INVESTIGATING THE ROLE OF FILTRATION UNIT FOR MICROPOLLUTANTS REMOVAL IN MUNICIPAL WASTEWATER TREATMENT PLANT USING INNOVATIVE NON-TARGETED SCREENING AND ENVIRONMENTAL RISK ASSESSMENT APPROACHES

By

Muhammad Sibtain

(0000277787)

Supervisor
Dr. Deedar Nabi

Institute of Environmental Science & Engineering
School of Civil & Environmental Engineering
National University of Sciences & Technology
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A thesis submitted in partial fulfillment of the requirement for the degree of Master of Science in Environmental Science

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Submitted by

Muhammad Sibtain

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Supervisor: _____
Associate Professor
Dr. Deedar Nabi
IESE, SCEE, NUST

GEC Member: _____
Dr. Zeshan
Associate Professor
IESE, SCEE, NUST

GEC Member: _____
Dr. Muhammad Ali Inam
Assistant Professor
IESE, SCEE, NUST

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To my Beloved Parents,

and Respectful Teachers

ACKNOWLEDGEMENTS

First and foremost, all praise to Allah Almighty Who is most merciful and the most beneficent Who is the ultimate source of knowledge and wisdom. He bestowed on me the ability and an opportunity to work on this research work.

Next, I express my utmost gratitude to my supervisor **Dr. Deedar Nabi**, who has supported and guided me throughout my research. His keen interest and valuable suggestions have helped me to overcome all the obstacles encountered during my research work and I will forever be thankful for his incredible guidance. I am also thankful for the meaningful advice and inspiring attitudes of my GEC members **Dr. Zeshan** and **Dr. Muhammad Ali Inam** which encouraged me to work harder during my research.

I would like to express my special gratitude to **Dr. Yasuyuki Zushi** of the National Institute of Advanced Industrial Science and Technology, Japan and **Dr. Farrukh Ahmad** from Environmental Health Solution California, USA for their extended support and valuable input throughout. I would like to thank the Al-Wathaba Veolia Besix, Abu Dhabi Executive Council, and Masdar Institute, Abu Dhabi for dispensing invaluable time and resources to carry out this research.

This acknowledgment would be incomplete if I do not pay my sincere and heartedly thanks to my cherished and loving parents for their sacrifices, prayers, and affections without which it would have been nearly impossible to achieve my goals. My sincerest thanks to all my friends at IESE and the research group for their continuous support and encouragement throughout my time at NUST. I would like to especially thank my best friend **Muhammad Usman Siddiqui** for being eternal support and staying with me in all highs and lows throughout this time. Last but not least I would like to thank all the laboratory staff at IESE for their help and cooperation.

I would also like to mention my group of friends namely **Suhaib Malik**, Kashif Imran, Amir Younus, Irfan Khawar, and Alfred Ndorwu Barnett for making my life at NUST the most memorable one. Along with them, I dedicate this thesis write-up to my 2018 session engineering class for helping and supporting me throughout my MS.

Muhammad Sibtain

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LIST OF ABBREVIATIONS/ KEYWORDS

TOF-MS	Time of Flight - Mass Spectrometer
NMF	Non-negative Matrix Factorization
WWTP	Wastewater Treatment Plant
HLC	Henry Law Constant
PDMS	Polydimethylsiloxane
POM	Polyoxymethylene
UNDP	United Nations Development Program
BCF	Bioconcentration Factor
BMF	Biomagnification Factor
Kow	Octanol/water Partitioning Coeficient
SARs	Structure-Activity Relationships
EPA	Environmental Protestation Agency
PAA	Peracetic Acid
DBS	Diffusion Bag Sampler
SPMD	Semipermeable Membrane Device
SPME	Solid-phase micro-extraction
EPI	Estimation Programs Interface
TWA	Time-weighted average
UNEP	United Nation Environmental Program
ECOSAR	Ecological Structure Activity Relationships
GC×GC	Comprehensive two-dimensional gas chromatography

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Abstract

The rise in population, urbanization and development around the globe has caused a massive deterioration in the ground water table and surface water which has led to the growth of many micropollutants and pathogens. The presence of these micropollutants and pathogens is alarming and has been causing a rise in multiple diseases. One of the most feasible and commonly used process to remove these micropollutants is the filtration process at a wastewater treatment facility. Filtration is an integral part of a typical wastewater treatment plant that removes particulate matters, suspended solids, dissolved solids, etc. Mechanistically they are supposed to remove micropollutants that occur in ultra-small concentrations, but various researches indicate that the filtration process has led to the formation of many other known and some new micropollutants which might pose a threat if present in alarming quantities. This research was undertaken to identify those micropollutants and to completely understand the complexity of their non-removal and evaluate the performance of a typical filtration system applied in an Al Wathba wastewater treatment plant, Abu Dhabi. To this end, silicon passive samplers have been deployed before and after the filtration process. The samples were analyzed using comprehensive two-dimensional gas chromatography (GC×GC) coupled with a time-of-flight mass spectrometric detector (TOFMS). The spectra were further analyzed using the non-matrix factorization (NMF) deconvolution technique. A non-targeted screening approach was applied to limit the identified analytes to 44 micropollutants. Using Estimation Program Interface (EPI-Suite) different modules, the research carried out a detailed risk assessment of identified micropollutants by checking their fate, behavior, transport, persistence, and toxicity, which showed that out of 44 chemicals, 12 are bio-accumulative, 18 persistent, and 24 are toxic by nature. The results also depict that newly identified chemicals and micropollutants require to be regulated and mainstreamed.

Keywords:

GC×GC, TOFMS, NMF deconvolution technique, chemical risk assessment, EPI-Suite

Chapter 1

1 Introduction

1.1 Background

Since the establishment of the industrial sector and with its revolution in the 19th century (Allen, 2017), the consumption of water has been ever increasing. The vitality of water is such that the existence of life depends on it. Earth is 70% water and water are considered a renewable and never diminishing source. However, the reality is quite the opposite as various regions on the earth's surface are water-scarce and some areas are vulnerable to water scarcity. Besides this, the quality of freshwater is deteriorating day by day due to several factors. Considering water as a non-renewable resource and ensuring its qualitative availability to the public must be the need of the hour.

As UNDP stated, the overall virtual accessibility of water around the globe is sufficient to fulfill day-to-day requirements. On average, the total water usage for domestic purposes is less than 10%, whereas other sectors like agriculture and industries use water much more than domestic (Islam & Susskind, 2015). The water right is only limited to some basic personal and domesticated needs. This basic need for water only makes a small portion of overall local use. Even in the context of climate change, which overall affects water availability, water for personal and domestic use can still be ensured if prioritized as required by human rights law. On average, 50 to 100 liters/capita per day is required and an absolute 20 liters/capita per day is the threshold limit. But with time, this availability is diminishing rapidly which arises a global concern among nations (Inocencio, Padilla, & Javier, 1999).

Water shortage and scarcity are rising around the globe and are becoming a major threat to multiple nations (Postel, 2014). According to the United Nations, around 30 countries out of 167 are facing water scarcity. Several factors like never-ending growth in population, urbanization, socio-economic advancements, and the change in the consumption behavior and pattern have contributed to the increase in water usage by 1 percent per year since the decade of 1980s. More than 2 billion humans live in countries that are highly water-stressed and about 4 billion humans are exposed to intensive water shortage for at least one month per year. If the demand for water increases and the impacts of climate changes escalate, the water stress levels will tend to increase (Hoekstra, Mekonnen, Chapagain, Mathews, & Richter, 2012).

1.2 Water Consumption

Every walk of life is undeniably dependent on water consumption. Water consumption around the globe is categorized into three sections which include domestic use, industrial use, and agricultural use. The agricultural usage of water mounts up to 70 % of total water consumption while domestic consumption is 7% and industrial usage is 23%. With the technological advancements in agricultural development, nations have been able to curb extensive usage of water and hence the yearly trend represents that agricultural consumption has not increased from 70% in the last decade (Massingham). But with the urbanization and industrial boom, consumption has been ever increasing over the last decade. Since 2014, industrial water usage has increased from 19% to 23%.

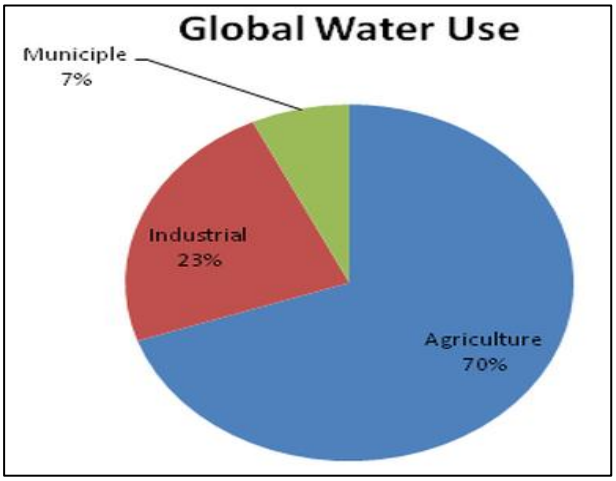


Figure 1: Global Water Consumption (Source: Aquastat. Fao)

These figures change in developed industrialized countries where more than 50 percent of water consumption is due to industrial activities. Belgium, for instance, uses 80 percent of the available water available for industry. Due to such massive usage of water, in the last 50 years, freshwater withdrawals have increased threefold.

1.3 Water Scarcity in Pakistan

Pakistan is considered an agricultural state with increasing water consumption on yearly basis. The obsolete practices for water consumption in each sector are still in use which has caused a massive surge in a water shortage. The availability of water in Pakistan has reduced to 935m3/person. Whereas, 70 years ago the water availability per person was 5,260 m3 (Bhatti & Nasu, 2010). The water availability will be further reduced to 860m3/person if any effective strategy will not be formed for water conservation. It is

believed by experts that water availability will be declined to 500m3/person by 2040. There are almost 167 countries in the world that are facing water scarcity. Of these 167 countries, Pakistan lies in 23rd number. Pakistan also is on the list with other 33 countries that are predicted to aspect acute water shortages in near future (Adeel & Wirsing, 2016).

It is expected that the water demand will increase to 274 MAF by 2025 whereas, the supply will be remained constant i.e. 191 MAF. It will cause a gap between demand and supply of about 83 MAF. Pakistan is a country that has a water usage rate fourth highest in the world. The economy of Pakistan is the most intensive in the world. It means that water utilized in GDP in Pakistan is the highest rate of water consumption in the world. It shows that productivity or efficiency is the bottommost in the world. According to NASA research, the Indus water basin is the second most over-stressed water channel in the world. It has maximum water exits with very low or no water added every year (Sharif, Jabbar, Niazi, & Mahr, 2016).

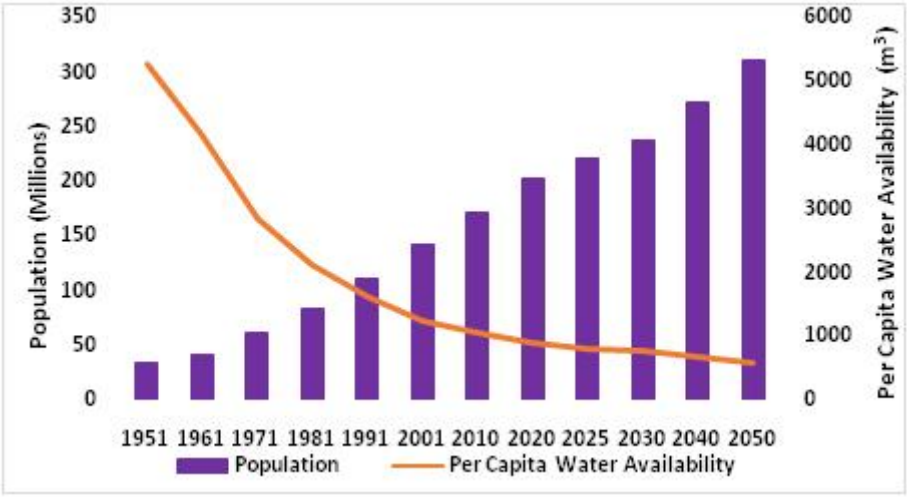


Figure 2: Per Capita Water Availability vs population (Source: https://www.worldometers.info/water/pakistan-water/)

The above figure identifies that the water available per capita is already less than 1000 m^3 and it will be decreasing further in the coming years. This is a testament that the negligence of the concerned authorities and the government is going to cost a lot. This will directly impact the economy as Pakistan is an agriculturally based economy. It is the need of the hour to take the water shortage seriously and work on the better management of water resources available in Pakistan.

1.4 Wastewater Production

As the worldwide consumption of water is increasing, the production of wastewater is also increasing. The critical component in the water cycle is wastewater. There is a need to manage wastewater in the whole water management cycle. It means that wastewater should be managed during the deliberation of freshwater, water treatment, usage, circulation, assortment, and post-treatment for its reuse and ultimate re-visitation of the climate. In ultimate return, the treated wastewater is used for replenishing the source of water abstraction. As per an article published by the United Nations University in 2021, from all over the world the yearly production of wastewater is about 359 billion m^3. This wastewater production rate is equivalent to 144 million swimming pools of Olympic size (Zhongming, Linong, Wangqiang, & Wei, 2021). This number shows the drastic nature of wastewater produced in the world due to domestic, agricultural, and industrial activities. The report also discusses the amount of wastewater being treated and reused around the globe. According to the report, only 52% of the produced wastewater is being treated and 48% of that wastewater is untreated and released into the streams (Jones, van Vliet, Qadir, & Bierkens, 2021). This is much lower than the frequently cited figure of 80 percent. Besides this research, the author warned that the rate of treatment in developing countries is still very low.

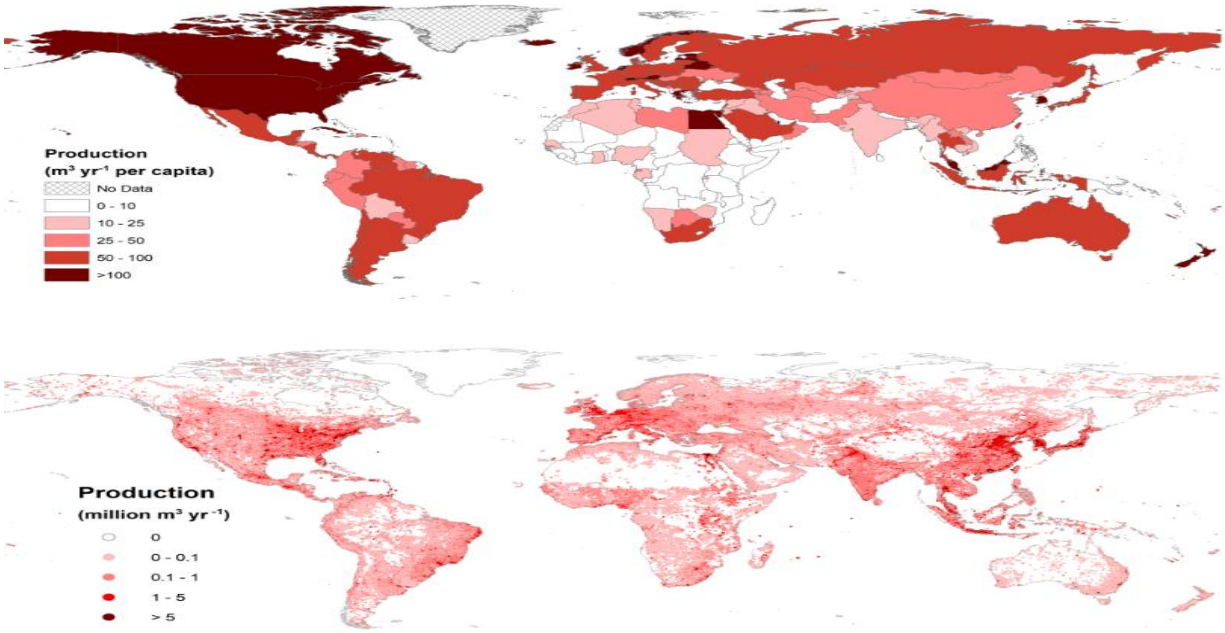


Figure 3: Wastewater Production Around the Globe (Source: https://inweh.unu.edu/wastewater-treatment-status-by-countries-and-economies/)

1.4.1 Industrial Wastewater Production

The rate of industrial wastewater generation is unknown to a larger extent. The data and information collected for volume wastewater all over the world are very few. This data is not enough for any result. Whereas some information is present which is stronger. There is limited data in European Union which indicates that there is a general decrease in wastewater generation. The data indicates that among all industrial sectors manufacturing is the greatest wastewater generator. However, there are few countries whose data show that the major polluter of water is industry. Also, only a little portion of wastewater is treated before discharge.

1.4.2 Domestic and Agricultural Wastewater Production

With the technological advancements, the domestic and agricultural water usage systems have decreased the overall wastewater generation. Rather, a beneficial approach to using treated wastewater in agricultural activities is rising globally. To apprehend the wastewater production of domestic and agricultural activities is quite challenging as multiple factors are constantly changing. For example, the characteristics of wastewater like its strength and composition vary with time i.e. the variations are hourly, daily, and seasonal. The strength is also dependent on the habits, diet, water usage per capita, and lifestyle. The usage of water for domestic purposes is the basic reason for variation in water usage. To collect all these intricate details in a tough process and therefore, no certain number to indicate the production of wastewater due to domestic and agricultural activities has been established. But some information present establishes that the wastewater production for developing countries is larger than that of developed nations.

1.5 Wastewater Generation in Pakistan

In Pakistan, according to official data, the volume of wastewater generated every year is 4.36 billion m3. From this generated wastewater only 1.30 BCM is generated by industry whereas the remaining 3.06 BCM is generated by domestic water use. Currently, not even 1% of the total wastewater gets treated before its disposal. From this generated wastewater 1.02 BCM is used in irrigation (Qureshi, 2005). This wastewater used for irrigation is untreated. Every year almost 32,000 ha of agricultural land is irrigated by using this untreated wastewater. About 1.43 BCM wastewater is discharged into the rivers without treatment every year. Due to this contamination of

water annual income loss is faced by the country. Also, the waterborne diseases cause the deaths of many children under 5 due to this contaminated water (Cissé, 2019).

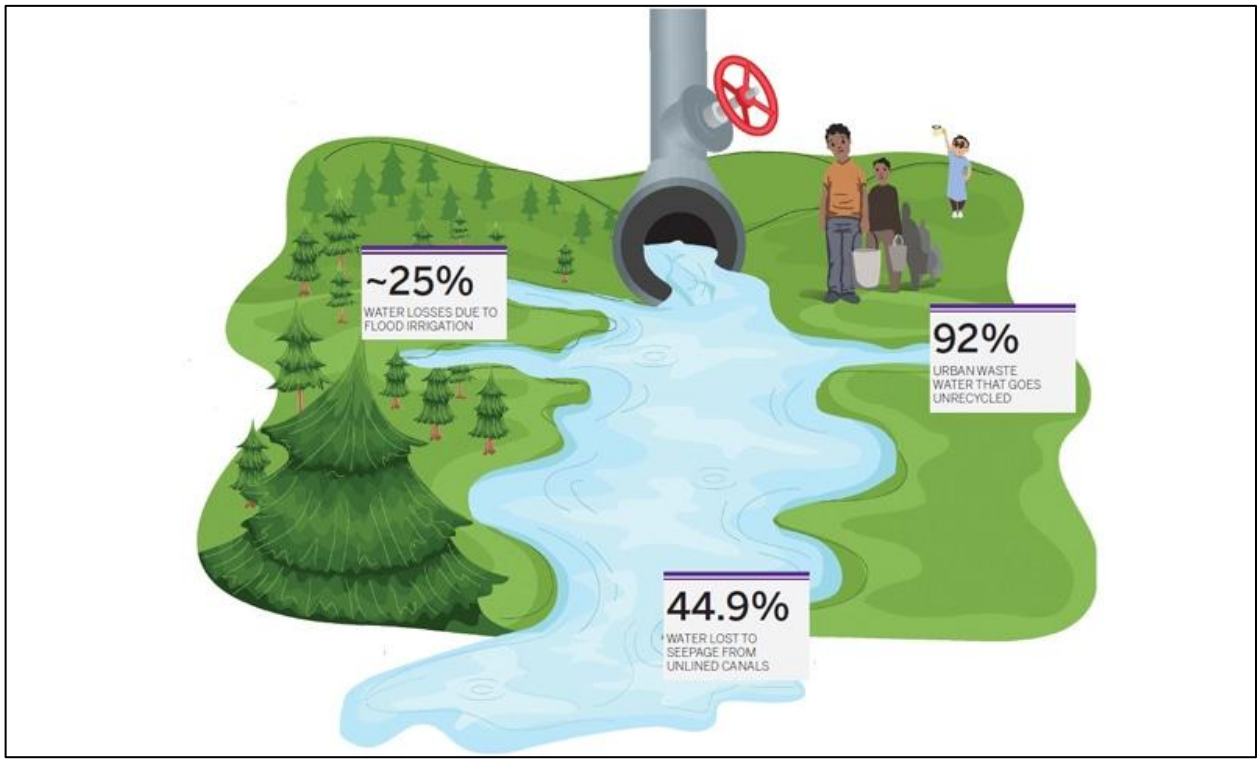


Figure 4: Fresh Water loss and Untreated Wastewater in Pakistan (Source: https://www.dawn.com/news/1428966)

In Pakistan, it is a general trend that wastewater generated from households containing human waste is directly discharged into a sewer or nearby water body, field, or to an internal septic tank. In Pakistan, there are biological treatment plants for the treatment of domestic wastewater which treat only a small portion of wastewater in Karachi and Islamabad. Whereas all other cities do not have these treatment plants and discharge untreated wastewater. If it is assumed that all the treatment plants are working at full capacity, even in such a situation they only treat 8% of the urban wastewater. Whereas there are other estimates according to them this percentage is no more than 1%. This treated wastewater is not used for agriculture or in other processes. It is simply discharged into the drain (Murtaza & Zia, 2012).

1.6 Wastewater Treatment

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

came about. After that advances in wastewater treatment plants began by introducing physiochemical and biological treatments. The twentieth century experienced key development in this field, and the understanding of wastewater has changed since the 20th century (Lofrano & Brown, 2010).

Usually, two types of treatment plants are present that are biological wastewater plants and physical or chemical wastewater plants. Biomass and microorganisms are used in biological treatment to break down the waste. While physical or chemical wastewater treatment involves the use of different chemical reactions along with various physical processes. The wastewater treatment plant comprises 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 before the discharge of effluent, the final stage of the wastewater treatment plant is disinfection which removes pathogens from effluent (Hendricks & Pool, 2012).

1.7 Sampling Techniques

For the detection of micropollutants and pathogens 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 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 (Petrović, Gonzalez, & Barceló, 2003).

International water quality monitoring programmers commonly used spot or grab sampling procedures for the determination of pollutant levels in the water. This technique has different disadvantages such as it being quite costly, giving the analysis of currently present contamination in water, is unable to give the result of seasonal, sporadic, and tidal contamination, and unable to measure the concentration of dissolved contaminants accurately.

1.7.1 Passive Sampling

Over the past two eras, different other strategies have been sought 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 pollutants in an aqueous environment is passive sampling (Namieśnik, Zabiegała, Kot-Wasik, Partyka, & Wasik, 2005). 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 to observe the water quality like European WFD (Water Framework Directive). Generally, passive sampling is dependent upon the free progression of analyte particles from the mechanism of sampling to the means of collection. It is performed because of the chemical potential difference between two media analytes. The flow between two media is continued until the equilibrium is established or the sampling session reaches its end (Górecki & Namieśnik, 2002).

The passive sampling technique has several advantages as compared to spot or grab sampling technology. They have the potential to uptake freely dissolved components of chemicals present in the marine environment and help in measuring the chemical activity of containment in trace amounts. Furthermore, passive sampling results can be used as a measure of chemical bioaccumulation, bioavailability, and ecotoxicity. Different types of passive sampling devices are presently based on different sorbents materials. There is a wide series of compounds in water for sampling. for sampling. Such as semipermeable membrane devices (SPMD), low-density poly-ethylene (LDPE) film, polyoxymethylene (POM) devices, and polyurethane foam (PUF) devices, and polydimethylsiloxane (PDMS) fibers (Prokeš).

1.8 GC X GC-TOF-MS

The authenticity of various analytical applications is offered by the coupling of gas chromatography with time-of-flight mass spectrometry, as well as the analysis of food quality, and the presence of organic matter present in wastewater. Gas chromatograph-mass spectrometer is used in almost every field like; packaging, research, environmental science, food, health and safety, and many others (Sparkman, Penton, & Kitson, 2011). Gas chromatography is a technique on which many of the analytical methods are based that are used for quantification of emerging contaminants. In these

methods, chromatography is used with mass-spectrometry. The physiochemical properties of analytes will determine which kind of chromatography will be used i.e. gas or liquid. GC X GC is mostly used for the analysis of PCPIs. It is used because many compounds present have high lipophilicity. Whereas in most of the published methods of analysis of PCPI and other compounds having the same properties the method is based on GC X GC-TOFMS.

1.9 EPI Suite

Estimation Programs Interface known as EPI Suite is a window-dependent program designed through OPPT for the screening of new chemicals that are deficient in 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 is absorbed in the atmosphere, water, soil, etc. For the risk assessment of a chemical, estimation of its properties is very crucial (Card et al., 2017).

Chapter 2

2 Literature Review

This chapter encompasses all the research studied to fully understand the background, current scenario, and future planning of this undertaken research work. The data gathered from these studies paved a linear way to enhance the spectrum of the undertaken research work to provide a novel approach to mitigate the existential problems identified in the research work. The data gathered is presented in the following paragraphs.

2.1 Presence of Micropollutants in Wastewater

All over the world, the presence of micropollutants in the water or marine system is a major issue. For example, 143,000 chemicals were listed in 2012 in the European marketplace. From these compounds, many of them have entered the water system at any point in their life. These compounds are mostly not transformed into any other compound or eliminated by the treatment process. These compounds are persistent in the aquatic system or when reacts with humic matter these compounds are from new species in the presence of sunlight. These compounds are bioactive, and they can also bioaccumulate. These compounds are present in water is very low concentrations so that they become undetectable. It is generally measured in ppb i.e., parts per billion. The existence of these compounds in water is determined by different factors like genotoxicity, estrogenicity, and mutagenicity (Molander, Breitholtz, Andersson, Rybacka, & Rudén, 2012). The pharmaceutical wastewater is generated mostly from households i.e., 70%. Whereas from livestock, hospitals, and non-point sources the pharmaceutical wastewater generation is about 20%, 5%, and 5% respectively. Whereas other variations like seasonal and geographical occur. The physical properties like octanol-water partition coefficient, solubility, and Henry's coefficient determine the micropollutants' fate in wastewater (Margot, Rossi, Barry, & Holliger, 2015).

2.2 Removal of Micro-pollutants:

Mostly suspended particles, nutrients, and dissolved organics are removed in the municipal WWTP. In a WWTP, the basic units are primary and secondary treatments. Whereas tertiary treatment is an optional method of treatment that is used for the optimal treatment of wastewater. The primary treatment involves alum, polymers, and

ferric chlorides as coagulants. These coagulants effectively remove colloidal particles and suspended solids. In the process of coagulation, the organic matter is attached with the humic substance dissolved and other particles that can be removed. Whereas, pollutants are removed with the help of aerobic bacteria by keeping these microbes dispersed in the secondary treatment process. The waste produced from these primary and secondary treatment units known as sludge is then thickened. This thickened sludge is digested anaerobically before disposing of it. In some treatment processes activated carbon adsorption and ozonation are used as the tertiary treatment methods. This final treatment is done for the removal of trace concentrations of organics.

The processes used for removing these micro pollutants in WWTP involve the adsorption of these particles on the suspended matter and humic substances. Whereas the process used for the removal of these particles are coagulation, flocculation, adsorption, membrane filtration, biodegradation, and advanced oxidation. The Henry constant of these pollutants is very low ($<10^{-5}$ atm-m3/mol) due to this volatilization of them is negligible (Bidleman, 1988).

2.3 Sedimentation of Micropollutants:

The efficiency of the wastewater treatment plant is usually improved by using coagulation and flocculation. These are used for the removal of colloids, dissolved organics, and suspended solids that do not settle. In the process of coagulation, the phenomenon of destabilization is used i.e. colloids were stabilized by using different coagulants. This coagulant may be metal salt or synthetic organic polymer. They follow the mechanism of adsorption, charge neuralization, double-layer compression, and interparticle bridging. The phenomenon of coagulation is affected by pH, coagulant dose, and ionic solution strength. Generally found that the process of coagulation and flocculation is not very useful for the micropollutants removal. Whereas there is an exception in some cases. Few studies have reported that the micro pollutants can be removed by using coagulation and flocculation. In determining the removal efficacy by using flocculation and coagulation the major factor contributing is the hydrophobicity of the chemical (log K_{ow}). It was detected that the chemicals having log $K_{ow} \geq 4$ at pH 7 to 8 have the highest removal of 20 – 50%. Whereas fore step for removing micropollutants in coagulation is MPs adsorption and collides on suspended solids. So,

the efficiency of the removal of micropollutants is connected with the suspended solids removal efficiency (Das et al., 2017).

2.4 Removal of Micro-pollutants by Filtration:

For the filtration of micro pollutants, the membrane process is divided into certain membrane-based systems like; direct, integrated, and combined direct. Mostly the membrane process is driven by pressure. This process involves nanofiltration, ultrafiltration, microfiltration, and reverse osmosis. These membrane processes are used for the treatment of different kinds of effluents. From these processes, nanofiltration and reverse osmosis are high-pressure processes whereas, microfiltration and ultrafiltration are low-pressure processes. These membrane processes are effectively used as tertiary treatment (Tay, Liu, Cornelissen, Wu, & Chong, 2018). For the removal of MPs, the membrane process is used. There are different factors on which the removal of MPs depends. These factors involve membrane characteristics, MP, characteristics of the solute, membrane fouling, and operating conditions. Membrane filtration works on mechanisms like; electrostatic repugnance, adsorption on the fouling sheet, size rejection, and adsorption due to hydrophobic interaction (Cho, Amy, & Pellegrino, 1999). The most applicable process for noncharged MPs is size exclusion. However, the shape of particles should also be considered. The contributors to the micropollutant's adsorption on the membrane surface are hydrogen bonding and hydrophobic interaction. The adsorption is also increased by fouling of the membrane. Also, the adsorption is increased when dissolved organic carbons are present. This changes the pore size and surface characteristics of the membrane. Between the compounds and membrane surface, there are electrostatic interactions. The electrostatic exclusions are raised between membrane surfaces having like charges due to these interactions. . There are certain advantages of the membrane process. These advantages include no harmful intermediates, a high removal rate, good adaptability, and robustness (Das et al., 2017).

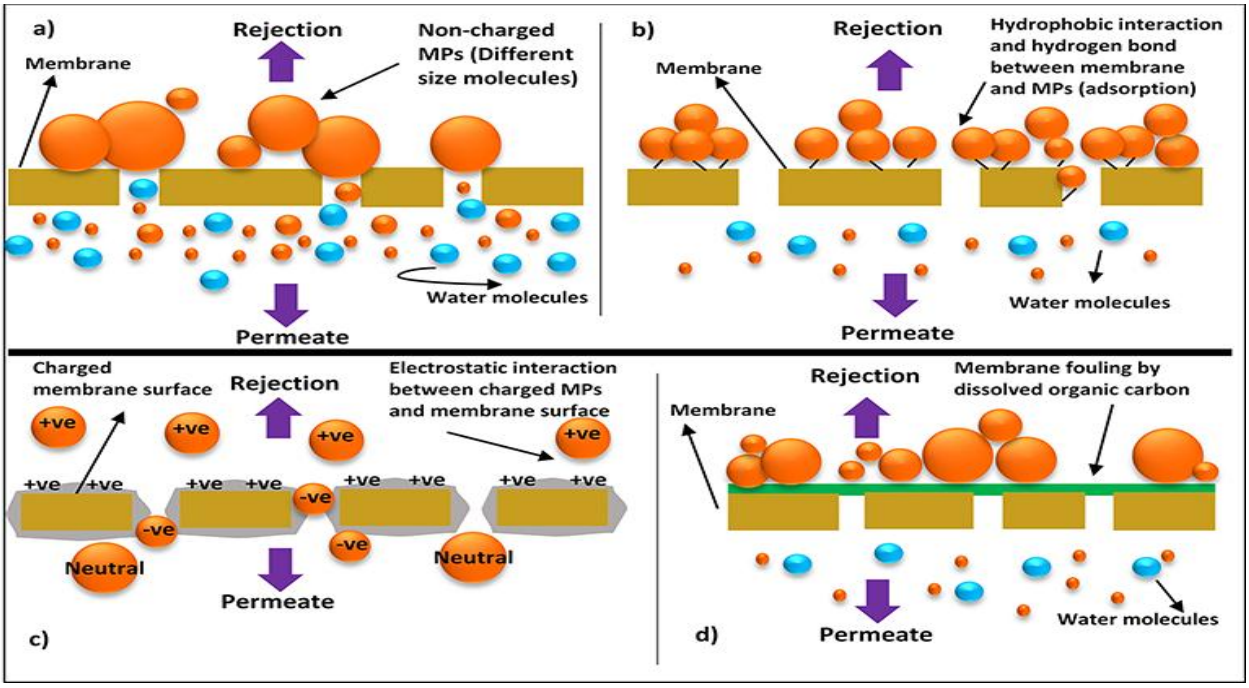


Figure 5: Removal of MPs in Filtration (Source: Rocca DGD et al, 2021)

This was the general method explained for the removal of micropollutants but at Al Wathba (2) wastewater treatment plant dual filter media is used for the filtration purpose instead of membrane filtration which also works on the principle of ab/adsorption. In dual media sand and pumice stone are used. This dual filter media of sand and pumice stone is very efficient in turbidity removal and moderate in total dissolved solid removal but we will check how much it is effective in micropollutants removal.

2.5 Persistent Micropollutants:

The wastewater treatment for the removal of micropollutants is complex. It is difficult to access because of the cost-intensive and tedious analysis. Whereas estimation of these processes is made based on physical properties like; solubility, pKa, and K_{ow}. Adsorption on suspended and colloidal particles and resulting evacuation in muck might happen for chemicals with log $K_{ow} > 4$. Generally, the activated sludge process is not effective for the removal of these MPs. So, the removal of these MPs can be better in membrane bioreactors. This removal is because of the greater adaptability and diversity of microorganisms. There is significant removal of compounds that have biodegradation constant <0.0042 L/gss/h and transformation is greater than 90% for compounds with rate constants greater than 0.4 L/gss/h (Das et al., 2017).

Some compounds can be removed partially in wastewater treatment. These compounds involve personal care and pharmaceutical compounds. Mostly these compounds and products produced by their degradation are out of control. There are very few compounds that are covered under the legal regulations. The target compounds are among the compounds that are non-regulated by law, along with non-target chemicals that can be observed. In the literature, different articles were present on several target compounds, determining their growth. It is a present-day challenge to effectively protect the aquatic ecosystem, reduction of negative impacts on the health of humans, and preservation of their good condition.

The main purpose of waste-water treatment is the removal of compounds that affect human and environmental health adversely. But the research indicates that the processes used are insufficient for the treatment of wastewater. As a result of insufficient removal, there are chances that hazardous materials may enter the surface water. The main purpose of the legislation is to eliminate or reduce the emissions to the environment. Whereas the majority of the compounds remained beyond the legitimate rules (Cameron & Abouchar, 1991).

2.6 Sampling Strategies

Basic sampling strategies and techniques to collect water or wastewater sample are dependent on the sample scale and time for the collection of the sample. These techniques are discreet sampling and composite sampling. Discrete sampling is only used to collect a singular sample in a designated individual sample collection container. The sample is collected in a special container to preserve the actual chemical and physical properties of the sample and that sample is representative of these properties of the sample size for that time only. While the other strategy used for sampling is composite or passive sampling. In this method, multiple smaller samples are collected at different predetermined time intervals and then mixed in the same container.

2.6.1 Passive Sampling

Because of the difference in chemical potential, this type of sampling is dependent on the analytes' free stream from the examined media to the gathering medium. This sampling method is used for identifying different organic and inorganic compounds from different matrices involving, air, soil, and water. For passive sampling, the devices

used are generally grounded in diffusion through a barrier or membrane permeation. Living organic entities can likewise be taken as detached examples. The sample preparation and general sampling are simplified during passive sampling in most cases. Also, during this process power requirement is eliminated which also reduces the cost of analysis significantly. Mostly this technique is applied for calculating the concentrations of the time-weighted average. Generally, the passive devices used today for the sampling of water are divided into two categories. These categories are the passive samplers for gases, layer, and dispersion with the previous being more extensive and more spread.

Sampling does not require any other energy source but only the chemical potential difference between the media. Reference or receiving phases are the analytes that are captured or retained within the passive sampler in any appropriate medium. This stage can be any adsorptive, chemical analyte, or solvent. Receiving phase is exhibited in the aqueous phase, but not for quantitative extraction of dissolved contaminants.

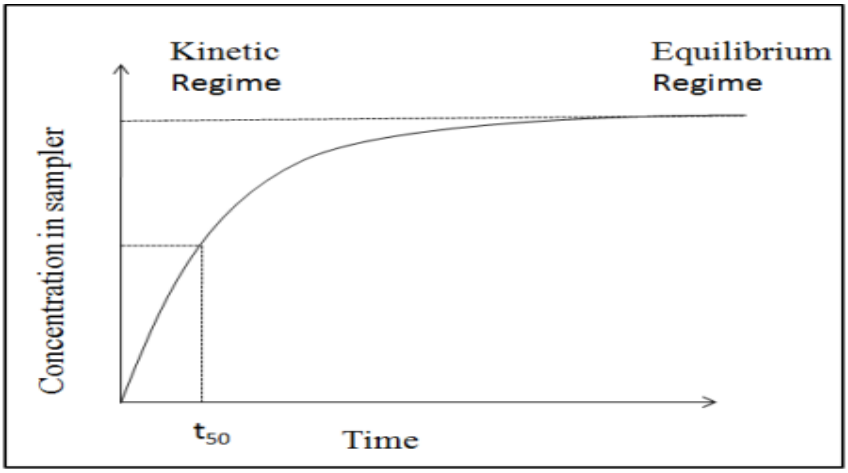


Figure 6: Time vs Concentration in Sample (Source: http://guweb2.gonzaga.edu/faculty/cronk/CHEM101pub/kinetics-equilibrium.html)

The exchange of kinetic among the aqueous phase and passive sampler can be depicted through a 1st order – mathematical model of the compartment. Equation 2.1 is shown below

$$C_S\,(t) = C_W \frac{k_1}{k_2}\,(1 - e^{-k_2 t})$$

Eqn. 2.1

In above equation $C_S\,(t)$ is the analyte concentration in a passive sampler at revealing time t, $C_W$is the concentration of the analyte in water and k1, and k2 are uptake and offload rate constants respectively. While in-field deployment, two major accumulation schemes, equilibrium or kinetics can be differentiated in the passive sampler operation.

2.6.2 Equilibrium-Passive Samplers

In this sampling, the exposure time is to the point of permitting a thermodynamic harmony established between the aqueous and the reference stage. In such condition, equation 2.1 is reduced to:

$C_S = C_W \frac{k_1}{k_2} = C_w\,\mathrm{K}$

Eqn.2.2

Knowing the partition coefficient (K) for the water phase allows for estimating the concentration of analytes that are dissolved.

The basic prerequisite for the equilibrium sampling method is to achieve a steady concentration after an acknowledged response time. The capacitance of the sampler is held below the capacity of the sample to avoid reduction through the descent procedure and the reaction time of the device requires to be briefer than any variations in the environmental medium. To calculate VOCs in the water passive diffusion bag sampler (PDBS) has been widely used (Vrana et al., 2005).

2.6.3 Kinetic Passive Samplers

By this sampling, it is presumed that the mass transfer rate to the reference stage is linearly relative to the linear ratio between the chemical activity of the contaminant in the aqueous stage and the chemical activity of the contaminant in the getting stage. At the underlying stage of sampler openness, the desorption pace of the analytes from the reference stage to the water is insignificant and the sampler works in a linear take-up state (Vrana et al., 2005). In such condition, equation 2.1 is reduced to:

$C_s(\mathrm{t}) = C_w k_1 \mathrm{t}$

Eqn.2.3

Equation 2.3 can also be set up for an equal relation:

$M_s\,(\mathrm{t}) = C_w\,R_s\,\mathrm{t}$

Eqn.2.4

In above equation M_s (t) is analyte mass gathered in the getting stage after an openness time [t] where R_s in the equation is the proportionality consistent i.e examining rate, which is obtained as a result of the first request rate steady for take-up of contaminant [k1] and amount of water having the comparative compound acts as the volume of the reference stage. $R_s$can be taken as the amount of water free from the analytes by the latent sampler per unit of openness time. C_w that is the time-weighted normal (TWA) convergence of a contaminant in the fluid stage can be determined if the upsides of R_s (examining rate), t (season of openness) and M_s (t) (the mass of analytes) amassed by the reference stage are known

In most equipment working in a kinetic model, the value of R_s(sampling rate) does not change with C_w but water or turbulence, biofouling, and the temperature usually affect its value (Booij, Van Bommel, Mets, & Dekker, 2006). The benefit of using kinetic sampling is that it 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 contaminants over prolonged periods.

2.6.4 Calibration of Passive Samplers

As previously we have described the theoretical background knowledge of passive sampling in the water. By using two different methods we can find the phase water partition coefficient (K), substance-specific kinetic constants k1 and k2 (Byrns, 2001).

In theory, semi-empirical relationships between hydrodynamic parameters, mass-transfer coefficients, and physiochemical properties chiefly diffusivities in several mediums can be used to calculate the kinetic parameters illustrating the analyte absorption. But during exposure to the water flow around passive sampling instruments, there are different complications generally in non-streamlined objects which make it difficult to calculate absorption constraints from first principles. The more specific knowledge about K can be found in literature, which depicts the chemical attraction of contaminants to the acceptance media compared to water. Through experimentally, passive sampling switch over kinetics calibration can be carried out at known exposure concentrations in the laboratory. To predict the concentration of TWA water contaminants from the levels cumulated in the passive sampler device, several standardization studies are required to characterize the absorption of compounds under

numerous disclosure situations. The kinetics of chemicals absorption depends upon the properties of the sampler as well along with the diffuser's physicochemical properties (Vrana, Mills, Dominiak, & Greenwood, 2006).

2.7 Environmental Factors Affecting Passive Sampling

Transportation of analyte atoms from the surrounding medium to the passive sampling gadget is a many steps transport process that relies upon a few variables. Various aspects like the presence of water turbulence, flow conditions, temperature, humidity rate, and temperature are some of the environmental factors that affect all passive sampling devices (Seethapathy, Gorecki, & Li, 2008).

The absorption of chemicals also relies on temperature and flow conditions. In most cases, sampling rates are low by lowering the temperature and showing a high rate at the higher temperature. To avoid such variations, sampling temperature must be optimized in the 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 affect further analysis process. In some cases, hydrophobicity can significantly change the results. Water turbulence impacts the viscosity of unstirred water layers, which results in the formation of the limiting diffusion barrier nearby the sampler surface and therefore also shows the impact on the mass transport rate of the analyte. Biofouling is the creation of a thick coating of microorganisms on the exposed side of the water. It can increase the thickness of the impediment and can block the pores which are filled with water in the membranes of passive samplers and thus decreasing the mass transfer rate of the sampler. If membranes are made up of a biodegradable material, these colonizing organisms may impair the membrane surface (Alvarez et al., 2004).

2.8 Types of Passive Samplers

Several different sorts of passive samplers are available that can be utilized to sample numerous chemicals in various conditions, so choosing the right passive sampling device is critical. Different types of passive sampling devices are presently based on different sorbents materials. Such as semi-permeable membrane devices [SPMD], low-density polyethylene [LDPE] film, polyoxymethylene (POM) devices, polyurethane foam (PUF) devices, and polydimethylsiloxane (PDMS) fibers.

2.9 Non-Targeted Screening

The detection and quantification of various chemicals are focused on target analysis. Whereas, because of the presentation of wastewater into the climate, the risk assessment of quantitative estimation of targeting synthetic compounds in the treated wastewater isn't adequate. There are many unknown substances in wastewater. The identification of many hazardous compounds is done by the screening of obscure mixtures present in the wastewater. This screening is done for maintaining surface water purity to s suitable level (Ibáñez, Sancho, Hernández, McMillan, & Rao, 2008). Determination of many specific compounds is focused on most scientific research. For the detection of these non-target pollutants in the wastewater following treatment, there are only a few reports present.

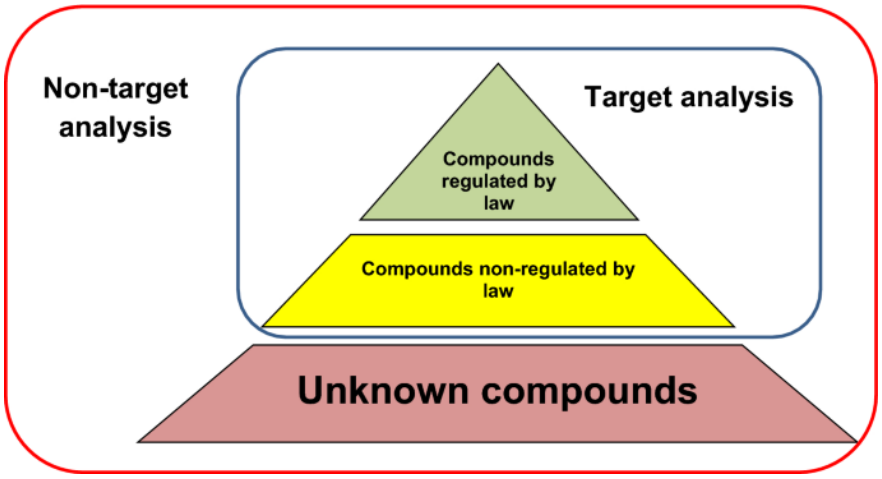


Figure 7: Non-Targeted Screening

In many applications such as toxicology, food safety, and the 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 put on to the screening, detection, and classification of organic pollutants in the aquatic environment (Díaz, Ibáñez, Sancho, & Hernández, 2012).

2.10 Role of EPI-Suite in Risk Analysis

The EPI Suite is a window-centered program designed by OPPT for the screening of new chemicals that are deficient in any experimental data. This program helps in identifying physical and chemical characteristics i.e melting point, fume/vapor pressure, etc. Chemical environmental fate can also be determined by this program such as whether the chemical is absorbed in the atmosphere, water, soil, etc. For the risk assessment of a chemical, estimation of its properties is very crucial.

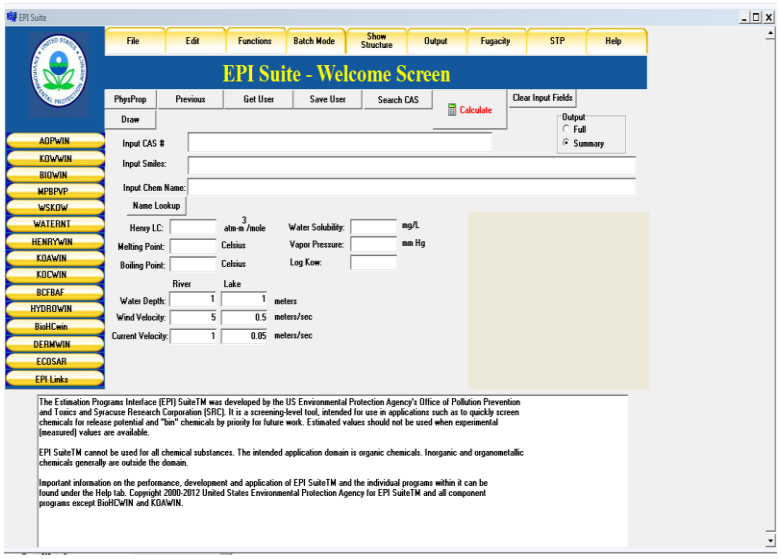


Figure 8: EPI-Suite Welcome Screen (Source: EPI-Sutie Software)

2.10.1 EPI-Suite Descriptors

US EPA developed the EPI suite. The EPI Suite is based on two modules involving BIOWIN and AOPWIN. These segments are utilized for the assessment of the destinies of natural synthetic substances in the climate. The compound's Simplified Molecular Input Line Entry System documentation is expected to contribute to utilizing EPI Suite. There are 13 discrete models of which EPI Suite consists (Card et al., 2017). These models are listed below.

- ✓ BIOWIN: estimates biodegradation probability
- ✓ BCFBAF: estimates bioconcentration factor and biotransformation rate

- ✓ ECOSAR: estimates aquatic toxicity (LD50, LC50)
- ✓ AOPWIN: estimates atmospheric oxidation rates
- ✓ BioHCwin: estimates biodegradation of hydrocarbons
- ✓ HENRYWIN: evaluations of Henry's law constant
- ✓ KOAWIN: evaluations octanol to air partitioning coefficient
- ✓ KOWWIN: evaluates octanol to water partitioning coefficient
- ✓ WSKOWWIN: evaluates water solubility [Kow]
- ✓ KOCWIN: estimates soil sorption coefficient [Koc]
- ✓ HYDROWIN: approximates the aqueous hydrolysis rates
- ✓ MPBPVP: evaluates vapor pressure, melting and boiling points
- ✓ WATERNT: estimates the solubility of water

2.10.2 BIOWIN

For Microsoft Windows, the probability bio-degradation program model [BIOWIN] was established by Syracuse Research Corporation [SRC]. It was established at the end of the US EPA in 1980. The probability of rapid aerobic biodegradability was estimated with this BIOWIN model. The probability of rapid aerobic biodegradability was estimated with this BIOWIN7 model in the presence of heterogeneous microbes, which is an exception. There are seven models in BIOWIN. BIOWIN3 is used in the EPI Suite for estimating the chemical fate by default (Boethling et al., 2004). The depiction of each BIOWIN module is as per the following:

- ✓ BIOWIN1; model of the linear probability
- ✓ BIOWIN2; model of non-linear probability
- ✓ BIOWIN3; model for ultimate biodegradation of expert survey
- ✓ BIOWIN4; model for primary biodegradation of expert survey
- ✓ BIOWIN5; model for linear MITI
- ✓ BIOWIN6; model for nonlinear MITI
- ✓ BIOWIN7; model for anaerobic biodegradation

Thousands of notifications of pre-manufacturing are reviewed by US EPA for distinguishing their possible impacts on human wellbeing and the climate. The synthetics aside from food added substances, medications, and pesticides are directed under the demonstration of Toxic Substance Control by the US EPA.

2.10.3 AOPWIN

AOPWIN is the Microsoft Windows Program for Atmospheric Oxidation. The rate constants between organic chemicals and photo-chemically produced hydroxyl radicals in the air under environmental conditions. The constant rate among olefinic particles and ozone are evaluated with the help of AOPWIN. The half-life of organic matter present in the environment is estimated with the help of these constants. Different methods were developed for the estimation of the concentration of OH-radicals in the environment since the 1980s (Liu & He, 2020). In the AOPWIN model, the rate constants of hydroxyl radical with organic compounds are calculated.

2.11 Problem Statement

Conventional filtration units are not efficient in removing micropollutants from the wastewater streams and are known to be the hotspots for the migration of micropollutants, and the whole spectrum of these micropollutants cannot be identified by conventional sampling and analytical techniques, which pose an unknown risk due to leftover micropollutants to the receptors

2.12 Objectives

The objectives concerning the problem statement of this research are

- To evaluate a smart non-targeted screening approach of micropollutants in a mega municipal wastewater treatment filtration unit.
- To assess the efficiency of the filtration unit in removing/transforming micropollutants.
- To carry out the risk assessment of micro-pollutants not removed during the filtration process.

Chapter 3

3 Materials and Methodology

This chapter explains the formulation, deployment, extraction, and valuation of the passive samplers. The process for the preparation of PDMS passive sampler, collection of samples, analysis, and risk assessment process is given below.

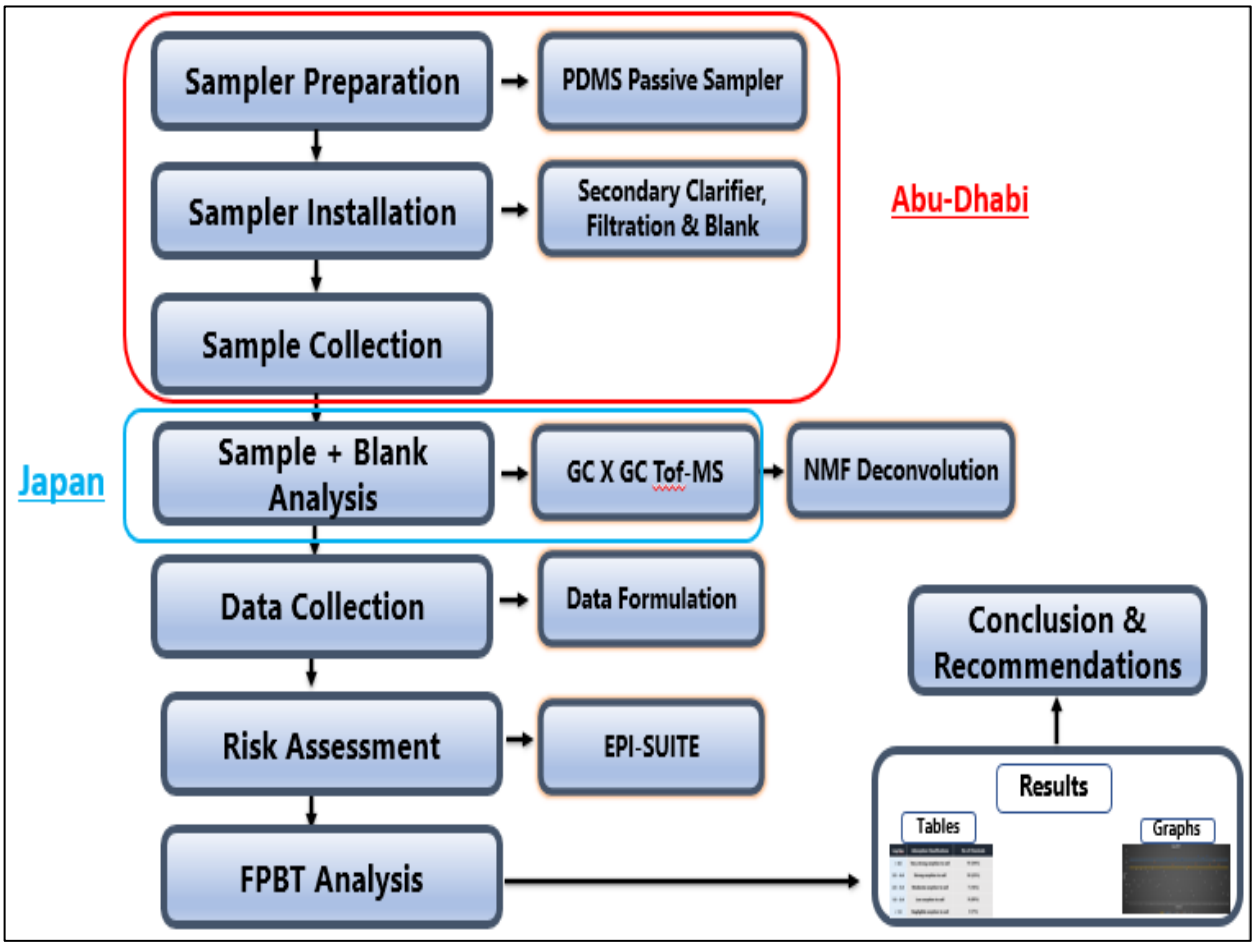


Figure 9:Methodology

First prepared the PDMS passive samplers and then installed these samplers after the secondary clarifier and filtration unit and prepared a blank sample that was not installed in the wastewater stream but was exposed to similar environmental conditions. After 15 days the samples were collected, and all of this was done in Abu Dhabi. Then all the samples collected were analyzed on GCxGC Tof MS and this was done in Japan back in 2016. Then applied the NMF deconvolution, collected and formulated the data obtained in different layers. Finally carried out the risk assessment through Epi. Suite Software where Performed the Fate, Behavior, Transport, Bioconcentration Potential,

Persistence, and Toxicity analysis. Then formulated all the results and concluded the results.

3.1 Study Area

The research was carried out at The Al Wathba WWTP in Abu Dhabi whose capacity is 300,000 m^3/day and is intended for a Residents Equivalent of over 1,500,000 units. Its purpose is to treat the wastewater produced in Abu Dhabi and to reuse the treated wastewater for irrigation of the green areas.

Figure 10: Al Wathba wastewater treatment plant (Source: https://www.veolia.nl/sites/g/files/dvc2496/files/document/2014/11/4128_Photo_Book_v5_LR.pdf)

3.1.1 Wastewater Treatment Train

The wastewater treatment train of Al Wathba WWTP is like the conventional Activate Sludge Process as shown below in the figure.

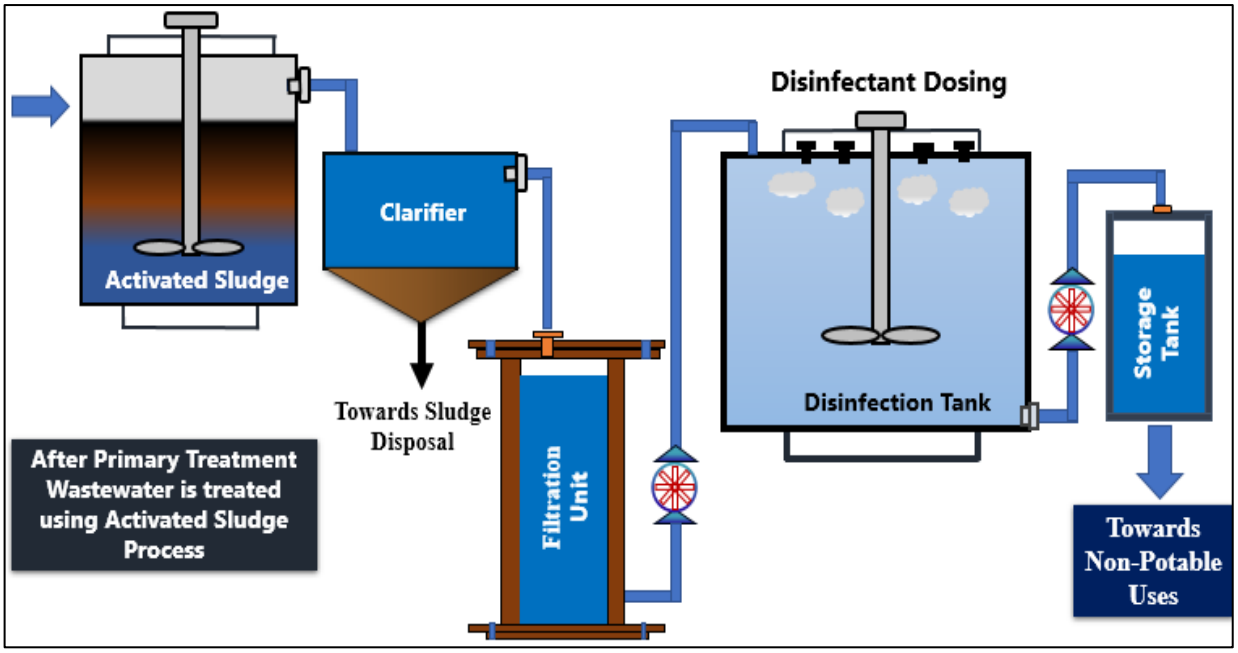


Figure 11: Al Wathba Wastewater Treatment Plant Train

After primary treatment, the wastewater goes to the coagulation tank and then to the secondary clarifier. From the secondary clarifier wastewater moves towards the filtration unit where a dual media filter of sand and pumice stone is used. After the filtration process, the effluent is pumped towards the Disinfection tank, and after the disinfection, it goes towards storage and then is distributed for non-portable uses.

For the assessment of filtration unit efficiency, we have installed passive samplers after the secondary clarifier and after the filtration unit. The passive samplers installed were in replicates for quality assurance. Because these are installed in series so if a chemical is reported in replicate 1 it should be reported on replicate 2 otherwise it can be due to some external interference or due to a false peak.

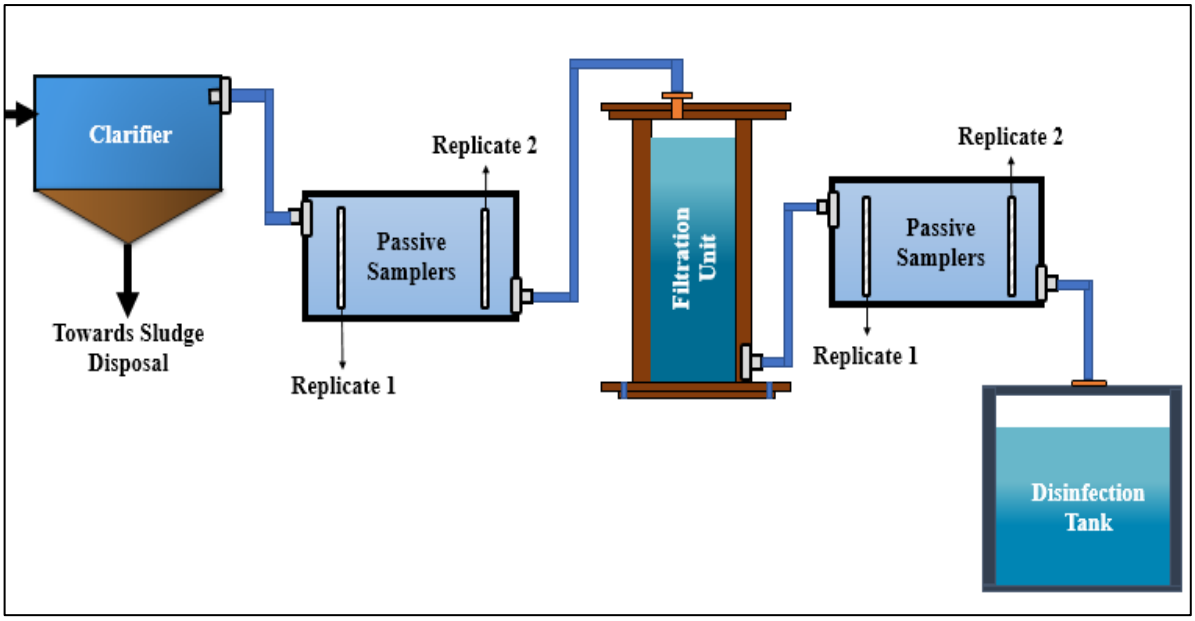


Figure 12: Passive Samplers Installation

3.2 Preparation of PDMS Passive Sampler

1. Cut 9 strips of PDMS (3mm thickness), each of around 21.5x16 cm^2 (3.77 g) with scissors.
2. Immerse these strips in acetone: hexane (1:1) mixture under the 200 rpm shuddering for 24 hours
3. Then, immerse these strips in methanol under the 200 rpm shuddering for another 24 hours
4. Rinse and store in Milli-Q water until deployment in an airtight glass bottle.
5. Perform steps 2 and 3 for aluminum mesh but 2 hours each.

3.3 Passive Sampling

Over the past two eras, different other strategies have been sought 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 pollutants in an aqueous environment is 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 this type of sampling can perform an important part in legislative frameworks for water quality monitoring like the European Water Framework Directive (WFD). This sampling strategy will be characterized in this article as any examining procedure because of a free progression of analyte particles from the tested medium to a gathering

medium, in light of a distinction in synthetic possibilities of the analyte between the two media. The net progression of analyte particles from one medium to the next goes on until balance is laid out in the framework, or until the inspecting meeting is ended by the user.

3.3.1 Advantages

The passive sampling technique has several advantages as compared to spot or grab sampling technology. They have the potential to uptake freely dissolved components of chemicals present in the aquatic environment and help in measuring the chemical activity of containment in trace amounts. Furthermore, passive sampling results can be used as a measure of chemical bioaccumulation, bioavailability, and ecotoxicity. Different types of passive sampling devices are presently based on different sorbents materials for sampling a diverse range of compounds in water. Such as semipermeable membrane devices (SPMD), low-density polyethylene (LDPE) film, polyoxymethylene (POM) devices, and polyurethane foam (PUF) devices, and polydimethylsiloxane (PDMS) fibers.

3.4 Deployment of PDMS (Polydimethylsiloxane) Passive Sampler

1. Enwrap passive sampling strips in aluminum mesh
2. Moor these wrapped strips via a string in the influent and effluent wastewater channels.
3. Treat one passive sampling strip as field blank by exposing it identically to deployed strips except in step 2.

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

3.4.1 Passive sampler strips distribution

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

3.4.2 Blank passive sampler strips

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

3.4.3 Field passive sampler strips

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

3.4.4 Experimental passive sampler strips

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

3.5 Collection of Aqueous Wastewater Samples

1. Rinse 1 L glass bottles (n=5) sequentially with tap water, Milli-Q water, acetone, DCM, and hexane.
2. Wrap these bottles with aluminum foil.
3. Fill one bottle with Milli-Q and treat it as field blank.
4. Collect 2 liters of each influent and effluent wastewater.
5. Add sodium azide (100 mg/L) to suppress the microbiology on site.
6. Store samples at 4 degrees until analysis.

3.6 Sample Analysis:

The samples acquired were analyzed through GCTOFMS, NMF Deconvolution technique, and data was retrieved from this analysis which was further run through EPISUITE to achieve the desired objectives of the study.

3.7 GC X GC-TOF-MS

It is a potent instrument that separates and quantifies thousands of compounds in a complex mixture. For the discovery of new particulates in the sample, an increase of throughput with fast chromatography, and quantifying of targeted compounds in the complex is an ideal method. For chemists, it is a challenging task to deal with environmental samples. In the complex cocktail of nature and anthropogenic compounds, these target compounds are trace present in trace amounts. For the calculation of these trace compounds accurately, the reduction of background is essential. Also, it is important for separating the target compounds from the residual mix and each other

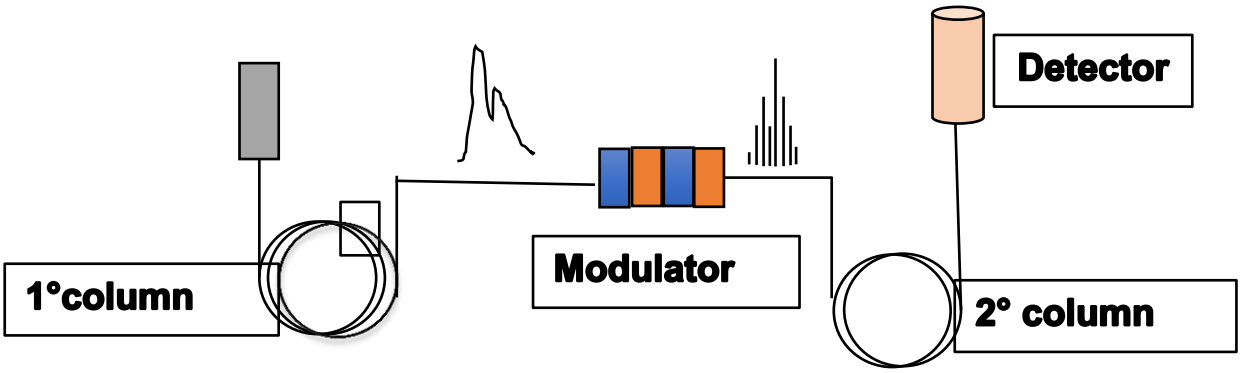


Figure 13: Schematics of GCTOFMS

This technique of two-dimensional GC[GCXGC] has evolved as a powerful technique for the separation of different types of compounds and isomers in the last few decades.

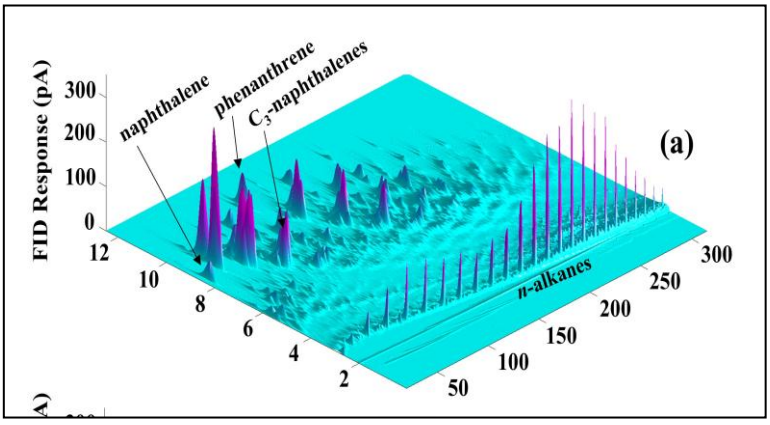


Figure 14: Two-Dimensional GC X GC (Source: Nabi, 2014

In this technique, two columns were used; one polar and another non-polar stationary phase, two individual separation modes polarity and volatility, that are used for the dispersion of compounds in 2D space. Cryogenic cooling is the base of the modulator mostly. This low cooling is utilized for centering and delivering bundles of material briefly division, which should be quick to acquire various samplings of every first-aspect top. This requires the utilization of a quick locator, for this situation, a TOFMS. To break down a more extensive extent of natural impurities GC×GC TOF-MS might be utilized for tests that have gone through at least an example tidy up.

3.8 Non-Negative Matrix Factorization (NMF) Deconvolution Technique

This is a gathering of algorithms in the multivariate investigation where a matrix V is factorized into (normally) two frameworks W and H, with the property that every one of the three networks has no bad components. This non-pessimism makes the subsequent frameworks more straightforward to examine. It permits clients to picture the GC × GC information, direct ghostly deconvolution, gauge properties, and investigate potential dangers because of laid out strategies. The homepage of the software used for deconvolution is shown below

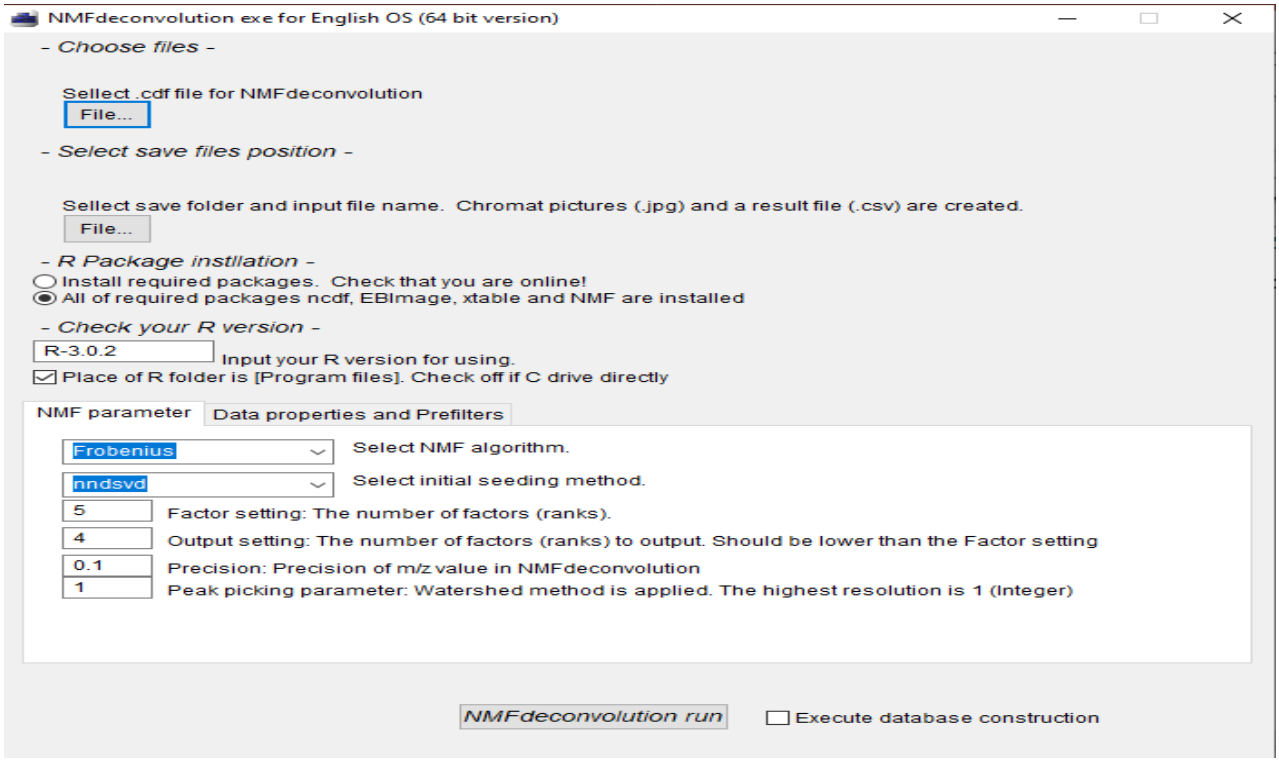


Figure 15: NMF Deconvolution (Source: NMF Deconvolution Software)

3.9 Risk Assessment

After GCxGC and NMF Deconvolution, got chemicals but how to tell they are risky or not for the environment, therefore, performed risk assessment through EPI suite. For this purpose, checked the Fate, Behavior, and Transport of these chemicals by Bioavailability, Hydrophobicity, and Volatility. Their bioconcentration potential by Bioconcentration Factor (BCF), Environmental Persistence through Biodegradation, and toxicity through Ecological Structure-Activity Relationships (ECOSAR).

1: Fate, Behavior, and Transport of the Chemicals

- Bioavailability (Koc), Hydrophobicity (Kow), and Volatility (HLC)

2: Bioconcentration Potential

- Bioconcentration Factor (BCF)

3: Environmental Persistence

- Biodegradation (BIOWIN)

4: Toxicity

- Ecological Structure-Activity Relationships (ECOSAR)

Chapter 4

4 Results and Discussions

4.1 Non-Targeted Screening Approach

4.1.1 GCxGC Chromatograms

The samples were first analyzed on GCxGC, and the raw chromatograms obtained from the analysis of samples in GCxGC are shown.

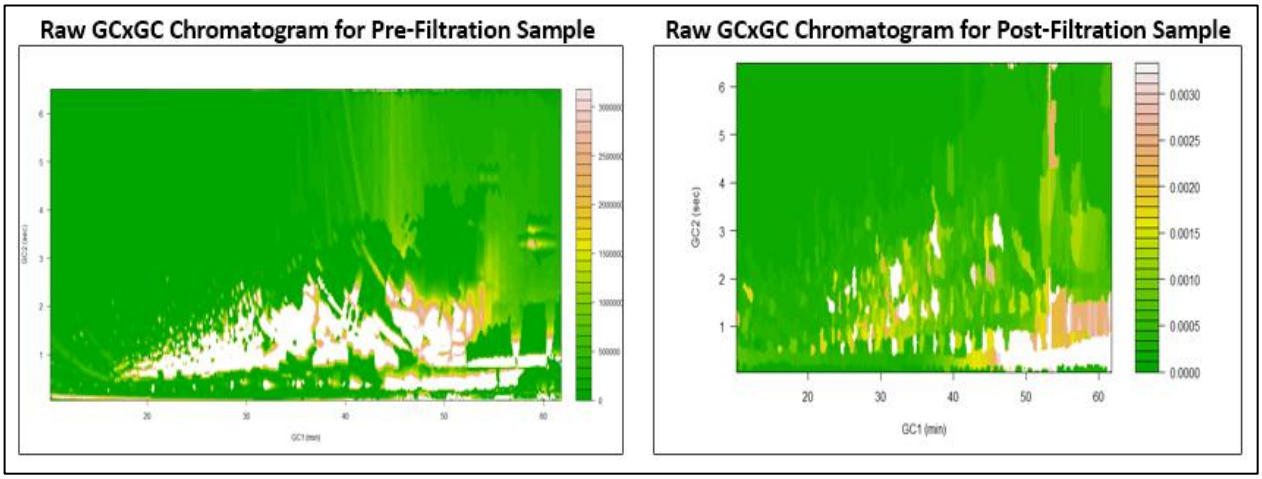


Figure 16: Raw GCxGC Chromatograms for Pre and Post Filtration Samples

The two chromatograms for pre- and post-filtration are listed above. From these chromatograms, it can be observed that the peaks identified in the post-filtration unit are less than in the pre-filtration unit because many chemicals are removed during the filtration process but still the peaks are diluted, and identification of compounds is not possible for the broad spectrum. However, for this problem, we have used a spectral deconvolution technique based on NMF.

4.1.2 NMF-Based Mass Deconvolution

The deconvolve chromatograms are analyzed in GC Image Software. After performing mass Deconvolution, the raw data is distributed into 4 sequence layers. In each layer, the number of peaks is decreased, and the interferences are removed. 35654 peaks were identified in the raw GCxGC data, but after deconvolution, there were 32552, 28262, 25045, and 20436 peaks in the 1st, 2nd,3^{rd,} and 4th layer respectively. After each layer, more and more false peaks are removed from the original data which ultimately results

in higher accuracy of the detected compound. The visual representation of the Post filtration unit sample and its deconvolve layers are shown below.

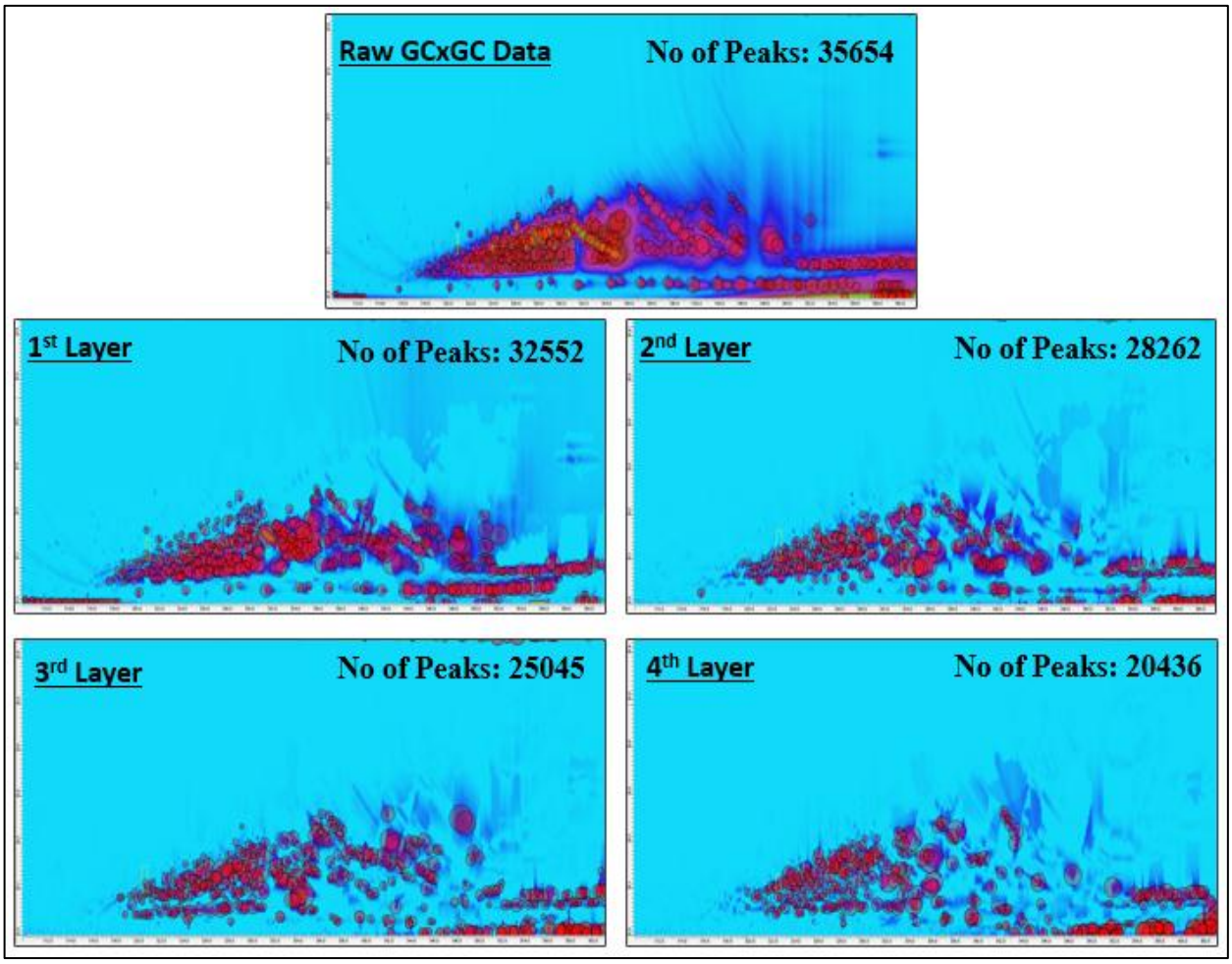


Figure 17: NMF Based Mass Deconvolution and Number of Identified Peaks in Each Layer

The mechanism of GC Image is that it compares the peak obtained from the GCxGC chromatogram with the Standard peaks in the library of NIST. The chemical peaks which are closer to the standard peaks in the library are given a score called a Match Factor. The higher the match factor, the higher will be the likelihood of the presence of that chemical. The Match factor scale shows that the match factor of >900 is excellent, >800 is good, and >700 is fair. The NMF based mass deconvolution helps in increasing the match factor by removing the false peaks or interferences.

4.1.3 Summary of Non-Targeted Screening Approach

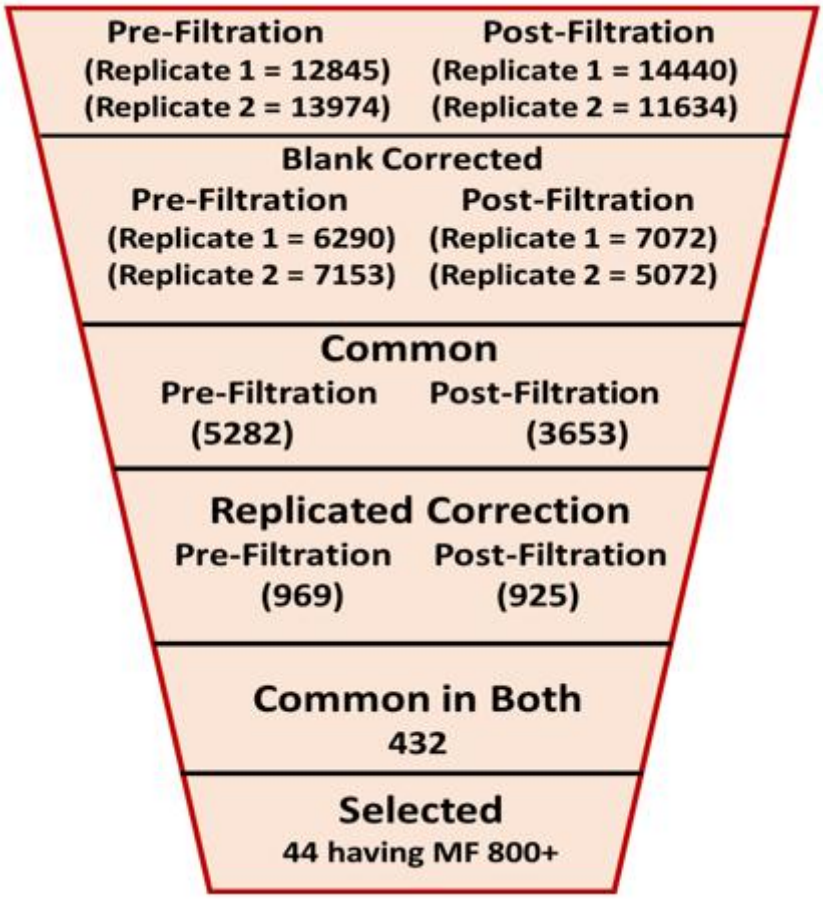


Figure 18: Summary of Non-Targeted Screening Approach

After GCxGC-TofMS, and NMF deconvolution, the data of different layers were compiled which shows that the number of chemicals at replicate 1 of the pre-filtration unit was more than 12000 and more than 13000 at replicate 2. For the post-filtration unit number of chemicals at replicates 1 and 2 were more than 14000 and 11000 respectively. By applying the blank correction, the number of chemicals for the replicates of both units decreased which means external interferences were removed. The common from the replicates of both units were taken as chemical reported in replicate 1 should be reported on replicate 2 otherwise, it could be due to some external interference or due to a false peak. After taking the common replicate correction was done for both units in which chemicals repeating in different layers are removed. Finally common from both pre and post-filtration units were taken which were 432 and out of which 44 were selected having a match factor above 800.

4.2 Identified Chemicals

The 44 identified chemicals are shown below with their match factors. Most of these chemicals are those which are used on daily basis such as chloroxylenol which is antiseptic and detergent. Chlorpyrifos is used as a pesticide and longifolene is an important component of perfumes. So, most of these are used on daily basis and, therefore, need to be monitored.

Table 1: Identified Chemicals with their CAS number and Match Factors

Sr No	Chemical Name	CAS No.	MF
1	Benzenaamine, 3,4-dichloro-	95-76-1	940
2	p-Chloroaniline	106-47-8	935
3	Chloroxylenol	88-04-0	902
4	Triphenylphosphine sulfide	3878-45-3	900
5	Quinoline, 2-methyl-	91-63-4	895
6	2,2'-Dimethylbiphenyl	605-39-0	895
7	Quinoline, 2,4-dimethyl-	1198-37-4	893
8	Chlorpyrifos	2921-88-2	889
9	3,5-Dichloro-2,4-dimethyl-1-methoxybenzene	0-00-0	875
10	Benzenamine, 2,5-dichloro-	95-82-9	873
11	Quinoline, 2,6-dimethyl-	877-43-0	872
12	Longifolene	475-20-7	859
13	Benzenemethanol, α,α,4-trimethyl-	1197-01-9	853
14	1-Hexanol, 2-ethyl-	104-76-7	852
15	Naphthalene, decahydro − 2,3 − dimethyl −	1008 − 80 − 6	847
16	3,5-Dimethyl-2,4,6-trichlorophenol	6972-47-0	841
17	Dichloroxylenol	133-53-9	840
18	5-Chloro-o-anisidine	95-03-4	835
19	Hexathiane	13798-23-7	834
20	1,1'-biphenyl, 2,4,6-trimethyl-	0-00-0	829
21	trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] −	0-00	829
22	10-Heneicosene (c,t)	95008-11-0	829
23	Heptacos-1-ene	15306-27-1	828
24	1,1,6,6-Tetramethylspiro[4.4]nonane	74054-92-5	828
25	Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) −	68039 − 35 − 0	822
26	4-Ethylbiphenyl	5707-44-8	821
27	3,5-Dimethyl-2,4,6-trichloroanisole	22921-84-2	821
28	Benzenemethanol, α,α-dimethyl-	617-94-7	821
29	3-Butyn-1-ol	927-74-2	820
30	Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl −	106988 − 87 − 8	818

Sr No	Chemical Name	CAS No.	MF
31	1,7-Dimethyl-4-(1-methylethyl)cyclodecane	645-10-3	815
32	$\text{Tricyclo}[20.8.0.0(7,16)]\text{triacontane}, 1(22),7(16)-\text{diepoxy}-$	00-0	810
33	4-tert-Octylphenol, TMS derivative	78721-87-6	809
34	Heneicosane	629-94-7	808
35	$\text{Cyclohexane}, 1,1,3-\text{trimethyl}-2-(3-\text{methylpentyl})-$	$54965-05-8$	807
36	Pyrene, 1-methyl-	2381-21-7	807
37	Hexane, 2-nitro-	14255-44-8	806
38	$\text{Cyclopenta}[g]-2-\text{benzopyran}, 1,3,4,6,7,8-\text{hexahydro}-4,6,6,7,8,8-\text{hexamethyl}-$	$1222-05-5$	805
39	Oleyl alcohol, trifluoroacetate	0-00-0	804
40	$\text{Naphthalene}, 1,2,3,4-\text{tetrahydro}-1,5,7-\text{trimethyl}-$	$21693-55-0$	804
41	Butane, 1-isothiocyanato-	592-82-5	803
42	Phthalic anhydride	85-44-9	803
43	Diazinone	333-41-5	801
44	Phenol	108-95-2	800

4.3 Filtration Efficiency for Removal of Micropollutants

Calculated the efficiency of the filtration unit in removing the micropollutants.

- Chemicals in Pre-Filtration (Secondary Clarifier) = 969
- Chemicals in Post-Filtration (Filtration) = 432

$$\%\ \boldsymbol{Efficiency} = \frac{\boldsymbol{Input} - \boldsymbol{Output}}{\boldsymbol{Input}} \times \mathbf{100}$$

The chromatogram of post-filtration shows that it has many chemicals present in it which are not removed by the filtration unit.

$$\text{Filtration efficiency for the removal of MP} = (969-432)/969 \times 100$$

Filtration efficiency for the removal of micropollutants = 55% which is not great

4.4 Risk Assessment

The following encompasses the obtained results from the analysis of the data set (Micro Pollutants present before and after filtration) in EPI-Suite. The modules used in this research are

1- KOCWIN (log Koc value)

2- KOWWIN (estimated and experimental values log Kow)

3- KOAWIN (log KOA value)

4- BCFBAF (log BCF)

5- HENRYWIN (estimated and experimental values of HLC)

6- BIOWIN (all values of 7 BIOWINS)

7- ECOSAR (LC50 and Chronic values for Fish, Daphnid, and Green Algae)

By utilizing above mentioned module in EPI Suite, Assessment was carried out for Fate, Behavior, and Transport of the chemicals (micropollutants) by Bioavailability, Hydrophobicity, and Volatility. Their bioconcentration potential by Bioconcentration Factor (BCF), Environmental Persistence through Biodegradation, and toxicity through Ecological Structure-Activity Relationships (ECOSAR).

4.4.1 Fate, Behavior, and Transport of the Micropollutants

It was assessed by Bioavailability (Koc), Hydrophobicity (Kow), and Volatility (HLC)

4.4.1.1 Log Koc (Bioavailability)

The Soil Adsorption Coefficient (Koc) gives a proportion of the capacity of a substance to sorb (adhere) to the organic part of the soil, silt, and sludge. Koc shows the potential for the substance to leach through soil and be brought into groundwater and segment among water and the suspended solids and residue in the water section. Solid adsorption to the soil will affect other destiny properties.

4.4.1.1.1 Interpreting Koc Results

If the value of log Koc is low then the contaminants

• Filters into the soil

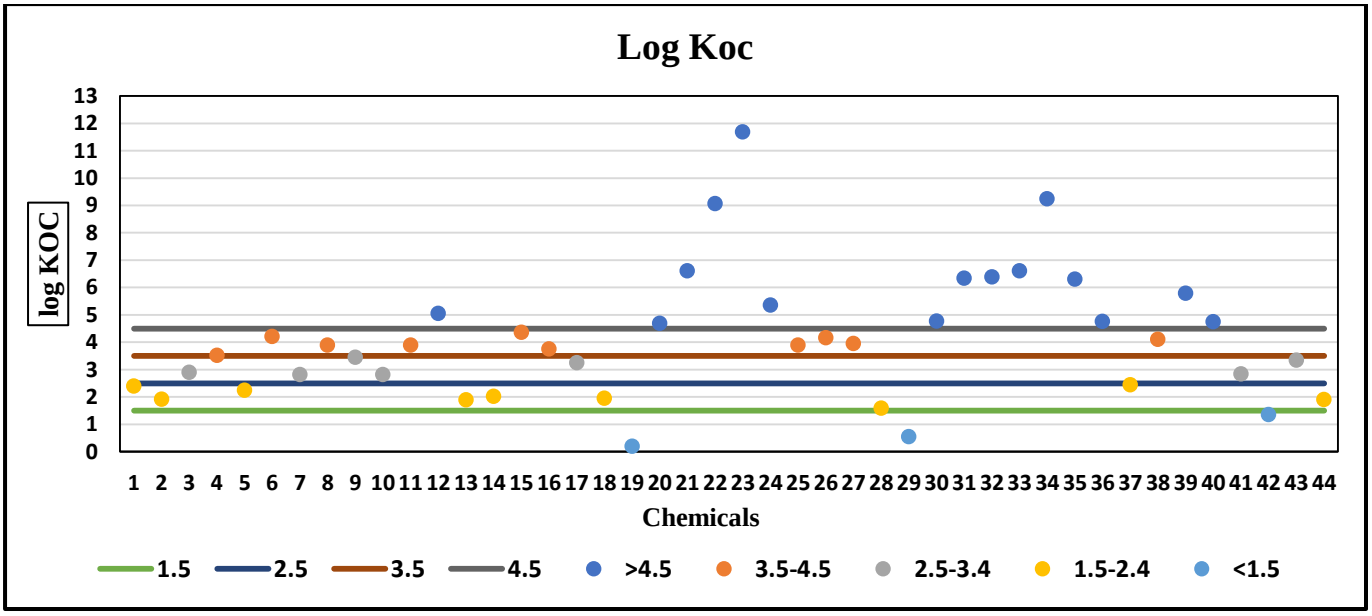
• Decreases the superficial fixation

• Possible pollution of groundwater

Table 2: Range of log Koc Vakues (Source: Manual 2012 EPA-748-B12-001)

Log Koc	Adsorption Classifications
> 4.5	Exceptionally strong sorption to soil/sediment, unimportant movement to groundwater (Less Bioavailable)
$3.5 - 4.4$	Strong sorption to soil/sediment, immaterial to ease back relocation to groundwater

Log Koc	Adsorption Classifications
2.5 – 3.4	Moderate sorption to soil/sediment, slow movement to groundwater
1.5 – 2.4	Low sorption to soil/sediment, moderate movement to groundwater
< 1.5	Insignificant sorption to soil/sediment, quick movement to groundwater (Highly Bioavailable)



Graph 1: Interpretation of log Koc values

4.4.1.1.2 Description

Table 3: Description of Results

Ranges	No of Chemicals	Names
> 4.5	15	Longifolene 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Heneicosane Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl −
3.5 - 4.4	10	Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl Chlorpyrifos Quinoline, 2,6-dimethyl- Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl −
2.5 - 3.4	7	Chloroxylenol Quinoline, 2,4-dimethyl- 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenamine, 2,5-dichloro- Dichloroxylenol Butane, 1-isothiocyanato- Diazinone
1.5 - 2.4	9	Benzenamine, 3,4-dichloro- p-Chloroaniline Quinoline, 2-methyl- Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- 5-Chloro-o-anisidine Benzenemethanol, α,α-dimethyl- Hexane, 2-nitro- Phenol

Ranges	No of Chemicals	Names
< 1.5	3	Hexathiane 3-Butyn-1-ol Phthalic anhydride

- 34% have Exceptionally strong sorption to soil/sediment and are less bioavailable, 23% have strong sorption to soil/sediment, 16% have moderate sorption to soil/sediment, 20% have low sorption to soil/sediment, 7% have insignificant sorption to soil/sediment and are highly bioavailable

4.4.1.2 Log Kow (Hydrophobicity)

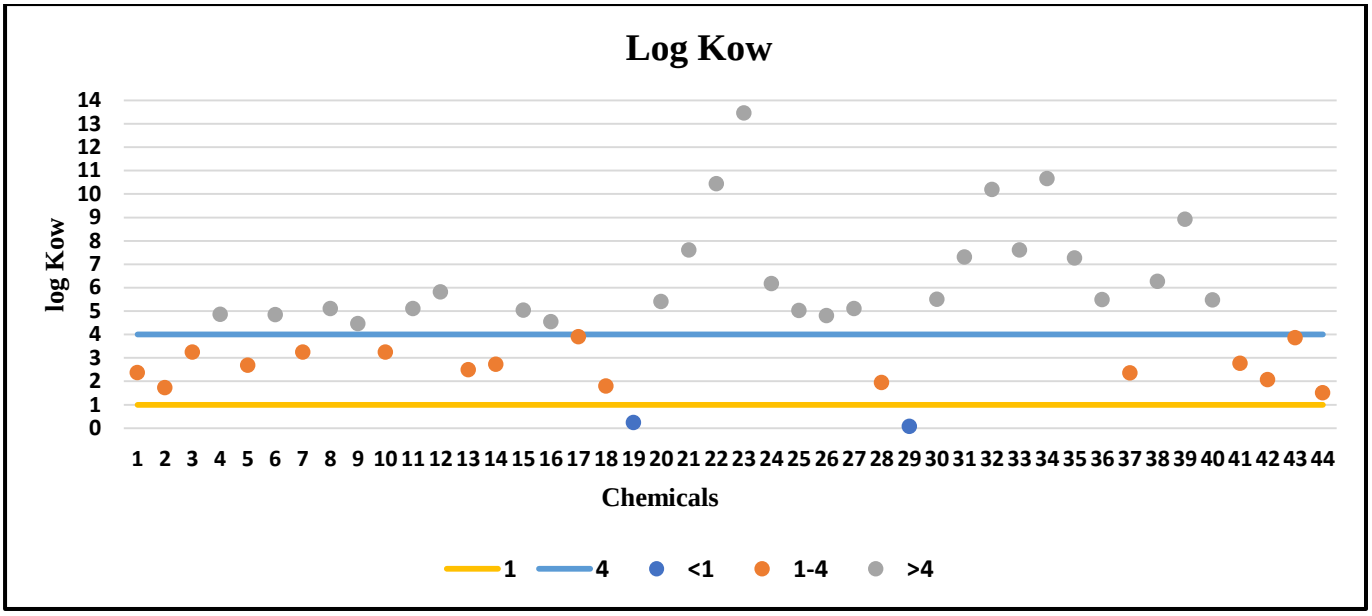
Octanol/water partition coefficient (Kow or P) gives data on how the compound will partition between octanol (which addresses the lipids or fats in biota) and water. The EPI Suite™ technique that estimates Kow is KOWWIN, and it utilizes a "fragment constant" strategy to foresee Kow. In the "fragment constant" strategy, a particle is partitioned into fragments (molecules or bigger utilitarian gatherings) and the allocated coefficient values for each fragment are added to give the Kow estimate, which is accounted for as a log.

4.4.1.2.1 Interpreting Results

log Kow tells the assessor assuming the substance has a fondness for water or fats/lipids or will be ingested through biological membranes. The ranges of Log Kow are:

Table 4: Ranges of log Kow values (Source: Manual 2012 EPA-748-B12-001)

Log Kow Value	Classification
< 1	Exceptionally soluble in water (hydrophilic)
> 4	Not extremely soluble in water (hydrophobic)
> 8	Not promptly bioavailable
> 10	Not bioavailable - challenging to gauge tentatively Partitioning in Biota



Graph 2: Interpretation of log Kow values

4.4.1.2.2 Description

Table 5: Interpreting log Kow Results

Ranges	No of Chemicals	Names
< 1	2	Hexathiane 4-Ethylbiphenyl
1-4	16	Benzenamine, 3,4-dichloro- p-Chloroaniline Chloroxylenol Quinoline, 2-methyl- Quinoline, 2,4-dimethyl- Benzenamine, 2,5-dichloro- Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- Dichloroxylenol 5-Chloro-o-anisidine Benzenemethanol, α,α-dimethyl- Hexane, 2-nitro- Butane, 1-isothiocyanato- Phthalic anhydride Diazinone Phenol
> 4	26	Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl Chlorpyrifos 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Quinoline, 2,6-dimethyl- Longifolene Naphthalene, decahydro – 2,3 – dimethyl – 3,5-Dimethyl-2,4,6-trichlorophenol

Ranges	No of Chemicals	Names
		1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Heneicosane Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Hexane, 2-nitro- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl − Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Butane, 1-isothiocyanato- Phthalic anhydride Diazinone Phenol
> 8	5	10-Heneicosene (c,t) Heptacos-1-ene Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − Heneicosane Oleyl alcohol, trifluoroacetate
> 10	4	10-Heneicosene (c,t) Heptacos-1-ene Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − Heneicosane

- 5% are exceptionally soluble in water (Hydrophilic), 26% are moderately soluble in water, 59% are not very soluble in water (Hydrophobic), 10% are not bioavailable

4.4.1.3 Henry's Law Constant HLC (Volatility)

Henry's Law Constant (HLC) is the ratio of a substance concentration in the gas stage to that in the fluid stage at harmony. HLC is communicated as $atm - m^3/mole$ or

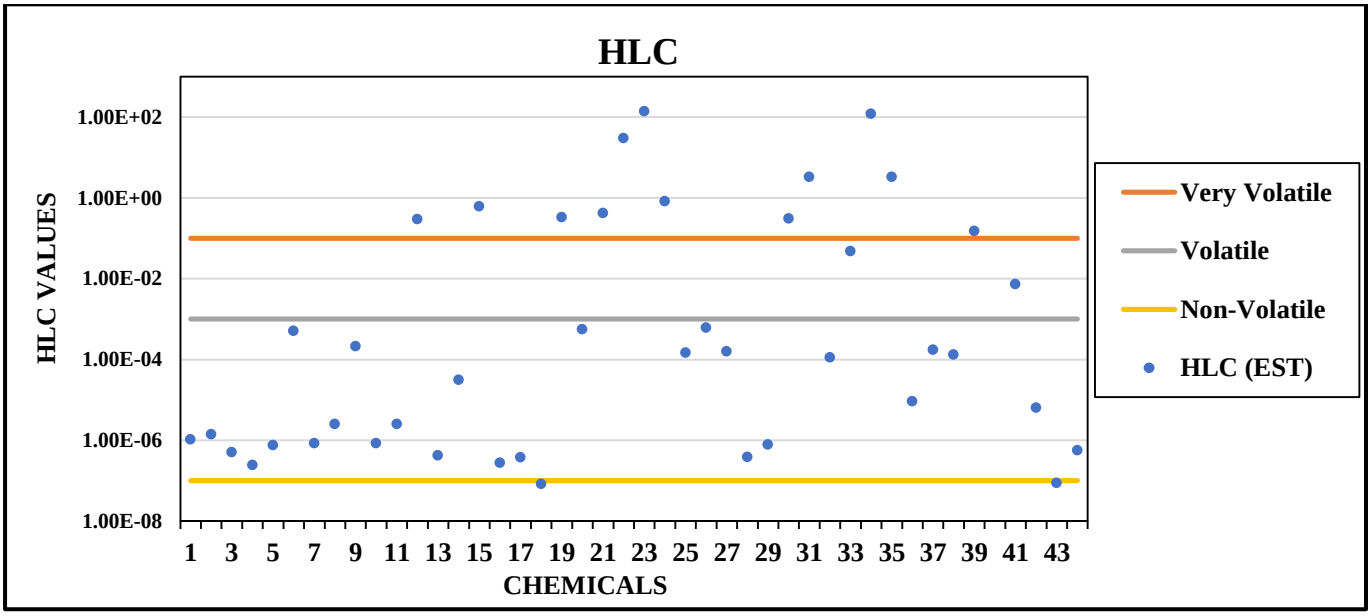
$Pa - m^3/mole$. HLC shows a substance's volatility from water and provides the assessor with a sign of likely environmental partitioning, expected expulsion in the sewage treatment plant, and potential courses of environmental openness.

4.4.1.3.1 Interpreting Results

The scopes of HLC values and the data they give about the substance are displayed underneath.

Table 6: Range Classification of HLC Values (Source: Manual 2012 EPA-748-B12-001)

HLC value (atm − m3 /mole)	**Classification**
$> 10^{-1}$	Very volatile from water
$10^{-1} - 10^{-3}$	Volatile from water
$10^{-3} - 10^{-5}$	Moderately volatile from water
$10^{-5} - 10^{-7}$	Slightly volatile from water
$< 10^{-7}$	Nonvolatile



Graph 3: Interpretation of HLC Values

4.4.1.3.2 Description

Table 7: Interpreting HLC Results

Ranges	No of Chemicals	Names
$> 10^{-1}$	12	Longifolene Naphthalene, decahydro − 2,3 − dimethyl − Hexathiane trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Heneicosane Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Oleyl alcohol, trifluoroacetate
10^{-1} - 10^{-3}	3	4-tert-Octylphenol, TMS derivative Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Butane, 1-isothiocyanato-
10^{-3} - 10^{-5}	10	2,2'-Dimethylbiphenyl 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene 1-Hexanol, 2-ethyl- 1,1'-biphenyl, 2,4,6-trimethyl- Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − Hexane, 2-nitro- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl −
10^{-5} - 10^{-7}	17	Benzenamine, 3,4-dichloro- p-Chloroaniline Chloroxylenol Triphenylphosphine sulfide Quinoline, 2-methyl- Quinoline, 2,4-dimethyl- Chlorpyrifos Benzenamine, 2,5-dichloro- Quinoline, 2,6-dimethyl- Benzenemethanol, α,α,4-trimethyl- 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Pyrene, 1-methyl-

Ranges	No of Chemicals	Names
		Phthalic anhydride Phenol
$< 10^{-7}$	2	5-Chloro-o-anisidine Diazinone

- 27% are very volatile from water, 7% are volatile from water, 23% are moderately volatile from water, 39% are slightly volatile from water, 4% are non-volatile from water

4.4.2 Bioconcentration Potential

It was assessed by Bioconcentration Factor (BCF)

4.4.2.1 Log BCF

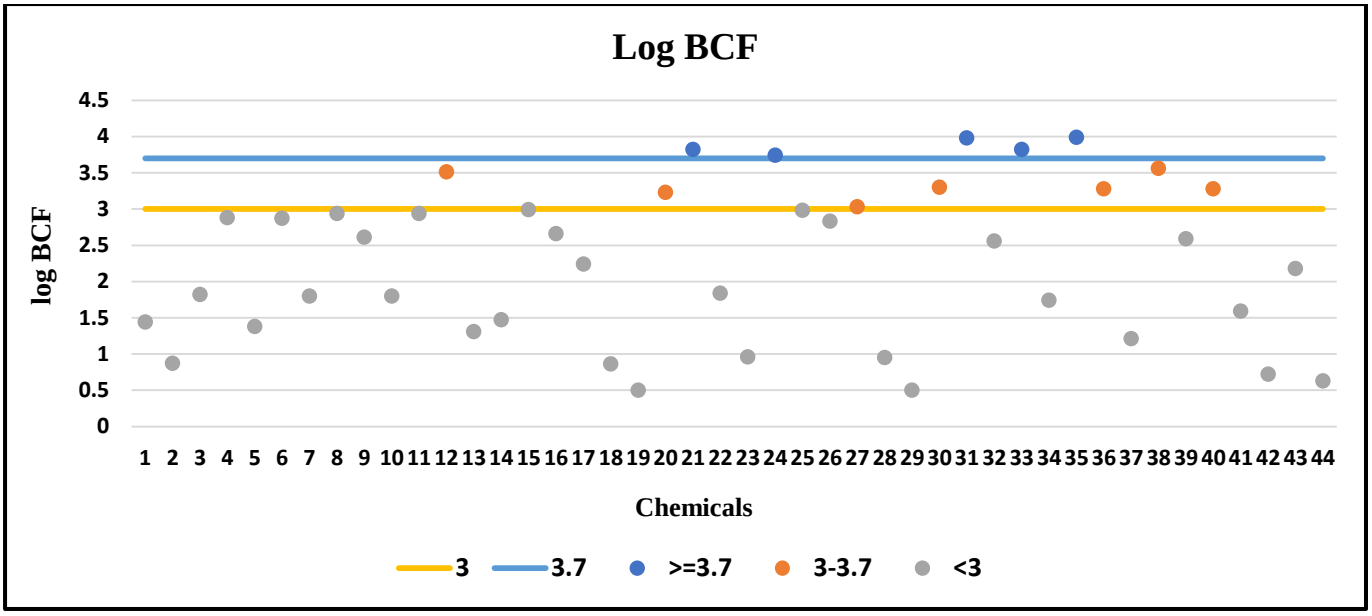
The Bioconcentration Factor (BCF) shows the potential for a chemical to bioconcentrate in lipids (greasy tissue) of organisms and is utilized as a substitute for bioaccumulation in higher trophic levels of the food web. Most BCF tests are finished utilizing amphibian organisms anyway assessors might extrapolate to earthbound organisms. BCF is assessed by BCFBAF, which is a SAR-based technique that utilizes Kow to estimate BCF.

4.4.2.1.1 Interpreting Results

compounds with a high BCF are less water-dissolvable and are supposed to bioconcentrate in sea-going organic entities. Alternately, low BCF shows higher water solvency.

Table 8: Range Classification of log BCF Values (Source: Manual 2012 EPA-748-B12-001)

Log BCF Value	Classification
$\geq$ 3.7	High bioconcentration potential
3	Moderate bioconcentration potential
$<$ 3	Low bioconcentration potential



Graph 4: Interpretation of log BCF values

4.4.2.1.2 Description

Table 9: Interpreting log BCF Results

Ranges	No of Chemicals	Names
≥ 3.7	5	trisiloxane, 1,1,1,5,5,5 – hexamethyl – 3 – [(trimethylsilyl)oxy] – 1,1,6,6-Tetramethylspiro[4.4]nonane 1,7-Dimethyl-4-(1-methylethyl)cyclodecane 4-tert-Octylphenol, TMS derivative Cyclohexane, 1,1,3 – trimethyl – 2 – (3 – methylpentyl) –
3-3.6	7	Longifolene 1,1'-biphenyl, 2,4,6-trimethyl- 3,5-Dimethyl-2,4,6-trichloroanisole Biphenylene, 1,2,3,6,7,8,8a, 8b – octahydro – 4,5 – dimethyl – Pyrene, 1-methyl- Cyclopenta[g] – 2 – benzopyran, 1,3,4,6,7,8 – hexahydro – 4,6,6,7,8,8 – hexamethyl – Naphthalene, 1,2,3,4 – tetrahydro – 1,5,7 – trimethyl –
< 3	32	Benzenamine, 3,4-dichloro- p-Chloroaniline Chloroxylenol Triphenylphosphine sulfide Quinoline, 2-methyl- 2,2'-Dimethylbiphenyl Quinoline, 2,4-dimethyl- Chlorpyrifos 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenamine, 2,5-dichloro- Quinoline, 2,6-dimethyl- Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl-

Ranges	No of Chemicals	Names
		Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol 5-Chloro-o-anisidine Hexathiane 10-Heneicosene (c,t) Heptacos-1-ene Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − Heneicosane Hexane, 2-nitro- Oleyl alcohol, trifluoroacetate Butane, 1-isothiocyanato- Phthalic anhydride Diazinone Phenol

- 11% have high bioconcentration potential, 73% have low bioconcentration potential and 16% have moderate bioconcentration potential,

4.4.3 Environmental Persistence

It was assessed by Biodegradation (BIOWIN)

4.4.3.1 BIOWIN:

Biodegradation, the degradation of a chemical substance by the activity of microorganisms, is assessed by EPI Suite™ utilizing seven models contained in BIOWIN. The potential for a chemical to biodegrade gives helpful data on the probable persistence of the chemical in soil, water, and silt, and its possible evacuation in sewage treatment plants. Chemicals with extremely lengthy biodegradation times might be profoundly tenacious in the climate. BIOWIN contains seven separate models. Version 4.10 assigns these models as follows:

Probability of Rapid Biodegradation

Biowin1: linear regression probability model

Biowin2: nonlinear regression probability model

Expert Survey Biodegradation

Biowin3: expert survey ultimate biodegradation model

Biowin4: expert survey primary biodegradation model

MITI Biodegradation Probability:

Biowin5: MITI linear regression model

Biowin6: MITI nonlinear regression model

Anaerobic Biodegradation Probability

Biowin7: anaerobic biodegradation model

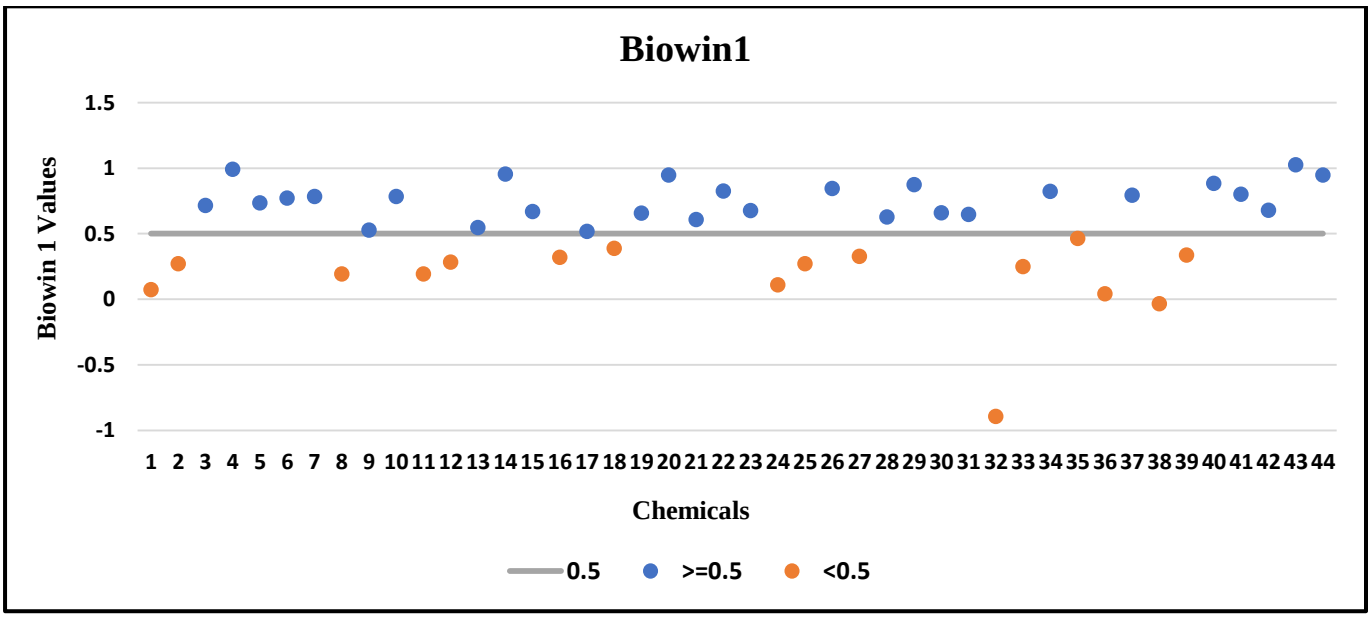
4.4.3.1.1 BIOWIN 1

4.4.3.1.1.1 Interpreting Results

Possibility of Rapid Biodegradation Biowin1 (linear regression probability model)

> 0.50 Likely to biodegrade rapidly

< 0.50 Not likely to biodegrade



Graph 5: Interpretation of BIOWIN 1 values

4.4.3.1.1.2 Description

Table 10: Interpreting BIOWIN 1 Results

Ranges	No of Chemicals	Names
> 0.50	26	Chloroxylenol Triphenylphosphine sulfide Quinoline, 2-methyl- 2,2'-Dimethylbiphenyl Quinoline, 2,4-dimethyl- 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenamine, 2,5-dichloro- Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- Naphthalene, decahydro − 2,3 − dimethyl − Dichloroxylenol Hexathiane 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 4-Ethylbiphenyl Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Heneicosane Hexane, 2-nitro- Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Butane, 1-isothiocyanato- Phthalic anhydride Diazinone Phenol
< 0.50	18	Benzenamine, 3,4-dichloro- p-Chloroaniline Chlorpyrifos Quinoline, 2,6-dimethyl- Longifolene 3,5-Dimethyl-2,4,6-trichlorophenol 5-Chloro-o-anisidine 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 3,5-Dimethyl-2,4,6-trichloroanisole Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative

Ranges	No of Chemicals	Names
		Cyclohexane, 1,1,3 – trimethyl – 2 – (3 – methylpentyl) –
		Pyrene, 1-methyl-
		Cyclopenta[g] – 2 – benzopyran, 1,3,4,6,7,8 – hexahydro – 4,6,6,7,8,8 – hexamethyl –
		Oleyl alcohol, trifluoroacetate

4.4.3.1.2 BIOWIN 2

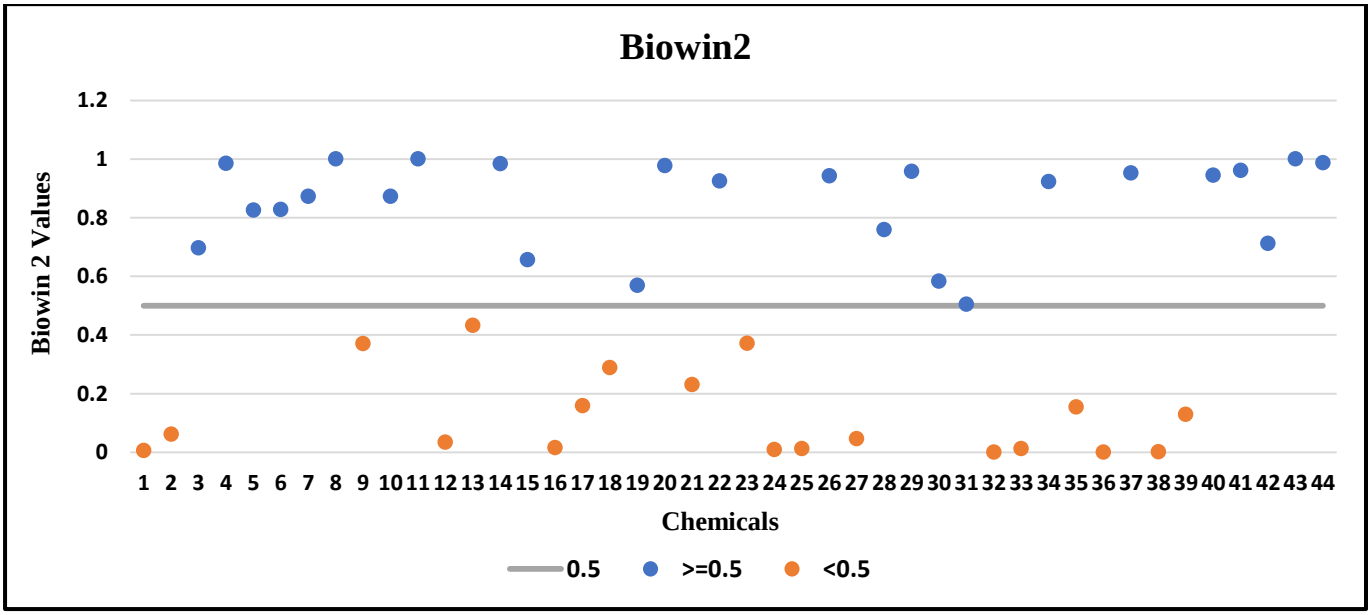
4.4.3.1.2.1 Interpreting Results

Possibility of Rapid

Biodegradation Biowin1 (Non – linear regression probability model)

> 0.50 Likely to biodegrade rapidly

< 0.50 Not likely to biodegrade



Graph 6: Interpretation of BIOWIN 2 values

4.4.3.1.2.2 Description

Table 11: Interpreting BIOWIN 2 Results

Ranges	No of Chemicals	Names
> 0.50	25	Chloroxylenol Triphenylphosphine sulfide

Ranges	No of Chemicals	Names
		Quinoline, 2-methyl- 2,2'-Dimethylbiphenyl Quinoline, 2,4-dimethyl- Chlorpyrifos Benzenamine, 2,5-dichloro- Quinoline, 2,6-dimethyl- 1-Hexanol, 2-ethyl- Naphthalene, decahydro − 2,3 − dimethyl − Hexathiane 1,1'-biphenyl, 2,4,6-trimethyl- 10-Heneicosene (c,t) 4-Ethylbiphenyl Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Heneicosane Hexane, 2-nitro- Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Butane, 1-isothiocyanato- Phthalic anhydride Diazinone Phenol
< 0.50	19	Benzenamine, 3,4-dichloro- p-Chloroaniline 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Longifolene Benzenemethanol, α,α,4-trimethyl- 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol 5-Chloro-o-anisidine trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Heneicosane Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl − Oleyl alcohol, trifluoroacetate

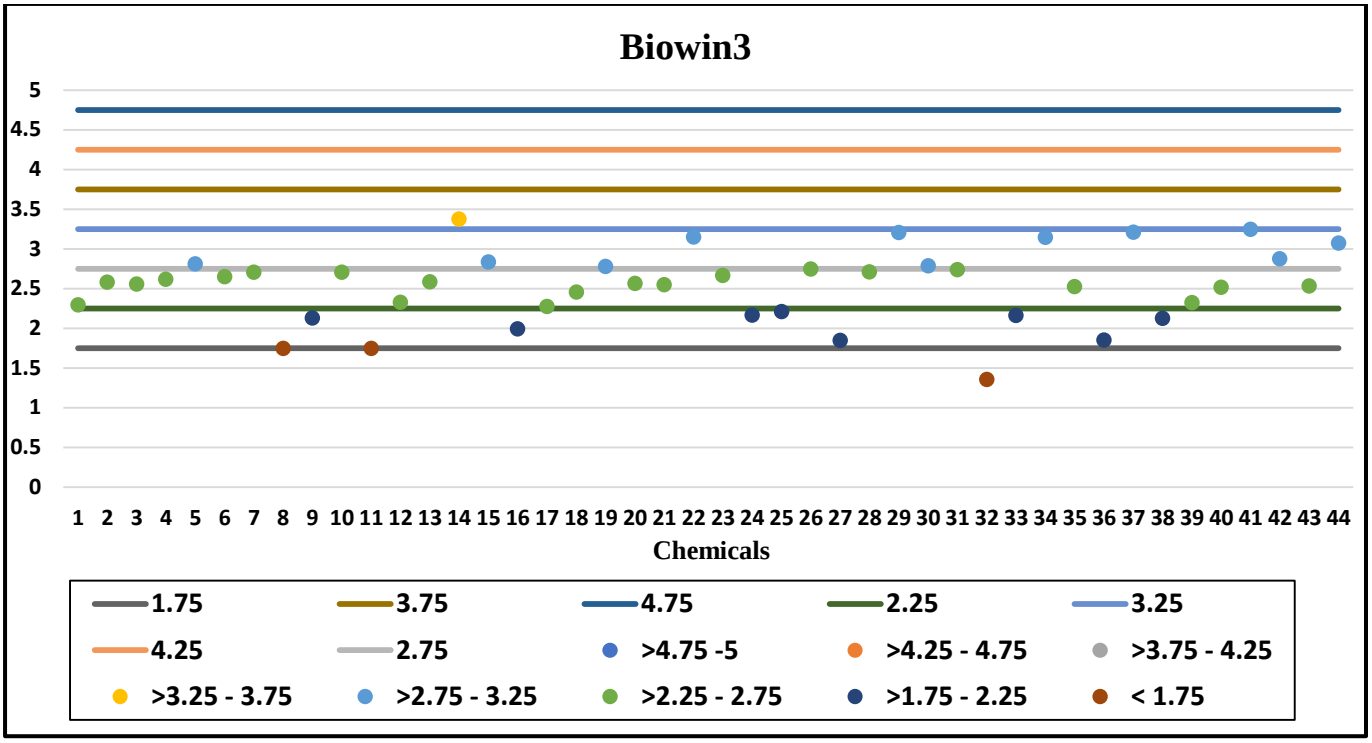
4.4.3.1.3 BIOWIN 3

4.4.3.1.3.1 Interpreting Results

Expert Survey Biodegradation Biowin3 (ultimate biodegradation model)

Table 12: Range Classification of BIOWIN 3 Values (Source: Manual 2012 EPA-748-B12-001)

Result	Time Required for Biodegradation
$> 4.75 - 5$	Hours
$> 4.25 - 4.75$	Hours – days
$> 3.75 - 4.25$	Days
$> 3.25 - 3.75$	Days – weeks
$> 2.75 - 3.25$	Weeks
$> 2.25 - 2.75$	Weeks – months
$> 1.75 - 2.25$	Months
< 1.75	Longer (recalcitrant)



Graph 7: Interpretation of BIOWIN 3 values

4.4.3.1.3.2 Description

Table 13: Interpreting BIOWIN 3 Results

Ranges	No of Chemicals	Names
>4.75 - 5	0	
>4.25 - 4.75	0	
>3.75 - 4.25	0	
>3.25 - 3.75	1	1-Hexanol, 2-ethyl-
>2.75 - 3.25	11	Quinoline, 2-methyl- Naphthalene, decahydro − 2,3 − dimethyl − Hexathiane 10-Heneicosene (c,t) 3-Butyn-1-ol Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − Heneicosane Hexane, 2-nitro- Butane, 1-isothiocyanato- Phthalic anhydride
>2.25 - 2.75	21	Benzenamine, 3,4-dichloro- p-Chloroaniline Chloroxylenol Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl Quinoline, 2,4-dimethyl- Benzenamine, 2,5-dichloro- Longifolene Benzenemethanol, α,α,4-trimethyl- Dichloroxylenol 5-Chloro-o-anisidine 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − Heptacos-1-ene 4-Ethylbiphenyl Benzenemethanol, α,α-dimethyl- 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Diazinone
>1.75 - 2.25	8	3,5-Dichloro-2,4-dimethyl-1-methoxybenzene 3,5-Dimethyl-2,4,6-trichlorophenol 1,1,6,6-Tetramethylspiro[4.4]nonane 3,5-Dimethyl-2,4,6-trichloroanisole 4-tert-Octylphenol, TMS derivative Pyrene, 1-methyl-

Ranges	No of Chemicals	Names
		Cyclopenta[g] – 2 – benzopyran, 1,3,4,6,7,8 – hexahydro – 4,6,6,7,8,8 – hexamethyl –
<1.75	3	Chlorpyrifos Quinoline, 2,6-dimethyl- Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) – diepoxy –

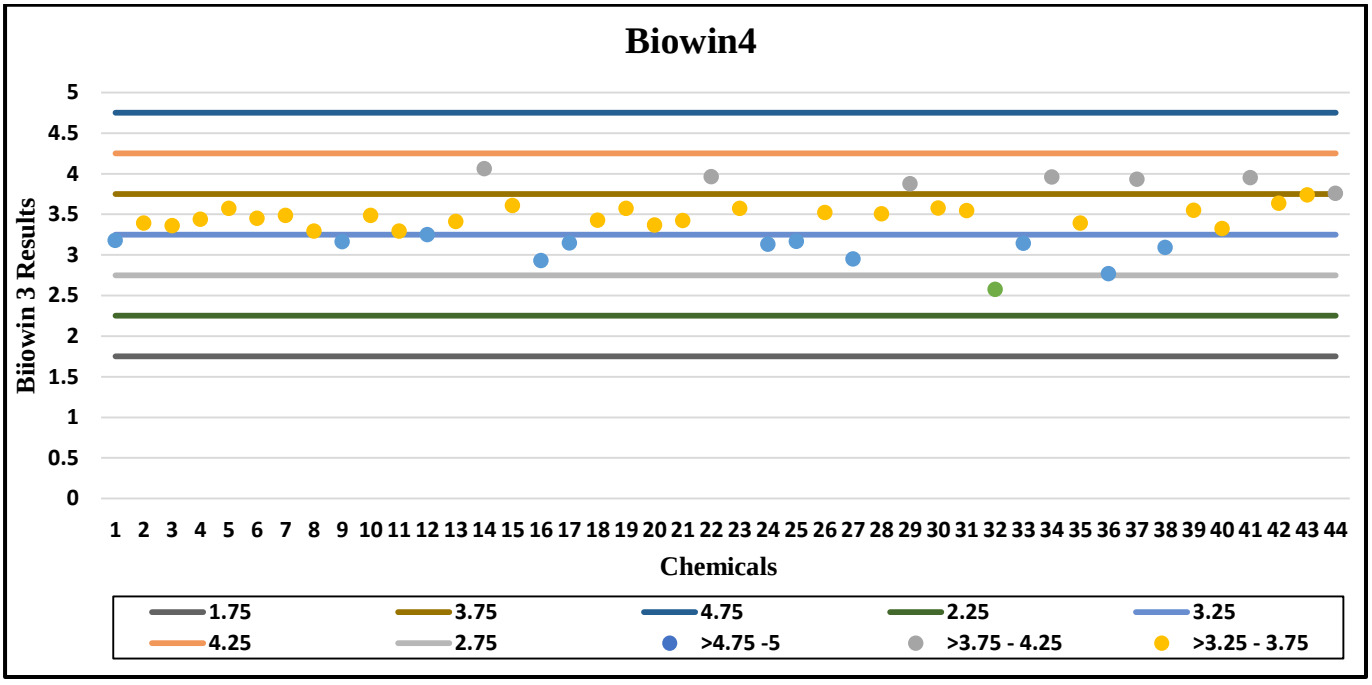
4.4.3.1.4 BIOWIN 4

4.4.3.1.4.1 Interpreting Results

Expert Survey Biodegradation Biowin4 (Primary biodegradation model)

Table 14: Range Classification of BIOWIN 4 Values (Source: Manual 2012 EPA-748-B12-001)

Result	Time Required for Biodegradation
> 4.75 – 5	Hours
> 4.25 – 4.75	Hours – days
> 3.75 – 4.25	Days
> 3.25 – 3.75	Days – weeks
> 2.75 – 3.25	Weeks
> 2.25 – 2.75	Weeks – months
> 1.75 – 2.25	Months
< 1.75	Longer (recalcitrant)



Graph 8: Interpretation of BIOWIN 4 values

4.4.3.1.4.2 Description

Table 15: Interpreting BIOWIN 4 Results

Ranges	No of Chemicals	Names
>4.75 - 5	0	
>4.25 - 4.75	0	
>3.75 - 4.25	7	1-Hexanol, 2-ethyl- 10-Heneicosene (c,t) 3-Butyn-1-ol Heneicosane Hexane, 2-nitro- Butane, 1-isothiocyanato- Phenol
>3.25 - 3.75	25	p-Chloroaniline Chloroxylenol Triphenylphosphine sulfide Quinoline, 2-methyl- 2,2'-Dimethylbiphenyl Quinoline, 2,4-dimethyl- Chlorpyrifos Benzenamine, 2,5-dichloro- Quinoline, 2,6-dimethyl- Benzenemethanol, α,α,4-trimethyl- Naphthalene, decahydro − 2,3 − dimethyl − 5-Chloro-o-anisidine Hexathiane 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − Heptacos-1-ene 4-Ethylbiphenyl Benzenemethanol, α,α-dimethyl- Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Pyrene, 1-methyl- Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Phthalic anhydride Diazinone
>2.75 - 3.25	11	Benzenamine, 3,4-dichloro- 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Longifolene 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) −

		3,5-Dimethyl-2,4,6-trichloroanisole 4-tert-Octylphenol, TMS derivative Pyrene, 1-methyl- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl −
>2.25 - 2.75	1	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy −
>1.75 - 2.25	0	
<1.75	0	

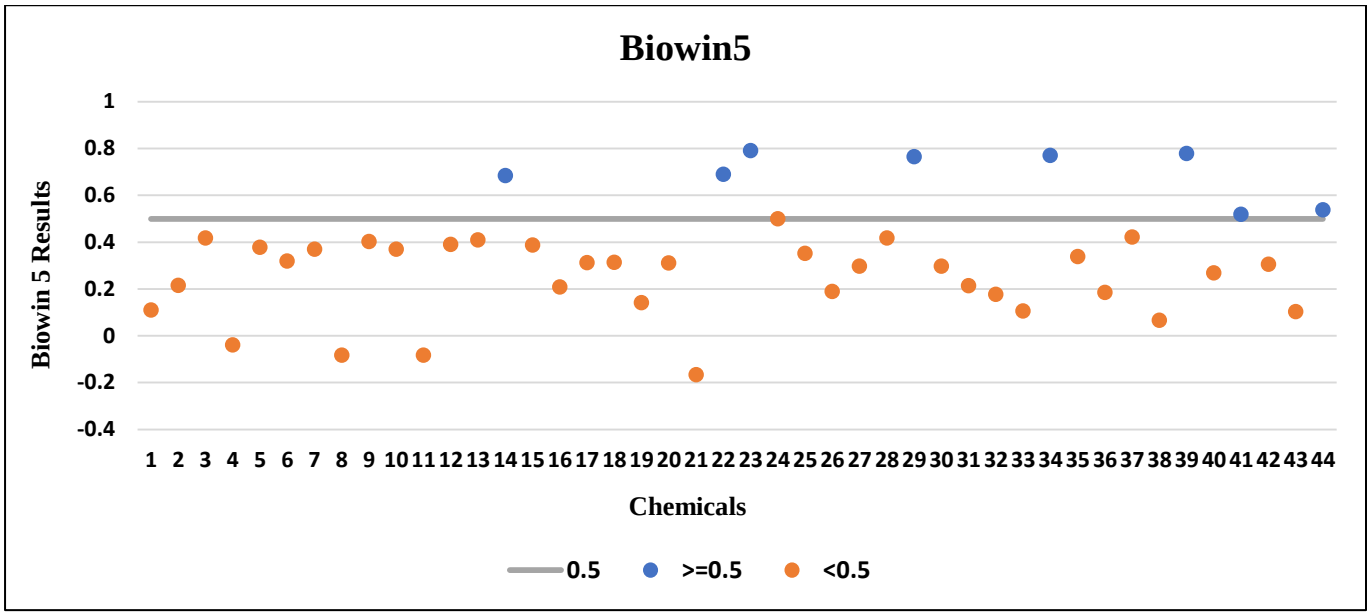
4.4.3.1.5 BIOWIN 5

4.4.3.1.5.1 Interpreting Results

For the Biowin5 (MITI linear regression model)

> 0.50 Likely to biodegrade rapidly

< 0.50 Not likely to biodegrade



Graph 9: Interpretation of BIOWIN 5 values

4.4.3.1.5.2 Description

Table 16: Interpreting BIOWIN 5 Results

Ranges	No of Chemicals	Names
> 0.50	8	1-Hexanol, 2-ethyl- 10-Heneicosene (c,t) Heptacos-1-ene 3-Butyn-1-ol Heneicosane Oleyl alcohol, trifluoroacetate

Ranges	No of Chemicals	Names
		Butane, 1-isothiocyanato- Phenol
< 0.50	36	Benzenamine, 3,4-dichloro- p-Chloroaniline Chloroxylenol Triphenylphosphine sulfide Quinoline, 2-methyl- 2,2'-Dimethylbiphenyl Quinoline, 2,4-dimethyl- Chlorpyrifos 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenamine, 2,5-dichloro- Quinoline, 2,6-dimethyl- Longifolene Benzenemethanol, α,α,4-trimethyl- Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol 5-Chloro-o-anisidine Hexathiane 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Benzenemethanol, α,α-dimethyl- Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Hexane, 2-nitro- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl − Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Phthalic anhydride Diazinone

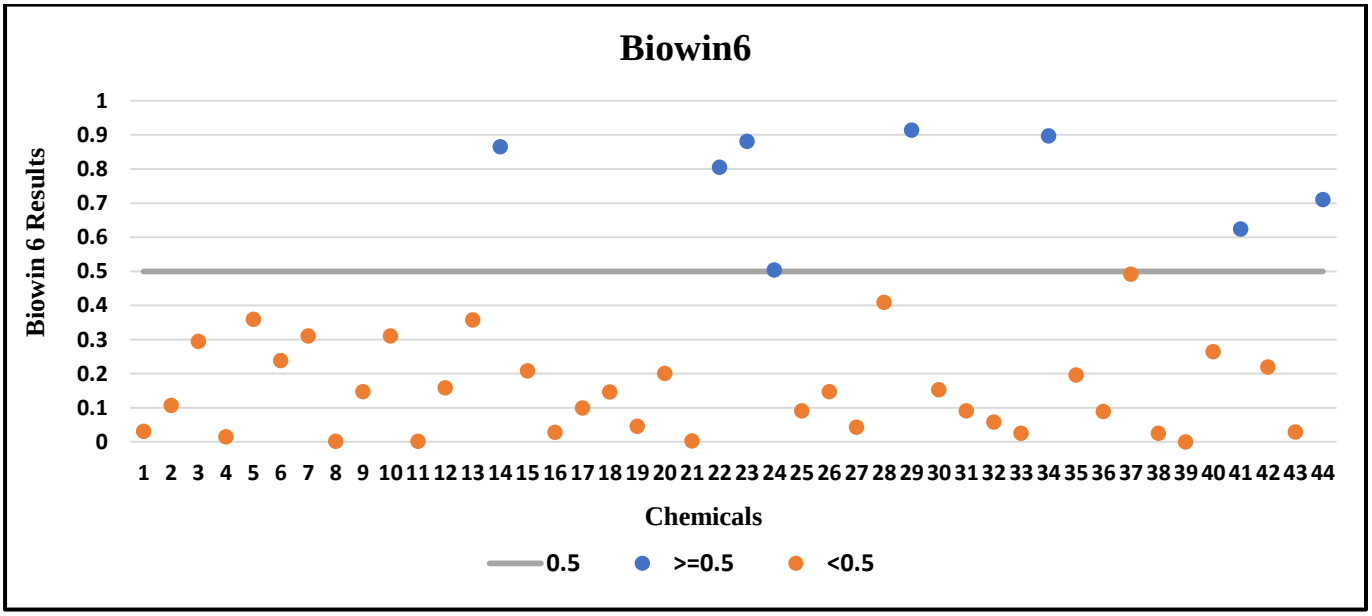
4.4.3.1.6 BIOWIN 6

4.4.3.1.6.1 Interpreting Results

For the Biowin6 (MITI Non-linear regression model)

> 0.50 Likely to biodegrade rapidly

< 0.50 Not likely to biodegrade



Graph 10: Interpretation of BIOWIN 6 values

4.4.3.1.6.2 Description

Table 17: Interpreting BIOWIN 6 Results

Ranges	No of Chemicals	Names
> 0.50	8	1-Hexanol, 2-ethyl- 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane 3-Butyn-1-ol 4-tert-Octylphenol, TMS derivative Butane, 1-isothiocyanato- Phenol
< 0.50	36	Benzenamine, 3,4-dichloro- p-Chloroaniline Chloroxylenol Triphenylphosphine sulfide Quinoline, 2-methyl- 2,2'-Dimethylbiphenyl Quinoline, 2,4-dimethyl- Chlorpyrifos 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenamine, 2,5-dichloro- Quinoline, 2,6-dimethyl- Longifolene

Ranges	No of Chemicals	Names
		Benzenemethanol, α,α,4-trimethyl- Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol 5-Chloro-o-anisidine Hexathiane 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Benzenemethanol, α,α-dimethyl- Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Hexane, 2-nitro- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl − Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Phthalic anhydride Diazinone

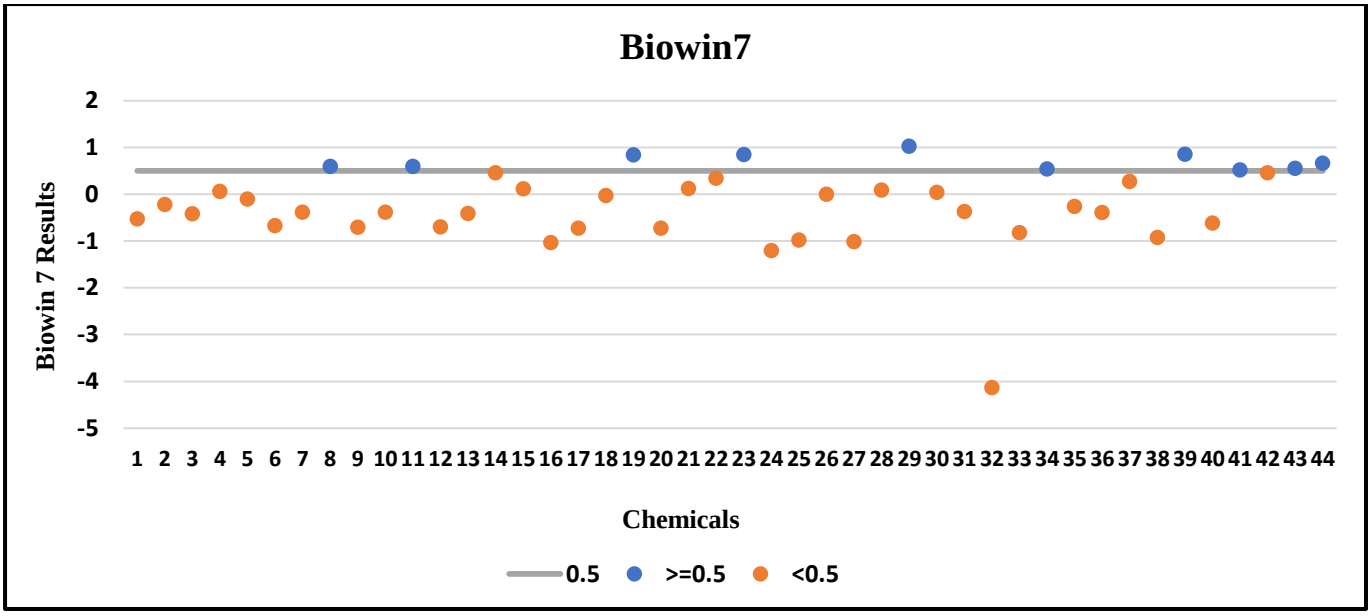
4.4.3.1.7 BIOWIN 7

4.4.3.1.7.1 Interpreting Results

For the Biowin7 (anaerobic biodegradation model)

$>$ 0.50 Likely to biodegrade rapidly

$<$ 0.50 Not likely to biodegrade



Graph 11: Interpretation of BIOWIN 7 values

4.4.3.1.7.2 Description

Table 18: Interpreting BIOWIN 7 Results

Ranges	No of Chemicals	Names
> 0.50	10	Chlorpyrifos Quinoline, 2,6-dimethyl- Hexathiane Heptacos-1-ene 3-Butyn-1-ol Heneicosane Oleyl alcohol, trifluoroacetate Butane, 1-isothiocyanato- Diazinone Phenol
< 0.50	34	Benzenamine, 3,4-dichloro- p-Chloroaniline Chloroxylenol Triphenylphosphine sulfide Quinoline, 2-methyl- 2,2'-Dimethylbiphenyl Quinoline, 2,4-dimethyl- 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenamine, 2,5-dichloro- Longifolene Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol 5-Chloro-o-anisidine

Ranges	No of Chemicals	Names
		1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Hexane, 2-nitro- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl- Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Phthalic anhydride

4.4.4 Toxicity

It was assessed by Ecological Structure-Activity Relationships (ECOSAR)

4.4.4.1 ECOSAR:

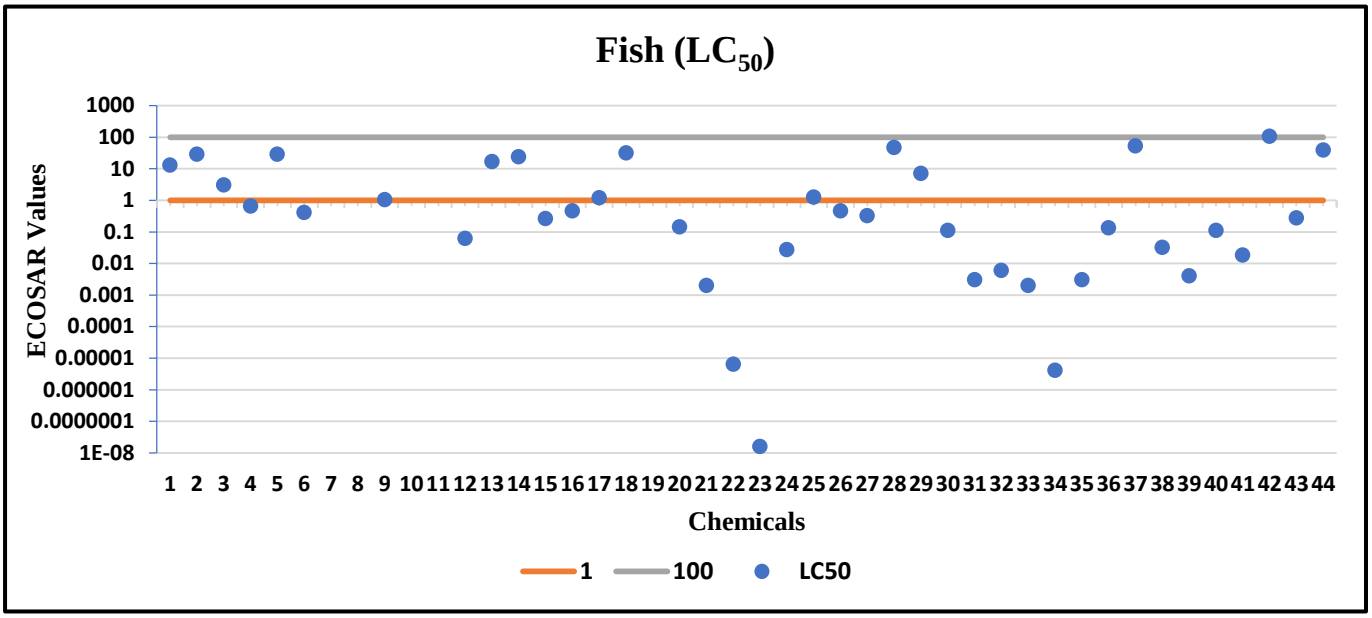
ECOSAR predicts the likely toxicity of modern chemicals to organisms living in the water body to which the chemicals are released. The model purposes estimated information to anticipate the toxicity of chemicals lacking information by utilizing Structure-Activity Relationships (SARs) and Quantitative Structure-Activity Relationships (QSARs) that gauge a chemical's acute (short-term) toxicity and when information are free, chronic (long-term or deferred) toxicity. QSARs incorporate acute and chronic toxicity endpoints for (1) fish, (2) aquatic spineless creatures (Daphnia), and (3) sea-going plants (green algae). These organisms are surrogate species addressing the aquatic food web.

4.4.4.1.1 Fish (LC_{50})

4.4.4.1.1.1 Interpreting Results

Table 19: LC_{50} Cut off values for Fish in ECOSAR (Source: Manual 2012 EPA-748-B12-001)

High Concern	
Acute value	< 1 mg/L
Moderate Concern	
Acute value	> 1 and < 100 mg/L
Low Concern	
Acute value	> 100 mg/L



Graph 3: Interpretation of LC50 Values of Fish from ECOSAR

4.4.4.1.1.2 Description

Table 20: Interpreting ECOSAR LC 50 Values of Fish

High Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
<1	**24**	Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl Longifolene Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane

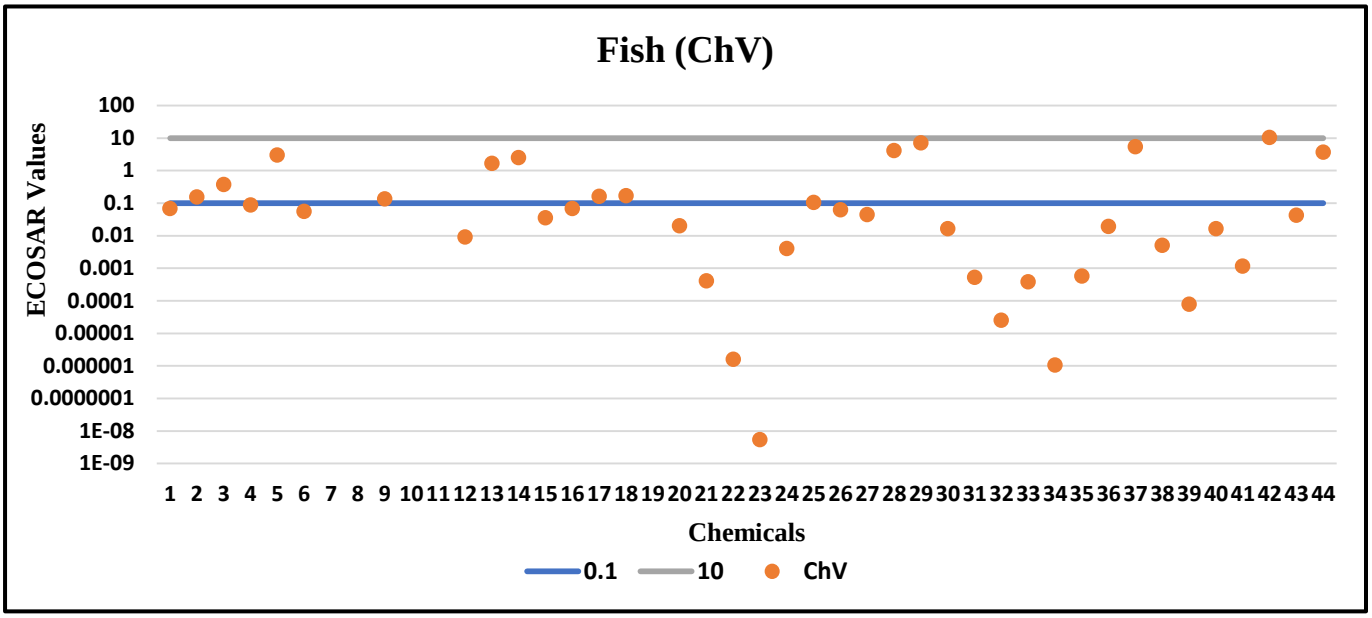
		4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Heneicosane Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl − Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Butane, 1-isothiocyanato- Diazinone
Moderate Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 1 and < 100	**14**	Benzenamine, 3,4-dichloro- p-Chloroaniline Chloroxylenol Quinoline, 2-methyl- 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- Dichloroxylenol 5-Chloro-o-anisidine Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Hexane, 2-nitro- Phenol
Low Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 100	**1**	Phthalic anhydride

4.4.4.1.2 Fish ChV

4.4.4.1.2.1 Interpreting Results

Table 21: Cut off values for Fish in ECOSAR (Source: Manual 2012 EPA-748-B12-001)

High Concern	
Chronic	< 0.1 mg/L
Moderate Concern	
Chronic	> 0.1 and < 10.0 mg/L
Low Concern	
Chronic	> 10.0 mg/L



Graph 4: Interpretation of Chronic Values of Fish from ECOSAR

4.4.4.1.2.2 Description

Table 22: Interpreting ECOSAR Chronic Values of Fish

High Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
< 0.1	**25**	Benzenamine, 3,4-dichloro- Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl Longifolene Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane

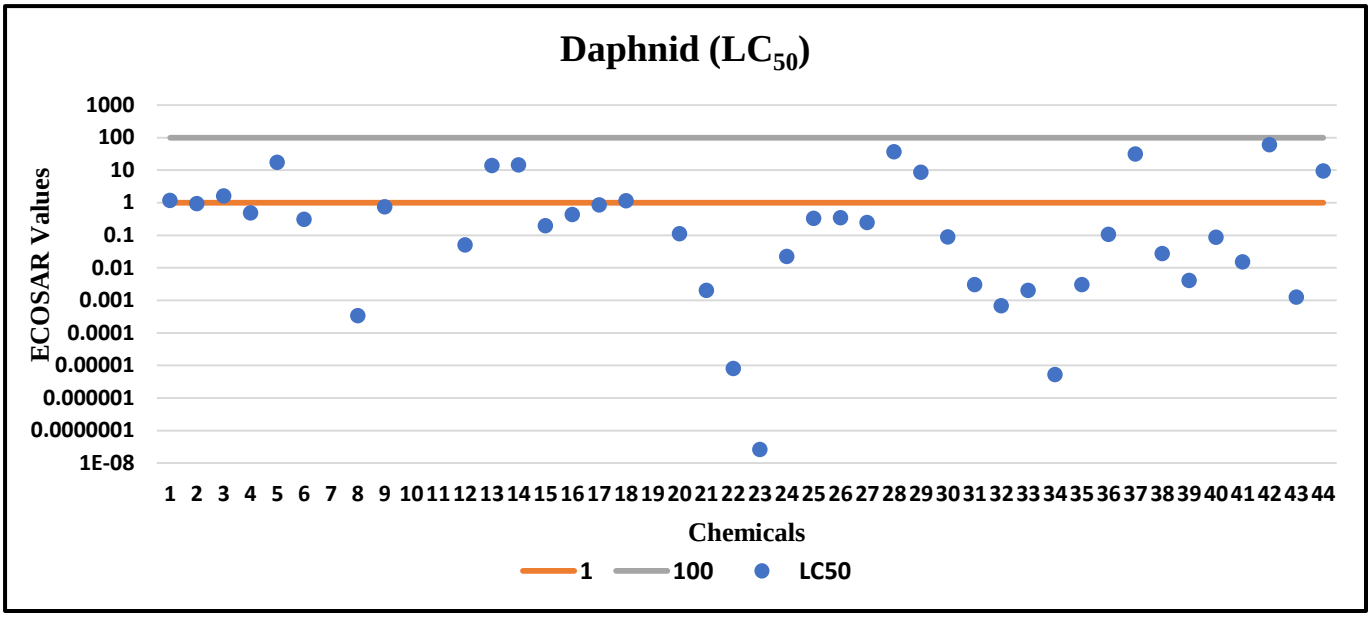
		4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Heneicosane Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl − Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Butane, 1-isothiocyanato- Diazinone
Moderate Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
>0.1 and <10.0	**13**	p-Chloroaniline Chloroxylenol Quinoline, 2-methyl- 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Longifolene Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- Dichloroxylenol 5-Chloro-o-anisidine Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Hexane, 2-nitro- Phenol
Low Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 10.0	**1**	Phthalic anhydride

4.4.4.1.3 Daphnia (LC_{50})

4.4.4.1.3.1 Interpreting Results

Table 23: Cut off values for Daphnid in ECOSAR (Source: Manual 2012 EPA-748-B12-001)

High Concern	
Acute value	< 1 mg/L
Moderate Concern	
Acute value	> 1 and < 100 mg/L
Low Concern	
Acute value	> 100 mg/L



Graph 5: Interpretation of LC50 Values of Daphnid from ECOSAR

4.4.4.1.3.2 Description

Table 24: Interpreting ECOSAR LC 50 Values of Daphnid

High Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
<1	**29**	p-Chloroaniline Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl Chlorpyrifos 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Longifolene Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane

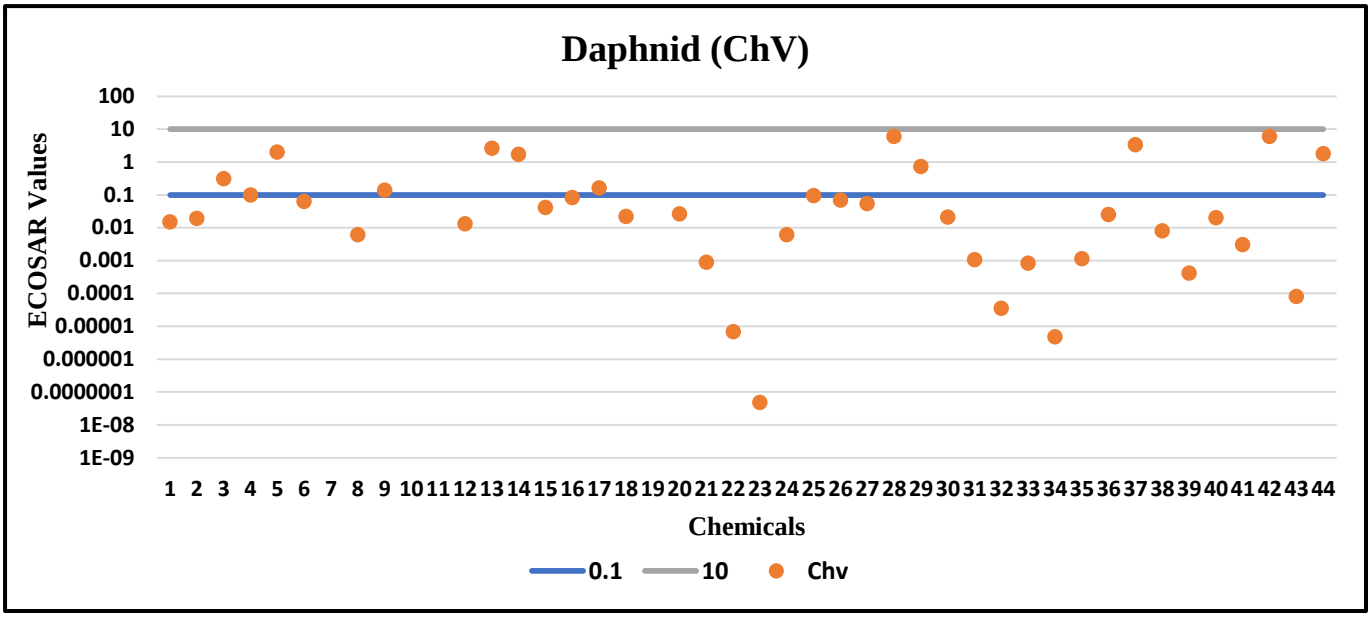
		Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Heneicosane Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl − Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Butane, 1-isothiocyanato- Diazinone
Moderate Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 1 and < 100	**11**	Benzenamine, 3,4-dichloro- Chloroxylenol Quinoline, 2-methyl- Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- 5-Chloro-o-anisidine Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Hexane, 2-nitro- Phthalic anhydride Phenol
Low Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 100	**0**	

4.4.4.1.4 Daphnia ChV

4.4.4.1.4.1 Interpreting Results

Table 25: Cut off values for Daphnid in ECOSAR (Source: Manual 2012 EPA-748-B12-001)

High Concern	
Chronic	< 0.1 mg/L
Moderate Concern	
Chronic	> 0.1 and < 10.0 mg/L
Low Concern	
Chronic	> 10.0 mg/L



Graph 6: Interpretation of Chronic Values of Daphnid from ECOSAR

4.4.4.1.4.2 Description

Table 26: Interpreting ECOSAR Chronic Values of Daphnid

High Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
< 0.1	**30**	Benzenamine, 3,4-dichloro- p-Chloroaniline Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl Chlorpyrifos 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Longifolene Naphthalene, decahydro – 2,3 – dimethyl – 3,5-Dimethyl-2,4,6-trichlorophenol 5-Chloro-o-anisidine 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 – hexamethyl – 3 – [(trimethylsilyl)oxy] – 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 – (2,3,4,7,8,8a – hexahydro – 3,6,8,8 – tetramethyl – 1H – 3a, 7 – methanoazulen – 5 – yl) – 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Biphenylene, 1,2,3,6,7,8,8a, 8b – octahydro – 4,5 – dimethyl –

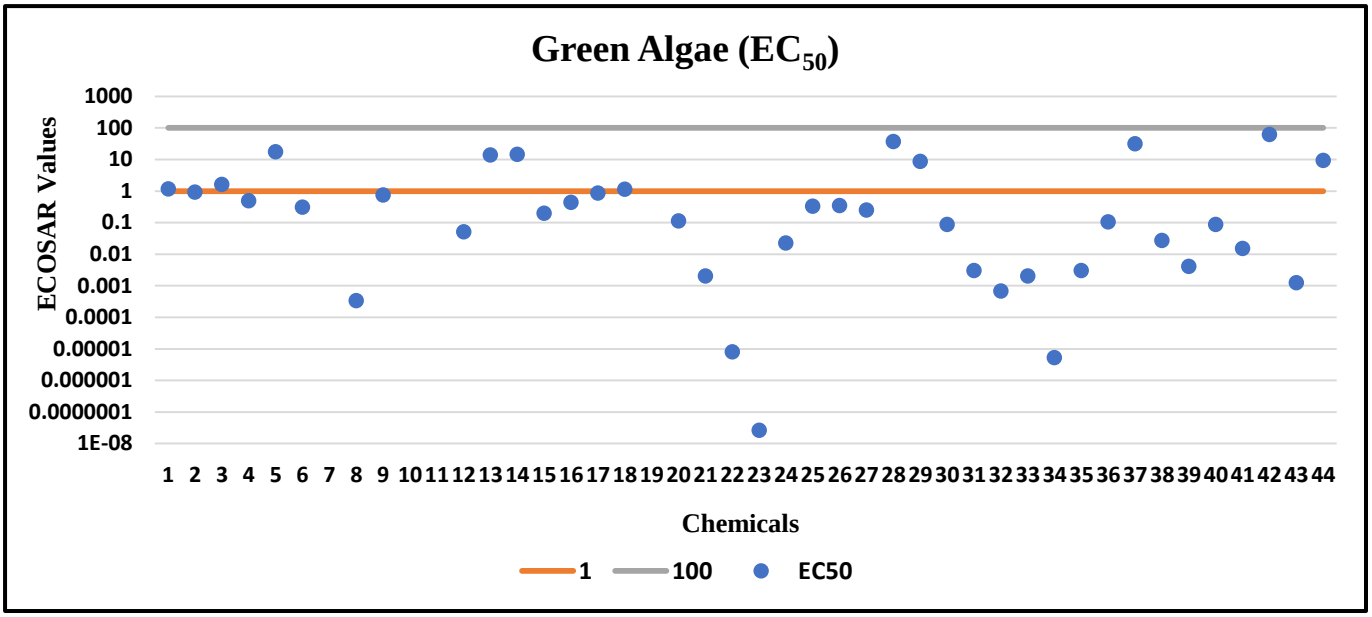
		1,7-Dimethyl-4-(1-methylethyl)cyclodecane Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) – diepoxy – 4-tert-Octylphenol, TMS derivative Heneicosane Cyclohexane, 1,1,3 – trimethyl – 2 – (3 – methylpentyl) – Pyrene, 1-methyl- Cyclopenta[g] – 2 – benzopyran, 1,3,4,6,7,8 – hexahydro – 4,6,6,7,8,8 – hexamethyl – Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 – tetrahydro – 1,5,7 – trimethyl – Butane, 1-isothiocyanato- Diazinone
Moderate Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
>0.1 and <10.0	**10**	Chloroxylenol Quinoline, 2-methyl- 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- Dichloroxylenol Benzenemethanol, α,α-dimethyl- Hexane, 2-nitro- Phthalic anhydride Phenol
Low Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 10.0	**0**	

4.4.4.1.5 Green Algae (EC_{50})

4.4.4.1.5.1 Interpreting Results

Table 27: Cut off values for Green Algae in ECOSAR (Source: Manual 2012 EPA-748-B12-001)

High Concern	
Acute value	< 1 mg/L
Moderate Concern	
Acute value	> 1 and < 100 mg/L
Low Concern	
Acute value	> 100 mg/L



Graph 7: Interpretation of EC50 Values of Green Algae from ECOSAR

4.4.4.1.5.2 Description

Table 28: Interpreting ECOSAR EC 50 Values of Green Algae

High Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
<1	**29**	p-Chloroaniline Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Longifolene Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol Dichloroxylenol 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane

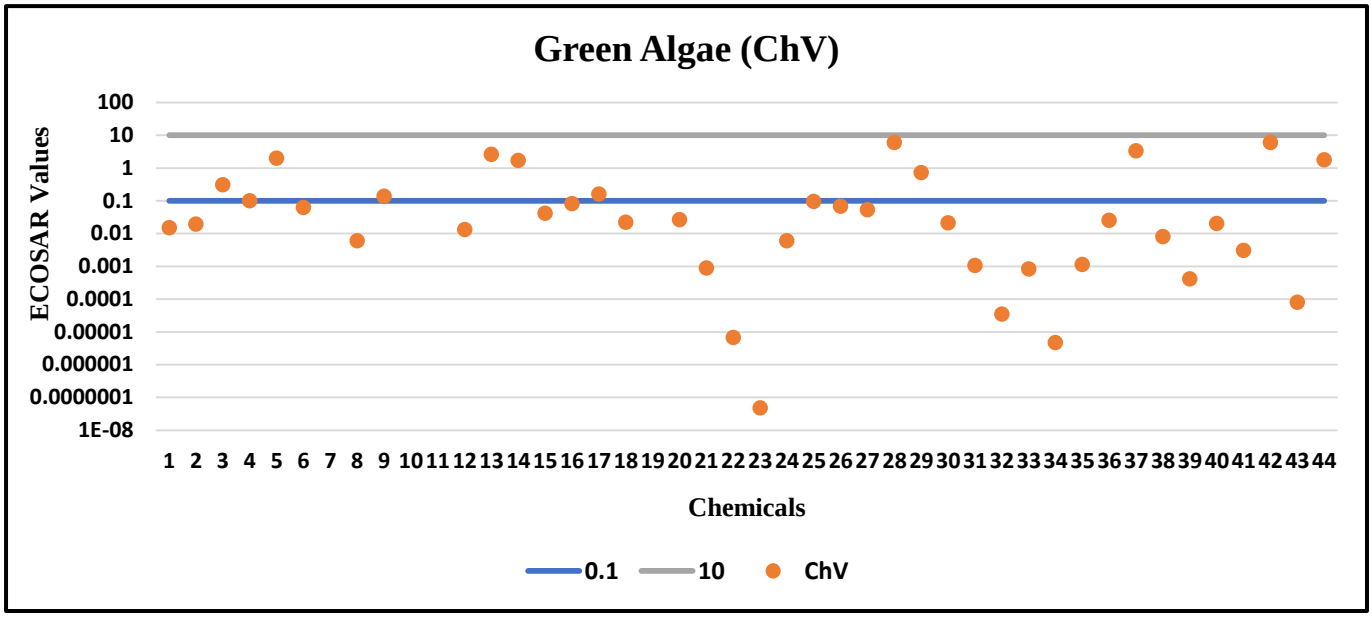
		Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) – diepoxy – 4-tert-Octylphenol, TMS derivative Heneicosane Cyclohexane, 1,1,3 – trimethyl – 2 – (3 – methylpentyl) – Pyrene, 1-methyl- Cyclopenta[g] – 2 – benzopyran, 1,3,4,6,7,8 – hexahydro – 4,6,6,7,8,8 – hexamethyl – Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 – tetrahydro – 1,5,7 – trimethyl – Butane, 1-isothiocyanato- Diazinone
Moderate Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 1 and < 100	**11**	Benzenamine, 3,4-dichloro- Chloroxylenol Quinoline, 2-methyl- Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- 5-Chloro-o-anisidine Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Hexane, 2-nitro- Phthalic anhydride Phenol
Low Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 100	**0**	

4.4.4.1.6 Green Algae ChV

4.4.4.1.6.1 Interpreting Results

Table 29: Cut off values for Green Algae in ECOSAR (Source: Manual 2012 EPA-748-B12-001)

High Concern	
Chronic	< 0.1 mg/L
Moderate Concern	
Chronic	> 0.1 and < 10.0 mg/L
Low Concern	
Chronic	> 10.0 mg/L



Graph 8: Interpretation of Chronic Values of Green Algae from ECOSAR

4.4.4.1.6.2 Description

Table 30: Interpreting ECOSAR Chronic Values of Daphnid

High Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
< 0.1	**28**	Benzenamine, 3,4-dichloro- p-Chloroaniline Triphenylphosphine sulfide 2,2'-Dimethylbiphenyl Chlorpyrifos Longifolene Naphthalene, decahydro − 2,3 − dimethyl − 3,5-Dimethyl-2,4,6-trichlorophenol 5-Chloro-o-anisidine 1,1'-biphenyl, 2,4,6-trimethyl- trisiloxane, 1,1,1,5,5,5 − hexamethyl − 3 − [(trimethylsilyl)oxy] − 10-Heneicosene (c,t) Heptacos-1-ene 1,1,6,6-Tetramethylspiro[4.4]nonane Ethanone, 1 − (2,3,4,7,8,8a − hexahydro − 3,6,8,8 − tetramethyl − 1H − 3a, 7 − methanoazulen − 5 − yl) − 4-Ethylbiphenyl 3,5-Dimethyl-2,4,6-trichloroanisole Biphenylene, 1,2,3,6,7,8,8a, 8b − octahydro − 4,5 − dimethyl − 1,7-Dimethyl-4-(1-methylethyl)cyclodecane

		Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16) − diepoxy − 4-tert-Octylphenol, TMS derivative Heneicosane Cyclohexane, 1,1,3 − trimethyl − 2 − (3 − methylpentyl) − Pyrene, 1-methyl- Cyclopenta[g] − 2 − benzopyran, 1,3,4,6,7,8 − hexahydro − 4,6,6,7,8,8 − hexamethyl − Oleyl alcohol, trifluoroacetate Naphthalene, 1,2,3,4 − tetrahydro − 1,5,7 − trimethyl − Butane, 1-isothiocyanato- Diazinone
Moderate Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
>0.1 and <10.0	**12**	Chloroxylenol Quinoline, 2-methyl- 3,5-Dichloro-2,4-dimethyl-1-methoxybenzene Benzenemethanol, α,α,4-trimethyl- 1-Hexanol, 2-ethyl- Dichloroxylenol Benzenemethanol, α,α-dimethyl- 3-Butyn-1-ol Hexane, 2-nitro- Phthalic anhydride Phenol
Low Concern		
Ranges (mg/L)	**No of Chemicals**	**Names**
> 10.0	**0**	

Conclusion

The conclusion of the research is that

- Wastewater samples are super complex even for multi-dimensional separation techniques. However, the use of passive samplers, GCxGC, ToFMS, and deconvolution algorithms help to reduce the complexity of chemicals. As there were more than 14000 chemicals at the starting point, by applying these techniques we narrowed it down to 44 chemicals.
- The filtration unit of Al Wathba WWTP is not doing a great job for the removal of micropollutants, and its filtration efficiency is only 55%.
- In terms of fate, behavior, and transport of the unremoved micropollutants 3 chemicals are highly bioavailable and 16 are moderate bioavailable, 26 chemicals are hydrophobic, and 15 are highly volatile which helps to identify the appropriate removal techniques such as AOP, AC, Air stripping.
- 5 chemicals have High, 7 moderate, and 32 low Bio- Concentration potential
- 26 chemicals are Persistent and do not biodegrade easily.
- According to LC50 Values: 24 chemicals for Fish and 29 chemicals each for Daphnia and Green Algae are Highly Toxic. According to Chronic Values: 29 chemicals for Fish, 29 for Daphnia, 30 for Green Algae are Highly Toxic

Limitations

In the end, some limitations found in this study are

- Only tentative identification of the chemicals is done and not the confirmation because for confirmation there is a need to buy analytical standards, then inject them, and then match with them to confirm. but to buy standards for 44 chemicals is easier than buying for more than 14000 chemicals.
- The risk quotient cannot be calculated because no quantification is done because for the risk quotient, we need to know the concentrations and we don't have concentrations of these chemicals.
- we used only silicon-based samplers. For some polar chemicals like antibiotics, the affinity of PDMS is not great so it will not absorb them effectively.

Recommendations

Some future recommendations for the improvement are given below,

- Use the other passive samplers such as polyethylene, Polyoxymethylene, and ODGT which are good for polar chemicals to improve and cross-check the reported Micro Pollutants.
- The performance reference compounds should be used to improve the quantification results.
- Some measures need to be taken to improve the efficiency of the Filtration unit as multimedia filtration can be used instead of dual media. If this is not possible the effluent should be treated by AC, Air stripping, or AOP.
- More detailed screening can be done based on the Abraham Solvation Model.

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