls
5- Steel scissor
6- Steel paper clips
7- Scotch tape
8- BBQ grills(stainless steel)
9- Iron rods(different lengths)
10- Wire auze
11- Conical flasks(1000 ml, 500 ml, 250 ml, 50 ml)
12- Measuring cylinder(500 ml, 100 ml)
13- Beakers(1000ml, 500 ml, 250 ml)

Flow Chart of Experimental Procedure



3.3 LDPE Passive samplers' preparation:

Passive sampler used in this experiment was Low Density Polyethylene (LDPE) sheet. LDPE large sheet (bought in a single batch to avoid any manufacturing error) was handled through following ways.

3.3.1 Cutting of passive sampler:

A single batch of large LDPE sheet was cut down into strips according to the size of BBQ grills (passive sampler holders) and requirement of experiment. Strips length, width and mass is noted for final calculation of different organic pollutants in water. Dimensions of passive samplers were important as to know about the ratio of passive sampler area to adsorption of organic pollutants or weight to adsorption of organic pollutants.

Figure 5: LDPE strips

3.3.2 Cleaning/Washing of passive sampler strips:

After cutting LDPE sheet into strips, first cleaned with tissue paper. Washing of passive sampler strips were carried out in different solvents as to clean it from all types of pollutants (wether organic or inorganic pollutants). Following sequence of solvents is used for washing passive sampler strips.

Figure 6: Washing of LDPE Strips

3.3.2.1 Tap water:

Passive sampler strips were rolled according to the size of beaker (500 ml) full of water. Then beaker was place in shaker for 24 hrs. Shaker rpms were 135 and temperature 25°C. Passive sampler strips were washed with tap water three times each for 24 hrs. Each time used solvent is replaced with fresh batch. Washing with tape water was done to remove dust particles or macro pollutants in passive sampler pores.

3.3.2.2 Dichloromethane (DCM):

After washing with tap water, passive sampler strips were thoroughly soaked with tissue paper and then again put into beaker. This time same washing procedure was carried out as done with tap water. Washing with DCM is carried out in order to remove organic pollutants if present on passive sampler strips.

3.3.2.3 Deionize water:

After washing with DCM, passive sampler strips were dried using tissue paper. Final washing was carried out with deionize water to remove remaining pollutants if present on passive sampler strips.

After washing passive sampler strips were dried with tissue paper, wrapped in aluminum foil and froze for further use in field.

3.3.3 Assembly washing:

Assembly of passive sampler strips consisted of BBQ grills, binding wire and paper pins. These things were first washed with water and cleaned from dirt and rust present on it. For further cleaning of these materials, dilute Hydrosulphuric acid used by spraying on it. After cleaning assembly was stored in clean cold storage for further use in field.

Figure 7: Complete Passive Sampler Assembly

3.4 Passive sampler strips distribution:

Before deployment of passive sampler in field, the strips were divided into three categories,

3.4.1 Blank passive sampler strips:

Blank passive sampler were separately stored in freezer after washing. There use was mainly as a standard for data analysis after GC-MS results. They were free from any type of pollutants.

3.4.2 Field passive sampler strips:

Field passive sampler strips were also stored separately in freezer for its use at the time of experimental passive sampler strips deployment. They were kept open in a beaker while assembly was under making process. There use was mainly for those pollutant which were most probably present in air or any other source (except deployment water body). Field strips were also used as standard after GC-MS results and analysis.

3.4.3 Experimental passive sampler strips:

Experimental passive sampler strips were separately stored after washing. These strips were the mainly for deployment in water for 15 days and 30 days.

3.5 Passive sampler deployment:

At the day of passive sampler deployment, whole assembly was prepared at the deployment site (Membrane Bioreactor or MBR, NUST). Field passive sampler strips were kept open in beaker for any contamination from air source. When the assembly got ready, it was immersed/deployed in water with the help of iron rods. Wire gauze was also wrapped around BBQ grills in order to avoid passive sampler loss in water. Passive sampler strips were fixed in BBQ grills using stainless steel paper pins. Passive samplers were deployed at the inlet and out let of MBR plant water flow for 15 days and 30 days separately. After deployment, field strips were again wrapped in aluminum foil and stored in freezer.

Figure 8: Deployment of Passive Sampler Assembly

3.6 Retrieval of Passive samplers:

After completion of 15 & 30 days respectively, passive sampler assemblies were taken out of water. Assemblies were carefully opened. The passive sampler strips were taken out of BBQ grills.

Strips at that time were too muddy because of mud sticking in its surface. Strips were cleaned from mud using tissue paper gently. Note that at the time of retrieving, field passive sampler strips were also kept open like at the time of deployment for any contamination from air source. After cleaning retrieved passive sampler strips, wrapped in aluminum foil and stored in freezer.

Figure 9: Retrieval of Passive Sampler Assembly

3.7 Extraction from passive sampler strips:

All three types of passive sampler strips which were stored separately in freezer were pit in 250 ml beaker. Ethyl acetate was used as solvent for extraction. The beaker containing strips and solvent were properly covered with aluminum sheet in order to avoid any photo catalytic reactions inside. Beakers were placed on shaker for 24 hrs in order to transfer pollutants from passive sampler strips to solvent. This extraction was carried out three times, each time adding fresh solvent for all three types of passive sampler strips. Each time used solvent i.e. Ethyl acetate was stored in glass bottles that ware properly covered with aluminum sheet.

Figure 10: Dilute Extracted Solutions

Figure 11: Rota-vap of Dilute Solutions

Figure 12: Reduced/Concentrated Solutions for GCMS Analysis

As the extracted solutions in glass bottles were very dilute, so to make it concentrated, each sample was reduced to 5ml through Rota vaporization technique. Total samples for this experiment were:

- Blank sample
- Field sample
- Inlet 15 days
- Outlet 15 days
- Inlet 30 days
- Outlet 30 days

All reduced volume sample were analyzed through GC-MS technique for further study and discussion.

Chapter-4

Results and Discussion

4.1 EPI-Suite Modelling for Risk Assessment

Risk assessment of the data that was being retrieved from GCMS, UFZ-LSER and EPI suite software. Attributes for risk assessment were toxicity, bioaccumulation and biodegradation. All of them can be defined as,

4.1.1 Toxicity:

The US Environmental Protection Agency defines toxic substance as the substance that have toxic effect when the concentration is greater than or equal to 0.1 mg / L.

4.1.2 Bioaccumulation:

In Accordance to EU REACH regulations, chemicals with bio concentration factor (BCF) ≥ 2000 (logBCF) 3 (BCF) ≥ 5000 (log BCF) greater than or equal to 3.7 are classified as bioaccumulation (B) and very bioaccumulation (vB), respectively (REACH 2007). BCF is defined as the equilibrium distribution in between the lipid pool and water of organisms (i.e. membrane plus storage lipids).

4.1.3 Bio-degradation:

In Accordance to ECHA guidelines for PBT assessment, a substance is considered to be potentially persistent (P or vP) when BIOWINN2 or BIOWINN7<0.5 and BIOWINN3 <2.2. If BIOWINN3 indicates a value between 2.2 and 2.7 (ECHA Guidelines, European Chemicals Agency R.7.9.4, R.7.9.5 and European Chemicals Agency R.11.1.3), the substance is considered to be critical.

As there were four points where passive samplers were deployed, each passive sampler has different set of non-targeted compounds. These compounds that were detected, assessed with different sets of parameters using Epi-Suite software.

4.2 Epi-Suite Modelling for Risk Assessment

Each DIB was run on UFZ-LSER software for the retrieval of smiley codes and CAS numbers. Chemicals/DIBs were divided into four sets according to the number of passive sampler points. The four sets are

- **Inlet-15**
- **Outlet-15**
- **Inlet-30**
- **Outlet-30**

Table 1: Details of Chemicals on all sample points

SN	Chemical Name	SMILES	Library CAS#	Library Formula
Inlet-15				
1	2-Octene, 3,7-dimethyl-, (Z)-	CC=C(C)CCCC(C)C	6874-32-4	$C_{10}H_20$
2	3-Carene	CC1=CCC2C(C1)C2(C)C	13466-78-9	$C_{10}H_{16}$
3	o-Cymene	CC1=CC=CC=C1C(C)C	527-84-4	C10H14
4	1-Hexanol, 2-ethyl-	CCCCC(CC)CO	104-76-7	C8H18O
5	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-	CC1=CCCC(=C)C2CC(C2CC1)(C)C	118-65-0	$C_{15}H_{24}$
6	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl-	CC1=CC=C(C=C1)C(C)CCC=C(C)C	644-30-4	$C_{15}H_{22}$
7	2-Tridecanone	CCCCCCCCCCCC(=O)C	593-08-8	$C_{13}H_{26}O$
8	Isovaleric acid, 3-ethylphenyl ester	CCC1=CC(=CC=C1)OC(=O)CC(C)C	0-00-0	$C_{13}H_{18}O_2$
9	(1S,6R,9S,10R,12S)-5,5,9,10-Tetramethyltricyclo[7.2.1.0(1,6)]dodecan-10,12-diol	CC1(CCCC23C1CCC(C2(C)O)(C(C3)O)C)C	0-00-0	$C_{16}H_{28}O_2$
10	1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl-, trans-	CC1(CC2C(C1)C(C=CC2(C)C)(C)C)C	54832-81-4	$C_{15}H_{26}$
11	2-Pentadecanone	CCCCCCCCCCCCCC(=O)C	2345-28-0	$C_{15}H_{30}O$

12	Heptacosane, 1-chloro-	CCCCCCCCCCCCCCCCCCCCCCCCCCCCl	62016-79-9	$C_{27}H_{55}Cl$
13	n-Heptadecanol-1	CCCCCCCCCCCCCCCCCO	1454-85-9	$C_{17}H_{36}O$
14	Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-	CC1COCC2=CC3=C(C=C12)C(C(C3(C)C)C)(C)C	1222-05-5	$C_{18}H_{26}O$
15	Phthalic acid, 4,4-dimethylpent-2-yl butyl ester	CCCCOC(=O)C1=CC=CC=C1C(=O)OC(C)CC(C)(C)C	0-00-0	$C_{19}H_{28}O_4$
16	Docosyl trifluoroacetate	CCCCCCCCCCCCCCCCCCCCCCOC(=O)C(F)(F)F	0-00-0	$C_{24}H_{45}F_3O_2$
17	9-Tricosene, (Z)-	CCCCCCCCCCCCCC=CCCCCCCCC	27519-02-4	$C_{23}H_{46}$
18	Octatriacontane, 1,38-dibromo-	C(CCCCCCCCCCCCCCCCCCCBr)CCCCCCCCCCCCCCCCCBr	102436-01-1	$C_{38}H_{76}Br_2$
19	2-Isopropenyl-5-methyl-6-hepten-1-ol	CC(CCC(CO)C(=C)C)C=C	13066-55-2	$C_{11}H_{20}O$
20	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-	C1CCCCC23CCCCCC45CCCCCCCCC4(O5)CCCCCC2(O3)CCC1	0-00-0	$C_{30}H_{52}O_2$
21	Octacosanol	CCCCCCCCCCCCCCCCCCCCCCCCCCCCO	557-61-9	$C_{28}H_{58}O$
22	Isobutyl tetratriacontyl ether	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCOCC(C)C	0-00-0	$C_{38}H_{78}O$
23	Triacontyl pentafluoropropionate	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCOC(=O)C(C(F)(F)F)(F)F	0-00-0	$C_{33}H_{61}F_5O_2$
24	2-Methyltetracosane	CCCCCCCCCCCCCCCCCCCCCCC(C)C	1560-78-7	$C_{25}H_{52}$
25	Bis(2-ethylhexyl) phthalate	CCCCC(CC)COC(=O)C1=CC=CC=C1C(=O)OCC(CC)CCCC	117-81-7	$C_{24}H_{38}O_4$
26	Tetracontane	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	4181-95-7	$C_{40}H_{82}$
27	Carbonic acid, decyl hexadecyl ester	CCCCCCCCCCCCCCCCOC(=O)OCCCCCCCCCC	0-00-0	$C_{27}H_{54}O_3$
28	2-Buten-1-one, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-	CC=CC(=O)C1C(C=CCC1(C)C)C	41436-42-4	$C_{13}H_{20}O$

29	Dotriacontyl pentafluoropropionate	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCOC(=O)C(C(F)(F)F)(F)F	0-00-0	$C_{35}H_{65}F_5O_2$
30	Myristyl myristate	CCCCCCCCCCCCCCOC(=O)CCCCCCCCCCCCC	3234-85-3	$C_{28}H_{56}O_2$
31	Tritriacontane, 3-methyl-	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC(C)CC	14167-69-2	$C_{34}H_{70}$
32	Nonadecyl heptafluorobutyrate	CCCCCCCCCCCCCCCCCCCOC(=O)C(C(C(F)(F)F)(F)F)(F)F	0-00-0	$C_{23}H_{39}F_7O_2$
33	Cholestan-3-ol, (3.beta.,5.beta.)-	CC(C)CCCC(C)C1CCC2C1(CCC3C2CCC4C3(CCC(C4)O)C)C	360-68-9	$C_{27}H_{48}O$
Outlet-15				
1	1,2-Cyclopentanediol, trans-	C1CC(C(C1)O)O	5057-99-8	$C_5H_{10}O_2$
2	2-Nonyne	CCCCCCC#CC	19447-29-1	C_9H_{16}
3	Decane	CCCCCCCCCC	124-18-5	$C_{10}H_{22}$
4	4-Undecene, 5-methyl-	CCCCCC/C(=C/CCC)/C	20634-43-9	$C_{12}H_{24}$
5	4-Undecene, 3-methyl-, (Z)-	CCCCCC/C=C\C(C)CC	74645-87-7	$C_{12}H_{24}$
6	1-Tridecene	CCCCCCCCCCCC=C	2437-56-1	$C_{13}H_{26}$
7	Undecane, 2,6-dimethyl-	CCCCCC(C)CCCC(C)C	17301-23-4	$C_{13}H_{28}$
8	Dodecane, 4,6-dimethyl-	CCCCCCC(C)CC(C)CCC	61141-72-8	$C_{14}H_{30}$
9	Eicosane, 10-methyl-	CCCCCCCCCCC(C)CCCCCCCCC	54833-23-7	$C_{21}H_{44}$
10	1-Tetradecene	CCCCCCCCCCCCC=C	1120-36-1	$C_{14}H_{28}$
11	Naphthalene, 1,3-dimethyl-	Cc1cc(c2ccccc2c1)C	575-41-7	$C_{12}H_{12}$
12	3-Hexadecene, (Z)-	CCCCCCCCCCCC/C=C\CC	34303-81-6	$C_{16}H_{32}$
13	1-Octadecene	CCCCCCCCCCCCCCCCC=C	112-88-9	$C_{18}H_{36}$
14	Octadecane, 5,14-dibutyl-	CCCCC(CCCC)CCCCCCCCC(CCCC)CCCC	55282-13-8	$C_{26}H_{54}$
15	Octadecane	CCCCCCCCCCCCCCCCCC	593-45-3	$C_{18}H_{38}$
16	7-Acetyl-6-ethyl-1,1,4,4-tetramethyltetralin	CCc1cc2c(cc1C(=O)C)C(CCC2(C)C)(C)C	88-29-9	$C_{18}H_{26}O$
17	Phthalic acid, 4,4-dimethylpent-2-yl isobutyl ester	CC(C)COC(=O)C1=CC=CC=C1C(=O)OC(C)CC(C)(C)C	0-00-0	$C_{19}H_{28}O_4$
18	1-Octadecanol	CCCCCCCCCCCCCCCCCCO	112-92-5	$C_{18}H_{38}O$
19	3-Pentadecanone	CCCCCCCCCCCCC(=O)CC	18787-66-1	$C_{15}H_{30}O$

20	Ergostane-3,5,6,12,25-pentol, 25-acetate, (3.beta.,5.alpha.,6.beta.,12.beta.)-	CC(CCC(C)C(C)(C)OC(=O)C)C1CCC2C1(C(CC3C2CC(C4(C3(CCC(C4)O)C)O)O)O)C	56053-00-0	$C_{30}H_{52}O_6$
21	Undecane, 4-cyclohexyl-	CCCCCCCC(CCC)C1CCCCC1	13151-79-6	$C_{17}H_{34}$
22	2,4-Difluorobenzene, 1-benzyloxy-	c1ccc(cc1)COc2ccc(cc2F)F	152434-86-1	$C_{13}H_{10}F_2O$
23	Undecane, 3-methylene-	CCCCCCCCC(C)CC	71138-64-2	$C_{12}H_{24}$
24	1-Cyclopentyleicosane	CCCCCCCCCCCCCCCCCCCCC1CCCC1	0-00-0	$C_{25}H_{50}$
25	Dotriacontyl heptafluorobutyrate	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCOC(=O)C(C(C(F)(F)F)(F)F)(F)F	0-00-0	$C_{36}H_{65}F_7O_2$
26	Dotriacontane, 1-iodo-	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCI	0-00-0	$C_{32}H_{65}I$
27	Docosyl pentyl ether	CCCCCCCCCCCCCCCCCCCCCCOCCCCC	0-00-0	$C_{27}H_{56}O$
28	3-Methylbutyl hexadecanoate	CCCCCCCCCCCCCCCC(=O)OCCC(C)C	81974-61-0	$C_{21}H_{42}O_2$
29	Octadecan-4-one	CCCCCCCCCCCCCC(=O)CCC	94307-14-9	$C_{18}H_{36}O$
30	Trihexadecyl borate	B(OCCCCCCCCCCCCCCC)(OCCCCCCCCCCCCCCC)OCCCCCCCCCCCCCCC	2665-11-4	$C_{48}H_{99}BO_3$
31	Hexacosane, 1-iodo-	CCCCCCCCCCCCCCCCCCCCCCCCCCI	0-00-0	Hexacosane
32	Squalene	CC(=CCCC(=CCCC(=CCCC=C(C)CCC=C(C)CCC=C(C)C)C)C)C	111-02-4	$C_{30}H_{50}$
33	Hexacontane	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	7667-80-3	$C_{60}H_{122}$
34	Tetrapentacontane	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	5856-66-6	$C_{54}H_{110}$
35	Tris(2,4-di-tert-butylphenyl) phosphate	CC(C)(C)C1=CC(=C(C=C1)OP(=O)(OC2=C(C=C(C=C2)C(C)(C)C)C(C)(C)C)OC3=C(C=C(C=C3)C(C)(C)C)C(C)(C)C)C(C)(C)C	95906-11-9	$C_{42}H_{63}O_4P$

36	Heptane, 2,2,3,3,5,6,6-heptamethyl-	CC(CC(C)(C)C(C)(C)C)C(C)(C)C	7225-67-4	$C_{14}H_30$
37	Isoamyl laurate	CCCCCCCCCCCC(=O)OCCC(C)C	6309-51-9	$C_{17}H_{34}O_2$
38	3-Methyltriacontane	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC(C)C	72227-01-1	$C_{31}H_{64}$
Inlet-30				
1	4-Octene, (E)-	CCCC=CCCC	14850-23-8	C_8H_{16}
2	.beta.-Pinene	CC1(C2CCC(=C)C1C2)C	127-91-3	$C_{10}H_{16}$
3	D-Limonene	CC1=CCC(CC1)C(=C)C	5989-27-5	$C_{10}H_{16}$
4	2,5-Dimethylhexane-2,5-dihydroperoxide	CC(C)(CCC(C)(C)OO)OO	3025-88-5	$C_8H_{18}O_4$
5	1,3-Cyclohexadien-5-ol, 1-phenyl-	C1C(C=CC=C1C2=CC=CC=C2)O	0-00-0	$C_{12}H_{12}O$
6	7-Tetradecenal, (Z)-	CCCCCCC=CCCCCCC=O	65128-96-3	$C_{14}H_{26}O$
7	Longifolene	CC1(CCCC2(C3C1C(C2=C)CC3)C)C	475-20-7	$C_{15}H_{24}$
8	Caryophyllene	CC1=CCCC(=C)C2CC(C2CC1)(C)C	87-44-5	$C_{15}H_{24}$
9	Undec-10-ynoic acid, tetradecyl ester	CCCCCCCCCCCCCCOC(=O)CCCCCCCCCC#C	0-00-0	$C_{25}H_{46}O_2$
10	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-	CC1=CCC=C(CC=CC(CC1)(C)C)C	0-00-0	$C_{15}H_{24}$
11	Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]-	CC(=C)C1CCC2(CCCC(=C)C2C1)C	17066-67-0	$C_{15}H_{24}$
12	Butylated Hydroxytoluene	CC1=CC(=C(C(=C1)C(C)(C)C)O)C(C)(C)C	128-37-0	$C_{15}H_{24}O$
13	.beta.-Bisabolene	CC1=CCC(CC1)C(=C)CCC=C(C)C	495-61-4	$C_{15}H_{24}$
14	Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	CC1CCC(C2=C1C=CC(=C2)C)C(C)C	483-77-2	$C_{15}H_2$
15	Cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene-, [S-(R*,S*)]-	CC(CCC=C(C)C)C1CCC(=C)C=C1	20307-83-9	$C_{15}H_{24}$
16	Carbonic acid, ethyl hexadecyl ester	CCCCCCCCCCCCCCCCOC(=O)OCC	0-00-0	$C_{19}H_{38}O_3$

17	3-Undecene, 3-methyl-	CCCCCCCC=C(C)CC	23381-94-4	$C_{12}H_{24}$
18	Benzene, (1-butylheptyl)-	CCCCCCC(CCCC)C1=CC=CC=C1	4537-15-9	$C_{17}H_{28}$
19	1,4-Benzenediol, 2-[(1,4,4a,5,6,7,8,8a-octahydro-2,5,5,8a-tetramethyl-1-naphthalenyl)methyl]-, [1R-(1.alpha.,4a.beta.,8a.alpha.	CC1=CCC2C(CCCC2(C1CC3=C(C=CC(=C3)O)O)C)(C)C	39707-55-6	$C_{21}H_{30}O_2$
20	Hexadecanal	CCCCCCCCCCCCCCCC=O	629-80-1	$C_{16}H_{32}O$
21	Tricyclo[4.3.0.0(7,9)]nonane, 2,2,5,5,8,8-hexamethyl-, (1.alpha.,6.beta.,7.alpha.,9.alpha.)-	CC1(CCC(C2C1C3C2C3(C)C)(C)C)C	54832-82-5	$C_{15}H_{26}$
22	Carbonic acid, octadecyl vinyl ester	CCCCCCCCCCCCCCCCCCOC(=O)OC=C	0-00-0	$C_{21}H_{40}O_3$
23	2-Octanol, 2-methyl-6-methylene-	CCC(=C)CCCC(C)(C)O	18479-59-9	$C_{10}H_{20}O$
24	Octadecane, 1-chloro-	CCCCCCCCCCCCCCCCCCCl	3386-33-2	$C_{18}H_{37}Cl$
25	Methyloctadecyldichlorosilane	CCCCCCCCCCCCCCCCCC[Si](C)(Cl)Cl	5157-75-5	$C_{19}H_{40}Cl_2Si$
26	2-Hexadecanone	CCCCCCCCCCCCCCC(=O)C	18787-63-8	$C_{16}H_{32}O$
27	Cyclopropane, 1-methyl-1-(2-methylpropyl)-2-nonyl-	CCCCCCCCCC1CC1(C)CC(C)C	41977-41-7	$C_{17}H_{34}$
28	2-Hexadecanol	CCCCCCCCCCCCCCC(C)O	14852-31-4	$C_{16}H_{34}O$
29	1-Heptatriacotanol	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCO	105794-58-9	$C_{37}H_{76}O$
30	1-Hexadecanethiol	CCCCCCCCCCCCCCCCS	2917-26-2	$C_{16}H_{34}S$
31	Octadecyl octyl ether	CCCCCCCCCCCCCCCCCCOCCCCCCCC	0-00-0	$C_{26}H_{54}O$
32	1-Eicosanol	CCCCCCCCCCCCCCCCCCCCO	629-96-9	$C_{20}H_{42}O$
33	2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester	CCCCC(CC)COC(=O)C=CC1=CC=C(C=C1)OC	5466-77-3	$C_{18}H_{26}O_3$
34	Heneicosane, 3-methyl-	CCCCCCCCCCCCCCCCCCCC(C)CC	6418-47-9	$C_{22}H_{46}$
35	Lanosterol	CC(CCC=C(C)C)C1CCC2(C1(CCC3=C2CCC4C3(CCC(C4(C)C)O)C)C)C	79-63-0	$C_{30}H_{50}O$

36	Docosyl pentafluoropropionate	CCCCCCCCCCCCCCCCCCCCCCOC(=O)C(C(F)(F)F)(F)F	0-00-0	$C_{25}H_{45}F_5O_2$
37	1-Docosanol, acetate	CCCCCCCCCCCCCCCCCCCCCCOC(=O)C	822-26-4	$C_{24}H_{48}O_2$
38	Cholest-14-en-3-ol, (3.beta.,5.alpha.)-	CC(C)CCCC(C)C1CC=C2C1(CCC3C2CCC4C3(CCC(C4)O)C)C	20780-35-2	$C_{27}H_{46}O$
39	5.beta.,14.beta.-Androstane-17.beta.-carboxylic acid, 3.beta.,14-dihydroxy-, .gamma.-lactone, acetate	CC(=O)OC1CCC2(C(C1)CCC3C2CCC4(C35CCC4C(=O)O5)C)C	10124-02-4	$C_{22}H_{32}O_4$
40	Prasterone-3-sulfate	CC12CCC3C(C1CCC2=O)CC=C4C3(CCC(C4)OS(=O)(=O)O)C	651-48-9	$C_{19}H_{28}O_5S$
41	Tritetracontane	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	7098-21-7	$C_{43}H_{88}$
42	Tetratriacontane	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	14167-59-0	$C_{34}H_{70}$
43	Carbonic acid, decyl heptadecyl ester	CCCCCCCCCCCCCCCCCOC(=O)OCCCCCCCCCC	0-00-0	$C_{28}H_{56}O_3$
44	1,13-Tetradecadien-3-one	C=CCCCCCCCCCC(=O)C=C	58879-40-6	$C_{14}H_{24}$
45	Pentacosane	CCCCCCCCCCCCCCCCCCCCCCCCC	629-99-2	$C_{25}H_{52}$
46	Nonyl octacosyl ether	CCCCCCCCCCCCCCCCCCCCCCCCCCCCOCCCCCCCCC	0-00-0	$C_{37}H_{76}O$
47	Octacosane, 1-iodo-	CCCCCCCCCCCCCCCCCCCCCCCCCCCCI	0-00-0	$C_{28}H_{57}I$
48	Ambrein	CC(=CCCC1C2(CCCC(C2CCC1(C)O)(C)C)C)CCC3C(=C)CCCC3(C)C	0-00-0	$C_{30}H_{52}O$
		Outlet-30		
1	Toluene	CC1=CC=CC=C1	108-88-3	C_7H_8
2	Decane, 2,2-dimethyl-	CCCCCCCCC(C)(C)C	17302-37-3	$C_{12}H_{26}$
3	Benzene, 1,4-dichloro-	C1=CC(=CC=C1Cl)Cl	106-46-7	$C_6H_4Cl_2$
4	Benzyl alcohol	C1=CC=C(C=C1)CO	100-51-6	C_7H_8O
5	Benzene, (iodomethyl)-	C1=CC=C(C=C1)CI	620-05-3	C_7H_7I
6	7-Tetradecene, (Z)-	CCCCCCC=CCCCCCC	41446-60-0	$C_{14}H_{28}$
7	3,3-Diethyltridecane	CCCCCCCCCCC(CC)(CC)CC	0-00-0	$C_{17}H_{36}$

8	3-Buten-2-one, 4-(2,5,6,6-tetramethyl-1-cyclohexen-1-yl)-	CC1CCC(=C(C1(C)C)C=CC(=O)C)C	79-70-9	$C_{14}H_{22}O$
9	5,9-methanobenzocycloocten-5(1H)-ol, 2,3,4,6,7,8,9,10-octahydro-2,2,8,8,9-pentamethyl-	CC1(CCC2=C(C1)CC3(CC2(CCC3(C)C)O)C)C	0-00-0	$C_{18}H_{30}O$
10	Heptadecane, 3-methyl-	CCCCCCCCCCCCCCC(C)CC	6418-44-6	$C_{18}H_{38}$
11	Tonalid	CC1CC(C2=C(C1(C)C)C=C(C(=C2)C(=O)C)C)(C)C	21145-77-7	$C_{18}H_{26}O$
12	6-Methyl-2-(4-methylcyclohex-3-en-1-yl)hepta-1,5-dien-4-ol	CC1=CCC(CC1)C(=C)CC(C=C(C)C)O	38142-56-2	$C_{15}H_{24}O$
13	3-Ethyl-3-methylheptadecane	CCCCCCCCCCCCCCC(C)(CC)CC	0-00-0	$C_{20}H_{42}$
14	l-(+)-Ascorbic acid 2,6-dihexadecanoate	CCCCCCCCCCCCCCCC(=O)OCC(C1C(=C(C(=O)O1)OC(=O)CCCCCCCCCCCCCCC)O)O	28474-90-0	$C_{38}H_{68}O_8$
15	Pentadecanal-	CCCCCCCCCCCCCCC=O	2765-11-9	$C_{15}H_{30}O$
16	Octadecanoic acid	CCCCCCCCCCCCCCCCCC(=O)O	57-11-4	$C_{18}H_{36}O_2$
17	3-Methyldotriacontane	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC(C)CC	20129-49-1	$C_{33}H_{68}$
18	Nonacos-1-ene	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC=C	18835-35-3	$C_{29}H_{58}$
19	Eicosyl isobutyl ether	CCCCCCCCCCCCCCCCCCCCCOCC(C)C	0-00-0	$C_{24}H_{50}O$
20	Docosyl nonyl ether	CCCCCCCCCCCCCCCCCCCCCCCCCOCCCCCCCCC	0-00-0	$C_{31}H_{64}O$
21	5,5-Diethylpentadecane	CCCCCCCCCCC(CC)(CC)CCCC	0-00-0	$C_{19}H_{40}$
22	2-Methylpentacosane	CCCCCCCCCCCCCCCCCCCCCCCCCC(C)C	629-87-8	$C_{26}H_{54}$
23	Cholest-5-ene, 3.beta.-chloro-	CC(C)CCCC(C)C1CCC2C1(CCC3C2CC=C4C3(CCC(C4)Cl)C)C	910-31-6	$C_{27}H_{45}Cl$
24	2-Methylheptacosane	CCCCCCCCCCCCCCCCCCCCCCCCCCCC(C)C	1561-00-8	$C_{28}H_{58}$
25	3,3-Diethylheptadecane	CCCCCCCCCCCCCCC(CC)(CC)CC	0-00-0	$C_{21}H_{44}$

26	Tridecane, 6-cyclohexyl-	CCCCCCCC(CCCCC)C1CCCCC1	13151-91-2	$C_{19}H_{38}$
27	Stigmastanol	CCC(CCC(C)C1CCC2C1(CCC3C2CCC4C3(CCC(C4)O)C)C)C(C)C	19466-47-8	$C_{29}H_{52}O$
28	3-Methyloctacosane	CCCCCCCCCCCCCCCCCCCCCCCCCCC(C)CC	65820-58-8	$C_{29}H_{60}$
29	Pentyl triacontyl ether	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCOCCCCC	0-00-0	$C_{35}H_{72}O$
30	Carbonic acid, decyl octadecyl ester	CCCCCCCCCCCCCCCCCCOC(=O)OCCCCCCCCC	0-00-0	$C_{29}H_{58}O_3$
31	2-Methylhentriacontane	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC(C)C	1720-12-3	$C_{32}H_{66}$

Once all the CAS number and smiley codes were retrieved and cross checked on PUBCHEM the attributes for risk assessment were selecting i.e. toxicity assessment using ECOSAR modelling from episuite was done, secondly Kow was retrieved for each dib to check if they are hydrophobic or hydrophilic, third using BIOWINN modelling from EPI-suite the biodegradability or persistence was checked, fourth using BCFBAF modelling from EPI-suite the bio-accumulation factor was checked.

4.2.1 Toxicity Assessment Using ECOSAR Modelling from Epi suite

For comparing the results for risk and fate analysis (REACH 2007) LIMITS were used as standard. The limit for toxicity is 0.1mg/l or higher are considered as highly toxic (REACH 2007).

4.2.1.1 Inlet-15 Toxicity Assessment

After applying the limit, 14 out of 50 analyzed chemicals were exceeding the cut-off limit. These compounds LC50 values were beyond the cut-off limit according to REACH 2007.

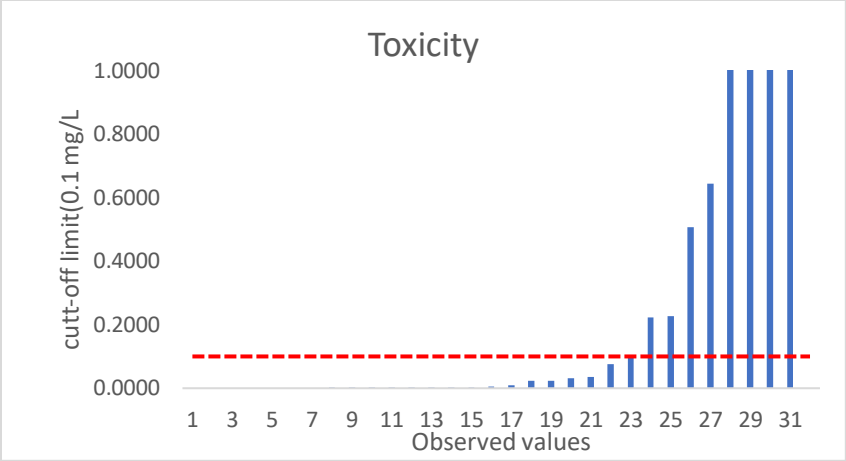


Figure 13: The graph showing the toxicity result, only 08 chemicals exceed cut-off limit

Table 2: List of chemicals exceeding the limit value in Inlet-15 sample

SN	Chemical Name	LC50 Fish (96 hours) ppm	ChV (ppm)
1	2-Octene, 3,7-dimethyl-, (Z)-	0.2230	0.03
2	Phthalic acid, 4,4-dimethylpent-2-yl butyl ester	0.2260	0.008
3	3-Carene	0.5060	0.066
4	2-Tridecanone	0.6440	0.084
5	o-Cymene	1.7760	0.216
6	Isovaleric acid, 3-ethylphenyl ester	1.8040	0.089
7	2-Buten-1-one, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-	4.3700	5.22E-01
8	1-Hexanol, 2-ethyl-	23.5500	2.49

4.2.1.2 Oulet-15 Toxicity Assessment

After applying the limit, 6 out of 38 analyzed chemicals were exceeding the cut-off limit. These compounds LC50 values were beyond the cut-off limit according to REACH 2007.

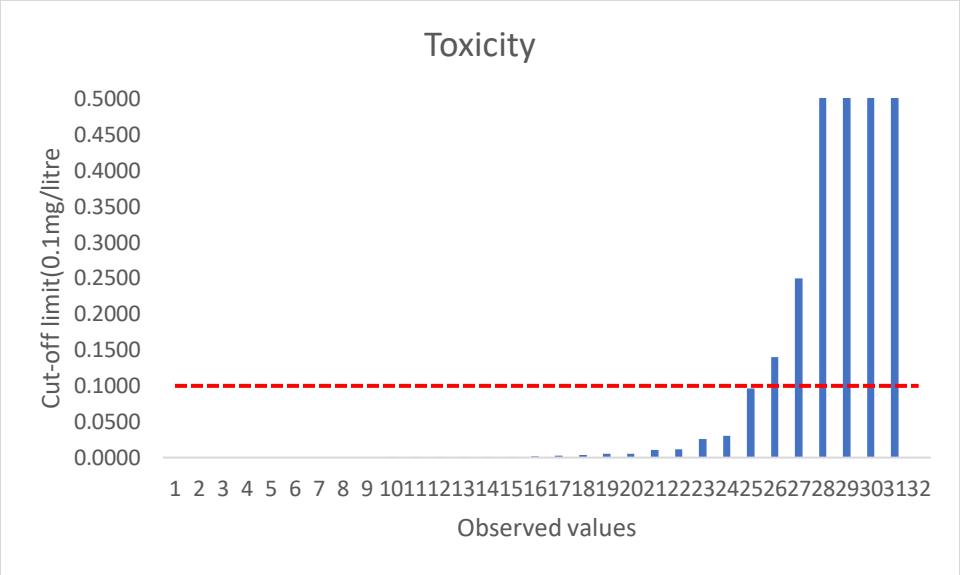


Figure 14: The graph showing the toxicity result, only six chemicals exceed cut-off limit

Table 3: List of chemicals exceeding the limit value in outlet-15 sample

SN	Chemical Name	LC50 Fish (96 hours) ppm	ChV (ppm)
1	Decane	0.1400	0.02
2	Phthalic acid, 4,4-dimethylpent-2-yl isobutyl ester	0.2500	0.008
3	Naphthalene, 1,3-dimethyl-	1.1900	0.149
4	2-Nonyne	1.4840	0.181
5	2,4-Difluorobenzene, 1-benzyloxy-	1.9830	0.246
6	1,2-Cyclopentanediol, trans-	########	401.148

4.2.1.3 Inlet-30 Toxicity Assessment

After applying the limit, 07 out of 32 analyzed chemicals were exceeding the cut-off limit. These compounds LC50 values were beyond the cut-off limit according to REACH 2007.

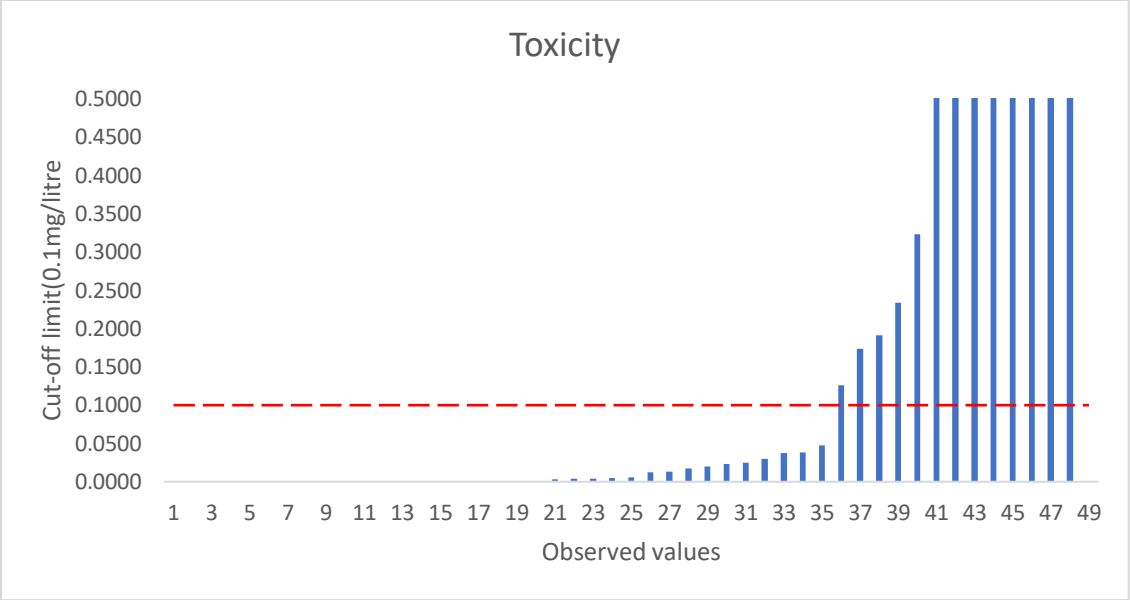


Figure 15: The graph showing toxicity result, only seven chemicals exceed cut-off limit

Table 4: List of chemicals exceeding the limit value in Inlet-30 sample

SN	Chemical Name	LC50 Fish (96 hours) ppm	ChV (ppm)
1	Longifolene	0.1260	0.018
2	7-Tetradecenal, (Z)-	0.1740	0.007
3	D-Limonene	0.3230	0.043
4	1,13-Tetradecadien-3-one	0.7910	6.10E-02
5	.beta.-Pinene	0.8730	0.11
6	4-Octene, (E)-	1.3150	0.161
7	Prasterone-3-sulfate	5117.8780	4.31E+02

4.2.1.4 Outlet-30 Toxicity Assessment

After applying the limit, 04 out of 22 analyzed chemicals were exceeding the cut-off limit. These compounds LC50 values were beyond the cut-off limit according to REACH 2007.

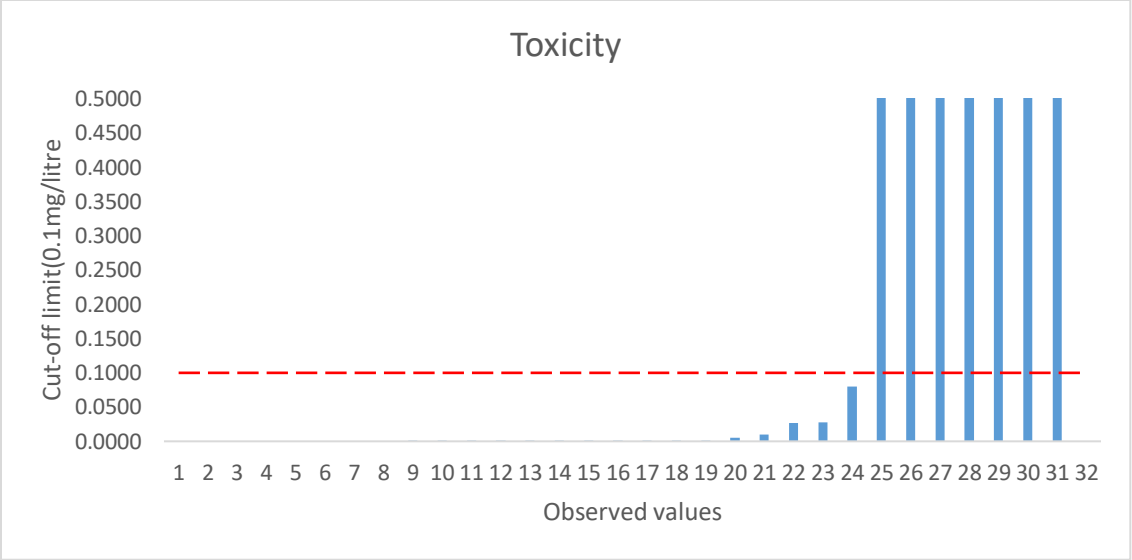


Figure 16: The graph showing toxicity result, only four chemicals exceed cut-off limit

Table 5: List of chemicals exceeding the limit value in Inlet-30 sample

SN	Chemical Name	LC50 Fish (96 hours) ppm	ChV (ppm)
1	Benzene, (iodomethyl)-	0.6100	0.241
2	Benzene, 1,4-dichloro-	8.5200	0.958
3	Toluene	24.7600	2.57
4	Benzyl alcohol	213.8700	15.536

4.2.2 Hydrophobic Contaminant on Basis of Kow Value

If Log Kow lesser than 1 the chemical or compound is considered hydrophilic i.e. it will show affinity towards water, but if the log Kow is greater than 3 then they are termed as hydrophobic (REACH 2007).

4.2.2.1 Hydrophobicity Inlet-15

Out of 31 Chemicals, 30 are hydrophobic as there value is Kow value is greater than 3.

Table 6: Hydrophobic chemicals result on basis of logKow values

SN	Compound Name	Log Kow
1	5,5,9,10-Tetramethyltricyclo[7.2.1.0(1,6)]dodecan-10,12-diol	3.72
2	o-Cymene	4
3	Isovaleric acid, 3-ethylphenyl ester	4.03
4	2-Buten-1-one, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-	4.16
5	3-Carene	4.61
6	2-Tridecanone	4.68
7	2-Octene, 3,7-dimethyl-, (Z)-	5.02
8	2-Pentadecanone	5.66
9	Phthalic acid, 4,4-dimethylpent-2-yl butyl ester	5.9
10	1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl-, trans-	6.1
11	Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-	6.26
12	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl-	6.29
13	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-	6.3
14	n-Heptadecanol-1	7.23
15	Bis(2-ethylhexyl) phthalate	8.39

16	Cholestan-3-ol, (3.beta.,5.beta.)-	8.82
17	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-	10.19
18	Docosyl trifluoroacetate	11.1
19	Nonadecyl heptafluorobutyrate	11.26
20	9-Tricosene, (Z)-	11.42
21	Carbonic acid, decyl hexadecyl ester	12.02
22	2-Methyltetracosane	12.55
23	Octacosanol	12.63
24	Myristyl myristate	12.65
25	Heptacosane, 1-chloro-	13.86
26	Triacontyl pentafluoropropionate	16
27	Tritriacontane, 3-methyl-	16.97
28	Dotriacontyl pentafluoropropionate	16.98
29	Isobutyl tetratriacontyl ether	17.67
30	Octatriacontane, 1,38-dibromo-	19.69

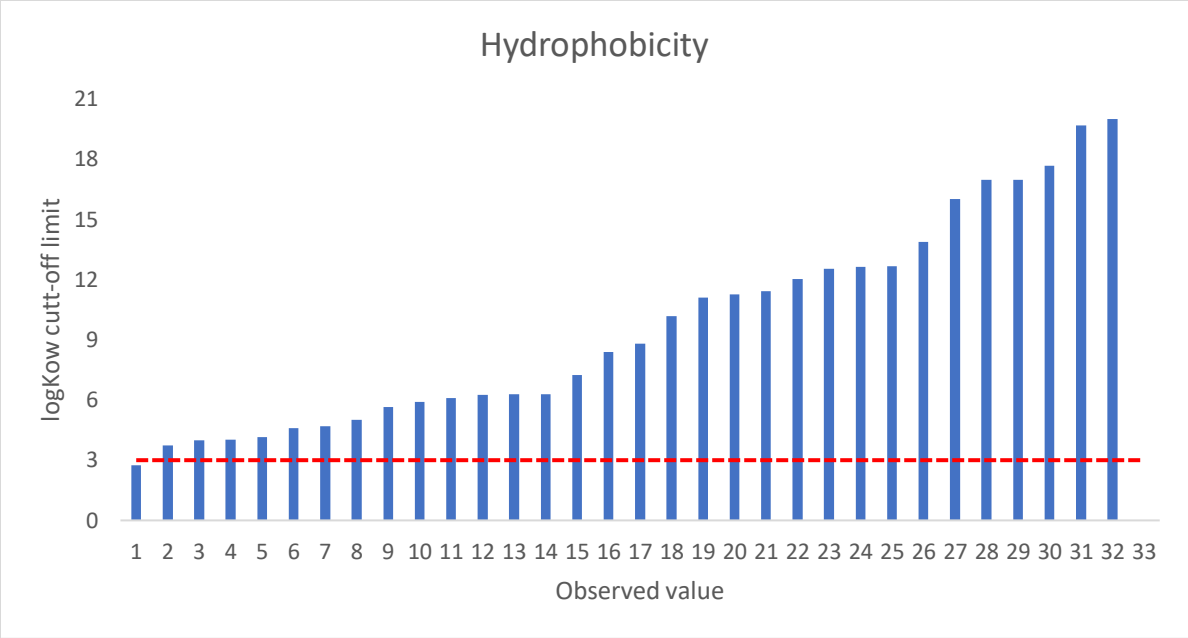


Figure 17: The graph showing the hydrophobic chemicals result on basis of logKow values

4.2.2.2 Hydrophobicity Outlet-15

Out of 31 Chemicals, 30 are hydrophobic as there value is Kow value is greater than 3.

Table 7: Hydrophobic chemicals result on basis of logKow values

SN	**Compound Name**	**Log Kow**
1	2-Nonyne	4.05
2	2,4-Difluorobenzene, 1-benzyloxy-	4.18
3	Naphthalene, 1,3-dimethyl-	4.26
4	Decane	5.25
5	3-Pentadecanone	5.66
6	Phthalic acid, 4,4-dimethylpent-2-yl isobutyl ester	5.83
7	4-Undecene, 5-methyl-	6.08
8	Undecane, 3-methylene-	6.16
9	Undecane, 2,6-dimethyl-	6.58

10	1-Tridecene	6.59
11	Dodecane, 4,6-dimethyl-	7.07
12	1-Tetradecene	7.08
13	Octadecan-4-one	7.13
14	1-Octadecanol	7.72
15	3-Hexadecene, (Z)-	7.98
16	Undecane, 4-cyclohexyl-	8.43
17	1-Octadecene	9.04
18	3-Methylbutyl hexadecanoate	9.14
19	Octadecane	9.18
20	Eicosane, 10-methyl-	10.58
21	Docosyl pentyl ether	12.34
22	1-Cyclopentyleicosane	12.43
23	Octadecane, 5,14-dibutyl-	12.96
24	Hexacosane, 1-iodo-	13.87
25	Squalene	14.12
26	3-Methyltriacontane	15
27	Dotriacontane, 1-iodo-	16.82
28	Dotriacontyl heptafluorobutyrate	17.65
29	Trihexadecyl borate	20.2
30	Hexacontane	29.81

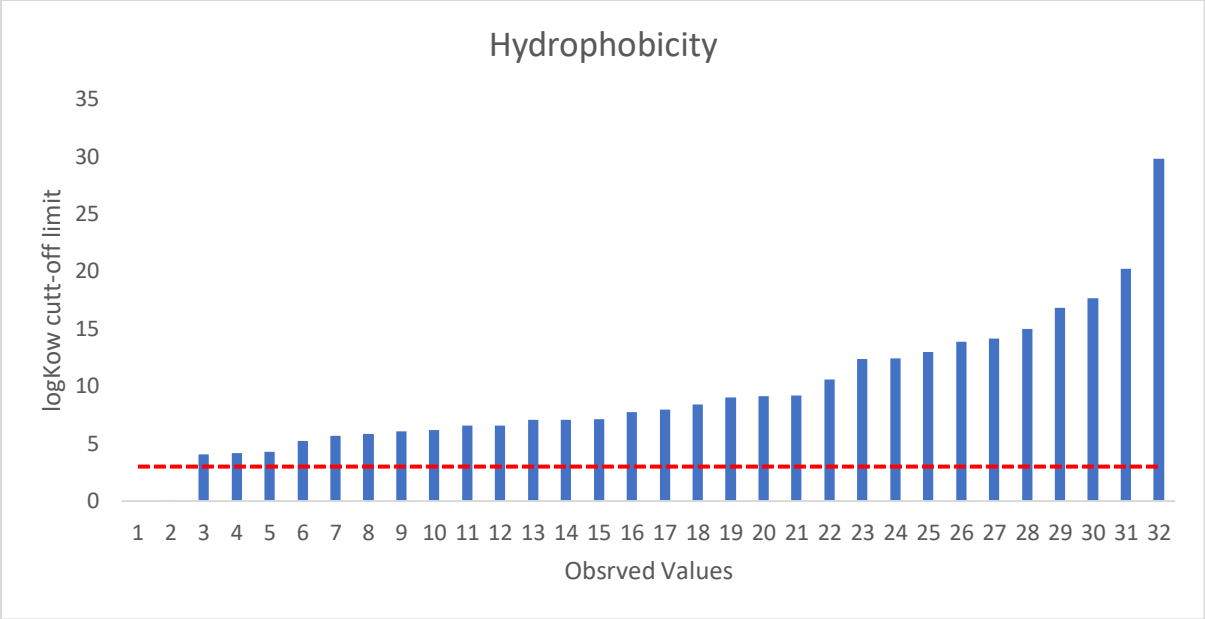


Figure 18: The graph showing the hydrophobic contaminant results on basis of logKow value

4.2.2.3 Hydrophobicity Inlet-30

Out of 32 Chemicals, 31 are hydrophobic as there value is Kow value is greater than 3.

Table 8: Hydrophobic chemicals result on basis of logKow values

SN	Compound Name	Log Kow
1	4-Octene, (E)-	4.06
2	.beta.-Pinene	4.35
3	D-Limonene	4.83
4	1,13-Tetradecadien-3-one	5.18
5	Longifolene	5.48
6	7-Tetradecenal, (Z)-	5.51
7	2-Hexadecanone	6.15

8	Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	6.25
9	Caryophyllene	6.3
10	Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]-	6.38
11	2-Hexadecanol	6.66
12	Hexadecanal	6.71
13	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-	6.95
14	Cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene-, [S-(R*,S*)]-	6.99
15	.beta.-Bisabolene	7.12
16	Benzene, (1-butylheptyl)-	7.38
17	1-Hexadecanethiol	8.14
18	1-Eicosanol	8.7
19	Carbonic acid, octadecyl vinyl ester	8.94
20	Octadecane, 1-chloro-	9.44
21	Undec-10-ynoic acid, tetradecyl ester	10.41
22	1-Docosanol, acetate	10.69
23	Heneicosane, 3-methyl-	11.07
24	Octadecyl octyl ether	11.85
25	Docosyl pentafluoropropionate	12.07
26	Carbonic acid, decyl heptadecyl ester	12.51
27	Pentacosane	12.62

28	Octacosane, 1-iodo-	14.85
29	Tetratriacontane	17.04
30	Nonyl octacosyl ether	17.26
31	Tritetracontane	21.46

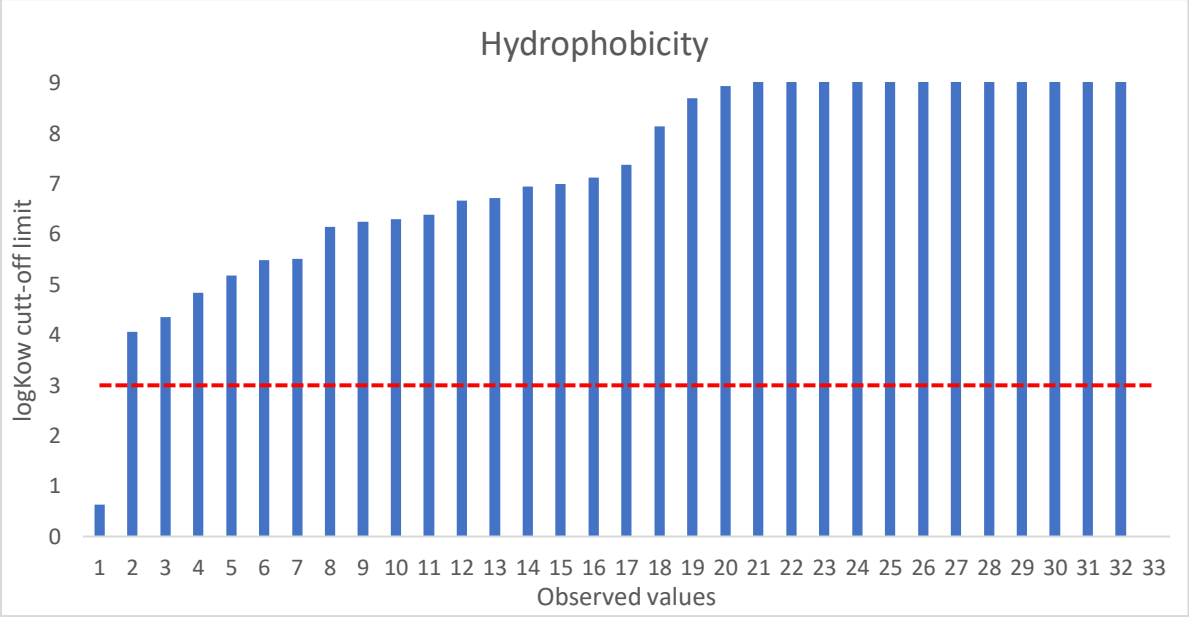


Figure 19: The graph showing the hydrophobic contaminant results on basis of logKow value

4.2.2.4 Hydrophobicity Outletlet-30

Out of 31 Chemicals, 20 are hydrophobic as there value is Kow value is greater than 3.

Table 9: Hydrophobic chemicals result on basis of logKow values

SN	**Compound Name**	**Log Kow**
1	Benzene, 1,4-dichloro-	3.28
2	Benzene, (iodomethyl)-	3.3

3	Decane, 2,2-dimethyl-	6.12
4	7-Tetradecene, (Z)-	7
5	Octadecanoic acid	7.94
6	3,3-Diethyltridecane	8.58
7	Tridecane, 6-cyclohexyl-	9.41
8	5,5-Diethylpentadecane	9.56
9	3,3-Diethylheptadecane	10.54
10	Eicosyl isobutyl ether	10.8
11	l-(+)-Ascorbic acid 2,6-dihexadecanoate	11.26
12	Carbonic acid, decyl octadecyl ester	13
13	2-Methylpentacosane	13.04
14	2-Methylheptacosane	14.02
15	Docosyl nonyl ether	14.31
16	Nonacos-1-ene	14.45
17	3-Methyloctacosane	14.51
18	2-Methylhentriacontane	15.98
19	Pentyl triacontyl ether	16.27
20	3-Methyldotriacontane	16.47

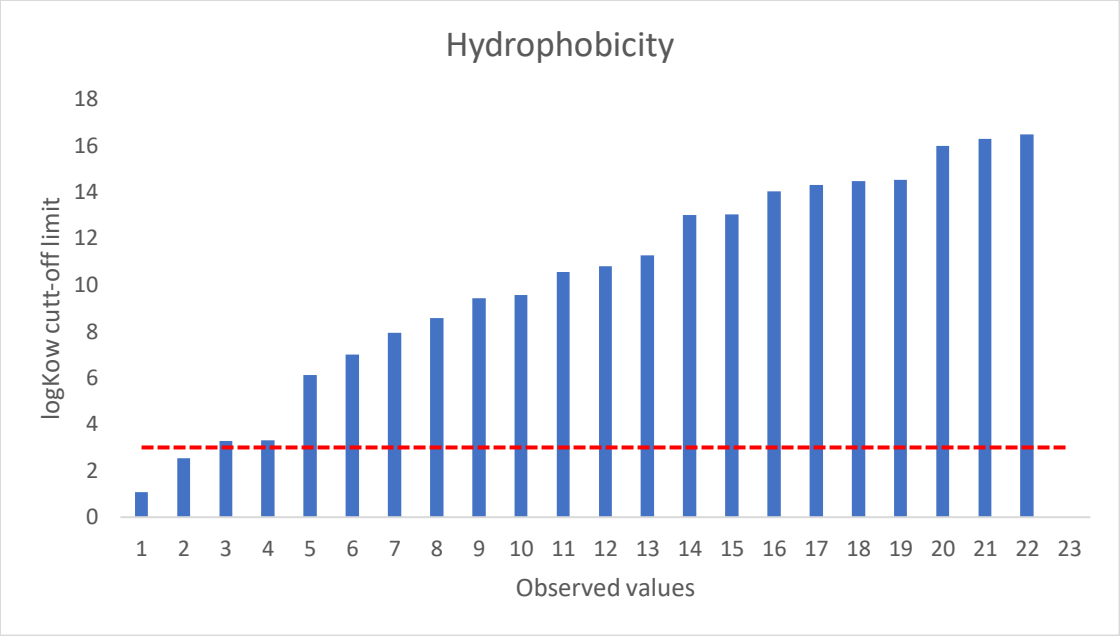


Figure 20: The graph showing hydrophobic contaminants result on basis of kow value

4.2.3 Bioaccumulation via BCBAF

BCBAF modelling for bioaccumulation was used, the threshold limits are if log BCF is greater than 3 then the chemical is considered or treated as highly bio accumulative.

4.2.3.1 Bioaccumulation Inlet-15

When FCBAF modelling applied on inlet-15 chemicals, 08 out of 31 were highly bio accumulative and hazardous.

Table 10: Bio accumulative chemicals on the basis of LogBCF values

SN	Compound Name	Log BCF
1	Bis(2-ethylhexyl) phthalate	3.23
2	Cholestan-3-ol, (3.beta.,5.beta.)-	3.23
3	n-Heptadecanol-1	3.42
4	Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-	3.56

5	Phthalic acid, 4,4-dimethylpent-2-yl butyl ester	3.56
6	1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl-, trans-	3.69
7	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-	3.82
8	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl-	3.82

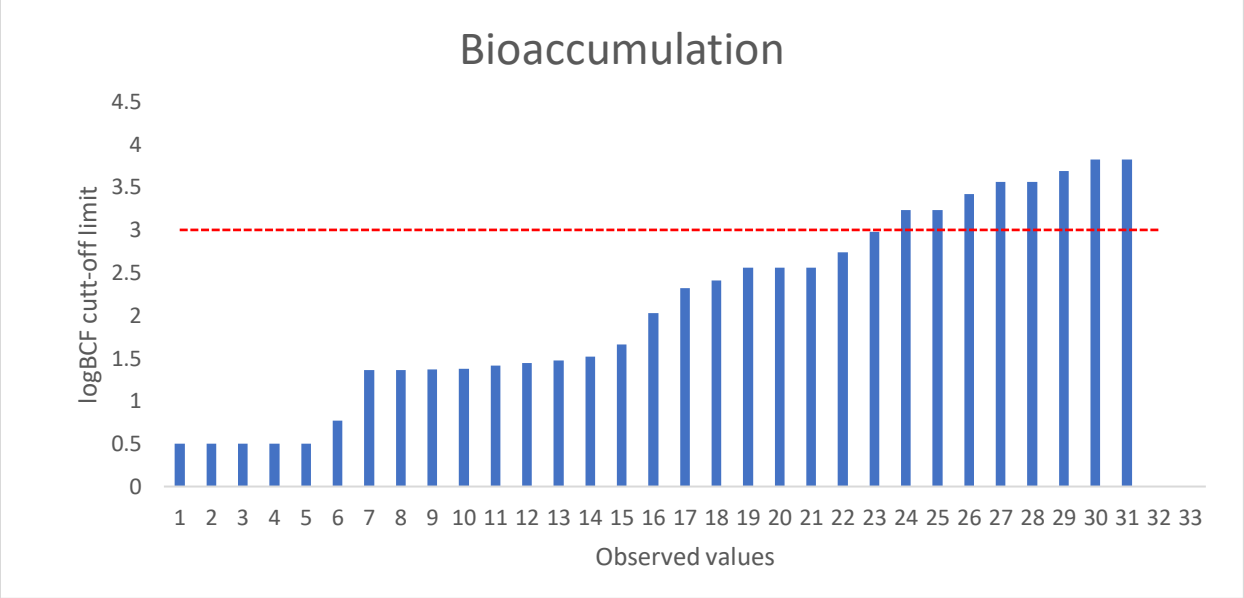


Figure 21: The graph showing Bio accumulative chemicals result on basis of logBCF values

4.2.3.2 Bioaccumulation Onlet-15

When FCBAF modelling applied on outlet-15 chemicals, 06 out of 31 compound were highly bio accumulative and hazardous.

Table 11: Bio accumulative chemicals on the basis of LogBCF values

SN	Compound Name	Log BCF
1	3-Hexadecene, (Z)-	3.05
2	1-Octadecanol	3.18
3	Octadecan-4-one	3.46

4	Dodecane, 4,6-dimethyl-	3.49
5	1-Tridecene	3.49
6	Phthalic acid, 4,4-dimethylpent-2-yl isobutyl ester	3.51

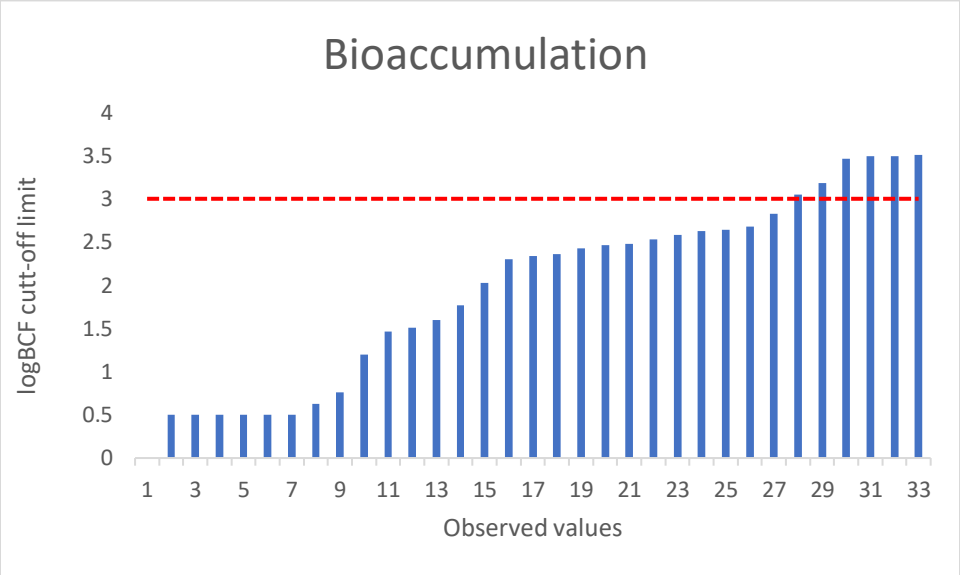


Figure 22: The graph showing Bio accumulative chemicals result on basis of logBCF values

4.2.3.3 Bioaccumulation Inlet-30

When FCBAF modelling applied on inlet-30 chemicals, 08 out of 32 compound were highly bio accumulative and hazardous.

Table 12: Bio accumulative chemicals on the basis of LogBCF values

SN	Compound Name	Log BCF
1	Longifolene	3.28
2	Benzene, (1-butylheptyl)-	3.31
3	Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	3.79
4	Caryophyllene	3.82

5	Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]-	3.88
6	.beta.-Bisabolene	4.06
7	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-	4.25
8	Cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene-, [S-(R*,S*)]-	4.28

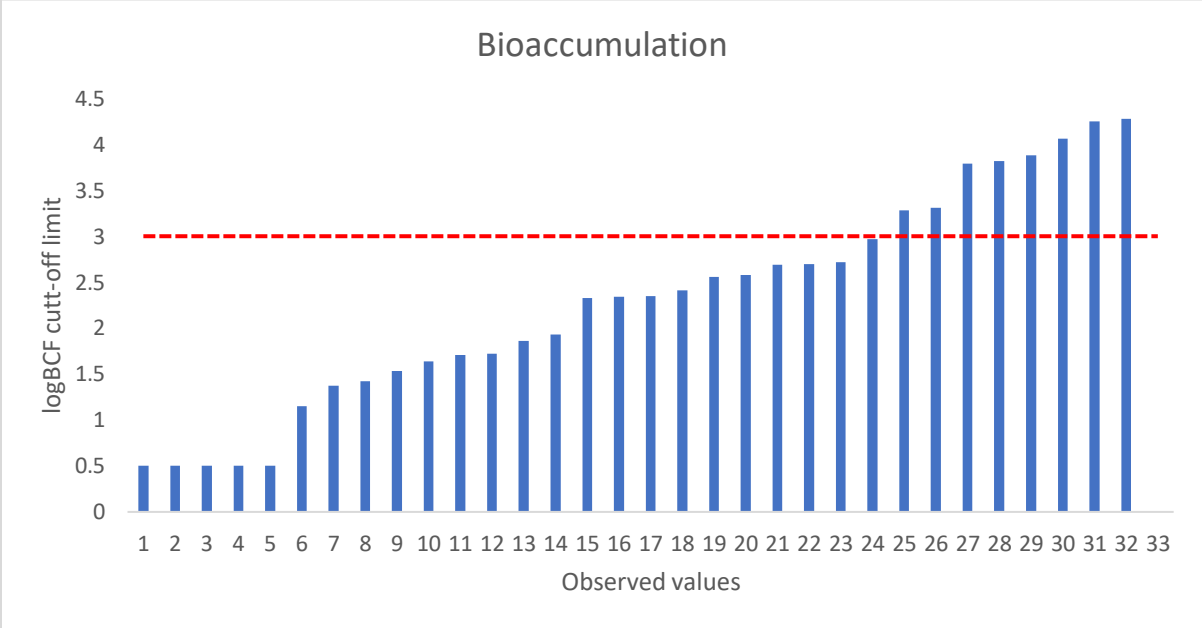


Figure 23: The graph showing Bio accumulative contaminants result on basis of logBCF values

4.2.3.4 Bioaccumulation Outlet-30

When FCBAF modelling applied on outlet-30 chemicals, 1 out of 22 chemical were highly bio accumulative and hazardous.

Table 13: Bio accumulative chemicals on the basis of LogBCF values

SN	**Compound Name**	**Log BCF**
1	7-Tetradecene, (Z)-	3.53

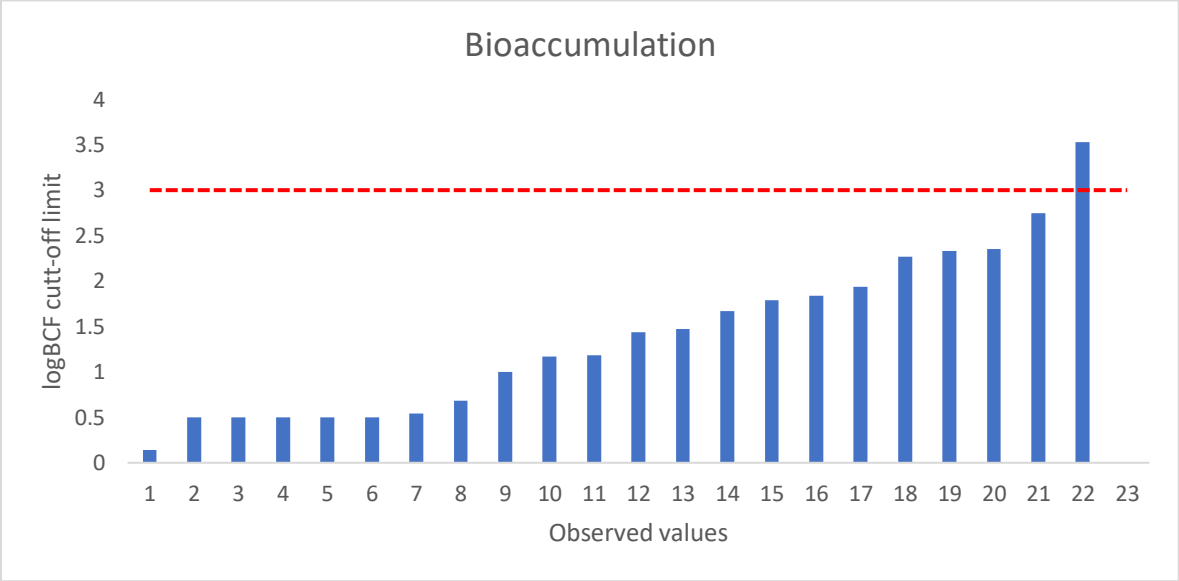


Figure 24: The graph showing Bio accumulative chemicals result on basis of logBCF values

4.2.4 Biodegradability Via BIOWINN Modelling

The biodegradability or persistence was checked using BIOWINN modelling from EPI-suite. BIOWIN contains seven separate models, out of which six were selected for analysis. Version 4.10 designates these models as follows:

4.2.4.1 Biodegradability via BIOWINN for Inlet-15

4.2.4.1.1 BIOWINN1

BIOWINN1 limit value was less than 0.5(REACH2007). 13 out of 31 Chemicals are identified as persistent according to results from BIOWINN1. 13 chemicals are shown in table.

Table 14: BIOWINN1 Chemicals result Inlet-15

SN	Chemicals/DIBs
1	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-
2	Nonadecyl heptafluorobutyrate
3	Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-
4	Dotriacontyl pentafluoropropionate

5	Triacontyl pentafluoropropionate
6	1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl-, trans-
7	Isobutyl tetratriacontyl ether
8	Docosyl trifluoroacetate
9	Octatriacontane, 1,38-dibromo-
10	Cholestan-3-ol, (3.beta.,5.beta.)-
11	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-
12	2-Buten-1-one, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-
13	3-Carene

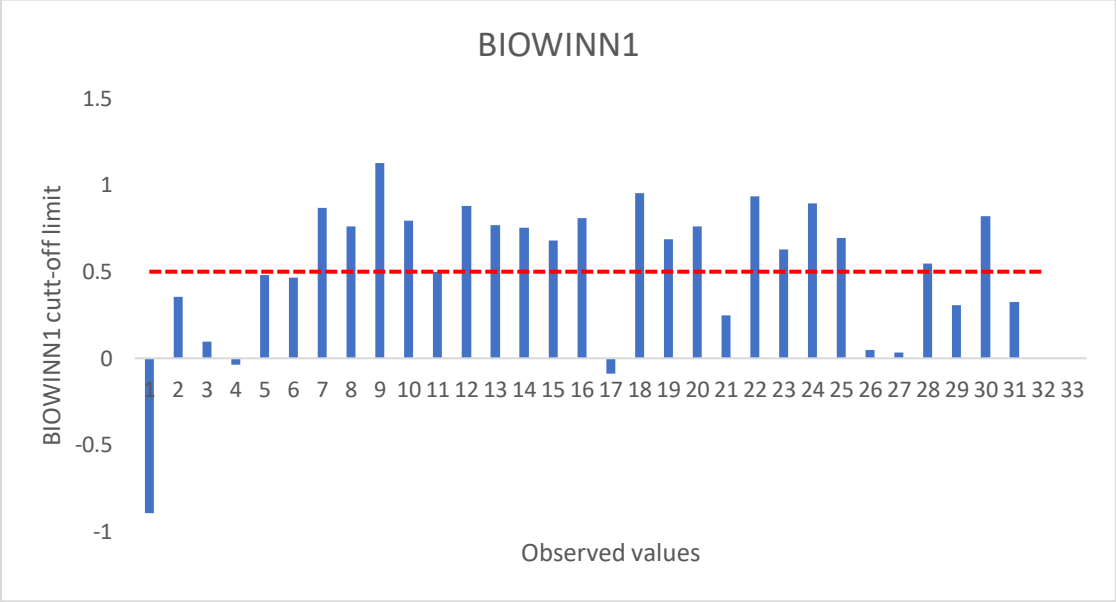


Figure 25: The graph showing the persistency of the chemicals from BIOWINN1

4.2.4.1.2 BIOWINN2

BIOWINN2 model is for non-degradability of chemicals/DIBs if the value is less than 0.5. This non-linear biodegradation limit set by REACH 2007. Results reported that 17 out of 31 chemicals falls under category of persistent (REACH 2007) results from BIOWINN2 for these are less than 0.5

Table 15: BIOWINN2 Chemicals result Inlet-15

SN	Chemicals/DIBs
1	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-
2	Octatriacontane, 1,38-dibromo-
3	Dotriacontyl pentafluoropropionate
4	Nonadecyl heptafluorobutyrate
5	Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-
6	Triacontyl pentafluoropropionate
7	Isobutyl tetratriacontyl ether
8	1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl-, trans-
9	Cholestan-3-ol, (3.beta.,5.beta.)-
10	Heptacosane, 1-chloro-
11	Docosyl trifluoroacetate
12	Tritriacontane, 3-methyl-
13	2-Buten-1-one, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-
14	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-
15	Tetracontane
16	3-Carene
17	2-Methyltetracosane

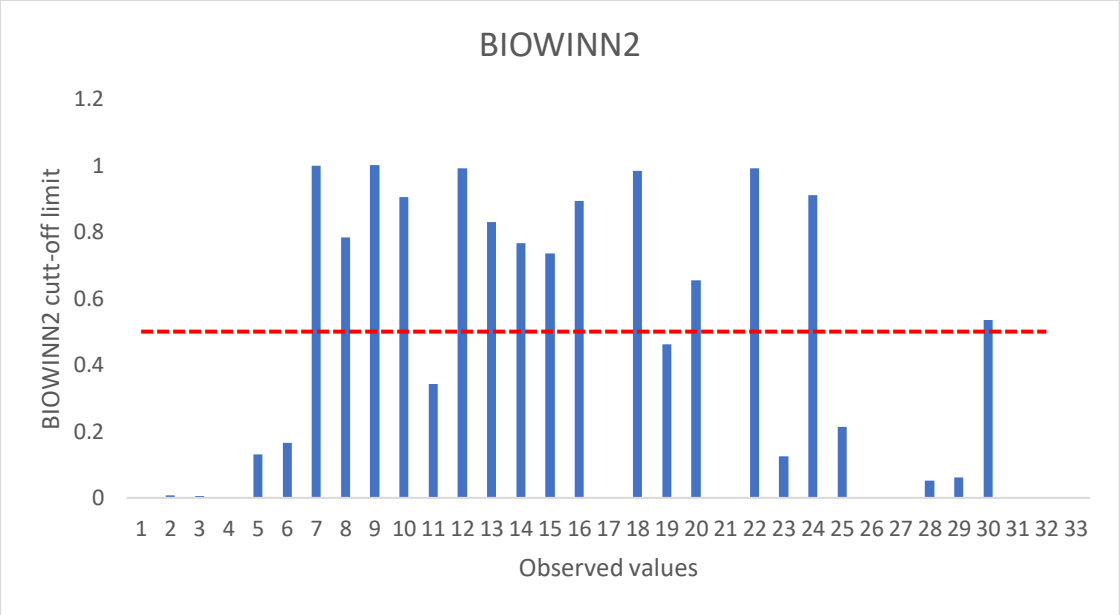


Figure 26: The graph showing the persistency of the chemicals from BIOWINN2

4.2.4.1.3 BIOWINN3

BIOWINN3 limit value was less than 1.7, considered highly persistent. Reported from our results, 4 out of 50 chemicals were highly persistent and non-biodegradable.

Table 16: BIOWINN3 Chemicals result Inlet-15

SN	Chemicals/DIBs
1	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-
2	Dotriacontyl pentafluoropropionate
3	Triacontyl pentafluoropropionate
4	Nonadecyl heptafluorobutyrate

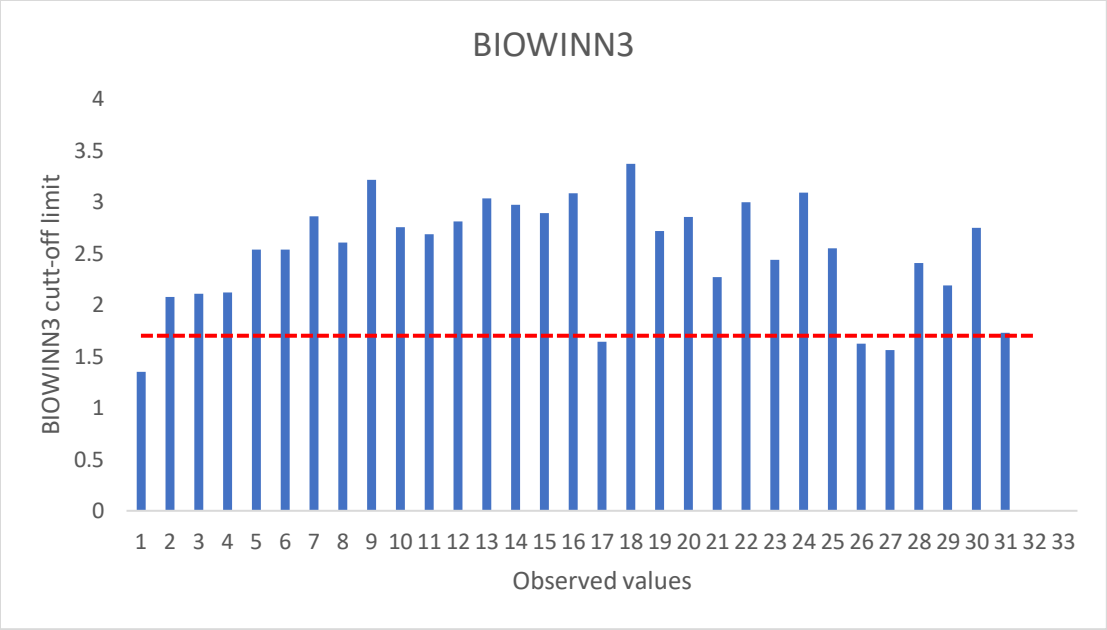


Figure 27: The graph showing the BIOWINN3 results, 4 chemicals show persistency

4.2.4.1.4 BIOWINN4

BIOWINN4 limit value was less than 1.7 (highly persistent for BIOWINN4). No chemical was persistent in primary degradation.

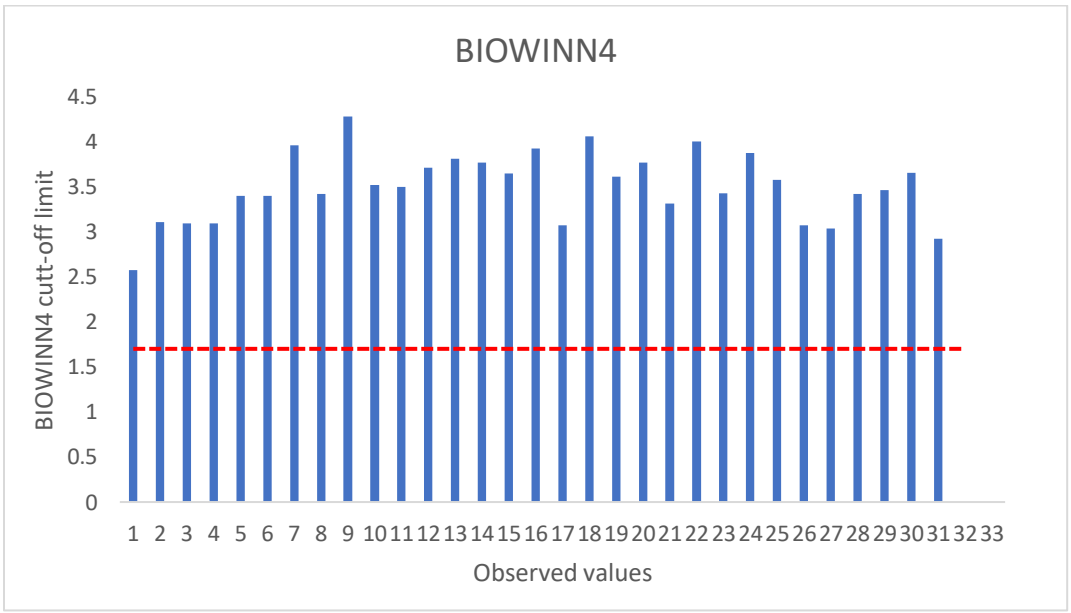


Figure 28: The graph showing the BIOWINN4 results, no chemical shows persistency

4.2.4.1.5 BIOWINN5

BIOWINN5 limit value was less than 0.5(BIOWINN5 persistent). 11 out of 31 chemicals were found persistent.

Table 17: BIOWINN5 Chemicals result Inlet-15

SN	Chemicals/DIBs
1	Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-
2	Cholestan-3-ol, (3.beta.,5.beta.)-
3	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-
4	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl-
5	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-
6	o-Cymene
7	1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl-, trans-
8	2-Buten-1-one, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-
9	2-Octene, 3,7-dimethyl-, (Z)-
10	Isovaleric acid, 3-ethylphenyl ester
11	3-Carene

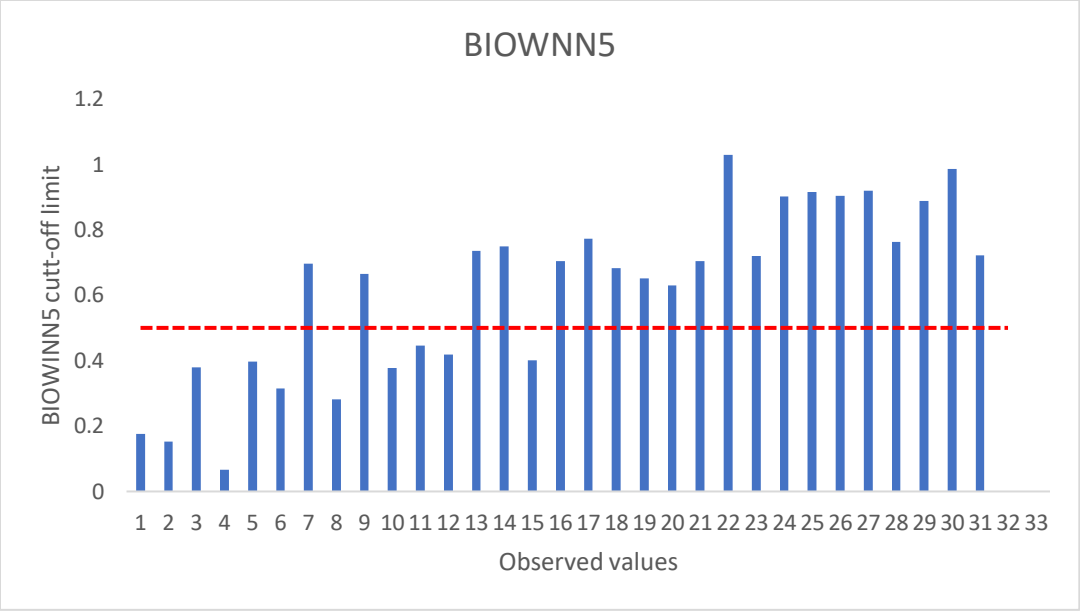


Figure 29: The graph showing BIOWINN5 results, 11 chemicals show persistency

4.2.4.1.6 BIOWINN7

BIOWINN7 limit value was less than 0.5(BIOWINN7 persistent). 18 of them are considered persistent as shown in table.

Table 18: BIOWINN7 Chemicals result Inlet-15

SN	Chemicals/DIBs
1	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-
2	Cholestan-3-ol, (3.beta.,5.beta.)-
3	1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl-, trans-
4	Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-
5	2-Buten-1-one, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-
6	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-
7	Phthalic acid, 4,4-dimethylpent-2-yl butyl ester
8	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl-

9	Bis(2-ethylhexyl) phthalate
10	o-Cymene
11	3-Carene
12	Isovaleric acid, 3-ethylphenyl ester
13	2-Tridecanone
14	2-Pentadecanone
15	2-Octene, 3,7-dimethyl-, (Z)-
16	9-Tricosene, (Z)-
17	Nonadecyl heptafluorobutyrate
18	1-Hexanol, 2-ethyl-

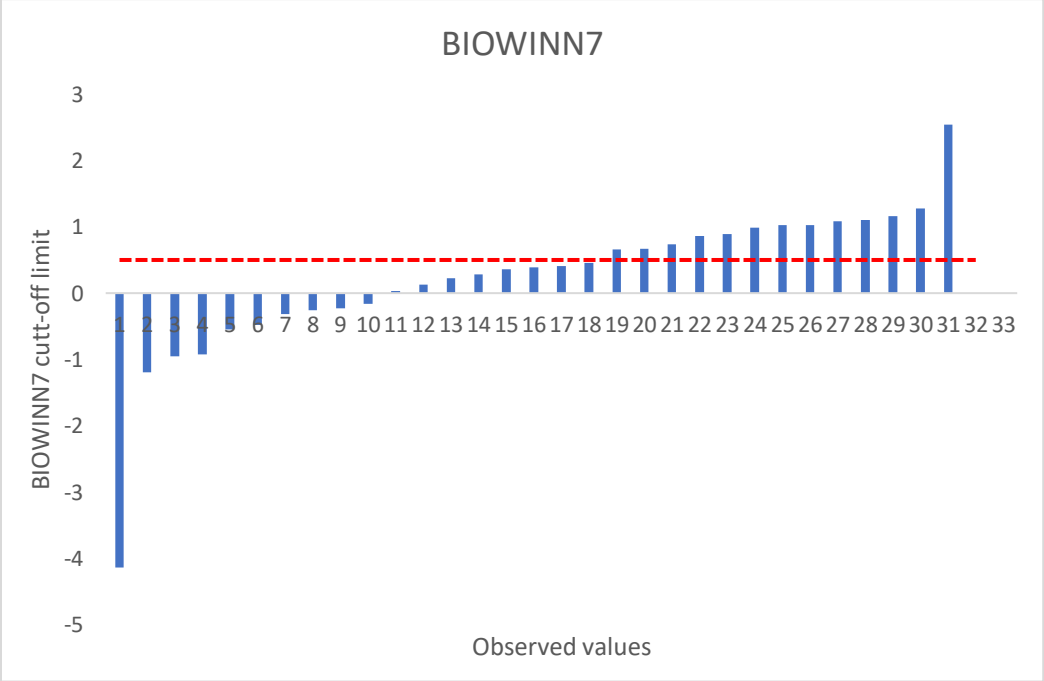


Figure 30: The graph showing BIOWINN7 results, 18 compounds show persistency

4.2.4.2 Biodegradability via BIOWINN for Outlet-15

4.2.4.2.1 BIOWINN1

BIOWINN1 limit value was less than 0.5(REACH2007). 03 out of 31 Chemicals are identified as persistent according to results from BIOWINN1. 03 chemicals are shown in table.

Table 19: BIOWINN1 Chemicals result Outlet-15

SN	Chemicals/DIBs
1	2,4-Difluorobenzene, 1-benzyloxy-
2	Dotriacontyl heptafluorobutyrate
3	Docosyl pentyl ether

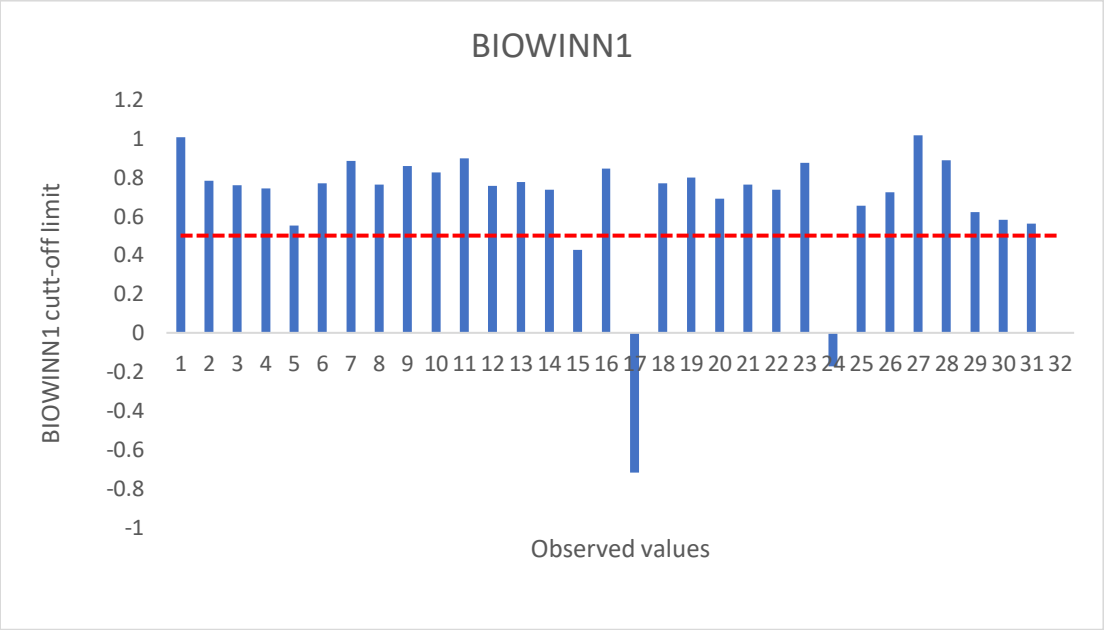


Figure 31: The graph showing persistency of the chemicals from BIOWINN1

4.2.4.2.2 BIOWINN2

BIOWINN2 model is for non-degradability of chemicals/DIBs if the value is less than 0.5. This non-linear biodegradation limit set by REACH 2007. Results reported that 10 out of 31 chemicals falls under category of persistent (REACH 2007) results from BIOWINN2 for these are less than 0.

Table 20: BIOWINN2 Chemicals result Outlet-15

SN	Chemicals/DIBs
1	2,4-Difluorobenzene, 1-benzyloxy-
2	Dotriacontyl heptafluorobutyrate
3	Hexacontane
4	Dotriacontane, 1-iodo-
5	Squalene
6	Docosyl pentyl ether
7	Hexacosane, 1-iodo-
8	Trihexadecyl borate
9	3-Methyltriacontane
10	1-Cyclopentyleicosane

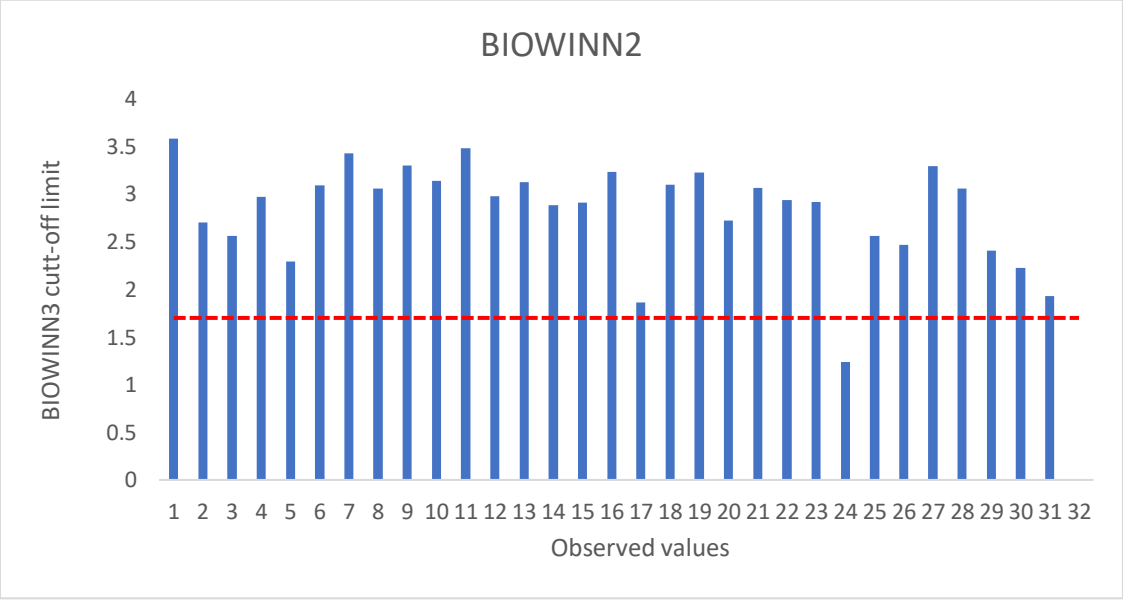


Figure 32: The graph showing persistency of the chemicals from BIOWINN2

4.2.4.2.3 BIOWINN3

BIOWINN3 limit value was less than 1.7, considered highly persistent. Reported from our results, 1 out of 31 chemical was highly persistent and non-biodegradable.

Table 21: BIOWINN3 Chemicals result Outlet-15

SN	Chemicals/DIBs
1	Dotriacontyl heptafluorobutyrate

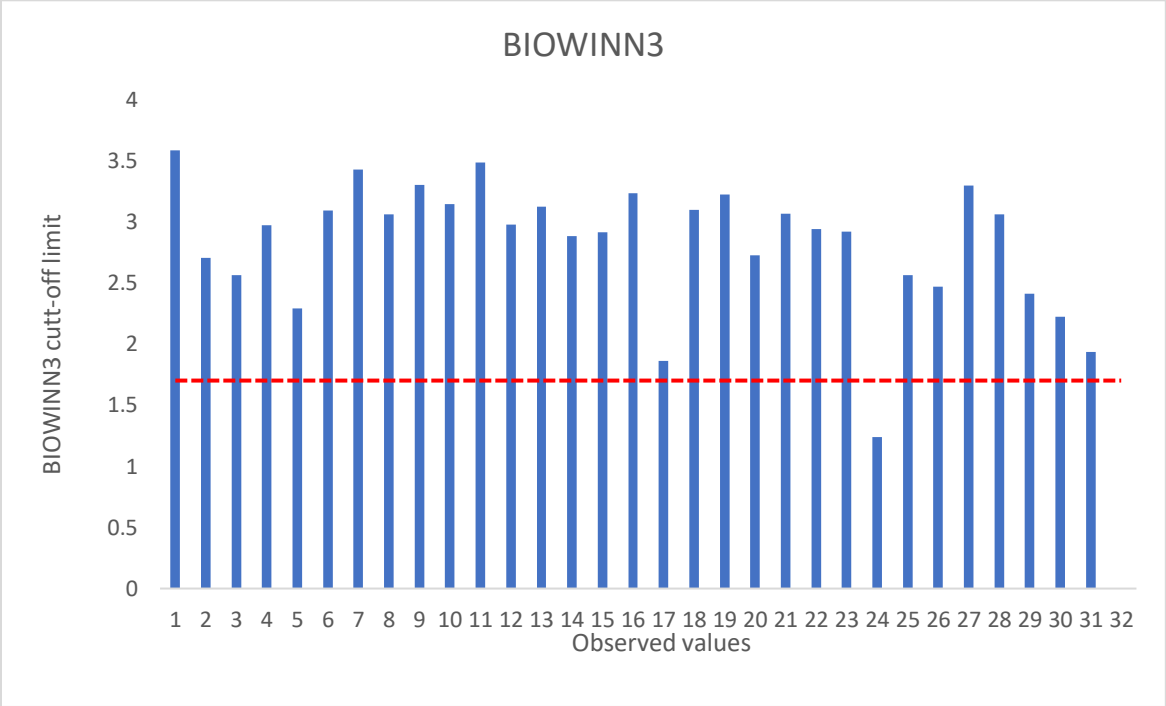


Figure 33: The graph showing BIOWINN3 results, 1 chemical shows persistency

4.2.4.2.4 BIOWINN4

BIOWINN4 limit value was less than 1.7 (highly persistent for BIOWINN4). No chemical was persistent in primary degradation.

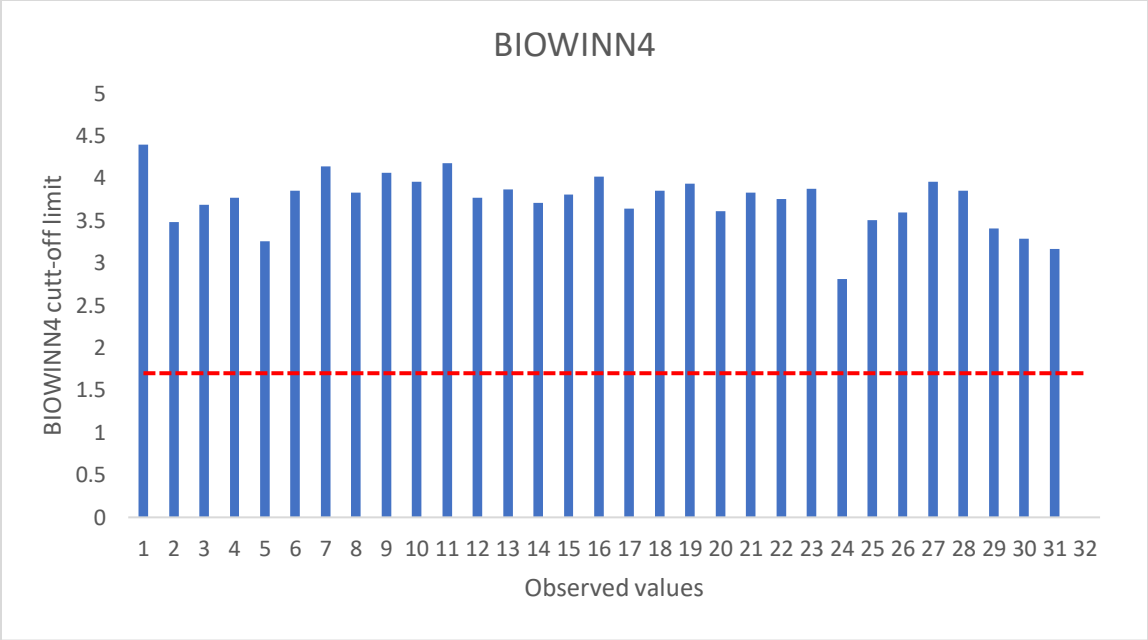


Figure 34: The graph showing BIOWINN4 results, no chemical shows persistent

4.2.4.2.5 BIOWINN5

BIOWINN5 limit value was less than 0.5(BIOWINN5 persistent). 7 out of 31 chemicals were found persistent.

Table 22: BIOWINN5 Chemicals result Outlet-15

SN	Chemicals/DIBs
1	Squalene
2	2,4-Difluorobenzene, 1-benzyloxy-
3	Naphthalene, 1,3-dimethyl-
4	Undecane, 2,6-dimethyl-
5	Dodecane, 4,6-dimethyl-
6	Undecane, 4-cyclohexyl-
7	Hexacosane, 1-iodo-

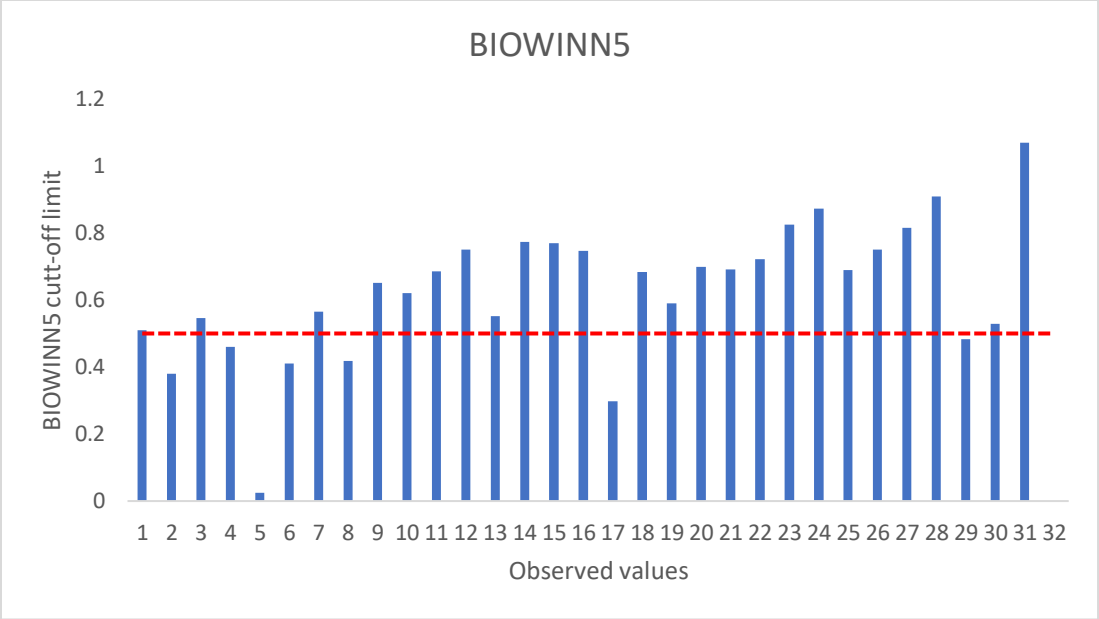


Figure 35: The graph showing BIOWINN5 results, 07 chemicals show persistency

4.2.4.2.6 BIOWINN7

BIOWINN7 limit value was less than 0.5(BIOWINN7 persistent). 20 of them are considered persistent as shown in table.

Table 23: BIOWINN7 Chemicals result Outlet-15

SN	Chemicals/DIBs
1	Octadecane, 5,14-dibutyl-
2	Naphthalene, 1,3-dimethyl-
3	Phthalic acid, 4,4-dimethylpent-2-yl isobutyl ester
4	Undecane, 4-cyclohexyl-
5	Squalene
6	Undecane, 2,6-dimethyl-
7	4-Undecene, 5-methyl-
8	Dodecane, 4,6-dimethyl-

9	3-Hexadecene, (Z)-
10	Eicosane, 10-methyl-
11	Decane
12	3-Pentadecanone
13	Undecane, 3-methylene-
14	Octadecan-4-one
15	Docosyl pentyl ether
16	Octadecane
17	2,4-Difluorobenzene, 1-benzyloxy-
18	1-Tridecene
19	2-Nonyne
20	1-Cyclopentyleicosane

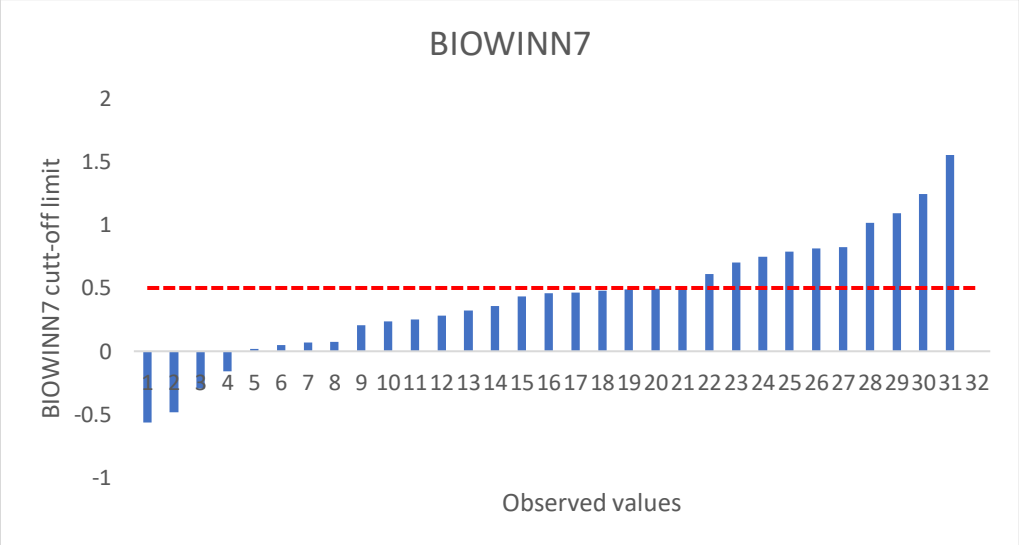


Figure 36: The graph showing BIOWINN7 results, 20 chemicals show persistency

4.2.4.3 Biodegradability via BIOWINN for Inlet-30

4.2.4.3.1 4.5.4.1 BIOWINN1

BIOWINN1 limit value was less than 0.5(REACH2007). 09 out of 32 Chemicals are identified as persistent according to results from BIOWINN1. 09 chemicals are shown in table.

Table 24: BIOWINN1 Chemicals result Inlet-30

SN	Chemicals/DIBs
1	Docosyl pentafluoropropionate
2	Prasterone-3-sulfate
3	Longifolene
4	Nonyl octacosyl ether
5	Octadecyl octyl ether
6	Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]-
7	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-
8	Caryophyllene
9	.beta.-Pinene

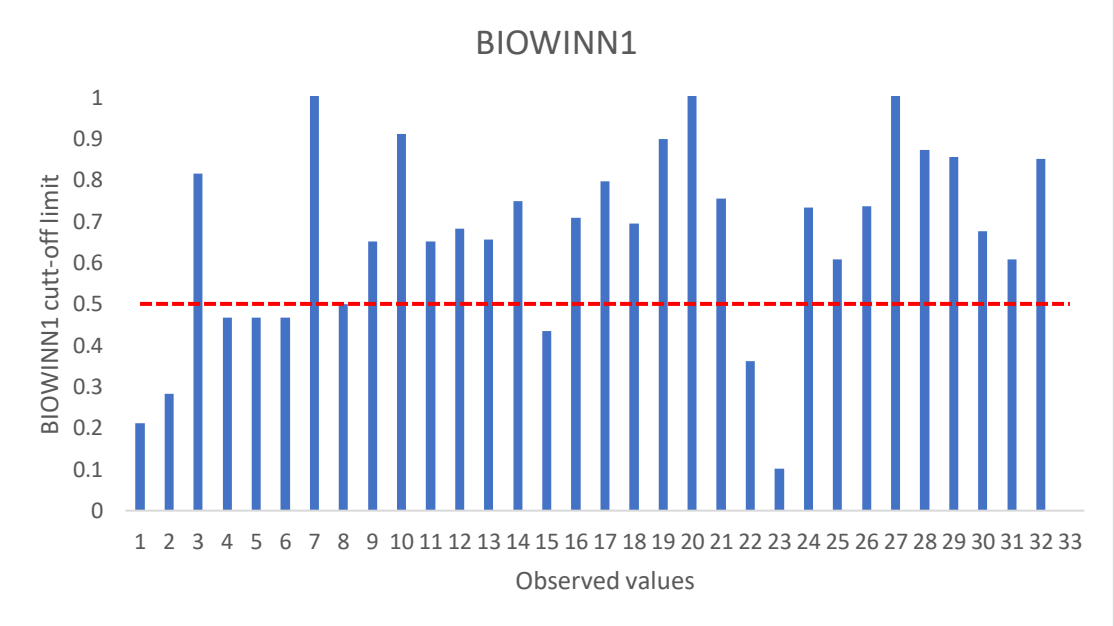


Figure 37: The graph showing persistency of the chemicals from BIOWINN1

4.2.4.3.2 BIOWINN2

BIOWINN2 model is for non-degradability of chemicals/DIBs if the value is less than 0.5. This non-linear biodegradation limit set by REACH 2007. Results reported that 14 out of 32 chemicals falls under category of persistent (REACH 2007) results from BIOWINN2 for these are less than 0.5.

Table 25: BIOWINN2 Chemicals result Inlet-30

SN	Chemicals/DIBs
1	Prasterone-3-sulfate
2	Docosyl pentafluoropropionate
3	Nonyl octacosyl ether
4	Longifolene
5	Octacosane, 1-iodo-
6	Octadecyl octyl ether
7	Tritetracontane
8	Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]-
9	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-
10	Caryophyllene
11	Octadecane, 1-chloro-
12	.beta.-Pinene
13	1,13-Tetradecadien-3-one
14	Tetratriacontane

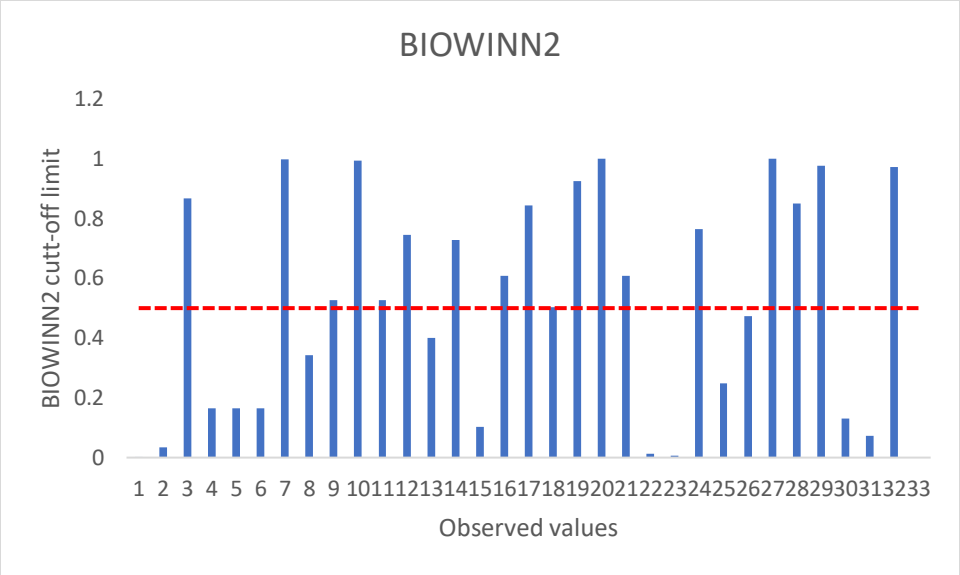


Figure 38: The graph showing persistency of the chemicals from BIOWINN2

4.2.4.3.3 BIOWINN3

BIOWINN3 limit value was less than 1.7, considered highly persistent. Reported from our results, no chemical was highly persistent and non-biodegradable.

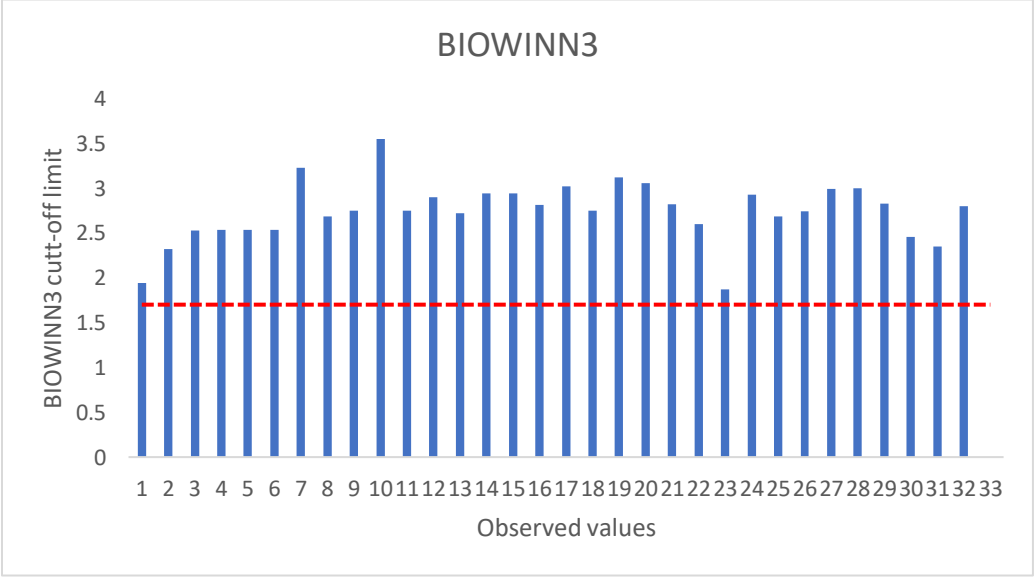


Figure 39: The graph showing BIOWINN3 results, no chemical shows persistency

4.2.4.3.4 BIOWINN4

BIOWINN4 limit value was less than 1.7 (highly persistent for BIOWINN4). No chemical was persistent in primary degradation.

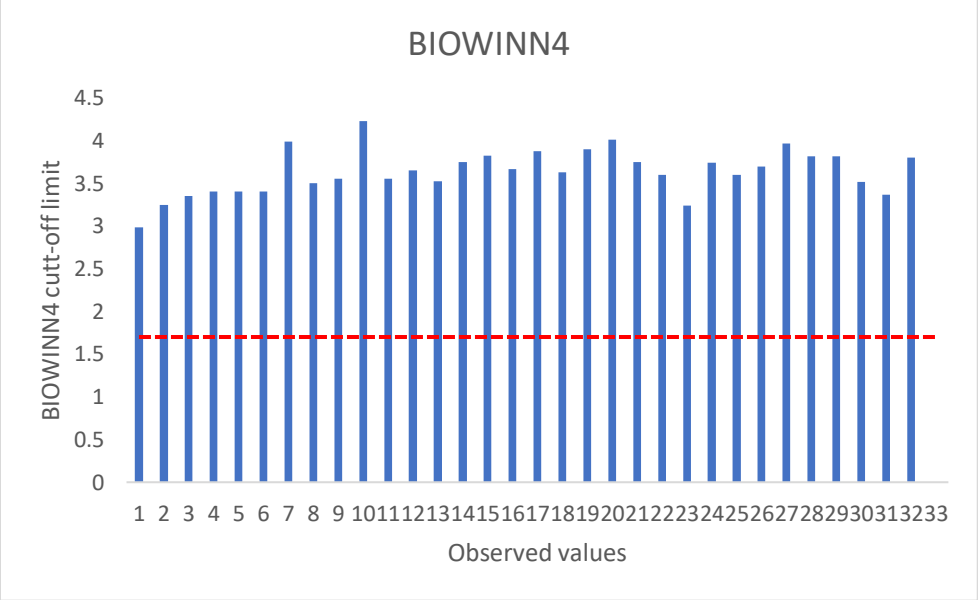


Figure 40: The graph showing the BIOWINN4 results, no chemical shows persistency

4.2.4.3.5 BIOWINN5

BIOWINN5 limit value was less than 0.5(BIOWINN5 persistent). 12 out of 32 chemicals were found persistent.

Table 26: BIOWINN5 Chemicals result Inlet-30

SN	Chemicals/DIBs
1	Prasterone-3-sulfate
2	Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-
3	Cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene-, [S-(R*,S*)]-
4	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-
5	.beta.-Bisabolene

6	Caryophyllene
7	Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]-
8	Longifolene
9	D-Limonene
10	Benzene, (1-butylheptyl)-
11	.beta.-Pinene
12	Octacosane, 1-iodo-

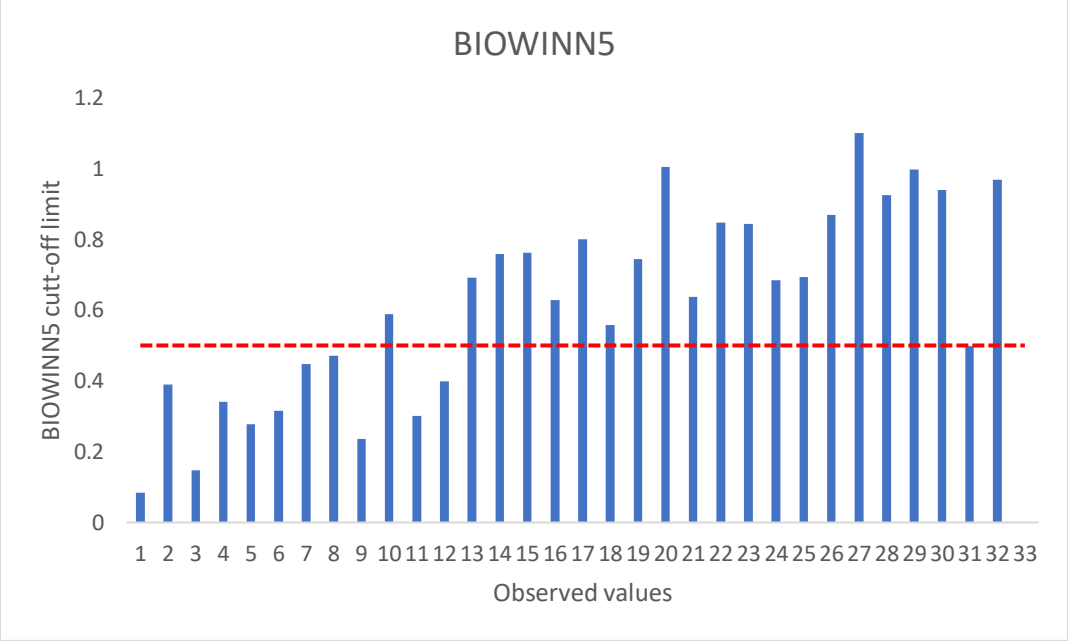


Figure 41: The graph showing BIOWINN5 results, 12 chemicals show persistency

4.2.4.3.6 BIOWINN7

BIOWINN7 limit value was less than 0.5(BIOWINN7 persistent). 15 out 32 considered persistent as shown in table.

Table 27: BIOWINN7 Chemicals result Inlet-30

SN	Chemicals/DIBs
1	Prasterone-3-sulfate
2	Longifolene
3	Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-
4	Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]-
5	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-
6	Caryophyllene
7	Benzene, (1-butylheptyl)-
8	.beta.-Pinene
9	Cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene-, [S-(R*,S*)]-
10	4-Octene, (E)-
11	.beta.-Bisabolene
12	D-Limonene
13	1,13-Tetradecadien-3-one
14	2-Hexadecanone
15	Octadecyl octyl ether

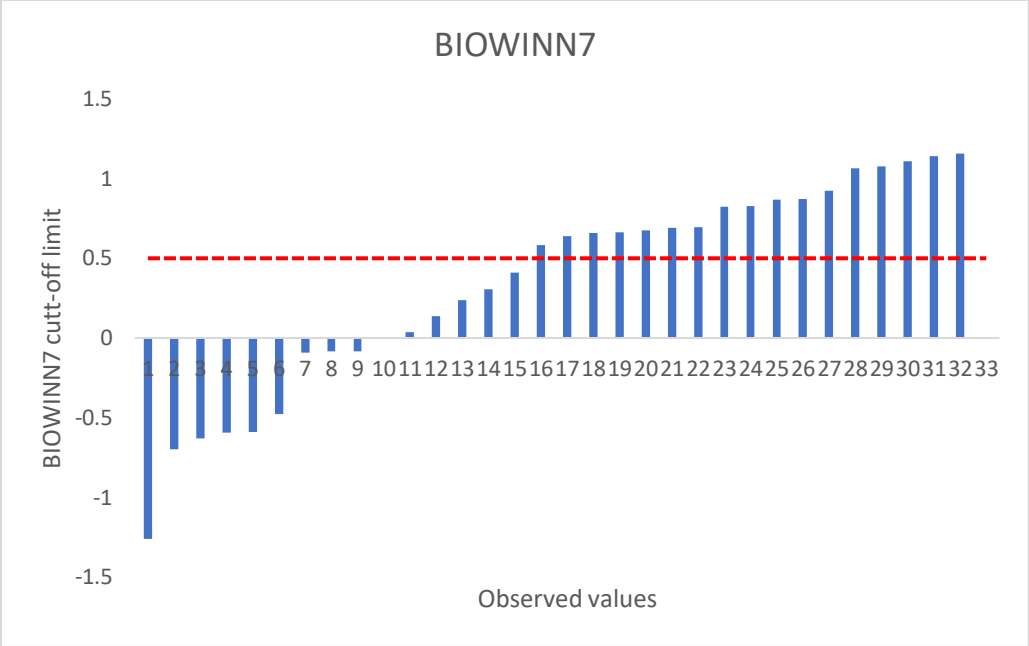


Figure 42: The graph showing BIOWINN7 results, 15 chemicals show persistency

4.2.4.4 Biodegradability via BIOWINN for Outlet-30

4.2.4.4.1 BIOWINN1

BIOWINN1 limit value was less than 0.5(REACH2007). 04 out of 22 chemicals are identified as persistent according to results from BIOWINN1. 04 chemicals are shown in table.

Table 28: BIOWINN1 Chemicals result Outlet-30

SN	Chemicals/DIBs
1	Benzene, 1,4-dichloro-
2	Eicosyl isobutyl ether
3	Pentyl triacontyl ether
4	Docosyl nonyl ether

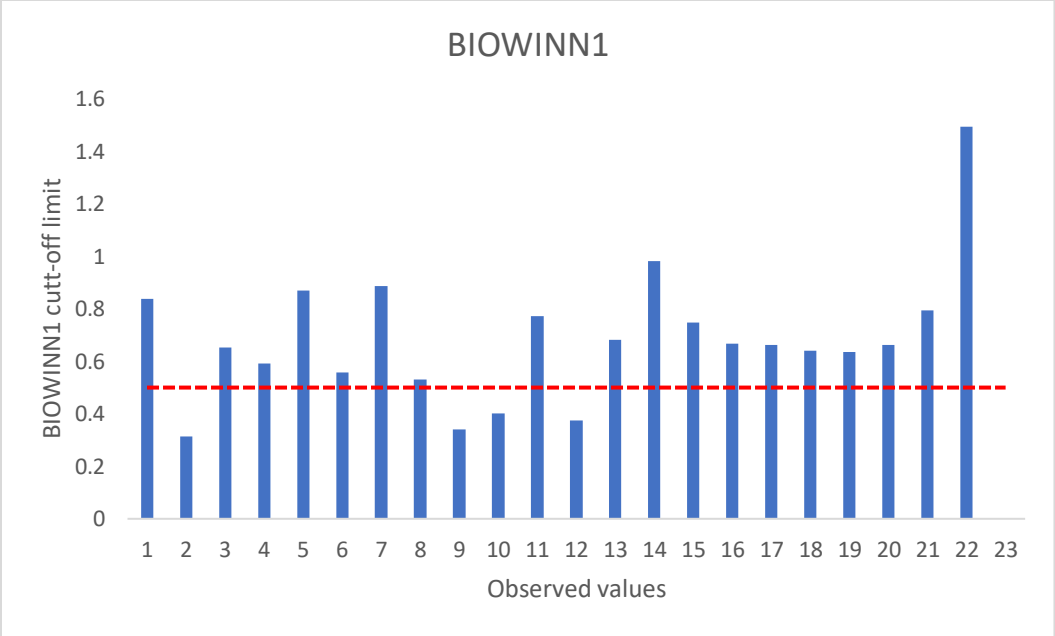


Figure 43: The graph showing persistency of the chemicals from BIOWINN1

4.2.4.4.2 BIOWINN2

BIOWINN2 model is for non-degradability of chemicals/DIBs if the value is less than 0.5. This non-linear biodegradation limit set by REACH 2007. Results reported that 12 out of 22 chemicals falls under category of persistent (REACH 2007) results from BIOWINN2 for these are less than 0.5

Table 29: BIOWINN2 Chemicals result Outlet-30

SN	Chemicals/DIBs
1	Pentyl triacontyl ether
2	Eicosyl isobutyl ether
3	Docosyl nonyl ether
4	Benzene, 1,4-dichloro-
5	3-Methyldotriacontane
6	2-Methylhentriacontane

7	3,3-Diethylheptadecane
8	3-Methyloctacosane
9	Nonacos-1-ene
10	2-Methylheptacosane
11	2-Methylpentacosane
12	3,3-Diethyltridecane

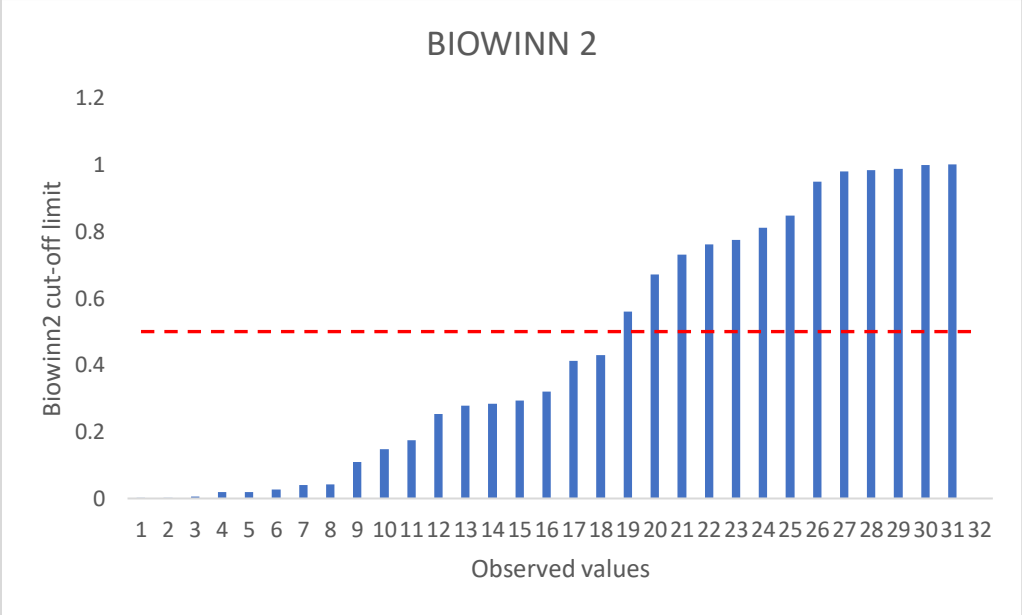


Figure 44: The graph showing persistency of the chemicals from BIOWINN2

4.2.4.4.3 BIOWINN3

BIOWINN3 limit value was less than 1.7, considered highly persistent. Reported from our results, no chemicals were found highly persistent and non-biodegradable.

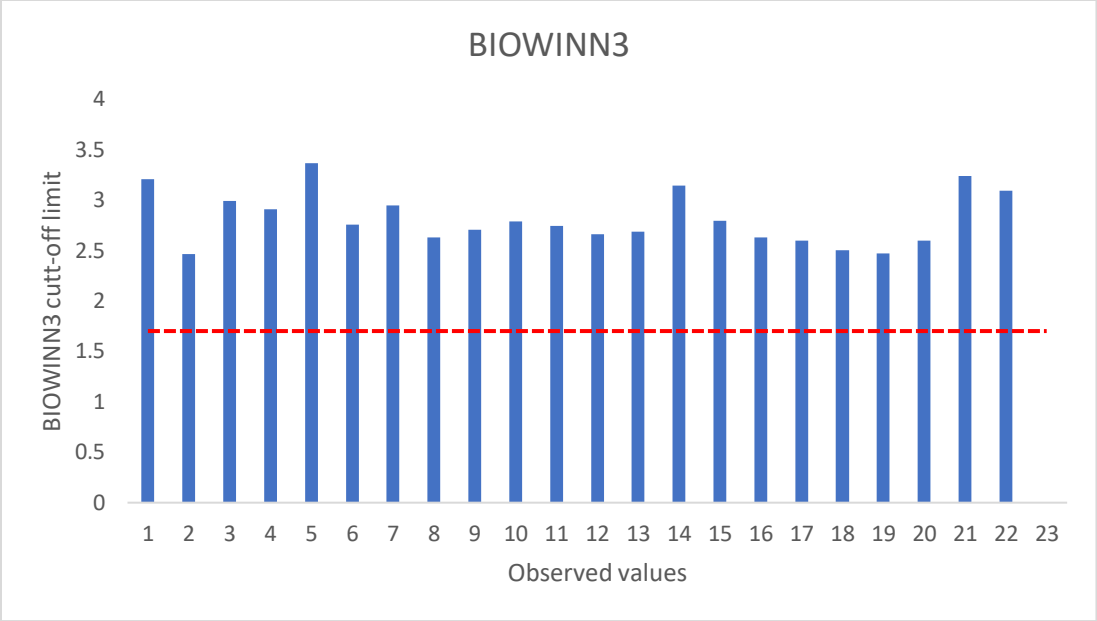


Figure 45: The graph showing BIOWINN3 results, no chemical shows persistency

4.2.4.4.4 BIOWINN4

BIOWINN4 limit value was less than 1.7 (highly persistent for BIOWINN4). No chemical was persistent in primary degradation.

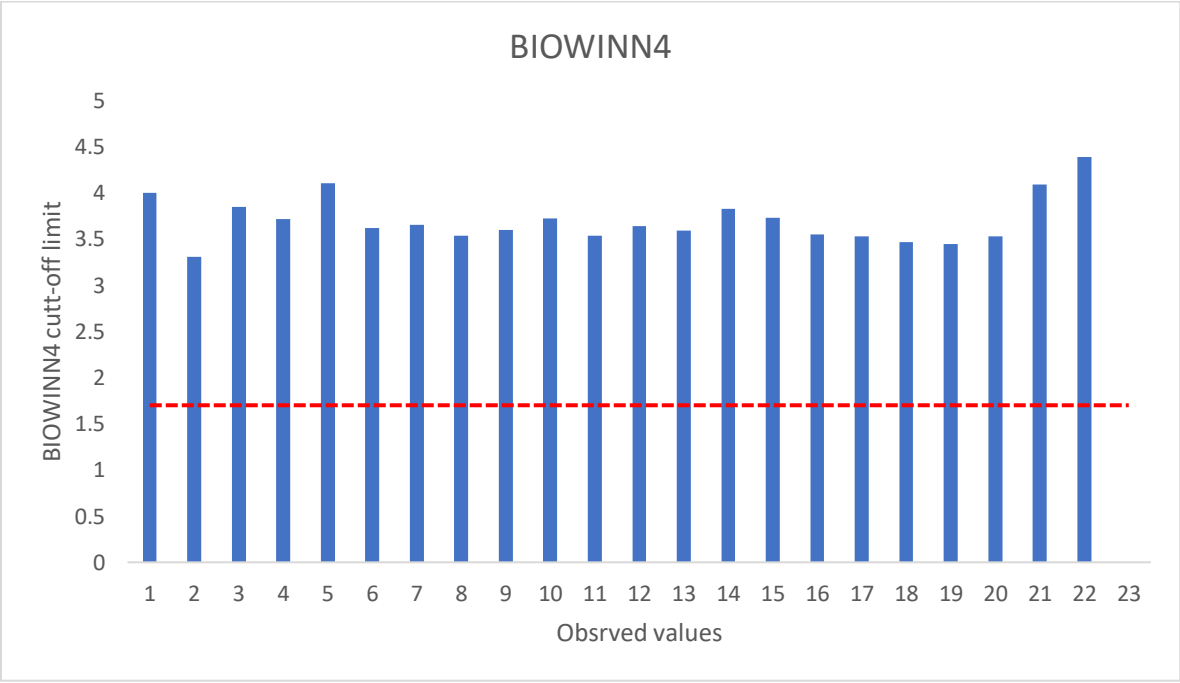


Figure 46: The graph showing BIOWINN4 results, no chemical shows persistency

4.2.4.4.5 BIOWINN5

BIOWINN5 limit value was less than 0.5(BIOWINN5 persistent). 03 out of 22 chemicals were found persistent.

Table 30: BIOWINN5 Chemicals result Outlet-30

SN	Chemicals/DIBs
1	Benzene, (iodomethyl)-
2	Benzene, 1,4-dichloro-
3	Tridecane, 6-cyclohexyl-

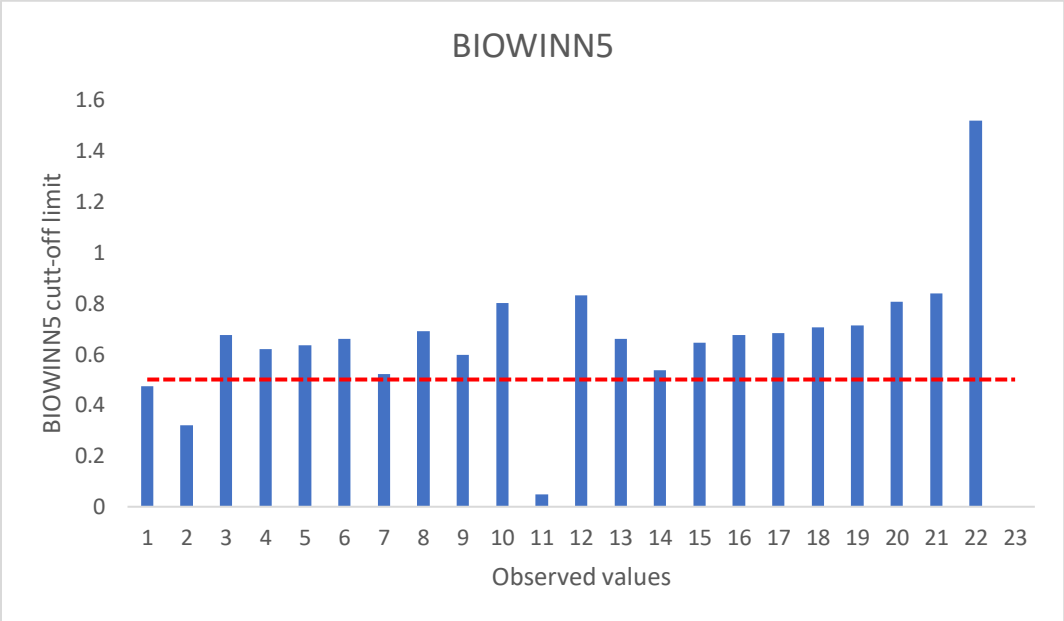


Figure 47: The graph showing BIOWINN5 results, 03 chemicals show persistency

4.2.4.4.6 BIOWINN7

BIOWINN7 limit value was less than 0.5(BIOWINN7 persistent). 09 out 22 considered persistent as shown in table.

Table 31: BIOWINN7 Chemicals result Outlet-30

SN	Chemicals/DIBs
1	Tridecane, 6-cyclohexyl-
2	Benzene, 1,4-dichloro-
3	5,5-Diethylpentadecane
4	Decane, 2,2-dimethyl-
5	7-Tetradecene, (Z)-
6	3,3-Diethyltridecane
7	Toluene
8	3,3-Diethylheptadecane
9	Eicosyl isobutyl ether

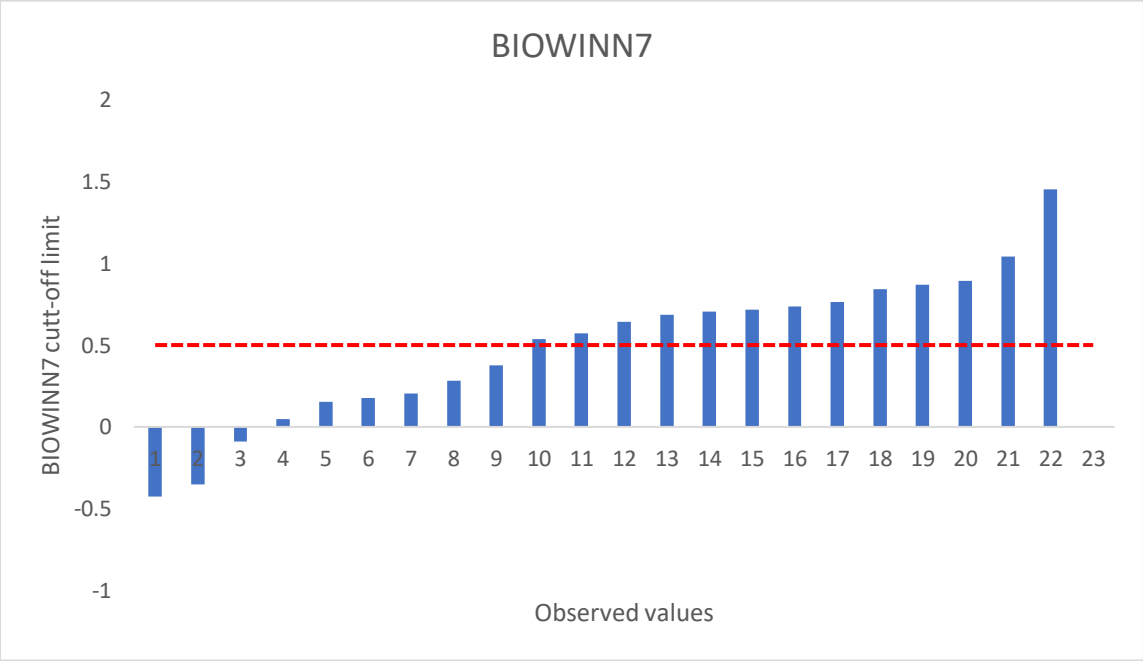


Figure 48: The graph showing BIOWINN7 results, 09 chemicalss show persistency

4.2.5 Result comparison of sample points:

From the results of different sample points it is clear that that different chemicals/DIBs were detected via GCMS at different points (excluding those which were detected in blank and field samples). List of those chemicals detected on all sample points is in the table.

Table 32: Chemicals present on all four sampling points (excluding blank and field sampling points)

S No.	Name	Blank	Field	O-15	I-15	O-30	I-30
1	1-Tetradecene	0	0	97	97	97	97
2	Octadecane	0	0	97	97	97	97
3	3-Pentadecanone	0	0	87	85	88	87
4	Octadecan-4-one	0	0	84	84	86	85

These chemicals were present on all sampling points, means filtration plant is unable to filter it. 1-Tetradecene is a serious eye and skin irritant. Octadecane May be fatal if swallowed and enters airways [Danger Aspiration hazard].

Table 33: Chemicals present on three sample points (O-30 excluded)

S No.	Name	Blank	Field	O-15	I-15	O-30	I-30
1	Squalene	0	0	88	95	0	95

Squalene is a chemical detected on all sample points except O-30. This chemical causes respiratory disorder if swallowed and can be fatal too if the amount swallowed is high. Its absence from O-30 may be due the short retention time on PDMS surface.

Table 34: Chemicals present on three sample points (I-30 excluded)

S No.	Name	Blank	Field	O-15	I-15	O-30	I-30
1	Naphthalene, 1,3-dimethyl-	0	0	83	88	86	0
2	Hexacontane	0	0	89	81	90	0

1,3-dimethyl- Naphthalene was present on all sampling sites except I-30. It is a serious environmental hazard for aquatic life (acute & long term hazard). Its absence from I-30 may be due to the reason of complex reactions going on when many chemicals come close together on PDMS surface.

Chapter 5

Conclusion and Recommendations

Conclusion

In present study, LDPE to water partition coefficients model was successfully developed which was used for non-targets screening of organic containments present in MBR wastewater treatment plant, Islamabad. Identification and location of MBR plant was kept anonymous due to commercial sensitivity and to avoid conflict of interest. Different experimental test via EPI-SUITE and UFZ-LSER were performed for screening of chemicals/DIBs.116 chemicals/DIBs were selected on all four sample points and their risk assessment was also done.

Chemicals that were identified from wastewater treatment plant such as Bis(2-ethylhexyl) phthalate may damage fertility, Naphthalene, 1,3-dimethyl-, Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-, 2-Tridecanone and 2-Buten-1-one, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)- have serious hazardous effects and very toxic for aquatic life Octacosanol is specifically caused skin irritation, serious eye irritation and respiratory irritation. In short it was concluded that the disinfected waste water is still not safe for potable and non-potable uses and can causes adverse health effects including cytotoxicity, carcinogenicity, mutagenicity, miscarriage, and even birth defects.

Limitation of our study are

- Chemicals/DIBs were not quantified, which need pure standards.
- We did not use performance reference compounds on passive samplers, which could have given better picture
- We only used Low density polyethene (LDPE). Other passive samplers such as Silicon, POM, PA could have been used as additional classifiers to improve the detection of compounds. However, since the results are still alarming therefore the conclusion can be derived with confidence based on this study.

Recommendations

Other disinfected methods should be used like the ultraviolet disinfection as it is not known to produce carcinogenic or toxic by-products or taste and odor problems. Different methods can also be used like removal or polishing method to clean the chlorination by product out of the waste water. The suggested method is that of activated carbons or TNTs.

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