NON-TARGETTED SCREENING OF WASTEWATER DISINFECTION BY PRODUCTS USING SILICONE PASSIVE SAMPLERS

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DEDICATION

This thesis is dedicated to my affectionate parents.

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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

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ABSTRACT

To reuse or not to reuse treated municipal wastewater effluent is still an open question. Answer of this question lies in detailed health and environmental risk-benefit analysis. Circularity of water is an emerging idea that is at the very heart of water conservation. Wastewater treatment offers treated wastewater with a quality that should be beneficial for reuse. Typically, wastewater treatment involves several steps such as biodegradation of organic matter, precipitation of suspended solids, nutrients removal, and disinfection to inactivate or kill pathogenic microorganisms. However, disinfection process produces a wide-range of chemicals referred to as disinfection by-products (DBPs), which are of health and environmental concern. Only a dozen of DBPs are regulated for monitoring in the developed world. Whereas the number of DBPs produced during disinfection may be in thousands. This makes complete health and environmental risk-benefit analysis of disinfected effluent a daunting challenge for monitoring agencies.

In this study, I illuminated a pathway which helps scientist overcome the challenge of resolving the complexity around the question of safe reuse of wastewater. I integrated innovative passive sampling, chromatographic, mass spectrometric and computational approaches for monitoring the complete spectrum of DBPs.

I started with the developing an estimation model to predict polydimethylsiloxane (PDMS)-water partition coefficient: a property needed to calculate the concentration in water phase by measuring concentration on passive sampling phase (PDMS). The model, which was based on 2-parameters linear free energy relationship (2p-LFER) between partition coefficients of PDMS-water, and octanol-water and air-water systems, exhibited $R^2 = 0.96$ and $RMSE = 0.38$ log unit.

Next, PDMS passive samplers deployed at Al-Wathba 2 Wastewater Treatment Plant, Abu Dhabi, United Arab Emirates for 30 days at the disinfection (chlorination) tank. Passive samplers were analyzed using comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-ToF-MS) technique at National Institute for Environmental Studies, Tsukuba, Japan. The raw chromatograms were deconvolved into five layers using Non-Negative Matrix Factorization (NMF)-based algorithm. Filters such as occurrence in replicates, absence in field blank, match score with the reference library were used to increase in the confidence of detection of DBPs. As a result, I screened 32 DBPs which might be present in the wastewater effluent with high probability.

Lastly, I carried out the risk assessment of detected DBPs for the attributes of persistence, bioaccumulation and toxicity (PBT) using U.S. Environmental Protection Agency's Estimation Program Interface (EPI Suite™) version 4.11. Several DBPs detected in the wastewater were flagged for the PBT concern, indicating the wastewater reuse for agriculture and landscaping might not be a safe practice. This indeed calls for further studies for targeted quantification and in-depth health and environmental risk assessment.

Chapter 1

Introduction

1.1 Background

With the rapid development of the world, many countries in the world are confronting the problem of fresh water supply and shortage of water resources and are becoming unable to meet water demand satisfactorily (Lyu, *et al.*, 2016). Increasing demand for water is because of rapid population growth, which may increase agricultural irrigation demand, pollution of surface and underground water, uneven water resources distribution and recurrent droughts worldwide due to global warming (Asano & Cotruvo, 2004). Moreover, the water crisis has listed as a global risk by the World Economic Forum for the world's population which have many devastating effects (Roccaro & Verlicchi, 2018). New sustainable water management program is the need of the hour. 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 (Metcalf, *et al.*, 2007). The reuse of waste water can fulfill many necessities such as irrigation requirements, industrial use, civil use and even drinking water demand. The UN Global Water Report in 2017, stated that wastewater reuse remains an available source for water supply and its pollution (Shahzad, *et al.*, 2017).

1.2 Waste Water 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 waste water 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 (Yehya, 2015).

Usually two type of treatment plants are present that is biological waste water plant and physical or chemical waste water plant. 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 (Akpor & Muchie, 2011).

1.3 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 (Burton, *et al.*, 2014). 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 (Bellar, *et al.*, 1974; Rook, 1974). DBPs have adverse health effects such as carcinogenicity, miscarriage, mutagenicity, cytotoxicity and in some cases causes even birth defects (Villanueva, *et al.*, 2015).

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 (Górecki & Namieśnik, 2002).

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 (Madrid & Zayas, 2007).

1.5 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. 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) (Jones, *et al.*, 2015). 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 (C_{free}) of chemical present in aquatic environment and help in measuring the chemical activity of containment in trace amount(Schäfer, *et al.*, 2008; Seethapathy, *et al.*, 2008) Furthermore, passive sampling results can be used as a measure of chemical bioaccumulation, bioavailability and ecotoxicity (Cui, *et al.*, 2013; Jahnke, *et al.*, 2008).

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) (Fries & Zarfl, 2012; Turgut, *et al.*, 2017), low density polyethylene (LDPE) film (Lu, *et al.*, 2004), polyoxymethylene (POM) devices (Beckingham & Ghosh, 2013), polyurethane foam (PUF) device (Nabi & Arey, 2017; Tuduri, *et al.*, 2006) and polydimethylsiloxane (PDMS) fibers (Zhang, *et al.*, 2014).

1.6 PDMS (Silicone) Passive Sampling

Polydimethylsiloxane (PDMS), also recognized as dimethylpolysiloxane or polydimethylsiloxane. It belongs to a group of compounds polymeric organosilicon generally known as silicones. PDMS is the utmost employed silicon-based organic polymer and is recognized for its uncommon flow properties. PDMS was demonstrated by the RIKZ company in the Netherlands as an excellent passive sampler material because of its high partition coefficient and low transport resistance, while having only a few identified disadvantages (Rusina, *et al.*, 2007). As compare to the bi-phasic SPMD, PDMS are single-phase samplers that are easy to construct, easy to incorporate into PRCs, and provide a simplified version of the contaminant absorption model (Smedes, *et al.*, 2007). Silicone rubber passive sampling devices are getting increasingly important in monitoring non-polar organic compounds.

The principle and feasibility of the proposed research were demonstrated by using 32 probe compounds and PDMS membrane-coated fibers. The system coefficient approach was used to study the solvent effects on the PDMS absorption of chemicals.

1.7 Analytic Methods for DBPs Analysis

There is a need for advance research to enhanced 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 PDMS samples were analyzed by two-dimensional gas chromatography (GC × GC) time of flight - mass spectrometer (TOF-MS)

1.8 Non target screening using GC×GC–Time of Flight - Mass Spectrometer (TOF-MS)

Non-target analysis can detect and identify a large number of harmful compounds that may be present in the environmental sample without prior information and does not require strict parameter for analysis. Whereas target analysis often does not provide a comprehensive overview of organic pollution patterns and needs a reference standard for analysis. Non-target screening

helps in providing information regarding target analysis and also improves identification rules to recognize chemicals of interest, which is important for evaluating mixtures.

Two-dimensional gas chromatography (GC x GC) is an emerging analytical technology that can easily detect and analyze a number of polar and semi-polar chemicals or compounds (Zushi & Hashimoto, 2018). GC×GC combined with high-resolution time-of-flight mass spectrometry permits for non-target analysis of chemicals. The GC×GC-MS can identify group types of chemicals using both GC×GC and mass spectrometry separation (Ochiai, *et al.*, 2011). They also have the enhanced detection capability because of the signal improvement after zone compression and large separation capacity. The most widely suitable MS for GC × GC is the high speed TOF-MS with unit-mass resolution. This is because the data acquiring rate of TOF-MS for very small peak width is over 100 Hz which is consider as ideal rate (van Deursen, *et al.*, 2000).

1.9 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 (Card, *et al.*, 2017).

1.10 Objectives of study

- To develop a robust, simple and powerful estimation model to predict PDMS to Water partition coefficients.
- To develop a reliable non-targeted screening approach to monitor disinfection by-products after chlorination of treated waste water.
- Risk assessment of detected DIB'S (disinfection by-products) for the attributes of persistence, biodegradation and toxicity using EPI suite (estimation modelling)

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 (Asano & Cotruvo, 2004).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 (Metcalf, *et al.*, 2007).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 (Anderson, 2003). 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 (Holden, *et al.*, 2014).

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 (Akpor, *et al.*, 2014).

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(Akpor & Muchie, 2011).

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(Abu-Orf*, et al.*, 2013).Ultraviolet radiation also applied for disinfection but only efficacious in low-polluting waters to avoid lamp infestation and provide proper lighting(Schwab, 2009). 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(Kitis*, et al.*, 2003). 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 (Golfinopoulos & Nikolaou, 2005).

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

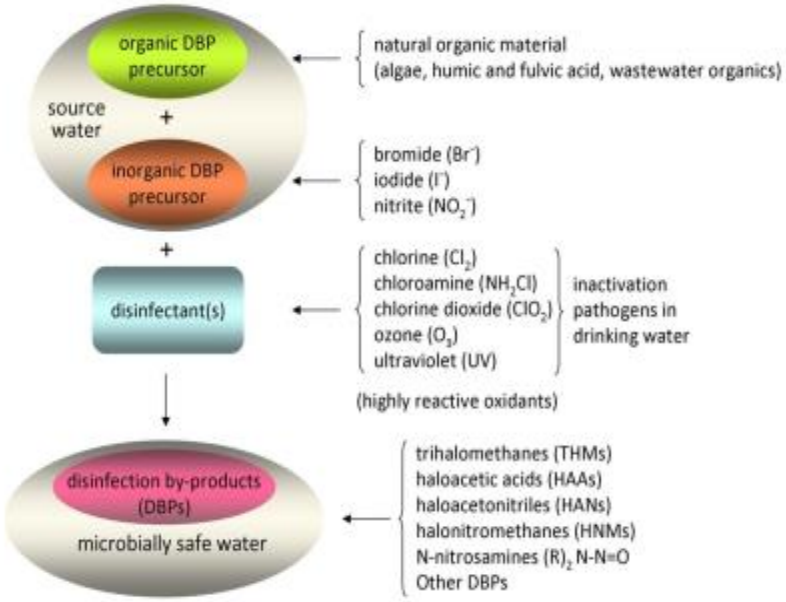


Figure 2.1 Schematic diagram of the formation of DBP from organic and/or inorganic and disinfectants precursors. Adopted from (Krasner, 2009)

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 (Bellar, *et al.*, 1974; Rook, 1974). 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 (NCI, 1976). Also, in the later 1970 it was shown that organic substances in drinking water causes mutation as was proven by

experiment on *Salmonella (*Loper, 1980*).* 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(Richardson, *et al.*, 2007). 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 (Allan, *et al.*, 2006). 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 (Greenwood, *et al.*, 2007). 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(Madrid & Zayas, 2007).

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 (Kot-Wasik, *et al.*, 2007).

- 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 (Leynen, *et al.*, 1999).

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 (Vrana, *et al.*, 2005).

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(Górecki & Namieśnik, 2002).

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.

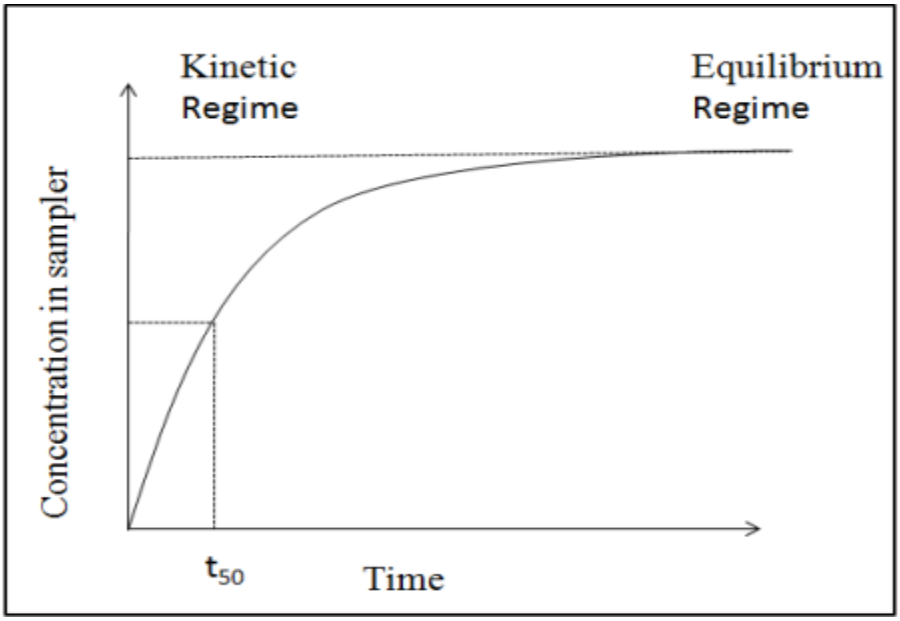


Figure 2.2 The general uptake in contaminant concentration over time for most passive samplers. Adopted from (Namieśnik, *et al.*, 2005)

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 k_1 is the uptake rate constant and k_2 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 (Kot-Wasik, *et al.*, 2007).

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:

$C_S = C_W \frac{k_1}{k_2} = C_w$ K Eqn.2.2

Knowing the phase water partition coefficient (K) can allow to estimate the concentration of dissolved analyte (Mayer, *et al.*, 2003).

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 (Harte, 2002).

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 (k_1) 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 (Stuer-Lauridsen, 2005).

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 (Booij, *et al.*, 2006). 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 different 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 (Stuer-Lauridsen, 2005). 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 (Gale, 1998; Pawliszyn, 2003). By using two different methods we can find the phase water partition coefficient (K), substance specific kinetic constants k_1 and k_2.

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 (Cussler, 2009). 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 (Huckins, *et al.*, 1999; Luellen & Shea, 2002). 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 (Vrana & Schüürmann, 2002).

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 (Huckins, *et al.*, 2002).

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 (Mitina, 2015). 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 (Huckins, *et al.*, 2006).

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)(Turgut, *et al.*, 2017), low density polyethylene (LDPE) film (Lu, *et al.*, 2004) (Fries & Zarfl, 2012), polyoxymethylene (POM) devices (Beckingham & Ghosh, 2013), polyurethane foam (PUF) device (Tuduri, *et al.*, 2006) (Nabi & Arey, 2017) and polydimethylsiloxane (PDMS) fibers (Zhang, *et al.*, 2014).

The application of polydimethylsiloxane (PDMS) in adsorption sampling and sample preparation is reviewed.

2.7 PDMS (Silicone) Passive Samplers

Polydimethylsiloxane (PDMS), also recognized as dimethylpolysiloxane or polydimethylsiloxane. It belongs to a group of compounds polymeric organosilicon generally known as silicones. PDMS is the utmost employed silicon-based organic polymer and is recognized for its uncommon flow properties. PDMS was demonstrated by the RIKZ company in the Netherlands as an excellent passive sampler material because of its high partition coefficient and low transport resistance, while having only a few identified disadvantages (Rusina, *et al.*, 2007). As compare to the bi-phasic SPMD, PDMS are single-phase samplers that are easy to construct, easy to incorporate into PRCs, and provide a simplified version of the contaminant absorption model (Smedes, *et al.*, 2007). Silicone rubber passive sampling devices are getting increasingly important in monitoring non-polar organic compounds.

The principle and feasibility of the proposed research were demonstrated by using 32 probe compounds and PDMS membrane-coated fibers. The system coefficient approach was used to study the solvent effects on the PDMS absorption of chemicals and was compared with Abraham solvation model.

2.7.1 Abraham Solvation Parameter Model

Abraham's solvation parameter model is the utmost suitable methods for analyzing and predicting partition and adsorption coefficients (Abraham, *et al.*, 1993; Abraham, Platts, *et al.*, 1999). 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 PDMS application, the logarithm of the solute's water-to fiber sorption coefficient, log $K_{PDMS-water}$ 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 (Abraham, 1993; Abraham, Le, *et al.*, 1999).

2.7.2 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 (Johanson, 2010).

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 (Schwarzenbach, *et al.*, 2016). 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 (Lohmann, *et al.*, 2011).

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 (Voutsas, 2007).

2.8 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 (Hernández, *et al.*, 2011).

2.9 Analytical Methodologies for Non-Targeted Screening of DBPs

There is a need for advance research to enhanced 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 (Weinberg, 2009).

2.9.1 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) (Lebel & Williams, 1995). In particular, in the discovery of DBPs in drinking water the GC-MS method plays a key role (Richardson, 2002). 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 (Brack, *et al.*, 2016; Richardson, 2002) .

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 (Zwiener & Richardson, 2005). It is believed that these species are the reason for an important part of the inexplicable TOX and misplaced DBP parts.

2.9.2 Emerging Analytical Technologies (two-dimensional gas chromatography (GC × GC)

Two-dimensional gas chromatography (GC x GC) is an emerging analytical technology that can easily detect and analyze a number of polar and semi-polar chemicals or compounds (Zushi & Hashimoto, 2018). Liu and Phillips discovered GC × GC 21 years ago (Liu & Phillips, 1991).

GC x GC allowed each sample constituent to enter two separate phases. In GC.GC the interface, also called as the modulator, incessantly take samples to the primary effluent and then delivers the primary effluent as a pulse to the head of the secondary column. The interval in between the sample transmissions is called as the modulation period. The width of the peak appearing from the primary column is usually analogous to modulation period. This permits to maintains most of the resolution developed by the primary column, but then it also means that the modulation time must be less than retention time range in the secondary column to avoid the mixing of components that are assorted by the primary column (Mitrevski & Marriott, 2012). Modulators are exclusive to GC×GC and they are still the subject of vivid exploitation. GC x GC employs two size resolutions to all sample components, but the secondary separation is performed on a time scale that is typically three orders of magnitude smaller as compare to the primary separation.

In utmost times, the primary separation is alike to a single column GC separation with elevated temperature, while the secondary separation is basically a series of rapid isothermal analyses performed with elevated temperatures (Khummueng, *et al.*, 2006).

In this study GC×GC combined with high-resolution time-of-flight mass spectrometry to achieve non-target (full scan mode) analysis of organic containments.

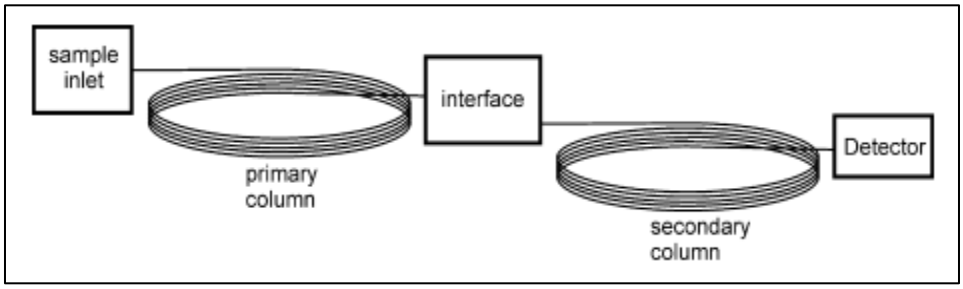


Figure 2.3. Schematic of a basic 2-D gas chromatograph. Adopted from (Seeley & Seeley, 2012)

Chapter 3

Materials and Methods

This chapter describes detailed information about materials and methods that are used for research purposes. The available data is analyzed by authentic computing software on the computer. Current study was performed in two phases, in first part robust computational model for the estimation of PDMS to water partition coefficients was developed. Second part of research was the experimental in which non targeting screening of DBPs was done using PDMS sampler and GC×GC time of flight MS.

COMPUTATIONAL METHODOLOGY

3.1 Data Acquisition

Experimental data of current research for biological phases involving multiple chemicals sets were taken from the published literature(Abraham & Ibrahim, 2006; Endo, *et al.*, 2011; Endo, *et al.*, 2012; Geisler, *et al.*, 2012). In order to avoid over-representation, the arithmetic mean was used to average multiple values reported by a single chemical. From the data set all inorganic values were excluded. The EPI Suite ^{TM} 4.1 – KOWWIN v1.68, Henry Win v3.20, KOCWIN v2.00 (US-EPA, 2018) was used for obtaining estimated values of Kow, K_{aw}, and $k_{oc.}$ The diversity of chemical groups employed in the study can be measured in term of wide range covered by Kow (8 orders of magnitude), Kaw (7 orders of magnitude), and K_{oc} (5 orders of magnitude).

3.2 Statistical analysis

R statistical environment (version - 3.5.3) (R (3.5.3), n.d.) was used to perform the statistical analyses such as multiple linear regression, Principle Component Analysis (PCA) and cross-validation. If the calculated t value of the variable coefficient is less than or equal to the critical t value reported at the significance level (p value < 0.05) at a given degree of freedom, then the contribution of the variable in the model is considered statistically significant (Dawid, 1977). To select the optimal number of variables in the model the Akaike Information Criterion (AIC) was used. AIC penalizes the model when adding new variables that do not provide enough information

for the model (Bozdogan, 1987). Therefore, the model with the smallest AIC value was selected. Correlation analysis was also performed to check for any overlapping information brought by different descriptors.

After selecting the variables, the regression diagnosis (Studentidized Residuals, Hat Values and Cook's Distance) was analyzed to determine the influential values in each of the models or methods presented in this study. The standard error of the fitting coefficients in to each model was calculated using a bootstrapping algorithm. Several models were formulated for each data set using various descriptor combinations. To evaluate the model's predictive power following cross-validation tests were performed: K-Fold, repeated K-Fold (r = 10), Leave-One-Out (LOO), and bootstrapping (n = 1000) , the data set is randomly divided into training and test sets for the internal validation of each model and external validation. To study the dimensionality in all data sets Principal Component Analysis (PCA) was performed.

3.3 Principle Component Analysis (PCA)

Principal component analysis is a dimensionality reduction tool that specifies important variables in a model. It is the data compression method and it highlights the more important set of variables which remain uncorrelated throughout the analysis. This analysis is used to develop orthogonal variables for additional processing, so it is a technique for obtaining maximum information without reduction of any information.

3.4 Cross Validation Techniques

Following tests were performed for cross validation.

3.4.1 Leave - One Out Cross Validation

In this method, an observation is removed from the data set and regression is performed on the remaining data sets. This exercise carried out numerous times and the final results were compared with the statistical indicators of the MLR model to test how close the results were to the best fit of the actual model. The R2 value is usually considered an indicator.

3.4.2 K - Fold Cross Validation Technique

This is another independent verification test. The model was validated by various fold and the final results were displayed within range the best fit indicator of the MLR analysis, which was done on the actual data set. It is employed for the internal validity of the model.

3.4.3 Repeated K - Fold Cross Validation Technique

In this method, cross-validation of the model confirms that the target chemical falls within the field of applicability and the model is valid internally by ensuring that the target chemical is clearly present multiple times.

3.4.4 Bootstrapping Technique:

Bootstrapping independent test is applies to check the internal validity of the model. In this method, the values from the results of RMSE and R2 are compare with the values of the original model by performing random sampling of the data set (N = 1000).

EXPERIMENTAL METHODOLOGY:

3.5 Sampling Locations

The Al Wathba 2 wastewater treatment plant built in the desert outside Abu Dhabi was selected for this study. This Plant has a treatment capacity of 300,000 m3 per day and is designed for a Population Equivalent of over 1,500,000 units. Total tolerance capacity of plant is 345,000 m3/d. Peak flow to pre-treatment of plant is 25,000 m3/hour.

3.6 PDMS Sample Preparation

For sample preparation silicone sheets (which are termed as PDMS) were taken. Each strip was cut precisely into strips of 6 inch by 2.5 inches. 3 strips were taken for 3 replicates and one for blank. Strips were washed or sterilized to make sure there was no cross contamination for accuracy of results.

For washing deionized water were taken in 100ml beaker. Then strips were immersed into the jar and secured it with aluminum foil. Then the jar was kept in shaker for 24hrs at 130 rpm. Same procedure was repeated it thrice by changing the deionized water with fresh deionized water. second washing was done using ethyl acetate. For this ethyl acetate was taken in 100ml amber

glass jar. Then the strips were immersed into the jar and secured the jar with aluminum foil. Then placed it on shaker for 24hrs at 130 rpm. After 24hrs, strips were removed and solvent was replaced with fresh solvent (ethyl acetate) and kept it for another 24hrs at 130rpm. The same procedure was repeated for third day. At the end of third wash, the strips were carefully removed with metallic forceps (sterilized with ethyl acetate) and the solvent was discarded properly. Then each strip was placed on aluminum sheet and was cleaned and dried with alcohol swabs, then the strips were secured and wrapped properly in aluminum foil and blank sample was wrapped separately in foil and was stored in the freezer of the lab.

The field replicates were transported to the field in icebox and deployed with the help of metallic gauze on the post-chlorination phase of waste water treatment plant.

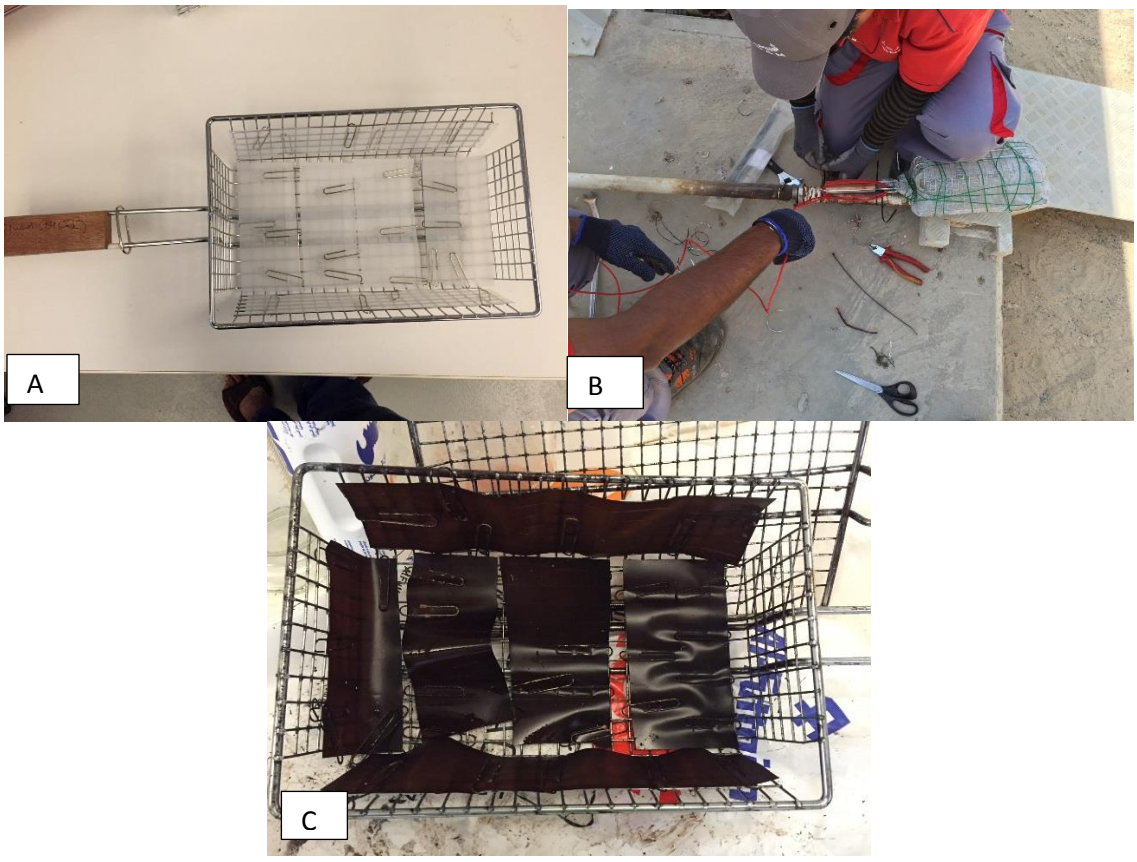


Figure 3.1 Post and pre-deployment of PDMS into Field (A) Before deployment into treated waste water, (B) Deployment into water (C) Collection after 30 days

3.7 PDMS Sample Extraction

Before the sample analysis extraction was done by using same solvent that is ethyl-acetate. For extraction the samples were carefully cut with sterilized cutters for each strip, and were being fully immersed in the amber jar of around 100ml used for each sample individually. Then all the samples along with blank were placed on the shaker at 130rpm in order to get the extracts out of the samples properly. Same procedure was repeated three time by collecting the extract in separate amber jar carefully and storing the extract after each collection and by securing it with aluminum foil in freezer.

When all the extracts were collected after 24×24×24hrs, these extracts were treated on rotary evaporator to get 5ml concentrate of each sample for GCxGC analysis. (from this rotary evaporator the advantage is recollection of pure ethyl acetate, can be reused.)

3.8 GC×GC–Time of Flight - Mass Spectrometer (TOF-MS)

After rotary evaporation samples were deported to National Institute for Environmental Studies, Tsukuba, Japan for comprehensive two-dimensional gas chromatography coupled with time-of flight mass spectrometry (GC×GC-ToF-MS) technique. The raw chromatograms were deconvolved into five layers using Non-Negative Matrix Factorization (NMF)-based algorithm

3.9 EPI-Suite Modelling for Risk Assessment

Risk assessment of the data that was being retrieved from GC×GC, NMF was done EPI suite. Attributes for risk assessment were toxicity, bio accumulation and biodegradation. All of them can be define as follow

3.9.1 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.

3.9.2 Bioaccumulation:

In Accordance to EU REACH regulations, chemicals with bioconcentration 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).

3.9.3 Bio-degradation:

In Accordance to ECHA guidelines for PBT assessment, a substance is considered to be potentially persistent (P or vP) when BioWin2 or BioWin6 <0.5 and BioWin3 <2.2. If BioWin3 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.

Chapter 4

Results and Discussion

COMPUTATIONAL

4.1 Two-parameter EPI Suite Model

Multiple linear regression was achieved with two descriptors, namely the K_{ow} partition coefficient of octanol-water and the K_{aw} partition coefficient of air-water. These descriptors come from the freely accessible software EPI Suite. A good model was established that led to Equation 4.1

$$log\ Kpdms - water = 0.06(\pm 0.05) + 0.95(\pm 0.01)\ log\ K_{ow} + 0.26(\pm 0.01)\ log\ K_{aw} \quad \text{Equi 4.1}$$

$$n = 173, R2 = 0.96, Adj.R2 = 0.96, RMSE = 0.38, PRESS\ RMSE = 0.38$$

Equation 4.1 illustrates the 95% variability of PDMS-water data with an RMSE of 0.404 log units. The model is valid internally, as shown by the RMSE and PRESS RMSE values and the closeness of R^2 and Q^2 values. Other cross-validation tests further support this. We use estimated values of the EPI Suite descriptor to train Equation 1, (n = 173) computed R^2 = 0.96 and RMSE = 0.38 log unit.

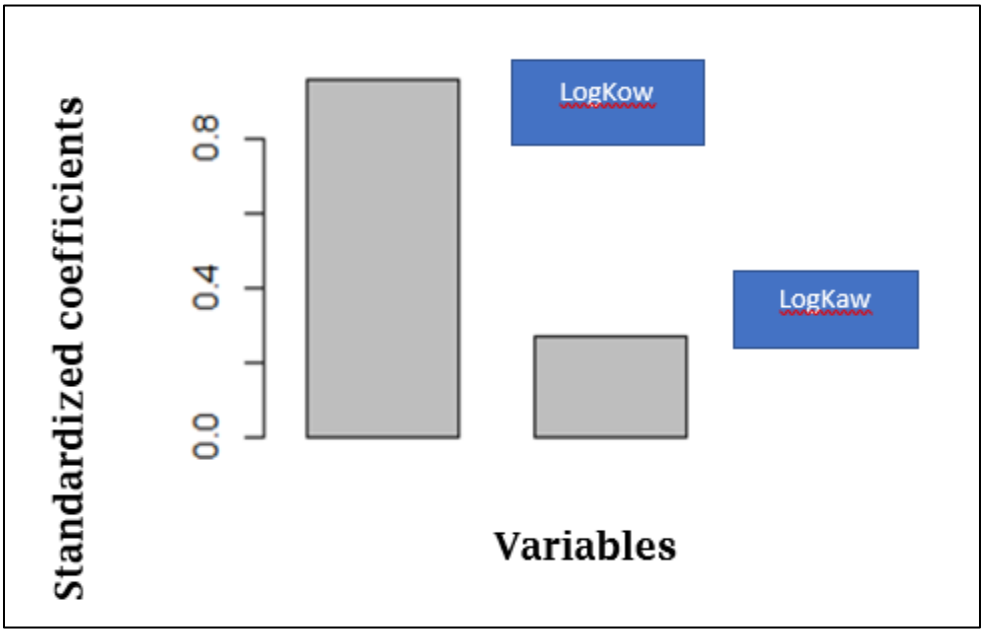


Figure 4.2 log K lipid-water, standardized coefficients

Figure 4.1 illustrates that Kow is exerting dominates effects on the PDMS-water partition coefficient, which can be easily rationalized because the higher the log Kow, the more hydrophobic compounds and more lipophilic compounds remain in the aqueous phase. Kaw compounds are low volatility compounds that will also remain in the lipid phase rather than the aqueous phase.

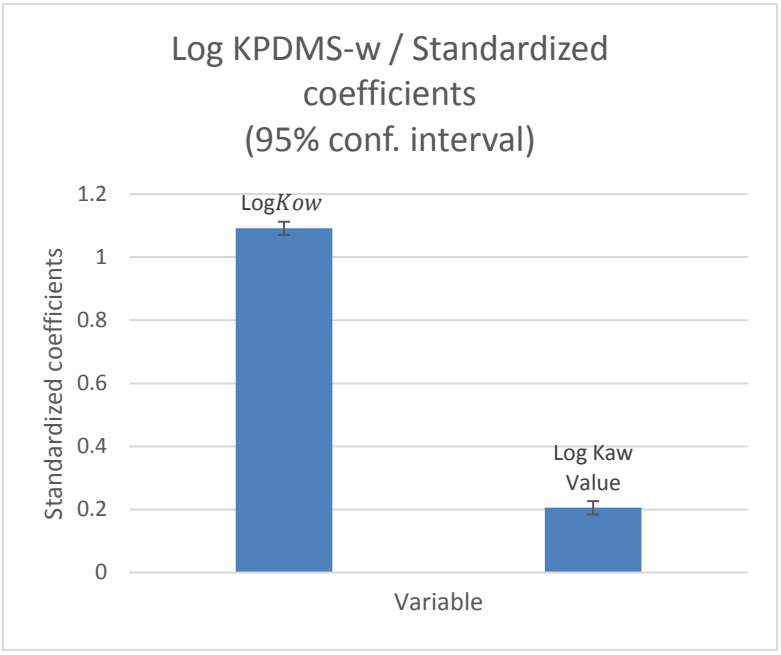


Figure 4.3 Log KPDMS-w / Standardized coefficients (95% conf. interval)

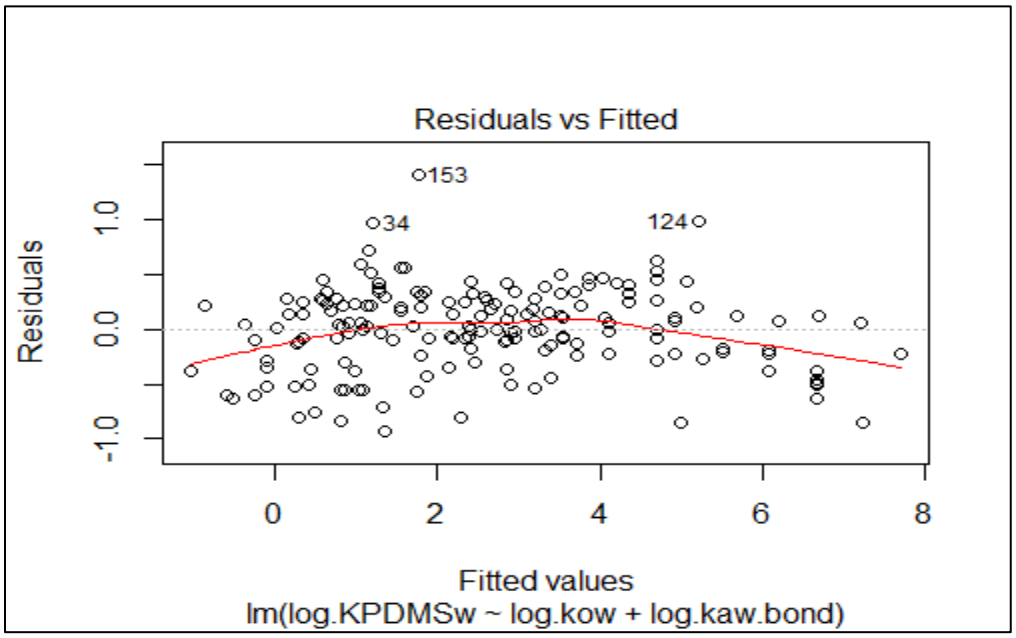


Figure 4.4 Regression Diagnostic - Residuals V/S Fitted Values

The graph in Figure 4.3 shows whether the residual has a nonlinear mode. There may be a nonlinear relationship between the predictor and the outcome variable, and if the model does not capture a nonlinear relationship, the pattern may appear in the graph. If equally spread residuals around a horizontal line without distinct patterns is found, that is a good indication that we don't have non-linear relationships.

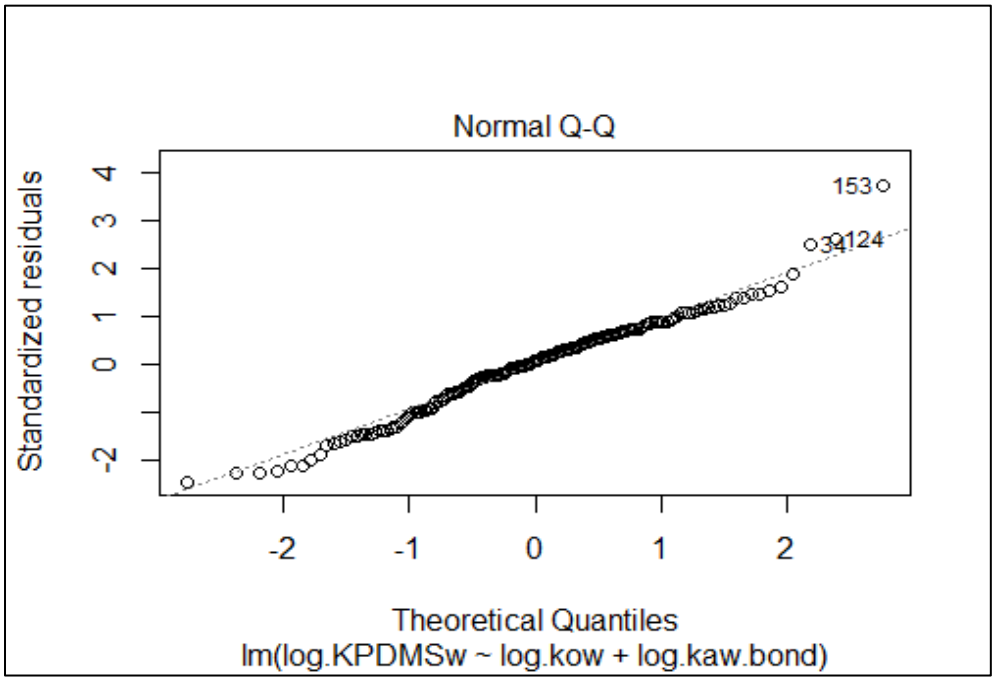


Figure 4.5 Regression Diagnostic – Normality Plot

It is known that a linear model has certain underlying assumptions, the first one is that the data should be normally distributed which can be gauged using q-q plot. As can be seen from plot (Figure 4.4), data set is normally distributed.

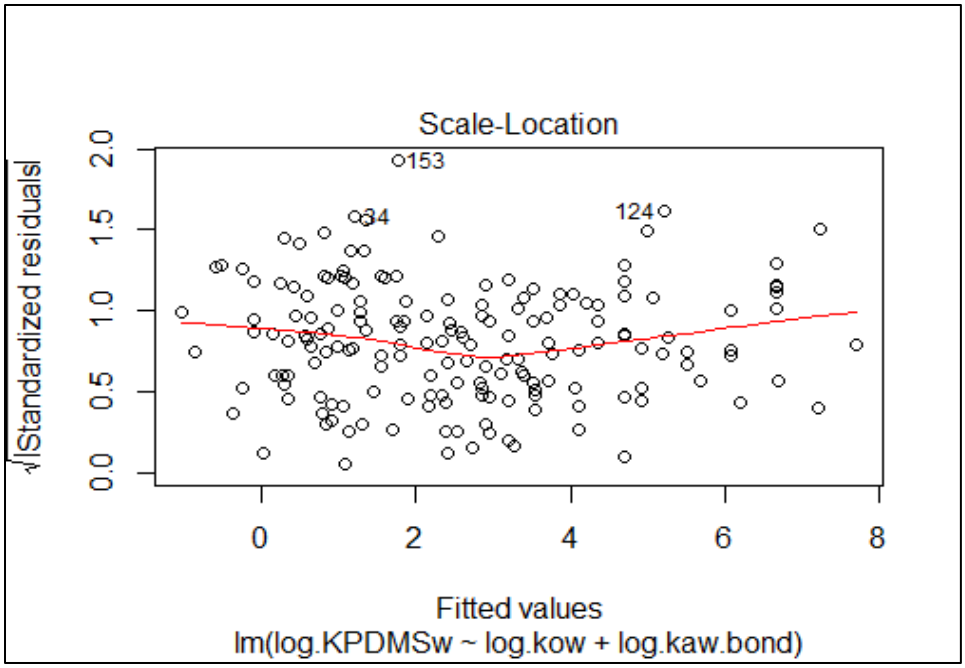


Figure 4.6 Regression Diagnostic – Scale Location

Important assumption for a linear model is homodescasity, which is the equal distribution of variance across the data space. From this plot (Figure 4.5) it can be seen that data set is respecting that requirement quite satisfactory.

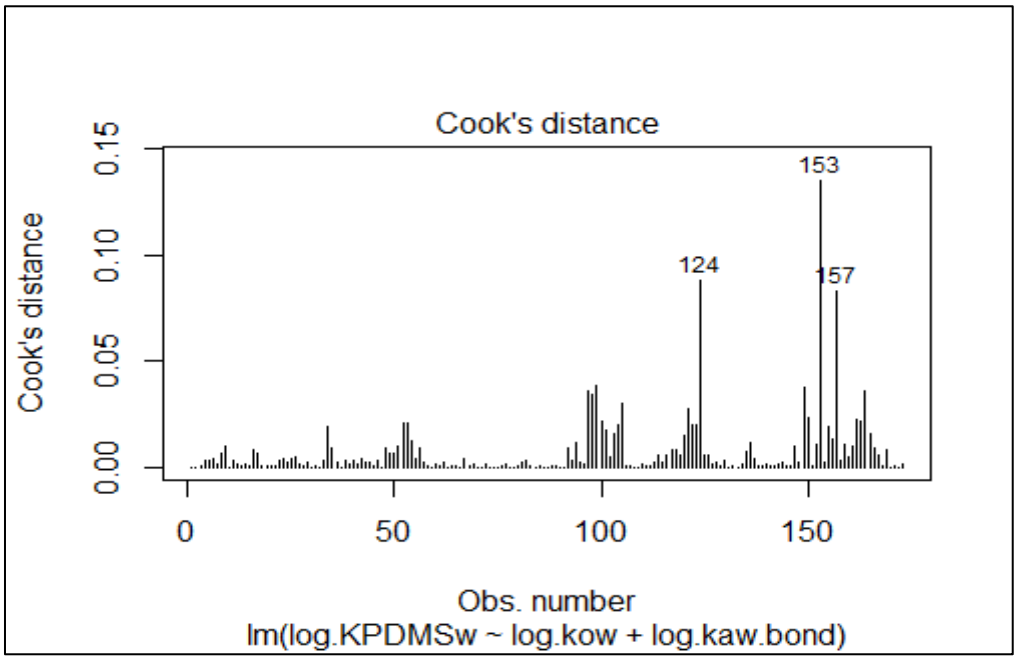


Figure 4.7 Regression Diagnostic – Cook's Distance

The other important diagnostic measure is the cook's distance that lets us identify influential data points, that can affect the regression line. As can be seen from this plot (Figure 4.6), there are few observations such as number 153,157.

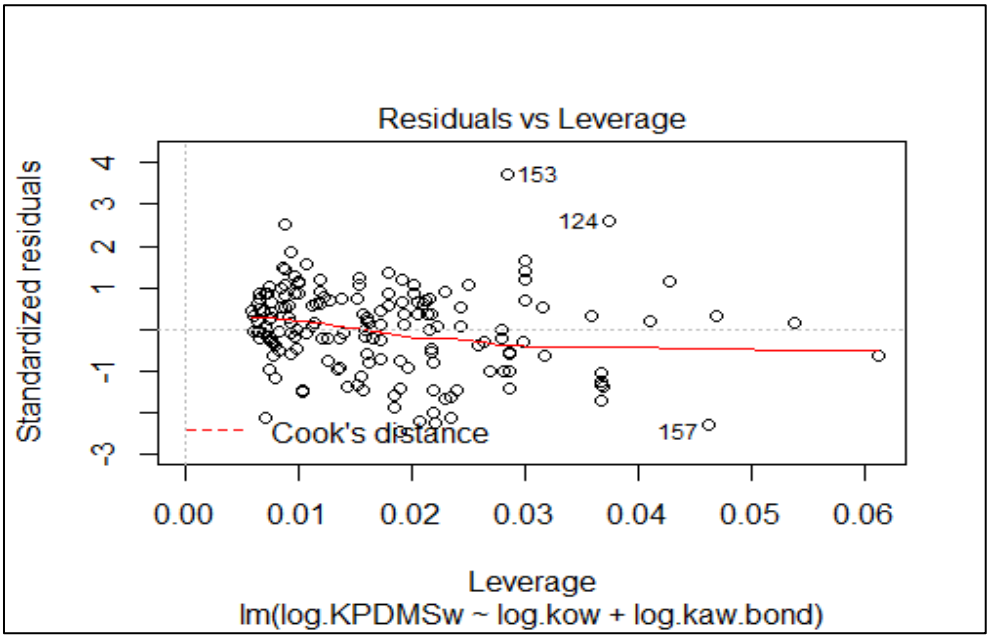


Figure 4.8 Regression Diagnostic – Residuals V/S Leverage

It is known that the leverages show the influence arising from the independent variables, that were used to train the model. On the other hand, studentized residuals shows the effect on the dependent variables.

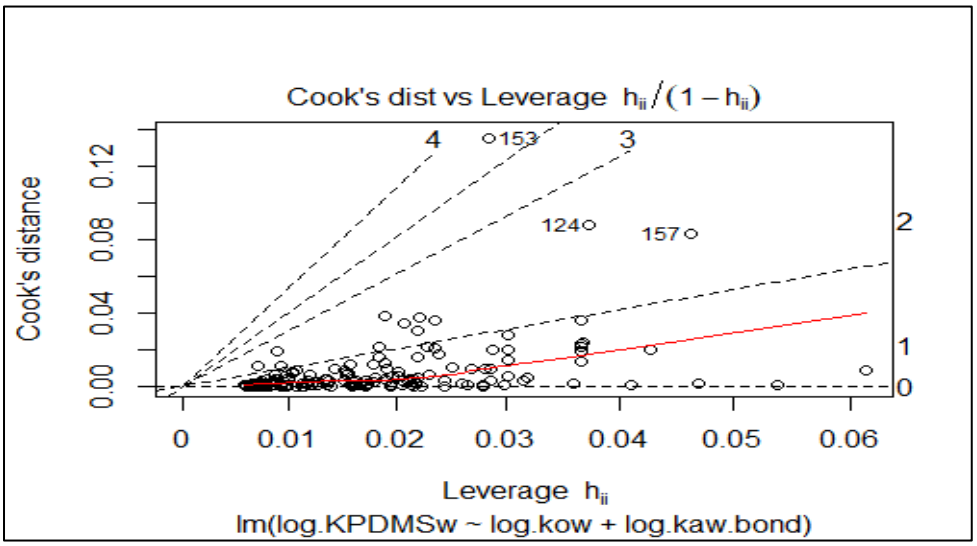


Figure 4.9 Regression Diagnostic – Cook's Distance V/S Leverage

This is another way of identifying with given different cut-off values. Highly influential data points, i.e. data points that can have a large effect on the outcome and accuracy of the regression.

Table 4.1 Estimated values of partitioning coefficients

Observation	Weight	Log Kow	Log Kaw Value	Log KPDMS-w	Pred(Log KPDMS-w)
Methane	1	0.780	1.430	1.160	1.134
Ethane	1	1.320	1.311	1.710	1.626
Propane	1	1.810	1.461	2.320	2.141
n-Butane	1	2.310	1.589	2.930	2.660
2-Methylpropane	1	2.230	1.687	2.880	2.608
n-Pentane	1	2.800	1.708	3.470	3.167
2,2-Dimethylpropane	1	2.690	2.179	3.230	3.184
n-Hexane	1	3.290	1.867	4.040	3.684
n-Heptane	1	3.780	1.913	4.610	4.171
n-Octane	1	4.270	2.118	4.700	4.701
n-Nonane	1	4.760	2.143	5.400	5.182
n-Decane	1	5.250	2.323	5.820	5.705
n-Undecane	1	5.740	1.897	6.270	6.068
n-Dodecane	1	6.230	2.524	6.820	6.709
n-Tridecane	1	6.730	2.071	7.270	7.074
n-Tetradecane	1	7.220	2.575	7.480	7.682
Cyclopropane	1	1.700	1.509	1.430	2.047
Cyclohexane	1	3.180	0.788	3.520	3.292
Ethene	1	1.270	0.969	1.343	1.488
Propene	1	1.680	0.904	1.800	1.868
But-1-ene	1	2.170	0.979	2.310	2.363
Isobutene	1	2.230	0.950	2.160	2.414
Buta-1,3-diene	1	2.030	0.478	1.780	2.095
Trichloromethane	1	1.520	-0.824	1.620	1.257
Trichloromethane	1	1.520	-0.824	1.710	1.257
Tetrachloromethane	1	2.440	0.052	2.840	2.380
1,1,1-Trichloroethane	1	2.680	-0.153	2.750	2.559
1,1,1,2-Tetrachloroethane	1	2.930	-0.991	2.660	2.580
1,1,2,2-Tetrachloroethane	1	2.190	-1.824	2.170	1.643
1,2-Dichloropropane	1	2.250	-0.938	2.100	1.935
Trichloroethene	1	2.470	-0.395	2.240	2.291
Trichloroethene	1	2.470	-0.395	2.410	2.291

Tetrachloroethene	1	2.970	-0.140	3.270	2.844
Chlorodibromomethane	1	1.700	-1.495	2.160	1.254
Trifluoromethane	1	0.580	0.590	0.600	0.718
2-Propanone	1	-0.240	-2.844	-0.670	-0.983
2-Butanone	1	0.260	-2.633	-0.320	-0.443
Pentan-2-one	1	0.750	-2.466	0.410	0.077
Hexan-2-one	1	1.240	-2.419	0.860	0.564
Hexan-3-one	1	1.240	-2.292	0.980	0.598
Heptan-2-one	1	1.730	-2.161	1.350	1.108
Cyclohexanone	1	1.130	-3.434	0.070	0.190
Acetophenone	1	1.670	-3.371	1.040	0.730
p-Chloroacetophenone	1	2.320	-3.527	1.640	1.319
Ethyl acetate	1	0.860	-2.261	0.271	0.237
Isobutyl acetate	1	1.770	-1.731	1.660	1.260
Phenyl acetate	1	1.590	-2.577	0.860	0.862
Methyl benzoate	1	1.830	-2.878	1.650	1.015
Ethyl benzoate	1	2.320	-2.523	2.120	1.584
Methyl 2-methylbenzoate	1	2.380	-2.805	2.150	1.568
Ethanol	1	-0.140	-3.689	-1.410	-1.109
Propan-1-ol	1	0.350	-3.519	-1.160	-0.589
Propan-2-ol	1	0.280	-3.480	-1.210	-0.647
Butan-2-ol	1	0.770	-3.431	-0.630	-0.159
2-Methylpropan-1-ol	1	0.770	-3.398	-0.390	-0.150
2-Methylbutan-1-ol	1	1.260	-3.239	-0.100	0.367
Benzene	1	1.990	-0.644	2.100	1.760
Benzene	1	1.990	-0.644	1.990	1.760
Toluene	1	2.540	-0.566	2.240	2.314
Toluene	1	2.540	-0.566	2.580	2.314
Ethylbenzene	1	3.030	-0.492	2.710	2.809
o-Xylene	1	3.090	-0.674	2.500	2.819
m-Xylene	1	3.090	-0.532	2.950	2.857
p-Xylene	1	3.090	-0.550	2.760	2.852
n-Propylbenzene	1	3.520	-0.367	3.140	3.317
Isopropylbenzene	1	3.450	-0.328	3.250	3.260
1,2,4-Trimethylbenzene	1	3.630	-0.599	2.940	3.363
1,3,5-Trimethylbenzene	1	3.630	-0.445	3.250	3.403
Styrene	1	2.890	-0.949	2.860	2.553
Chlorobenzene	1	2.640	-0.896	2.400	2.324
1,2-Dichlorobenzene	1	3.280	-1.105	2.870	2.890
1,3-Dichlorobenzene	1	3.280	-0.969	3.290	2.926
1,4-Dichlorobenzene	1	3.280	-1.006	2.930	2.916

1,2,3-Trichlorobenzene	1	3.930	-1.292	3.450	3.471
1,2,4-Trichlorobenzene	1	3.930	-1.236	3.480	3.486
1,3,5-Trichlorobenzene	1	3.930	-1.112	3.640	3.518
1,2,3,4-Tetrachlorobenzene	1	4.570	-1.508	3.900	4.035
1,2,3,5-Tetrachlorobenzene	1	4.570	-1.190	4.180	4.118
1,2,4,5-Tetrachlorobenzene	1	4.570	-1.388	4.090	4.066
Pentachlorobenzene	1	5.220	-1.542	4.620	4.656
Pentachlorobenzene	1	5.220	-1.542	4.420	4.656
Hexachlorobenzene	1	5.860	-1.158	5.010	5.378
2-Chlorotoluene	1	3.180	-0.836	3.070	2.864
4-Chlorotoluene	1	3.180	-0.747	2.870	2.887
2,4,5-Trichlorotoluene	1	4.470	-1.212	4.170	4.016
Bromobenzene	1	2.880	-0.996	2.510	2.531
Iodobenzene	1	3.160	-1.466	2.730	2.678
Methyl phenyl ether	1	2.070	-1.704	1.705	1.558
4-Chloroanisole	1	2.720	-2.016	2.370	2.106
Aniline	1	1.080	-4.083	0.010	-0.030
3,4-Dimethylaniline	1	2.170	-4.119	1.070	1.018
2-Chloroaniline	1	1.720	-3.657	1.040	0.703
4-Chloroaniline	1	1.720	-4.324	0.840	0.527
2,4-Dichloroaniline	1	2.370	-4.367	1.690	1.146
3,4-Dichloroaniline	1	2.370	-3.224	1.390	1.448
Nitrobenzene	1	1.810	-3.008	1.210	0.962
Phenol	1	1.510	-4.866	-0.530	0.180
m-Cresol	1	2.060	-4.456	-0.030	0.822
3,5-Dimethylphenol	1	2.610	-4.600	0.420	1.317
4-Ethylphenol	1	2.550	-4.500	0.600	1.286
3-Bromophenol	1	2.400	-5.040	0.460	0.998
2-Chlorophenol	1	2.160	-3.339	0.560	1.214
3-Chlorophenol	1	2.160	-4.851	0.310	0.815
Pentachlorophenol	1	4.740	-5.999	2.650	3.014
4-Fluorophenol	1	1.710	-4.540	-0.280	0.460
Biphenyl	1	3.760	-1.900	3.370	3.145
Naphthalene	1	3.170	-1.745	2.830	2.614
1-Methylnaphthalene	1	3.720	-1.677	3.260	3.166
2-Methylnaphthalene	1	3.720	-1.674	3.170	3.166
1,2-Dimethylnaphthalene	1	4.260	-1.582	3.470	3.714

2,6-Dimethylnaphthalene	1	4.260	-1.582	3.590	3.714
Acenaphthene	1	4.150	-2.124	3.630	3.465
Fluorene	1	4.020	-2.405	3.720	3.264
Phenanthrene	1	4.350	-2.762	4.000	3.490
Anthracene	1	4.350	-2.643	3.840	3.522
Fluoranthene	1	4.930	-3.441	4.260	3.874
Benz[a]anthracene	1	5.520	-3.309	4.770	4.481
Pyrene	1	4.930	-3.313	4.320	3.907
Chrysene	1	5.520	-3.670	4.690	4.385
Benz[b]fluoranthene	1	6.110	-4.571	5.160	4.720
Benzo[k]fluoranthene	1	6.110	-4.622	5.330	4.706
Benzo[a]pyrene	1	6.110	-4.729	5.240	4.678
Benzo[ghi]perylene	1	6.700	-4.869	5.500	5.213
Dibenz[ah]anthracene	1	6.700	-5.239	6.200	5.116
1-Methylphenanthrene	1	4.890	-2.696	4.500	4.031
Perylene	1	6.110	-3.826	4.980	4.916
Benzonitrile	1	1.540	-2.672	1.040	0.788
Dimethyl sulfide	1	0.920	-1.182	0.820	0.580
Helium	1	0.280	0.001	0.470	0.272
Neon	1	0.280	0.001	0.580	0.272
Argon	1	0.740	0.001	0.820	0.718
Krypton	1	0.890	0.001	0.980	0.863
Xenon	1	1.280	0.001	1.253	1.242
Nitrogen	1	0.670	-0.101	0.850	0.623
Nitrous oxide	1	1.380	-1.195	0.510	1.023
Carbon dioxide	1	0.830	-0.207	0.240	0.750
Tetrafluoromethane	1	1.190	2.323	1.570	1.767
Sulfur hexafluoride	1	1.640	2.267	2.100	2.189
Benzyl alcohol	1	1.080	-4.861	-0.350	-0.235
2-Phenylethanol	1	1.570	-4.980	0.120	0.208
3-Methylbenzyl alcohol	1	1.620	-5.008	0.170	0.250
2-chlorobiphenyl	1	4.400	-1.522	3.970	3.866
PCB 15	1	5.050	-2.090	4.590	4.347
PCB 28	1	5.690	-2.087	4.700	4.968
PCB 28	1	5.690	-2.087	5.030	4.968
PCB 17	1	5.690	-2.163	5.000	4.948
PCB 101	1	6.980	-2.434	5.710	6.128
PCB 52	1	6.340	-2.087	5.300	5.599
Limonene	1	4.830	0.115	4.140	4.715
Hexafluoroethane	1	2.150	2.919	2.400	2.856
Hydrogen sulphide	1	0.230	-0.449	0.300	0.105

camphor	1	3.040	-2.480	1.480	2.294
Acridine	1	3.320	-5.561	3.170	1.752
PCB 105	1	6.980	-1.937	5.890	6.259
PCB 138	1	7.620	-3.066	6.200	6.582
PCB 156	1	7.620	-2.233	6.280	6.801
PCB 180	1	8.270	-3.388	6.400	7.127
PCB 118	1	6.980	-1.929	5.870	6.261
Tribromomethane	1	1.790	-1.660	1.870	1.298
2,4,5-Trichloroaniline	1	3.010	-4.499	2.080	1.732
PCB 112	1	6.980	-2.423	5.710	6.131
PCB 153	1	7.620	-3.027	6.160	6.592
PCB 154	1	7.620	-2.553	6.170	6.717
PCB 155	1	7.620	-0.989	6.030	7.130
Propionaldehyde	1	0.330	-2.523	-0.867	-0.346
Butyraldehyde	1	0.820	-2.328	-0.289	0.181
Pyridine	1	0.800	-3.347	-0.454	-0.107
Thiophene	1	1.810	-1.032	1.748	1.483
1,2-Dichloroethane	1	1.830	-1.317	1.161	1.427
Benzonitrile	1	1.540	-2.672	0.859	0.788
Diethyl ether	1	1.050	-1.299	0.664	0.676
Ethanethiol	1	1.270	-0.732	1.115	1.039
PCB 65	1	6.340	-2.036	5.340	5.612

4.2 Regression Diagnostics of My Model

Table 4.2 Outliers of my model

chemicals	**studentized Res**	**Hat**	**Cooks D**
n-Dodecane	0.1611059	0.05379044	0.0004946691
n-Tridecane	-0.6156505	0.06124715	0.0082731536
Benzo[ghi]perylene	2.6511897	0.03737834	0.0878597325
Hexafluoroethane	3.8689827	0.02838792	0.1347154018

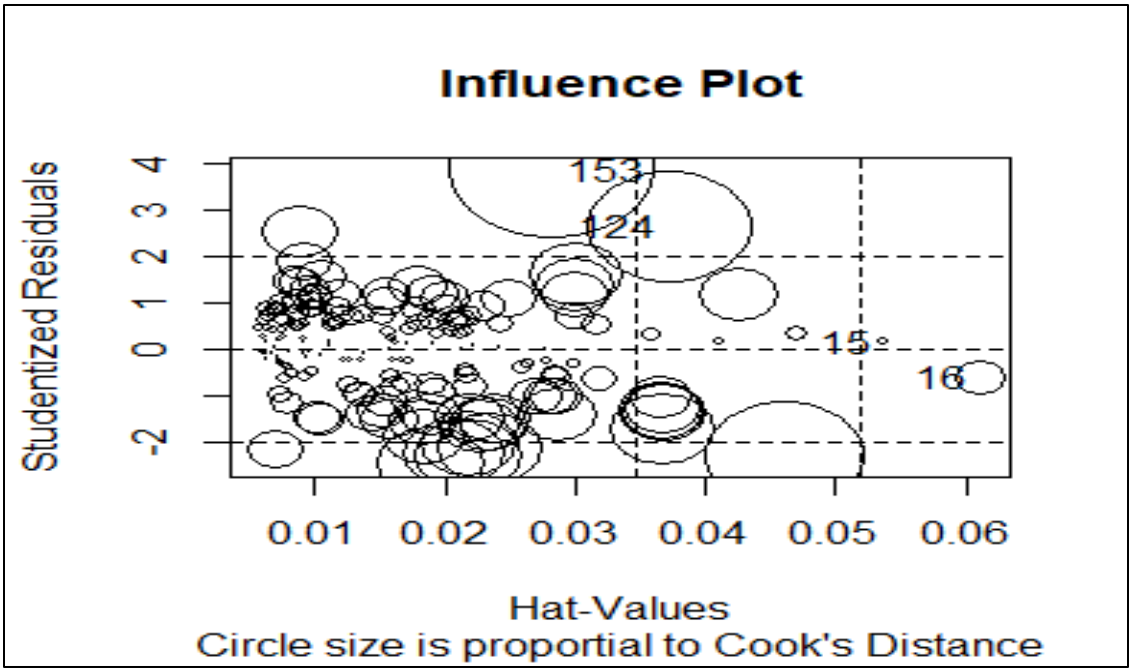


Figure 4.10 Influential values

Here is a plot that lets you see all the three important influence aspects together i.e., studentized residual on the y-axis, HAT values on the x-axis and the size of the circle that is proportional to the cook's distance. The data points that are flagged in this plot were curated very carefully again for their accuracies and we decided to keep them in our data set because they were bringing in real information.

Table 4.3 Results of cross validation techniques

Indicators	**LOOCV**	**K- Fold CV**	**Repeated K – Fold CV**		**Bootstrapping**		
			3 times	10 times	N= 100	N= 500	N= 1000
R2	0.96	0.96	0.96	0.96	0.96	0.96	0.96
RMSE	0.38	0.38	0.38	0.38	0.39	0.39	0.39
MAE	0.30	0.30	0.30	0.30	0.30	0.30	0.30

Table 4.4 Summary of model after bootstrapping (N=1000)

	Estimate	**Std. Error**	**t value**	**Pr(>|t|)**
Intercept	0.06356112	0.05827318	1.090744	2.769291e-01
log Kow	0.95512247	0.01476396	64.692842	1.167877e-121
log Kaw	0.26531640	0. 0.01460075	18.171427	1.086071e-41

Table 4.5 Summary of the Model

Data set	**Variables taken**	**Variables Retained**	**Highly influential variable**	**N**	**R2**	**Adj. R2**	**Q2**	**RMSE**	**Press RMSE**	**VIF**	**Internal validation**
PDMS-water	LogKow, LogKaw Bond LogKoa, LogKoc	logKow, log Kaw bond	logKow	173	0.96	0.96	0.96	0.38	0.38	LogKow= 1.001 logKaw bond = 1.001	**R^2 = Q^2;** 0.96=0.96**RMSE=PRESS** 0.38=0.38

EXPERIMANTAL RESULTS

4.3 Sample Analysis

we were reported with total of 85 DIBs after analysis results which were filtered on basis of following criteria.

1. Should only be reported in downstream i.e. in post chlorination and should not have been reported in filtration phase (another study in parallel was done on filtration phase reported chemicals from that phase were 5780)
2. After making sure the of DIBs reported from post-chlorination were absent and were not reported in filtration, the second filter was applied, making sure the reported DIBs were all present in 3 of replicates deployed.

3. Third criteria set was, the reported chemicals must not report from the blank samples.

4.4 NIST Library Match Factor

After all the three mentioned criteria were satisfied by my reported results, then moved towards the final check i.e. NIST library match factor. Only those chemicals were picked and considered for further assessment and risk factor which were in the range of 800-900 NIST library match factor.

Table 4.6 NIST library match results

SN	Blob ID	Compound Name	Library Match Factor	Library Reverse Match Factor	Library NIST ID
1	770	Benzenamine, 2,4-dichloro-	933	941	290760
2	787	Benzonitrile, 2,6-dichloro-	921	928	231349
3	1601	Naphthalene, 1-isocyano-	913	949	4954
4	660	Benzenamine, 2,3,4-trichloro-	905	909	231259
5	733	2-Bromo-4-chloroaniline	893	911	340990
6	127	Acetaldehyde, tribromo-	893	898	72931
7	1544	Bromodichloroacetaldehyde	888	900	288088
8	948	Benzaldehyde, 2,4-dichloro-	872	926	291093
9	985	Acetic acid, dibromo-, methyl ester	869	904	210925
10	1543	1H-Pyrazole, 3,4-dibromo-	869	908	157779
11	868	Acetaldehyde, tribromo-	865	901	72931
12	894	Benzenamine, 2,3,4-trichloro-	860	869	231259
13	710	4-Bromo-2,6-dichloroaniline	859	901	133729
14	1595	Bromodichloroacetaldehyde	856	885	288088
15	1699	Benzene, 1,1'-(bromomethylene)bis-	854	933	113358
16	1884	Benzene, 1,1'-(bromomethylene)bis-	854	932	113358
17	232	Chlorodibromoacetaldehyde	851	909	288089
18	882	4-Bromo-2,6-dichloroaniline	847	893	133729
19	1714	Hexane, 2-bromo-	841	883	236730
20	1598	Benzene, 1,1'-(bromomethylene)bis-	836	934	113358
21	957	Phenol, 4-chloro-	836	905	333415
22	959	Phenol, 2,4,6-tribromo-	834	930	133988
23	1007	2-Propanone, 1,1,3-trichloro-	832	864	108364
24	575	Acridine, 4,5-dibromo-	830	872	164917
25	156	Acetaldehyde, tribromo-	823	883	72931
26	1096	Tribromoacetic acid, methyl ester	821	898	288222
27	1472	1,1,3,3-Tetrabromoacetone	821	862	288210
28	750	2,4,6-Trichlorophenyl isocyanate	818	911	154625

29	1446	1H-Pyrazole, 3,4-dibromo-	815	891	157779
30	776	4-Bromo-2,6-dichloroaniline	815	863	133729
31	1571	Butanedinitrile	813	929	229071
32	564	Benzenamine, 2,4-dichloro-	812	889	135554

As it can be seen from above table the finally chosen chemicals were 32 in number (dibs) that fell in the range of 800-900.

4.5 Epi-Suite Modelling for Risk Assessment

For risk assessment, each DIB was run on UFZ website for the retrieval of smiley codes and CAS-number

Table 4.7 Shows CAS number and smiley codes results

SN	BlobID	Compound Name	SMILES	Library CAS#	Library Formula
1	770	Benzenamine, 2,4-dichloro-	Clc1ccc(c(c1)Cl)N	554-00-7	C6H5Cl2N
2	787	Benzonitrile, 2,6-dichloro-	N#Cc1c(Cl)cccc1Cl	1194-65-6	C7H3Cl2N
3	1601	Naphthalene, 1-isocyano-	c(ccc1c(c2)N#C)cc1cc2	1984-04-9	C11H7N
4	660	Benzenamine, 2,3,4-trichloro-	Nc1ccc(c(c1Cl)Cl)Cl	634-67-3	C6H4Cl3N
5	733	2-Bromo-4-chloroaniline	c1cc(c(cc1Cl)Br)N	873-38-1	C6H5BrClN
6	127	Acetaldehyde, tribromo-	O=CC(Br)(Br)Br	115-17-3	C2HBr3O
7	1544	Bromodichloroacetaldehyde	C(=O)C(Cl)(Cl)Br	34619-29-9	C2HBrCl2O
8	948	Benzaldehyde, 2,4-dichloro-	c1cc(c(cc1Cl)Cl)C=O	874-42-0	C7H4Cl2O
9	985	Acetic acid, dibromo-, methyl ester	COC(=O)C(Br)Br	6482-26-4	C3H4Br2O2
10	1543	1H-Pyrazole, 3,4-dibromo-	c1c(c([nH]n1)Br)Br	5932-18-3	C3H2Br2N2
11	868	Acetaldehyde, tribromo-	O=CC(Br)(Br)Br	115-17-3	C2HBr3O
12	894	Benzenamine, 2,3,4-trichloro-	Nc1ccc(c(c1Cl)Cl)Cl	634-67-3	C6H4Cl3N
13	710	4-Bromo-2,6-dichloroaniline	c1c(cc(c(c1Cl)N)Cl)Br	697-86-9	C6H4BrCl2N
14	1595	Bromodichloroacetaldehyde	C(=O)C(Cl)(Cl)Br	34619-29-9	C2HBrCl2O
15	1699	Benzene, 1,1'-(bromomethylene)bis-	c1ccc(cc1)C(c2ccccc2)Br	776-74-9	C13H11Br
16	1884	Benzene, 1,1'-(bromomethylene)bis-	c1ccc(cc1)C(c2ccccc2)Br	776-74-9	C13H11Br
17	232	Chlorodibromoacetaldehyde	C(=O)C(Cl)(Br)Br	64316-11-6	C2HBr2ClO
18	882	4-Bromo-2,6-dichloroaniline	c1c(cc(c(c1Cl)N)Cl)Br	697-86-9	C6H4BrCl2N
19	1714	Hexane, 2-bromo-	CCCCC(C)Br	3377-86-4	C6H13Br

20	1598	Benzene, 1,1'-(bromomethylene)bis-	c1ccc(cc1)C(c2ccccc2)Br	776-74-9	C13H11Br
21	957	Phenol, 4-chloro-	Oc1ccc(cc1)Cl	106-48-9	C6H5ClO
22	959	Phenol, 2,4,6-tribromo-	Brc1cc(Br)c(c(c1)Br)O	118-79-6	C6H3Br3O
23	1007	2-Propanone, 1,1,3-trichloro-	C(C(=O)C(Cl)Cl)Cl	921-03-9	C3H3Cl3O
24	575	Acridine, 4,5-dibromo-	c1cc2cc3cccc(c3nc2c(c1)Br)Br	209460-03-7	C13H7Br2N
25	156	Acetaldehyde, tribromo-	O=CC(Br)(Br)Br	115-17-3	C2HBr3O
26	1096	Tribromoacetic acid, methyl ester	COC(=O)C(Br)(Br)Br	3222-05-7	C3H3Br3O2
27	1472	1,1,3,3-Tetrabromoacetone	C(C(=O)C(Br)Br)(Br)Br	22612-89-1	C3H2Br4O
28	750	2,4,6-Trichlorophenyl isocyanate	c1c(cc(c(c1Cl)N=C=O)Cl)Cl	2505-31-9	C7H2Cl3NO
29	1446	1H-Pyrazole, 3,4-dibromo-	c1c(c([nH]n1)Br)Br	5932-18-3	C3H2Br2N2
30	776	4-Bromo-2,6-dichloroaniline	c1c(cc(c(c1Cl)N)Cl)Br	697-86-9	C6H4BrCl2N
31	1571	Butanedinitrile	N#CCCC#N	110-61-2	C4H4N2
32	564	Benzenamine, 2,4-dichloro-	Clc1ccc(c(c1)Cl)N	554-00-7	C6H5Cl2N

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 biodegridibility or persistence was checked, fourth using BCFBAF modelling from EPI-suite the bio-accumulation factor was checked.

4.5.1 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).

According to REACH guidelines, out of 32 analyzed chemicals only 5 were exceeding the cutoff limits.

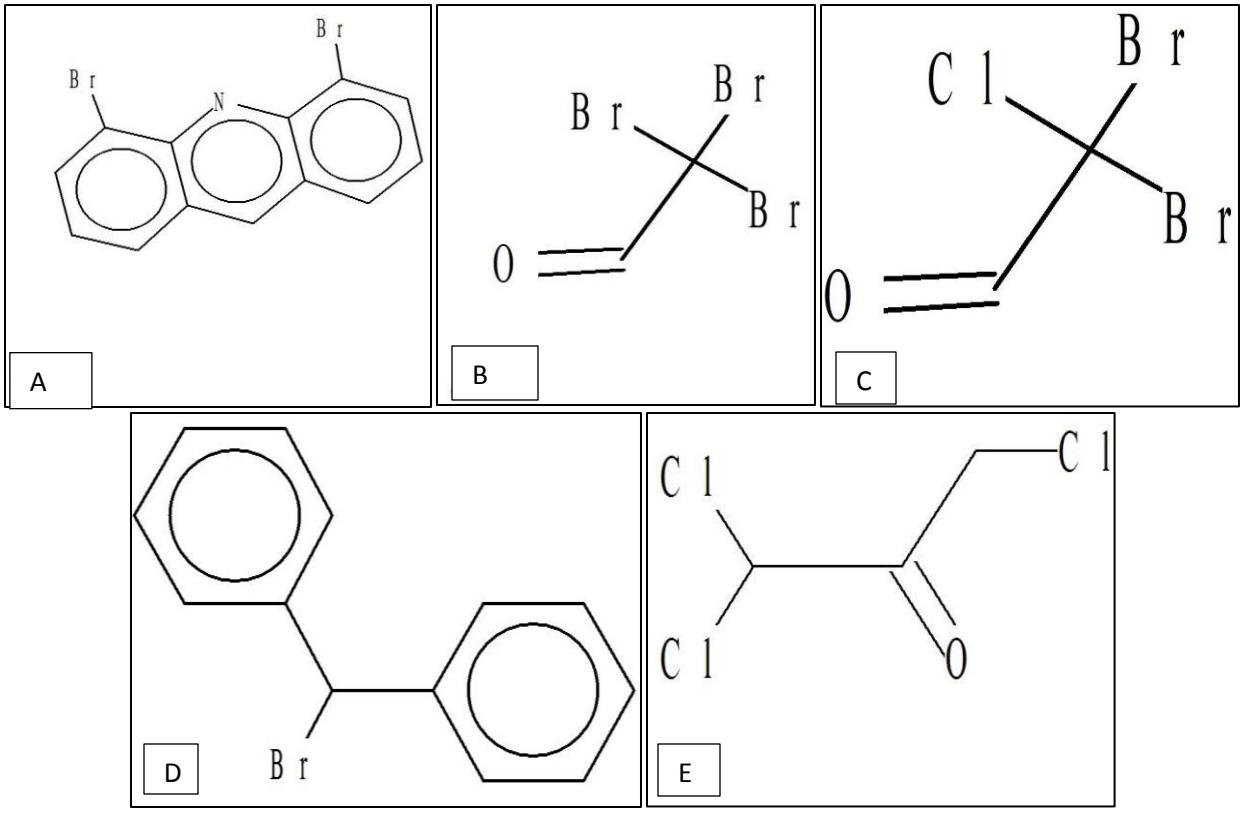


Figure 4.11 Chemical structures (A)Acridine, 4,5-dibromo, (B)Acetaldehyde,tribromo (C) Chlorodibromoacetaldehyde (D) Benzene, 1,1'-(bromomethylene)bis- (E) 2-Propanone, 1,1,3-trichloro

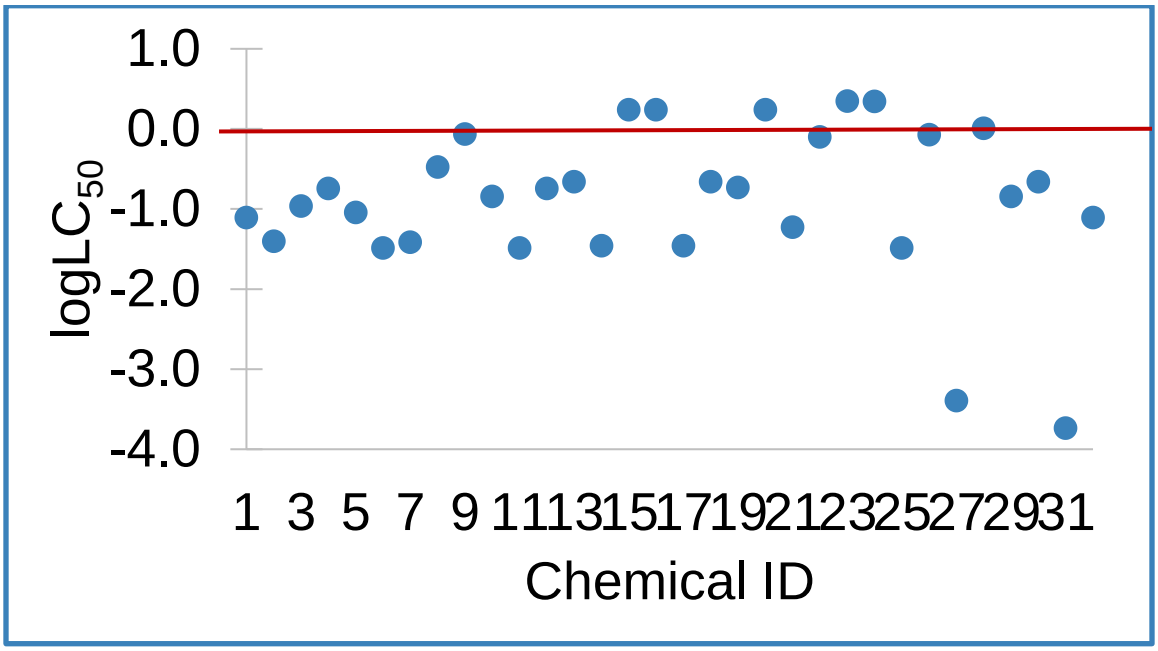


Figure 4.12 The graph showing the toxicity result, only five chemical exceeds cut off limit

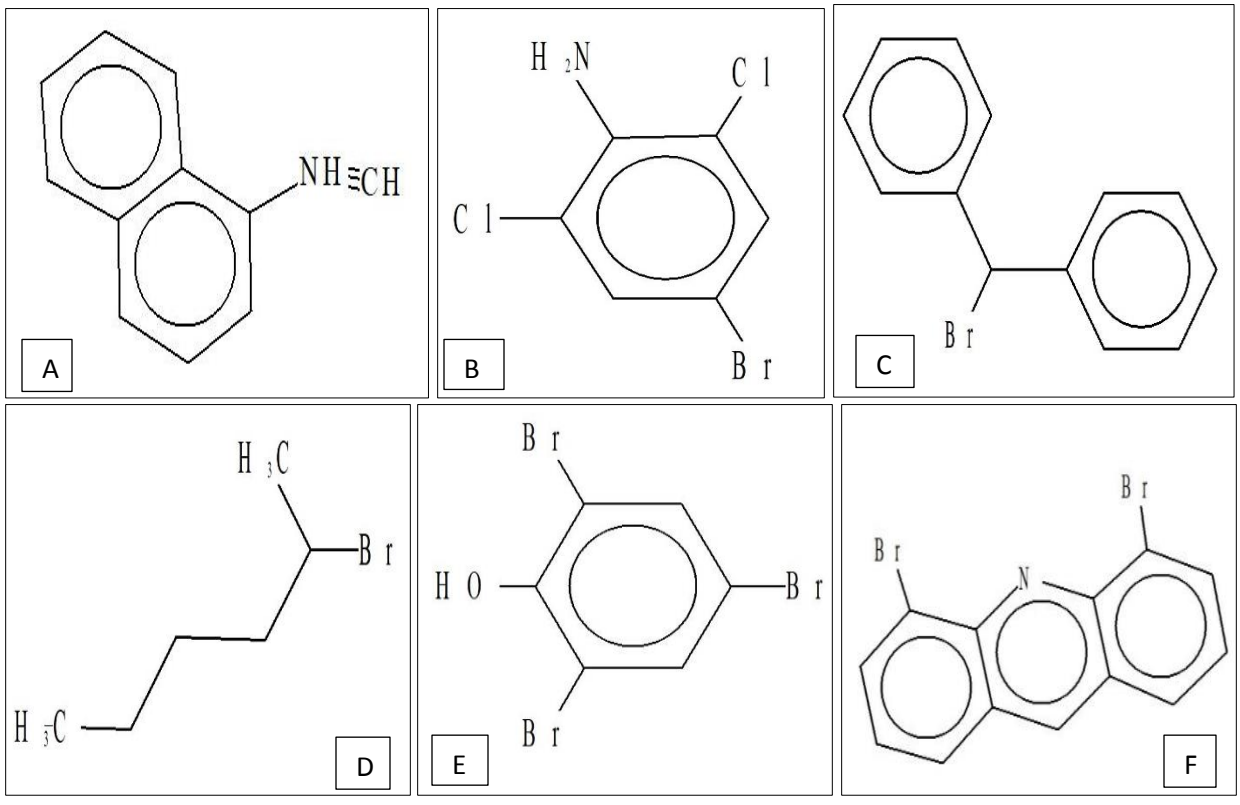
4.5.2 Hydrophobic Contaminant on Basis of Kow Value

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).

Table 4.8 Hydrophobic Contaminant results on Basis of Kow Value

SN	Blob ID	Compound Name	Log Kow
1	1601	Naphthalene, 1-isocyano-	3.27
2	710	4-Bromo-2,6-dichloroaniline	3.25
3	1699	Benzene, 1,1'-(bromo methylene)bis-	4
4	882	4-Bromo-2,6-dichloroaniline	3.25
5	1714	Hexane, 2-bromo-	3.56
6	1598	Benzene, 1,1'-(bromo methylene)bis-	4
7	959	Phenol, 2,4,6-tribromo-	4.18
8	575	Acridine, 4,5-dibromo-	5.1
9	750	2,4,6-Trichlorophenyl isocyanate	4.53
10	776	4-Bromo-2,6-dichloroaniline	3.25

Reported hydrophobic DIBs as per KOWWIN results were 10 as can be seen from above table. Limit is if Kow is greater than 3 than hydrophobic or least soluble in water.



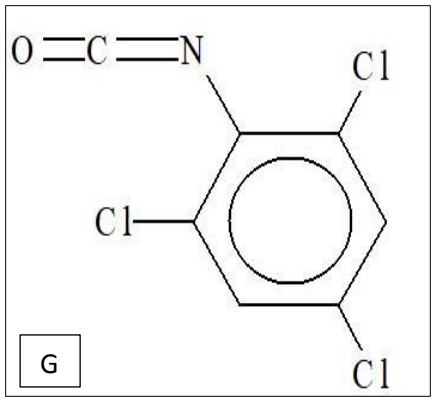


Figure 4.13 Chemical structures (A) Naphthalene, 1-isocyano-(B) 4-Bromo-2,6-dichloroaniline (C) Benzene, 1,1'-(bromo methylene)bis- (D) Hexane, 2-bromo- (E) Phenol, 2,4,6-tribromo- (F) Acridine, 4,5-dibromo- (G) 2,4,6-Trichlorophenyl isocyanate

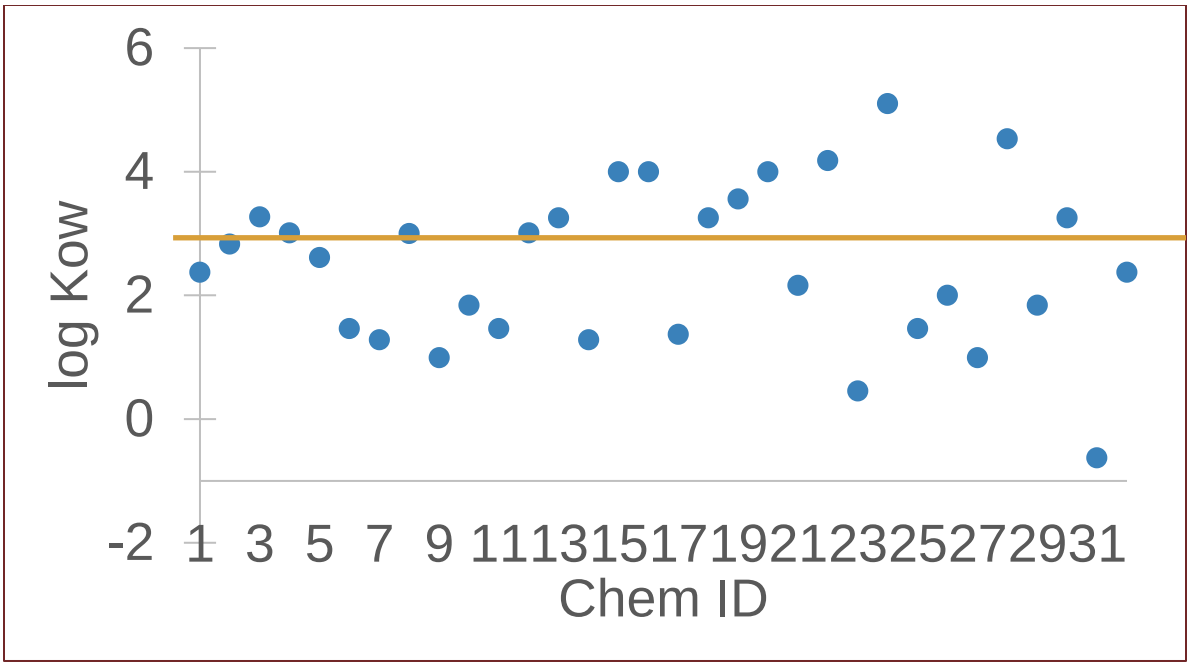


Figure 4.14 The graph showing the hydrophobic contaminant results on basis of kow value

It can be seen from the above graph and episuite results our chemicals are mix of hydrophobic and hydrophilic, so an efficient polishing method should be designed.

4.5.3 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, but fortunately none of the DIB crossed that limits as resulted from the EPI-suite model.

4.5.4 Biodegradability Via BIOWINN Modelling

The biodegradability or persistence was checked using BIOWINN modelling from EPI-suite. BIOWIN contains seven separate models. Version 4.10 designates these models as follows:

4.5.4.1 BIOWINN1

17 out of 32 dibs are identified as persistent according to results from BIOWINN1 as they are in range of less than 0.5 (REACH2007). 17 chemicals are shown in table

Table 4.10 BIOWINN1 results

s.no	Chemicals
1	Benzenamine, 2,4-dichloro-
2	Benzenamine, 2,3,4-trichloro-
3	2-Bromo-4-chloroaniline
4	1H-Pyrazole, 3,4-dibromo-
5	Benzenamine, 2,3,4-trichloro-
6	4-Bromo-2,6-dichloroaniline
7	Bromodichloroacetaldehyde
8	4-Bromo-2,6-dichloroaniline
9	Phenol, 2,4,6-tribromo-
10	2-Propanone, 1,1,3-trichloro-
11	Acridine, 4,5-dibromo-
12	Tribromoacetic acid, methyl ester
13	1,1,3,3-Tetrabromoacetone
14	2,4,6-Trichlorophenyl isocyanate
15	1H-Pyrazole, 3,4-dibromo-
16	4-Bromo-2,6-dichloroaniline
17	Benzenamine, 2,4-dichloro-

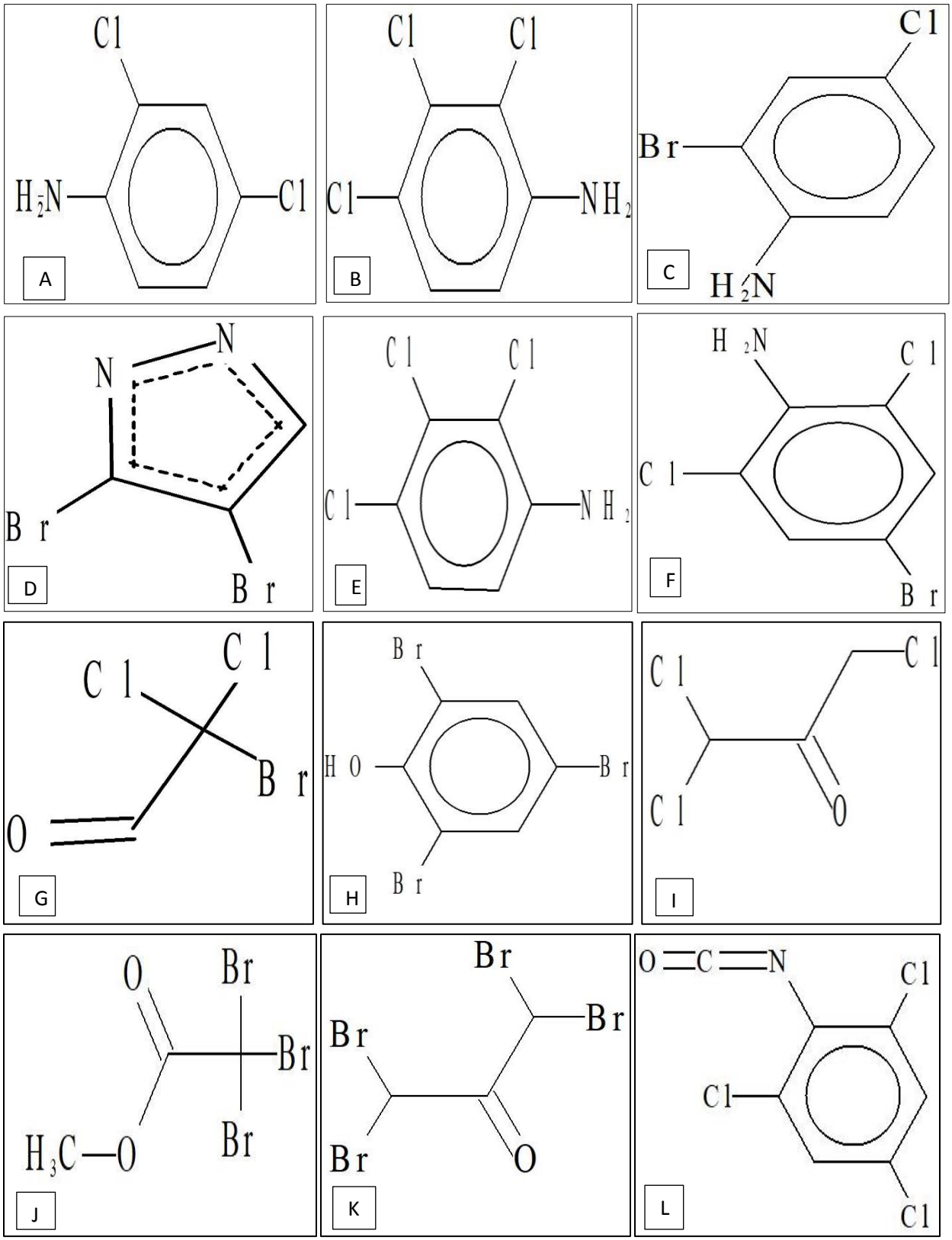


Figure 4.15 Chemical structures (A) Benzenamine, 2,4-dichloro- (B) Benzenamine, 2,3,4-trichloro- (C) 2-Bromo-4-chloroaniline (D) 1H-Pyrazole, 3,4-dibromo- (E) Benzenamine, 2,3,4-trichloro- (F) 4-Bromo-

2,6-dichloroaniline (G) Bromodichloro acetaldehyde (H) Phenol, 2,4,6-tribromo- (I) 2-Propanone, 1,1,3-trichloro (J) Tribromo acetic acid, methyl ester (K) 1,1,3,3-Tetrabromoacetone (L) 2,4,6-Trichlorophenyl isocyanate

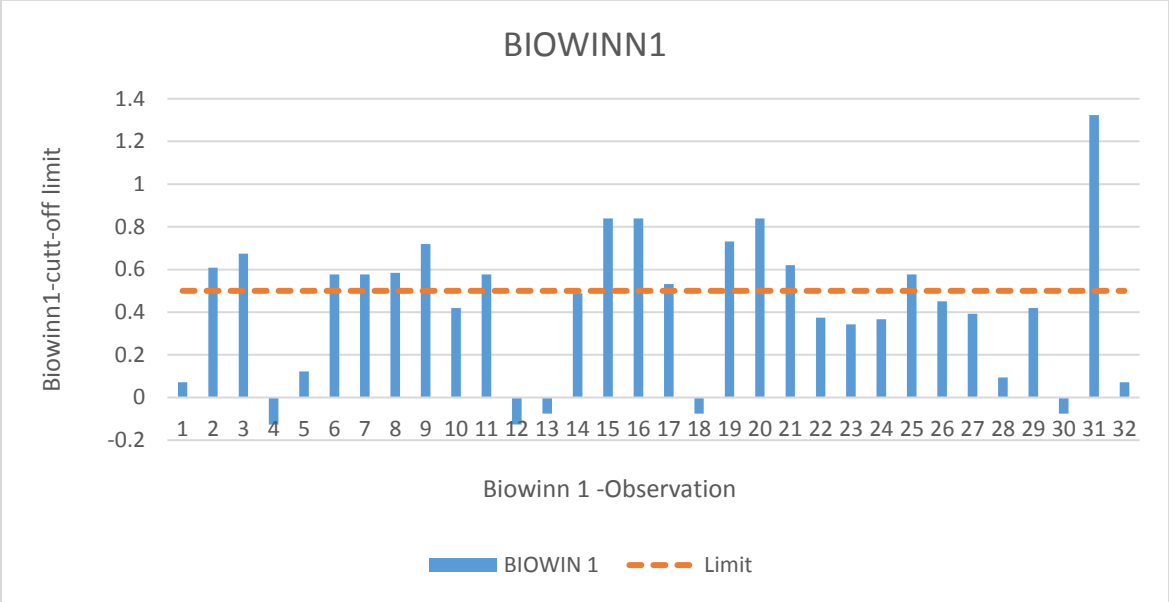


Figure 4.16 The graph showing the BIOWINN1 results, 17 compounds shows persistent

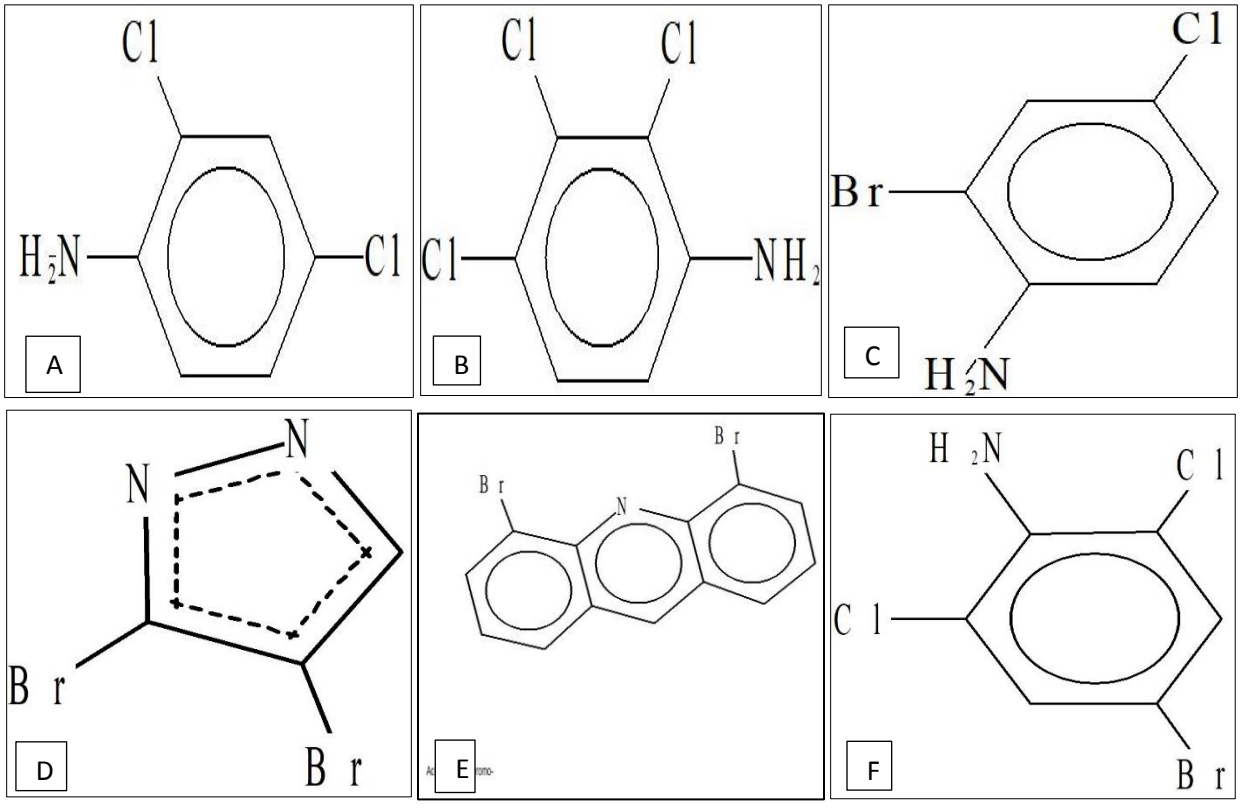
4.5.4.2 BIOWINN2

Chemicals are non-biodegradable or persistent if less than 0.5 results from biowinn2 model i.e. non-linear biodegradation limit set by REACH 2007. results Reported that 27 out of 32 chemicals falls under category of persistent (REACH 2007) results from biowinn2 for these are less than 0.5

Table 4.9 BIOWINN2 results

SN	Chemical
1	Benzenamine, 2,4-dichloro-
2	Benzenamine, 2,3,4-trichloro-
3	2-Bromo-4-chloroaniline
4	Acetaldehyde, tribromo-
5	Bromodichloroacetaldehyde
6	Acetic acid, dibromo-, methyl ester
7	1H-Pyrazole, 3,4-dibromo-
8	Acetaldehyde, tribromo-
9	Benzenamine, 2,3,4-trichloro-

10	4-Bromo-2,6-dichloroaniline
11	Bromodichloroacetaldehyde
12	Benzene, 1,1'-(bromomethylene)bis-
13	Benzene, 1,1'-(bromomethylene)bis-
14	Chlorodibromoacetaldehyde
15	4-Bromo-2,6-dichloroaniline
16	Hexane, 2-bromo-
17	Benzene, 1,1'-(bromomethylene)bis-
18	Phenol, 4-chloro-
19	Phenol, 2,4,6-tribromo-
20	2-Propanone, 1,1,3-trichloro-
21	Acridine, 4,5-dibromo-
22	Acetaldehyde, tribromo-
23	Tribromoacetic acid, methyl ester
24	1,1,3,3-Tetrabromoacetone
25	2,4,6-Trichlorophenyl isocyanate
26	1H-Pyrazole, 3,4-dibromo-
27	4-Bromo-2,6-dichloroaniline



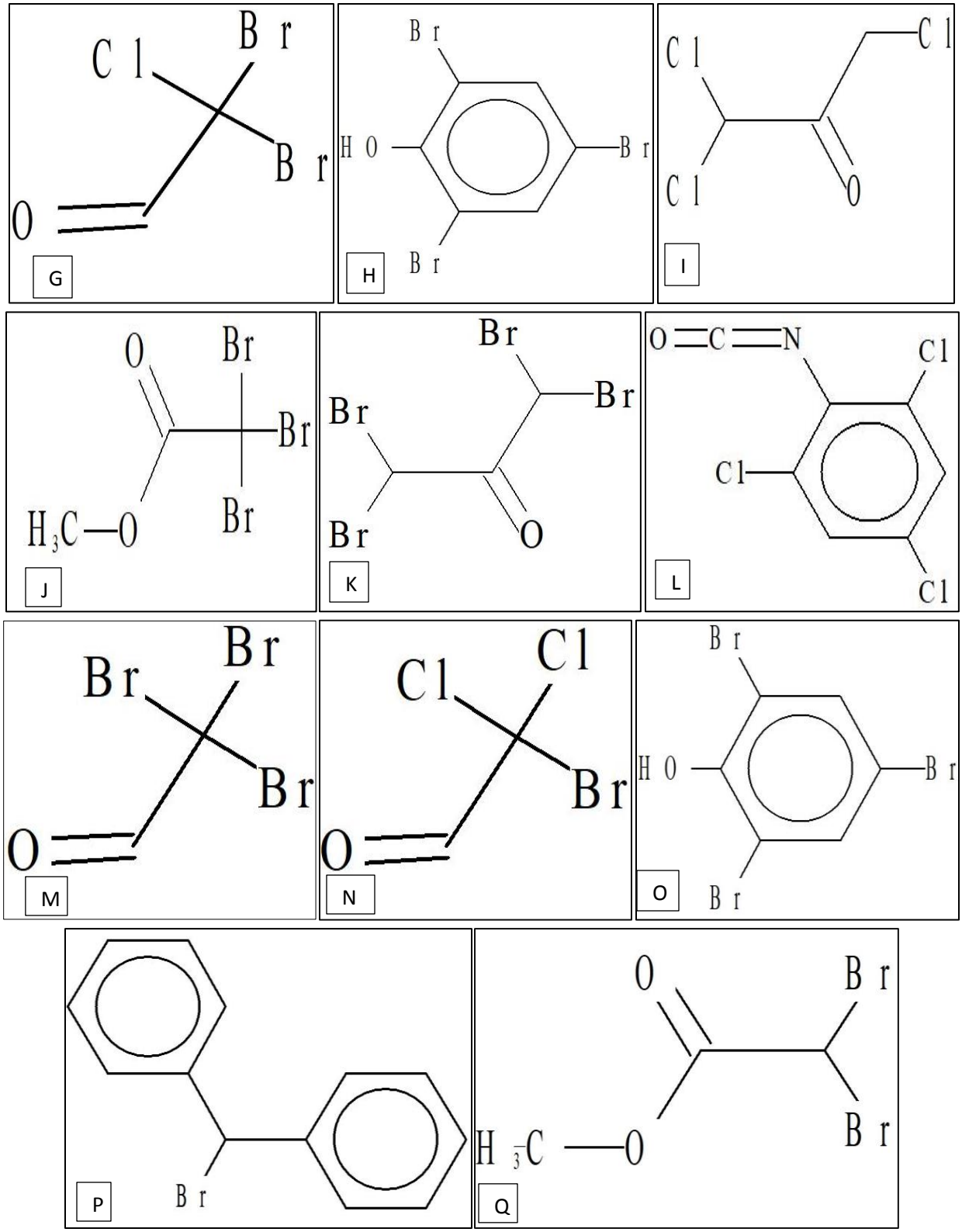


Figure 4.17 Chemical structures (A) Benzenamine, 2,4-dichloro- (B) Benzenamine, 2,3,4-trichloro- (C) 2-Bromo-4-chloroaniline (D) 1H-Pyrazole, 3,4-dibromo- (E) Acridine, 4,5-dibromo- (F) 4-Bromo-2,6-

dichloroaniline (G) Chlorodibromoacetaldehyde (H) Phenol, 2,4,6-tribromo- (I) 2-Propanone, 1,1,3-trichloro (J) Tribromoacetic acid, methyl ester (K) 1,1,3,3-Tetrabromoacetone (L) 2,4,6-Trichlorophenyl isocyanate (M) Acetaldehyde, tribromo- (N) Bromodichloroacetaldehyde (O) Phenol, 2,4,6-tribromo- (P) Benzene, 1,1'-(bromomethylene)bis- (Q) Acetic acid, dibromo-, methyl ester

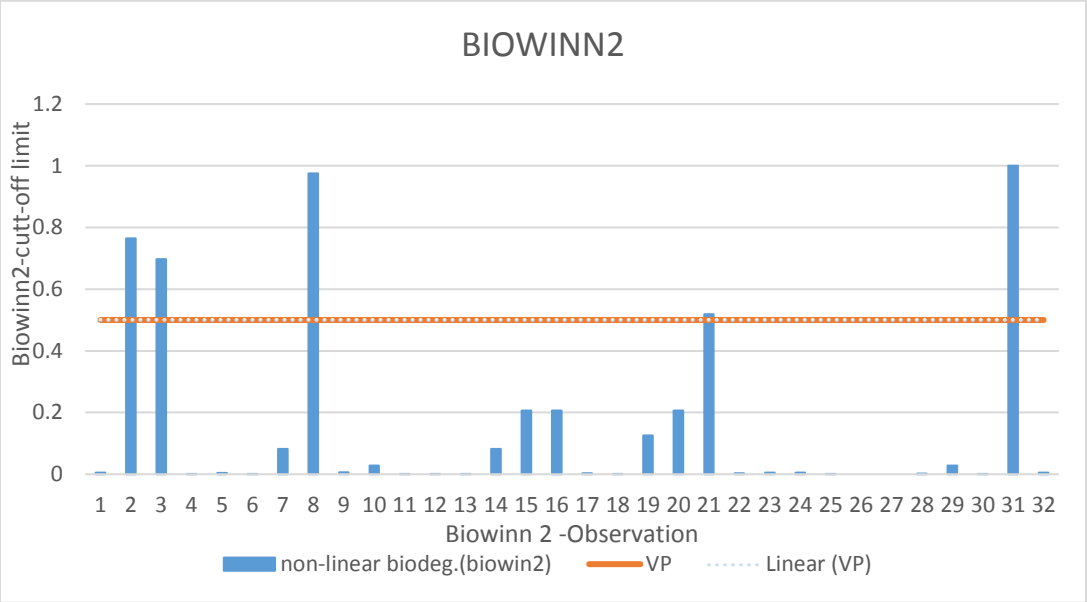


Figure 4.18 The graph showing the BIOWINN2 results, 27 compounds shows persistent

4.5.4.3 BIOWINN3

Limit set for biowinn3 was less than 1.7 considered highly persistent. Reported from our results, 6 out of 32 highly persistent and non-biodegradable from biowinn3.

Table 4.10 BIOWINN3 results

s.no	chemicals
1	Benzenamine, 2,3,4-trichloro-
2	4-Bromo-2,6-dichloroaniline
3	Benzenamine, 2,3,4-trichloro-
4	Phenol, 2,4,6-tribromo-
5	2,4,6-Trichlorophenyl isocyanate
6	Benzenamine, 2,4-dichloro-

.

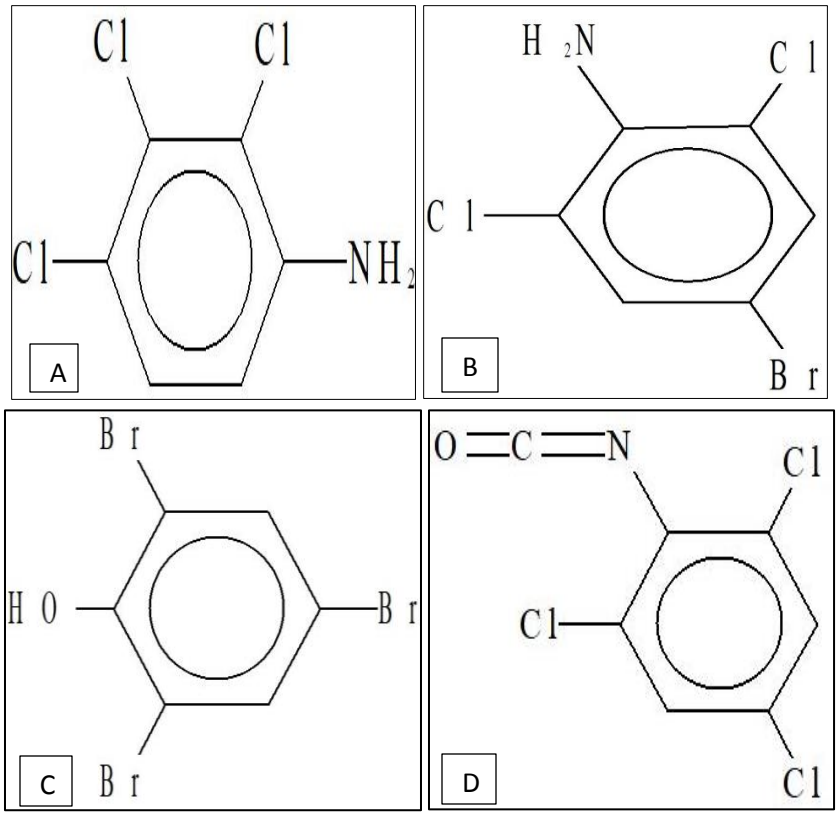


Figure 4.19 Chemical structures (A) Benzenamine, 2,3,4-trichloro (B) 4-Bromo-2,6-dichloroaniline (C) Phenol, 2,4,6-tribromo- (D) 2,4,6-Trichlorophenyl isocyanate

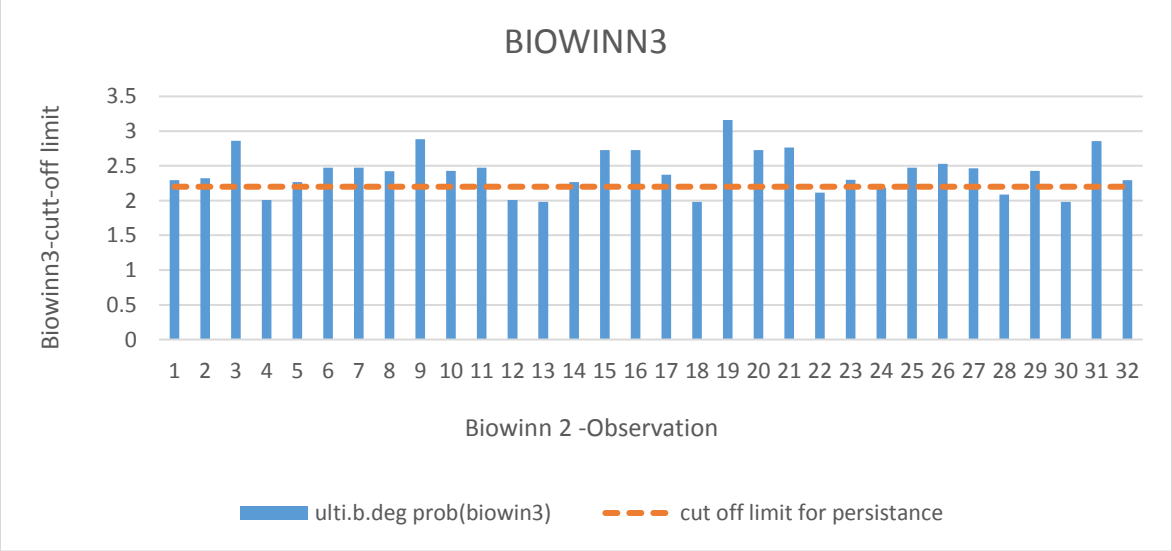


Figure 4.20 The graph showing the BIOWINN3 results, 6 compounds shows persistent

4.5.4.4 BIOWINN4

Limit set for persistence is less than 1.7 (count as highly persistent for biowinn4) no chemical is persistent in primary degradation or according to biowinn4.

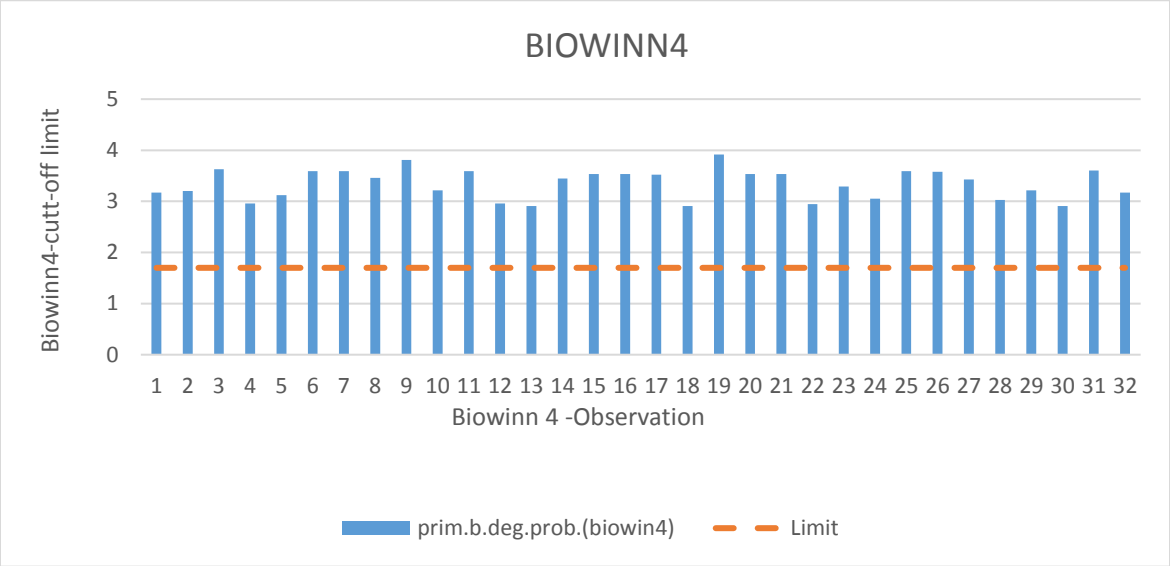


Figure 4.21 The graph showing the BIOWINN4 results, none compound show persistent

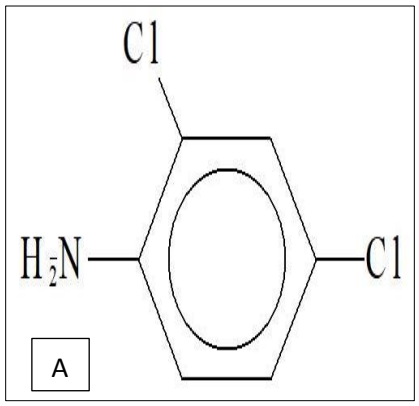
4.5.4.5 BIOWINN5

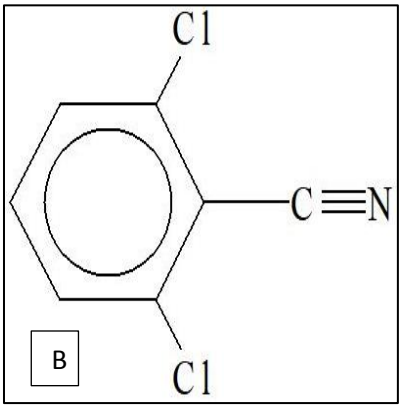
Limit set for biowinn5 is less than 0.5. results showed 22 out of 32 persistent.

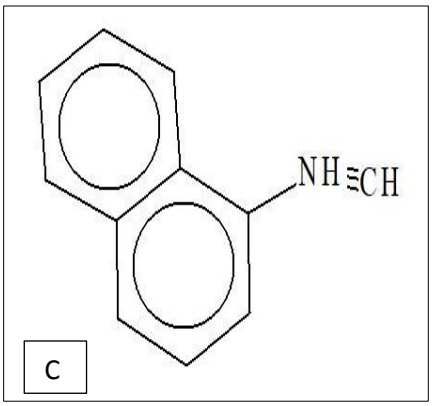
Table 4.11 BIOWINN5 results

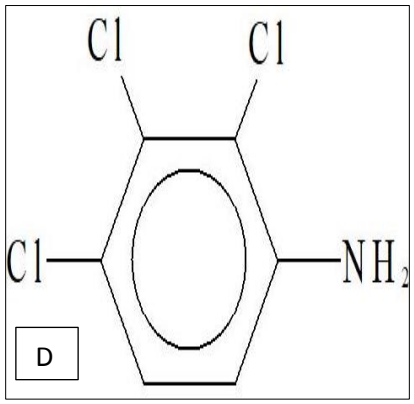
s.no	Chemicals
1	Benzenamine, 2,4-dichloro-
2	Benzonitrile, 2,6-dichloro-
3	Naphthalene, 1-isocyano-
4	Benzenamine, 2,3,4-trichloro-
5	2-Bromo-4-chloroaniline
6	1H-Pyrazole, 3,4-dibromo-
7	Acetaldehyde, tribromo-
8	Benzenamine, 2,3,4-trichloro-
9	Benzene, 1,1'-(bromomethylene)bis-
10	4-Bromo-2,6-dichloroaniline
11	Hexane, 2-bromo-
12	Benzene, 1,1'-(bromomethylene)bis-
13	Phenol, 4-chloro-

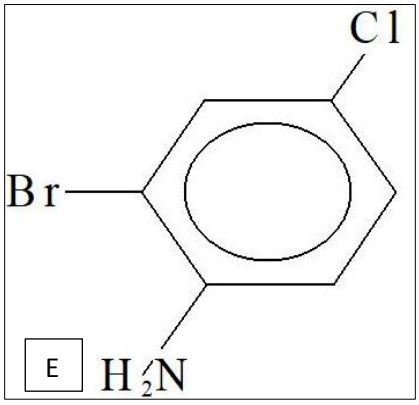
14	Phenol, 2,4,6-tribromo-
15	2-Propanone, 1,1,3-trichloro-
16	Acridine, 4,5-dibromo-
17	Tribromoacetic acid, methyl ester
18	1,1,3,3-Tetrabromoacetone
19	2,4,6-Trichlorophenyl isocyanate
20	1H-Pyrazole, 3,4-dibromo-
21	4-Bromo-2,6-dichloroaniline
22	Benzenamine, 2,4-dichloro-

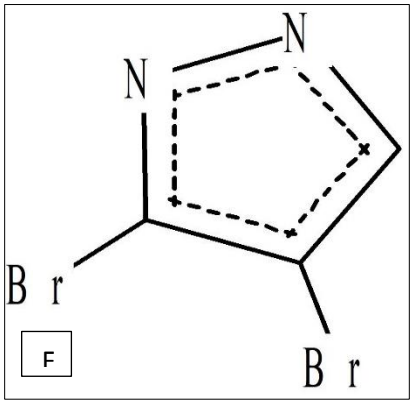


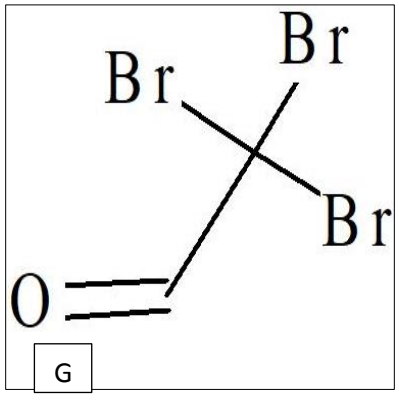


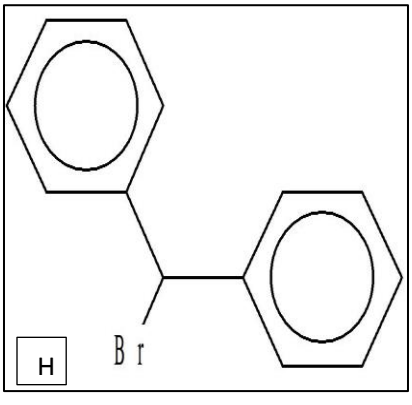


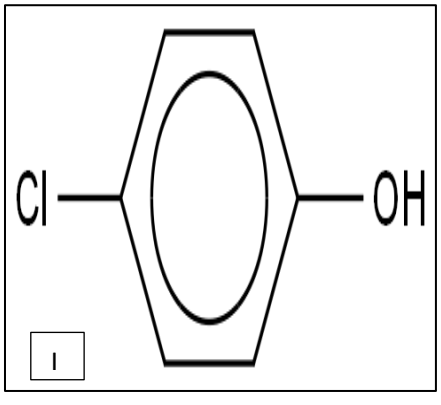












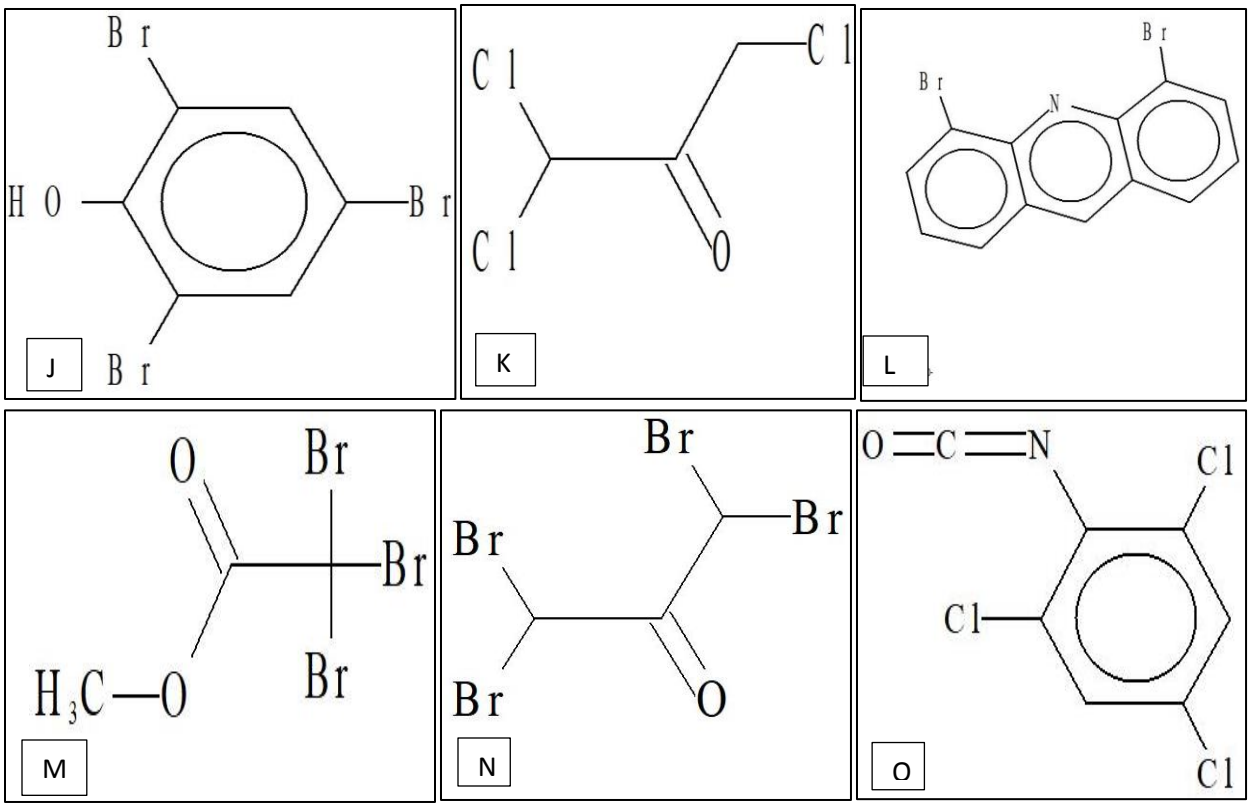


Figure 4.22 Chemical structures (A)Benzenamine, 2,4-dichloro-(B) Benzonitrile, 2,6-dichloro (C)Naphthalene, 1-isocyano- (D) Benzenamine, 2,3,4-trichloro- (E) 2-Bromo-4-chloroaniline (F) 1H-Pyrazole, 3,4-dibromo- (G) Acetaldehyde, tribromo- (H) Benzene, 1,1'-(bromo methylene)bis- (I) Phenol, 4-chloro-(J) Phenol, 2,4,6-tribromo-(K) 2-Propanone, 1,1,3-trichloro-(L) Acridine, 4,5-dibromo-(M)Tribromo acetic acid, methyl ester (N) 1,1,3,3-Tetrabromoacetone (O) 2,4,6-Trichlorophenyl isocyanate

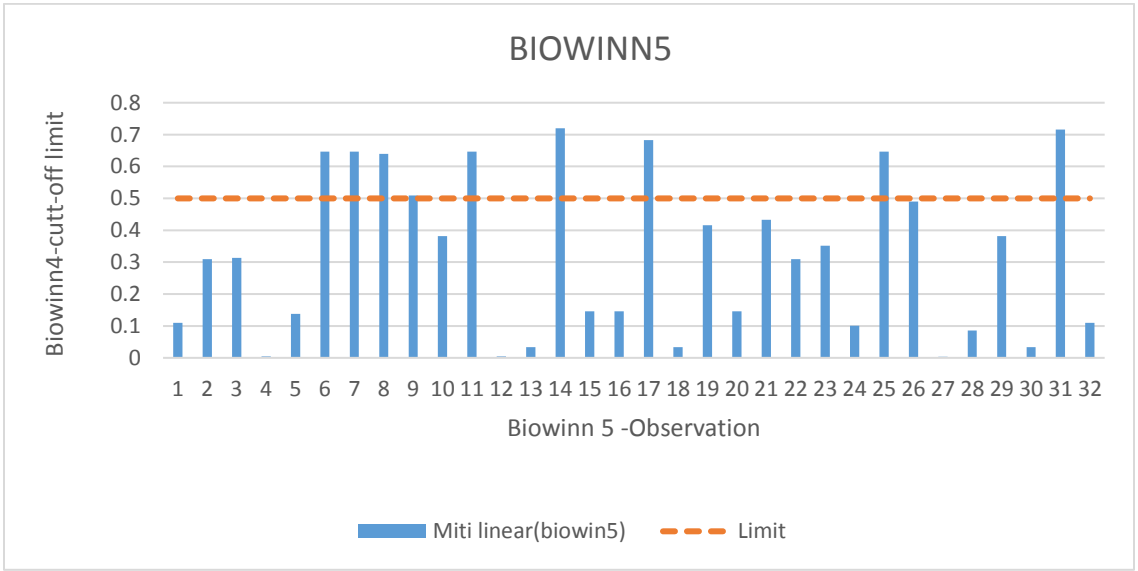


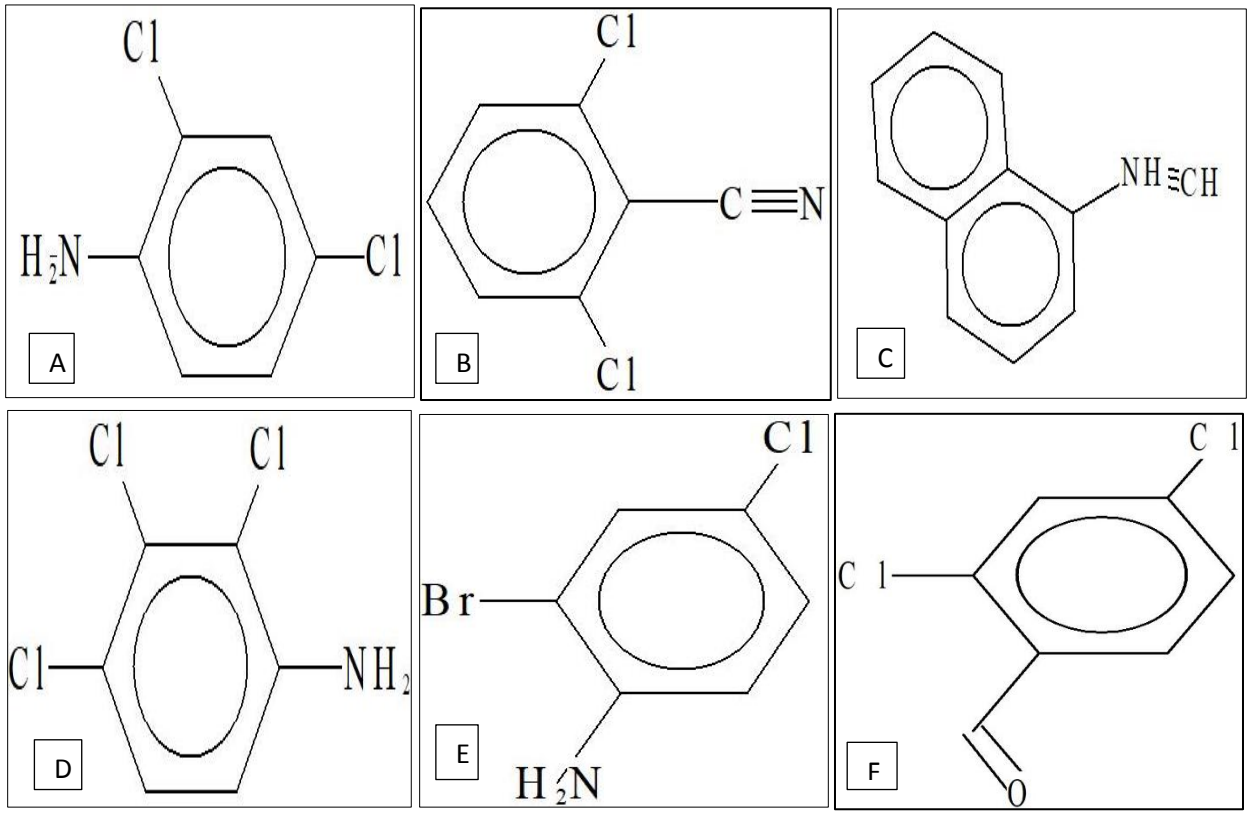
Figure 4.23 The graph showing the BIOWINN5 results, 22 compounds show persistent

4.5.4.6 BIOWINN7

Limit set for biowinn7 is less than0.5. 15 of them are considered persistent as shown in table.

Table 4.12 BIOWINN7 results

s.no	Chemicals
1	Benzenamine,2,4-dichloro-
2	Benzonitrile, 2,6-dichloro-
3	Naphthalene, 1-isocyano-
4	Benzenamine, 2,3,4-trichloro-
5	2-Bromo-4-chloroaniline
6	Benzaldehyde, 2,4-dichloro-
7	Benzenamine, 2,3,4-trichloro-
8	4-Bromo-2,6-dichloroaniline
9	4-Bromo-2,6-dichloroaniline
10	Phenol, 4-chloro-
11	Phenol, 2,4,6-tribromo-
12	2-Propanone, 1,1,3-trichloro-
13	2,4,6-Trichlorophenyl isocyanate
14	4-Bromo-2,6-dichloroaniline
15	Benzenamine, 2,4-dichloro-



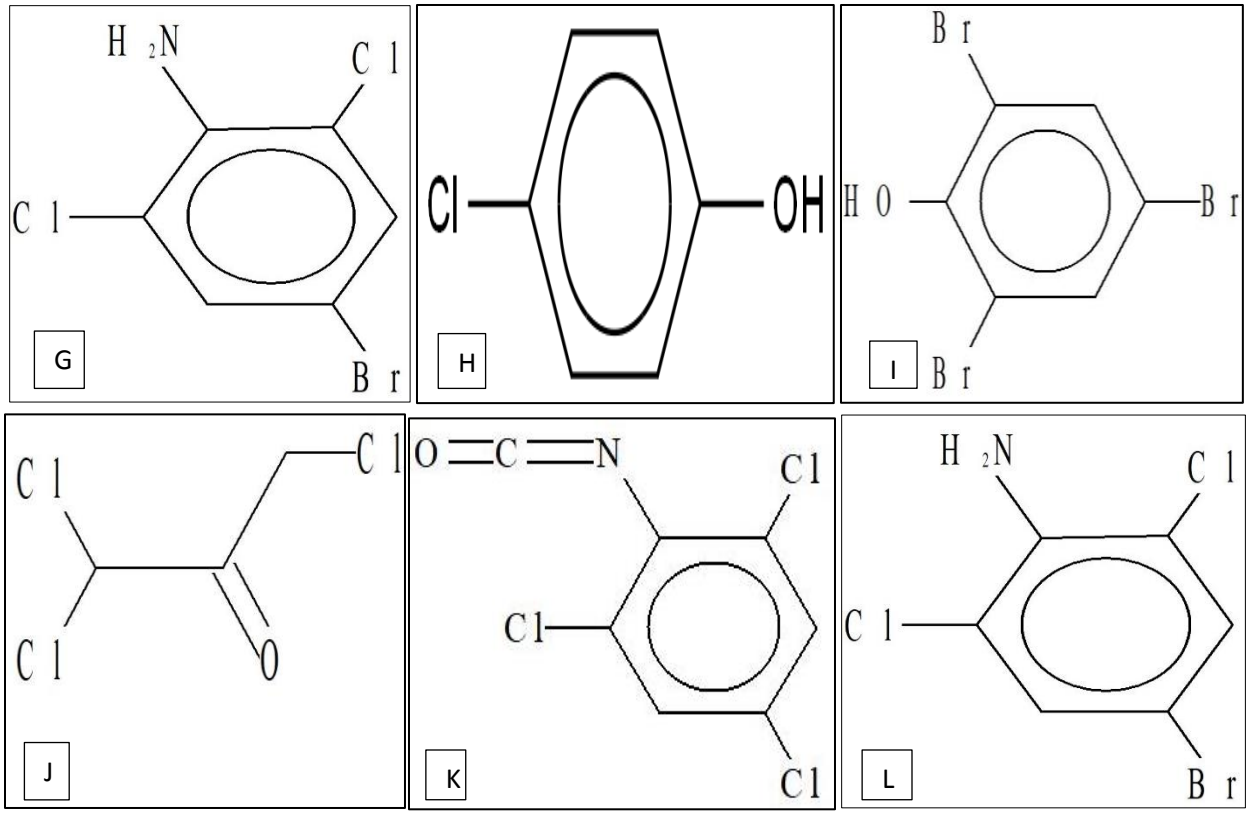


Figure 4.24 Chemical structures (A)Benzenamine, 2,4-dichloro-(B) Benzonitrile, 2,6-dichloro-(C)Naphthalene, 1-isocyano-(D) Benzenamine, 2,3,4-trichloro- (E) 2-Bromo-4-chloroaniline (F) Benzaldehyde, 2,4-dichloro-(G) 4-Bromo-2,6-dichloroaniline- (H) Phenol, 4-chloro (I) Phenol, 2,4,6-tribromo-(J)2-Propanone, 1,1,3-trichloro-(K) 2,4,6-Trichlorophenyl isocyanate (L) 4-Bromo-2,6-dichloroaniline

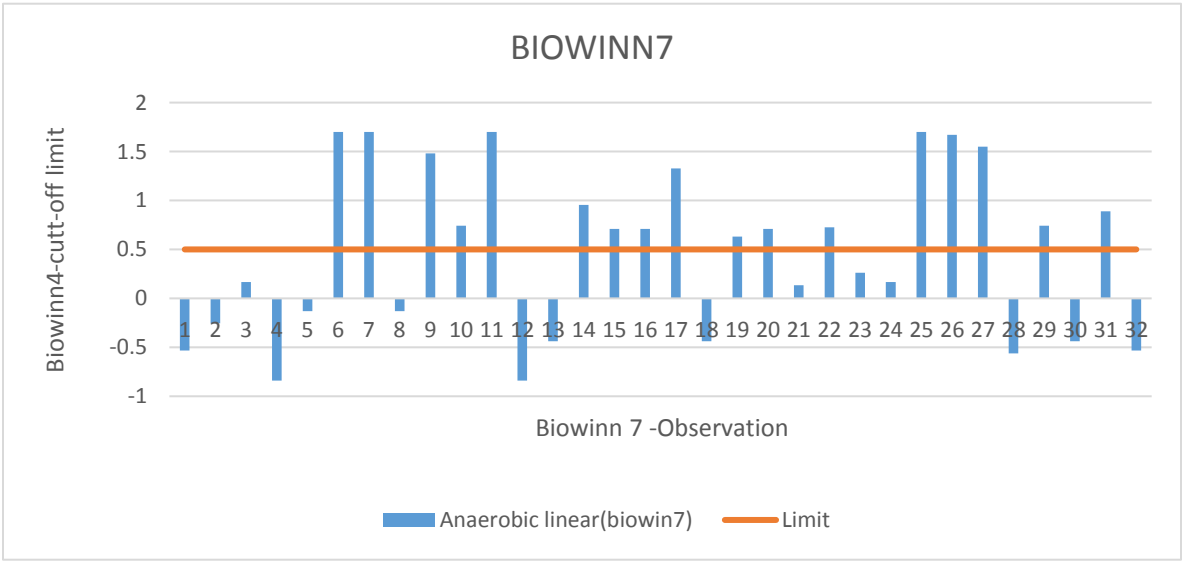


Figure 4.25 The graph showing the BIOWINN7 results, 15 compounds show persistent

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

In present study PDMS to water partition coefficients model was successfully developed which was needed to calculate the concentration in water phase by measuring concentration on passive sampling phase (PDMS). The model was based on 2-parameters linear free energy relationship (2p-LFER) between partition coefficients of PDMS-water, and octanol-water and air-water systems. Passive sampler was used for non-targets screening of organic containments present in Al-Wathba 2 Wastewater Treatment Plant, Abu Dhabi, United Arab Emirates wastewater treatment plant. Different chromatographic, mass spectrometric and computational approaches were used for monitoring the complete spectrum of DBPs. 32 DBPs were screened from waste water. Risk assessment of obtained DBPs was also done for the attributes of persistence, bioaccumulation and toxicity (PBT) using U.S. Environmental Protection Agency's Estimation Program Interface (EPI Suite™) version 4.11.

DBPs that were isolated from wastewater treatment plant have serious hazardous effects such as Phenol, 2,4,6-tribromo is serious eye irritant and very toxic to aquatic life, 1H-Pyrazole, 3,4-dibromo is acute toxic and causes respiratory irritation, Benzenamine, 2,4-dichloro is also acute toxic and causes damage to organs. In short it was concluded that the disinfected waste water is still not safe for potable and non-potable use and can causes adverse health effects including cytotoxicity, carcinogenicity, mutagenicity, miscarriage, and even birth defects.

Limitation of our study are

- We did not quantify DIBs, which need pure standards.
- We did not use performance reference compounds on passive samplers, which could have given better picture
- We only used silicone passive samplers. use of other passive sampling phases such as PE, POM, PA could have been used as additional classifiers to improve the detection of compounds.

5.2 Recommendations

New disinfected methods should be used like the use of 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 and carbon nanotubes (CNTs) an attractive adsorbent in wastewater treatment.

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