Understanding the chemodynamics of organic pollutants in microplastic phases using models based on intermolecular interactions

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A thesis submitted in partial fulfillment of the requirement for the degree of

Master of Science in Environmental Science

Institute of Environmental Sciences and Engineering
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Islamabad, Pakistan
2022

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based on intermolecular interactions"

Submitted by

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Dedication

This research is dedicated to my loving, caring, and industrious parents and my friends and seniors whose efforts and sacrifice have made my dream of having this degree a reality. words cannot adequately express my deep gratitude to them.
"O My Sustainer, Bestow on my parents your mercy even as they cherished me in my childhood".

Acknowledgements

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List of Abbreviations

PDMS	Polydimethylsiloxanes
LDPE	Low Density Polyethylene
PE	Polyethylene
K_{ow}	Octanol-Water Partition Coefficients
logP	Octanol-Water Partition Coefficient
K_{aw}	Air-Water Partition Coefficient
ASM	Abraham Solvation Model
ASD	Abraham Solvation Descriptors
WWTP	Waste Water Treatment Plant
T_g	Glass Transition Temperature
OECD	Organization for Economic Cooperation and Development
MTM	Mass Transfer Model
QSPR	Quantitative Structure-Property Relationship
pp-LFER	Poly Parameter Linear Free Energy Relationship
PCBs	Polychlorinated Biphenyls
SMILES	Simplified Molecular-Input Line-Entry System
CAS	Chemical Abstract Service
UFZ-LSER	Helmholtz Centre for Environmental Research-Linear Solvation Energy Relationships
MLR	Multiple Linear regression
AIC	Akaike Information Criterion
PCA	Principal Component Analysis

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ABSTRACT

Recently, micro- and Nanoplastic have attracted a substantial research interest due to ubiquitous presence in environment and even in human blood. It is critical to understand their fate, behavior, and transport in the environment. The chemicals that are added in plastic during their manufacturing are referred to as native chemicals. Once released in the environment, these plastic materials accumulate environmental pollutants, which are referred to as non-native chemicals. Understanding the leaching potential of these native and non-native pollutants is of fundamental importance for their environmental and human health risk assessment. The way these native and non-native chemicals interact with the environment is dictated by the basic principles of chemodynamics. However, this requires the information on the diffusivities of contaminants within the plastic material. The experimental database of diffusion coefficients is very limited. In this study, I introduced an easy and reliable method to estimate the diffusivity of organic pollutants in two widely used plastic materials: polydimethylsiloxanes (PDMS) and low-density polyethylene (LDPE). The estimation approach is based on a linear combination of $\log K_{ow}$ (octanol to water partition coefficient) and $\log K_{aw}$ (air to water partition coefficient). The new models successfully described the variance in the data of diffusivity of organic pollutants in PDMS and LDPE. The regression statistics for PDMS phase and LDPE phase depicted $R^2 = 0.70$, RMSE = 0.57 and $R^2 = 0.89$, RMSE = 0.15, respectively. The predictive performance of my models was in good agreement with the widely used Abraham Solvation Model (ASM). I extensively evaluated my models by applying a suite of machine learning techniques such as leave-one-out cross-validation, hold-out, k-fold, bootstrap, principal component analysis, and Pearson correlation analysis. The results of these analyses supported the theoretical footings taken to build these models. Moreover, good agreement was found between the train sets and test sets sampled using resampling techniques. Finally, I applied a mass transfer model to evaluate the leaching potential of diverse organic pollutants from the plastic materials as a function of their sizes and types. In summary, my models help better understand the chemodynamics of native and non-native chemicals present in the plastic phases. This insight is useful to carry out environmental and human health risk assessment.

Keywords: Microplastic; Nanoplastic; Plastic additives; Diffusion coefficients; Linear free energy relationship; Leaching potential; Polyethylene; Silicone

1. INTRODUCTION

1.1 Background

Oceanographers estimate that in 2015 approximately 15 trillion to 51 trillion microplastic shreds (< 5mm in size) floated freely in surface waters across the globe (Lim, 2021). Microplastics are everywhere, and their presence in diverse ecosystems can prove lethal for ecological systems and human health (Vivekanand *et al.,* 2021). These are synthetic particles with a size of less than 5mm in length and are categorized into two types according to their production. Plastics manufactured for specific purposes, such as microbeads for their use in cosmetics and other beauty products, are called primary microplastics. Similarly, the plastics formed after the degradation and fragmentation of larger plastics are called secondary plastics, including the formation of fibres from the degradation of synthetic fibres (Vivekanand *et al.,* 2021). The plastics either from primary or secondary sources are ultimately released into the environment, and approximately 5000 to 80000 tons of primary microplastics are discharged into the environmental compartments from households, as in cosmetics and cleaning products, from feedstocks that are used to produce these beauty products, and from pellets and powder that are used in air blasting (Jiang, 2018). Moreover, these plastics now enter into either natural or anthropogenic water cycles. Microfibers discharged from households accumulate in the inlet of WWTP, and because of their smaller size, these fibres pass through the screening phases and accumulate in outlets that are ultimately discharged into larger water bodies, rivers, and oceans (Carr *et al*., 2016).

These polymers have more comprehensive applications, such as PDMS, which is a rubber polymer used in medical sciences for its biocompatibility characteristics and in material sciences for its mechanical properties and in analytical chemistry for its high affinity with the wide range of hydrophobic chemicals (Narváez Valderrama *et al*., 2016). Similarly, polyethene has broader applications, such as packaging film, trash, and shopping bags, used in farming mulch, wire and insulation toys and various housewares. Passive sampling is a powerful tool for detecting environmental contaminants from water, sediments, soil, and air (Narváez Valderrama *et al*., 2016). In this context, Polydimethylsiloxanes and Polyethylene are polymers that are widely used

as passive samplers for the uptake of contaminants from the water bodies to know their concentrations. Because of their wider usage, they are produced in large quantities and ultimately disposed of in the environmental spheres.

Additionally, because of the ubiquitous and persistent nature of microplastics has become a growing concern worldwide, and their presence has adverse impacts on the ecosystem and human health (Vivekanand *et al.,* 2021). Furthermore, their interactions with other organic pollutants, especially in marine environments, increase their toxicity by 10 *(*Alberts, 2022*).* Microplastics have detrimental effects on the environment because of their small size, persistence, and chemical nature. The chemical nature of microplastics aggravates their deleterious impacts other than their ubiquitous presence and small sizes.

Microplastics are also used as native plasticizers, acting as additives, and loosely bonded to other microplastics. Whenever they enter into any environment, these chemicals leach out of the native plastics and are released into the environment. For instance, Phthalate esters are added to the microplastics for flexibility, but these are not chemically bonded, and upon disposal, they leach out into the environment (*Gigault et al.*, 2018). In contrast, non-native chemicals are those that are absorbed into the microplastics from surroundings, such as persistent organic pollutants. The movement of organic pollutants into the polymers depends on various factors, such as the availability of free volume in the polymer and the partial movement of the polymer chains. These properties of polymers are defined by the glass transition temperature (Tg) (Rusina *et al.*, 2010). The polymers with low Tg values have higher diffusivity, which means that more chemicals enter into the polymer; for instance, siloxane polymers have lower Tg values and therefore have the highest permeability for the organic substances. For instance, Polybrominated Diphenyl Ethers (PBDEs), flame retardents have higher diffusivity in PDMS than LDPE; therefore, the silicon-based polymer is used for sampling organic pollutants (Narváez Valderrama *et al.*, 2016). The risk assessment of passive samplers and the microplastics released into the environment requires a comprehensive understanding and calibration of the transport and interaction of organic pollutants and polymers. The diffusion process dominant the rate at which pollutants can cross biotic and polymer boundaries; hence, diffusion coefficients are a good measure of the uptake and release of contaminants from microplastics (Nabi & Arey, 2017).

Many researchers reported that the diffusivity decreases with an increase in molecular weight and size (Pintado-Herrera *et al*., 2016). Moreover, the molecule's shape also significantly influences the penetration ability of the diffusant. Generally, rigid molecules have less penetration power, whereas linear, flexible, and symmetrical compounds have higher mobility and, thus, higher diffusion rates *(Rusina et al., 2010)*.

1.2 Diffusion Coefficient

Diffusion is the random movement of molecules from higher concentration to low concentration along the concentration gradient. Fick's first law describes diffusion as:

$$J = -D\frac{-\partial C}{\partial x}$$ *Eq. 1.1*

J = diffusion flux, D = Diffusion Coefficient, C = Concentration, x = Change in position

D is measured in m2s-1

The diffusion coefficients 'D' is proportional to the mass transfer coefficients; then, the high value of D in polymer means that the higher the chemical transfer into polymers will occur.
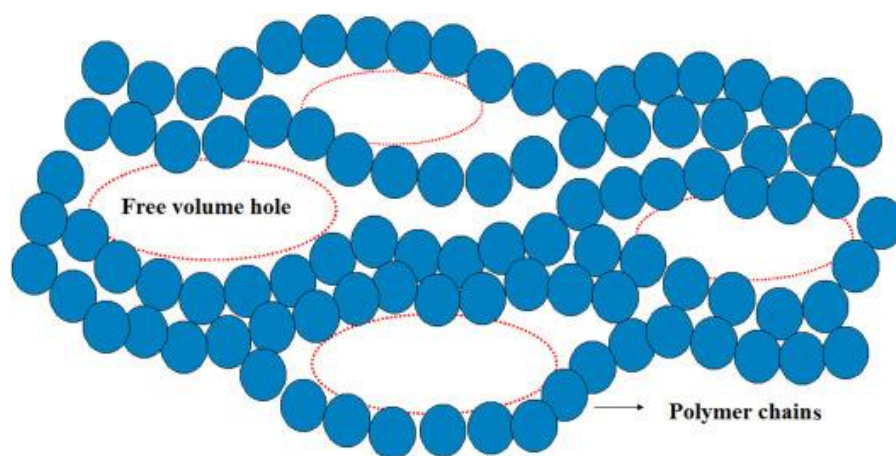
Figure 1.1 **Free volume in polymers and its relation with diffusion coefficients (Swapna et al., 2020)**

The free volume of a polymer can be described as the "empty internal space" This extra free volume tends to larger diffusion coefficients than would be expected if the polymer were in an equilibrium state. As the diffusion behaviour of chemicals depends on many factors, such as the free volume among polymer chains and segmental mobility, the measurement of the diffusivity of diverse organic compounds using experimental methods is arduous and time-consuming (Naseem *et al.* 2021).

Computational prediction models are developed based on the physicochemical properties of the compounds using already experimentally determined diffusivity values (Zhu et al., 2020). Additionally, various regulatory bodies such as Organization for Economic Cooperation and Development (OECD), World Health Organization (WHO) and the US Environmental Protection Agency (EPA) recommend the development of simulatio models for the estimation of chemical risk assessment in various environmental fields (Aakash, 2022; OECD, 2021). Consequently, numerous research across the world employed numerous in silico methods to determine the diffusivity of organic pollutants into various microplastics such as polyoxymethylene (POM), Polydimethylsiloxanes (PDMS), and Low-Density Polyethylene (LDPE).

Therefore, it is necessary to predict and evaluate the diffusivity potential of these polymers to know about their destructive potential to human beings and other aquatic organisms when they are released into the environment. Consequently, in this study, I have developed a model using polymers PDMS and LDPE because of the wide availability of data regarding the diffusion coefficients of these polymers. Because of the low glass transition temperature, these compounds are used in numerous experimental studies to determine the diffusivity of organic compounds in these polymers. This study is separated into two parts: the development of models for PDMS and PE and the development of a Mass Transfer Model (MTM) for polymers PDMS and PE using various thicknesses of macro, micro, and Nano plastic.

1. 3 Problem Statement

The Chemodynamics of native and non-native organic pollutants in microplastics has not been well-studied using the first principles of thermodynamics. Given millions of compounds, there is a need for easy estimation approaches available as of now.

1.4 Objectives

In accordance with the problem statement, the study was designed based on the following objectives.

- To investigate the role of intermolecular interaction parameters in describing the diffusivity of organic pollutants in the PDMS and PE.
- To come up with the best model for predicting the diffusivity of PDMS and PE using supervised and unsupervised machine learning techniques.
- To parameterize a mass transfer model for the estimation of organic pollutants from microplastics as a function of the size and nature of polymers.

2. LITERATURE REVIEW

Researchers use various approaches to determine the diffusion coefficients of various organic compounds. These include experimentation, molecular simulations and the development of quantitative structure-property relationships QSPRs (Lampic et al., 2019) (Lampic *et al*., 2019). Experimental methods are costly and time-consuming and need extensive data about emerging contaminants. Furthermore, molecular simulations are practical and faster methods to estimate diffusion coefficients of more minor compounds in polymers using molecular dynamics and Monte Carlo (MC) methods (Lampic *et al*., 2019; Gautieri *et al*., 2010; Sudibjo & Spearot, 2011). However, atomistic level simulation of large organic compounds is time taking, especially for the chemical to reach the equilibrium with a polymer. To solve this problem, multiple grouping atoms is done through the Coarse-grained simulation technique (Lampic *et al*., 2019; Gautieri *et al*., 2010), but these techniques are relatively complex and much less work is done on estimating the diffusion coefficients of organic compounds. In this regard, for the first time, Lampic developed molecular simulation models to predict the diffusivity of emerging pollutants (Lampic *et al*., 2019). Many researchers have developed Poly parameter Linear Free Energy Relationship (pp-LFER) (Abraham, 1993; Abraham et al., 2004; Abraham & Mcgowan, 1987) and QSPR models using various descriptors, but Abraham Solvation Models are accurate and used more frequently. However, few works have been done on the development of linear free energy relationship models regarding the diffusivity of organic compounds into PDMS and PE. For the development of models, different parameters are required to determine the rate-limiting step and the Abraham Solvation parameters. The Abraham descriptors are used to develop a model and are considered accurate to explain the information, but the values for these descriptors are available for limited compounds, approximately 8000 chemicals (Nabi & Arey, 2017).

Nevertheless, according to Kieran Mulvaney at Seeker reports, approximately 10 million new compounds are manufactured in a year. Therefore, the release of chemicals into the environment is more, and it is difficult to study every chemical, and it takes a lot of time, money, and resources.

In general, Abraham Solvation models are present in the following forms (Michael H. Abraham et al., 2004).

1. $logSP = c + sS + aA + bB + vV + lL$ *Eq. 2.1*
2. $logSP = c + eE + sS + aA + bB + vV$ *Eq. 2.2*
3. $logSP = c + eE + sS + aA + bB + lL$ *Eq. 2.3*
4. $logSP = c + sS + aA + bB + lL$ *Eq. 2.4*

The lowercase letter c is the y-intercept, and the other lowercase letters are regression coefficients referred to as system parameters. Different variations of Abraham parameters are based on the information covered in different phases. For instance, *Eq. 2.1* is used for diffusion between two condensed phases; while *Eq. 2.2* is used for determination of diffusion between the two different phases condensed and gas phases, and *Eq. 2.3* processed condensed and gas-condensed phase transfers (Michael H. Abraham et al., 2004).

Table 2.1 Significance of Abraham Descriptors (Michael H. Abraham et al., 2004)

Symbol	Descriptor
E	Excess Molar Fraction
S	Polarizability/Di polarity
A	Acidity
B	Basicity
V	McGowen Volume/ Cavity formation
L	Gas-Hexadecane Partition Coefficient

The response variable or dependent variable is logSP, which can be any specific dependent property; in my case, the dependent property is logDPDMS and logDPE. The other variables, such as E, S, A, B, V, and L, are predictor variables or independent variables that influence the value of logSP. These are also called Abraham Solvation descriptors, and their significance is demonstrated in *table 2.1*.

Since organic compounds penetrate into polymers when they come into contact with them, their interactions are prominently defined through dipole moment, molecular size, and the flexibility of compounds (Belles *et al*., 2018). Numerous studies have reported a positive correlation with the Octanol-water partition coefficient (logP), which is used as a proxy to determine the diffusivity in organic compounds (Narváez Valderrama *et al*., 2016) (Pintado-Herrera *et al*., 2016).

Belles *et al*. (2018) determined the diffusion coefficient of 145 organic compounds in Polydimethylsiloxanes (PDMS). As a result of their experiment, dipole moment, molecular size, and the flexibility of compounds are the prominent factors in defining the diffusion behaviour of organic substances. Furthermore, to improve interpretations derived from the developed experimental methods, the non-linear quantitative structure-property relationship (QSPR) model combined data with the available literature, making the total dataset of 198 compounds. The average value was calculated to avoid overlapping compounds collected experimentally or from literature. For developing the QSPR model, molecular volume, rotatable bonds, topological polar surface area, and the number of Oxygen (O) and Nitrogen (N) atoms are used as independent descriptors for the first time. A correlation coefficient (R2) of 0.81 and a mean absolute error of 0.26 log units were obtained, which implies that the mentioned descriptors explain 81 per cent of information on diffusion coefficients of organic compounds (Lampic *et al*. 2019).

$$\log_{DPDMS} = -4.1 \times 10^{-4}\, V_m^{1.48} + 0.028 R_0^{1.45} + 7.49 \times 10^{-5}\, TPSA^{2.34} - 0.041 N_0^{2.63} - 1.094$$
$$N_N^{0.73} - 9.417 \hspace{4cm} Eq.\ 2.5$$

where V_m = Molecular Volume, R_0 = Rotatable Bonds, TPSA = topological polar surface area, N_o = Number of Oxygen atoms, N_N = Number of Nitrogen atoms

Another model was developed by Lampic *et al*. (2019) to examine the abilities of different independent descriptors that can explain the diffusivity of organic pollutants in polymers, especially PDMS and Low-Density Polyethylene (LDPE). COSMO-RS sigma moment and simple molecular descriptors were used. The selection of descriptors was made meticulously, encompassing the diffusion behaviour of organic compounds. For those reasons, selected molecular descriptors demonstrate the main molecular properties that play an essential role in defining the diffusion rate in polymers such as polyethene and polydimethylsiloxanes. Similarly, sigma moment descriptors reflect the electron density distribution that includes the size of the molecule, charge,

polarizability, high-order variants, and dipole moment. Sigma moment descriptors are derived from quantum mechanical structure. With these descriptors, Lampic found that the sigma moment descriptors have the best predictive capability with a value of R2 = 0.85 with Root Mean Square Error (RMSE) of 0.36, whereas for the molecular descriptors QSPR model developed gave the value of correlation coefficient R2 = 0.78 and RMSE = 0.45.

On the other hand, for Low-density polyethene, the molecular descriptors gave the best results with a correlation coefficient of 0.86, and the root means a square error of 0.21. In contrast, sigma moment descriptors explained only 66 per cent of information with an error of 0.33. Molecular descriptors explain the size, polarity, flexibility, and capacity to form hydrogen. However, molecular descriptors did not describe the diffusivity of organic compounds in PDMS well. Therefore, sigma moment descriptors are reliable options for finding the diffusivity in PDMS. QSPR models developed (Lampic *et al*., 2019; Belles *et al*., 2018) gave the best results for determining diffusivity properties, but these determiners are challenging to obtain and computationally expensive. The molecular and sigma moment descriptors are difficult to obtain and are not readily available; therefore, computationally inexpensive and limited descriptors are required to explain complete information.

Furthermore, another computational approach is used by Zhu *et al*. (2020), where they developed poly-parameter Linear Free Energy Relationships (pp-LFER) model and a quantitative Structure-Property Relationships model for LDPE to predict the diffusivity of organic substances. (Zhu *et al*., 2020). The pp-LFER model using Abraham descriptors was developed with two descriptors of Abraham V and E, and it shows the best results. On further exploration of the diffusion coefficients of organic chemicals, a QSPR model with five descriptors was developed, and its R2 value was 0.949, and upon cross-validation using leave one out, the R2 value was 0.941 showing a good agreement between the training set and test set. However, the five descriptors used in this model are computationally expensive and are not readily available to the broader public. The equations for the LFER model with V and E descriptors Eq.1 of Abraham and five descriptors Eq.2 are shown here:

$$\log D_p = -0.881V - 0.262E - 10.79 \qquad Eq.\ 2.6$$

$$n=96,\ R^2_{Adj} = 0.815,\ RMSE = 0.059$$

Another QSPR model was also developed using the five descriptors ETA_Alpha, ASP-6, IC1, TDB6r and ATSC2v. These descriptors are described as 'Alpha values sum of all non-hydrogen vertices of a chemical (Zhu *et al*., 2020), Average simple path of order 6 , Information content index, topological distance-based autocorrelation - lag 6/weighted by covalent radius, Centered Broto-Moreau autocorrelation - lag 2/weighted by van der Waals volumes (Zhu *et al*., 2020). The results of these models presented high goodness of fit with $R^2 = 0.941$.

Log Dp = - 0.303 ETA_Alpha + 12.057ASP-6 + 0.111IC1 + 0.093 TDB6r + 0.000222 ATSC2v - 11.243   *Eq. 2.7*

n= 96, $R^2_{Adj} = 0.941$, RMSE = 0.016

Although these five descriptors have high predictive ability, it is a parameter intensive, and these parameters are not readily available to everyone. Therefore, we look into the parameters that explain maximum variability in fewer dimensions and whose experimental values are readily available. The molecular descriptors octanol to water partition coefficients (log Kow) and the air to water (log Kow) partition coefficients are widely used and readily available for an extensive range of organic compounds. However, mainly these descriptors are used to develop models based on partition coefficients. Belle et al. (2018) stated that the logP descriptor provides a positive correlation within the same compound class, though it has the opposite effect for the different compound families. It emphasizes that it explains the partial transport mechanism and does not cover the specific interactions. Therefore, I took another parameter log Kaw to describe the unexplained information and cover specific interactions.

3. METHODOLOGY

3.1 Data Acquisition

Experimental values for the diffusivity of logDPDMS and logDPE are acquired from the literature (Belles *et al.*, 2018; Rusina *et al.*, 2010). The data covered broader range of compounds such as Polybrominated diphenyl, Polychlorinated biphenyls (PCB), Poly Aromatic Hydrocarbons (PAHs), pesticides, and large chain Aliphatic hydrocarbons whose detail is given in table 3.2. After carefully curating and organising data from different literature, I collected the Simplified Molecular-Input Line-Entry System (SMILES) code and Chemical Abstracts Service (CAS) of each chemical from Chem Spider and PubChem databases. Later, I took values of Abraham descriptors of organic compounds from an online database source Helmholtz Centre for Environmental Research-Linear Solvation Energy Relationships (UFZ-LSER), which is free and easy to use. The values of Abraham Solvation Descriptors (ASDs), logKaw, and log Kow collected after careful examination are spread over several orders of magnitude, as displayed in table 3.1.

Table 3.1. Presenting the Range of ASDs, logKaw and logKow (Aakash, 2022)

Descriptor	Minimum value	Maximum value
E	-1.04	2.94
S	-0.52	1.98
A	0	1.12
B	0	2.04
V	0.068	3.14
L	-1.741	13.3
$logK_{ow}$	-2.11	9.87
$logK_{aw}$	-13.45	3.13

Table 3.2 Classes of compounds and the number of chemicals present in the PDMS and LDPE datasets (Lampic *et al.,* 2019; Belles *et al.,* 2018; Rusina *et al.,* 2010)

Chemicals	PDMS	LDPE
Polycyclic Aromatic Hydrocarbons (PAHs)	15	12
Polychlorinated Biphenyls	33	39
Volatile organic compounds (VOCs)	33	0
Polybrominated Diphenyl Ethers (PBDEs)	7	0
Alkanes	28	0
Pesticides compounds	43	2
Nitro-PAH	8	0
Flame Retardants	8	4
Fragrances	9	11
Miscellaneous compounds	13	11

The experimental data was collected from various sources although less experimental data is present but available for diverse set of classes. Therefore, the diversity in data set was ensured to include the chemicals from different classes of compounds. Below in a figure 3.1 a strip plot is given which depicts the diversity of dataset. The strip plot represents that almost fifty percent of the data lies in middle ranges near mean and median values. The lower end of the plot represents the first quartile and upper end elaborates the third quartile. In the plot the plus sign depicts the mean value, and the straight line depicts the median value. The points that are farther away from the mean value are outliers.
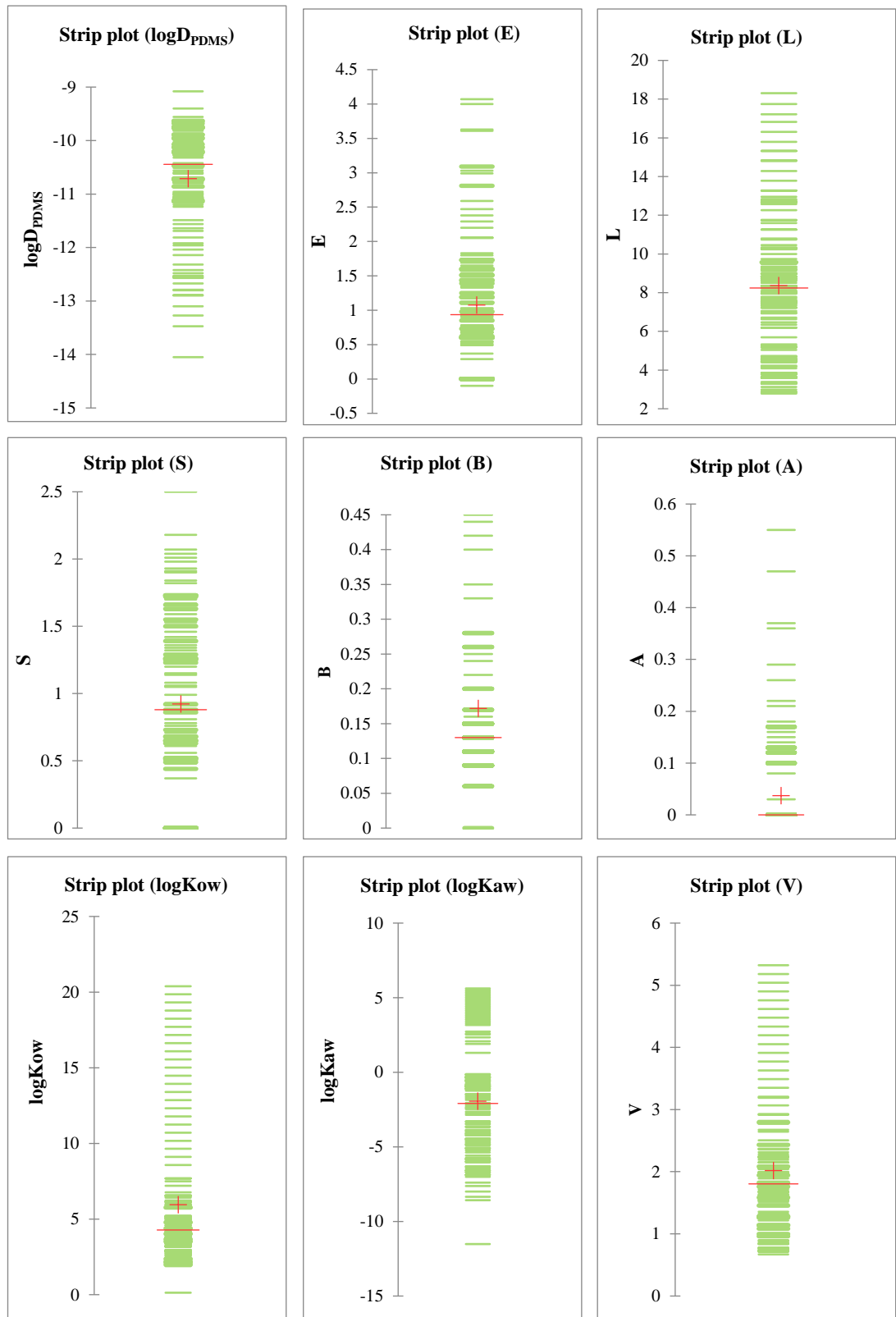
Figure 3.1 Diversity of dataset is represented in the form of strip plots.
Positive sign represents mean value
Straight line represents median value

3.2 Selection of Intermolecular descriptors

3.2.1 Intermolecular Forces

The attractive and repulsive forces that exist between the molecules of a compound or substance and within the molecules themselves are collectively called intermolecular forces. These forces define the physical and chemical properties of a compound for example, melting and boiling point of a substance depends on the intermolecular interactions. Similarly, there are different types of interactions that affect the behavior of molecular in different phases such as when the molecules are released into the marine environment, they interact in certain way according to their properties. When toxic chemicals are discharged into the environment most of the time they diffuse or partition in water phases. There are two governing processes hydrophobic and electrostatic interactions. Hydrophobic interactions where molecules have less compatibility with water. On the other hand, the molecules attract or repel the molecules on the basis of charges. Diffusivity of a substance depends on these intermolecular interactions and thermally activated motions. All molecules are in constant state of motion which leads to the collision between molecules and that produces kinetic energy. Sometimes enough kinetic energy is produced that molecules become able to break these intermolecular forces and molecules diffuse out of the system.

3.2.2 Octanol-Water Partition Coefficient (logP)

Numerous proxy methods are used to explain these intermolecular interactions so instead of experimental measures these proxies are used to model the diffusivity and partitioning of organic compounds. Octanol to water partition coefficient (K_{ow} and logP) frequently used to estimate the partitioning behavior and risk assessment of environmental contaminants. Octanol/water partition coefficient give information about hydrophobic interactions and can be used to estimate the fate of chemicals when these come into contact with different phases. Octanol to water partition coefficient consists of two phases where one phase is taken as hydrophobic phase such as octanol (proxy for lipids and fats in living organisms) while other phase is water (hydrophilic).

$$K_{ow} = \frac{C_o \; Equilibrium}{C_w \; Equilibrium} \qquad\qquad Eq. \; 3.1$$

Primarily, Kow is significant in determining the fate of chemicals in the

(a)   **(b)**
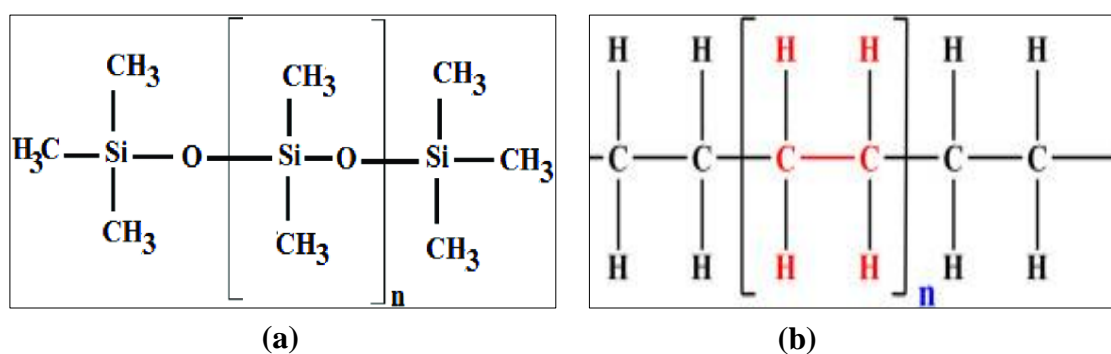
Figure 3.2 (a) Structure of PDMS having siloxanes bond depicting its partial polar nature and (b) structure of polyethylene depicting its hydrophobic nature (Sharada et al., 2022; Hamouni et al., 2019)

environment and the organism. For instance, the Kow values determine the bioaccumulation capacity and the toxicity of emerging pollutants. For this reason, the European Union's chemicals legislation REACH (Cumming & Rucker 2017) has made it compulsory to determine the value of Kow for every compound whose annual manufactured or imported weight is one ton or more. Therefore, experimental data is available for a large set of compounds, so this Octanol/Water partitioning coefficient is used to develop models. It is one of the reasons I selected the log Kow parameter to develop a model to examine the diffusivity values of organic compounds in PDMS and LDPE. PDMS is a mineral organic polymer partially ionic in nature because of its silicone oxygen bond, which makes it partially hydrophilic and hydrophobic at the same time. However, it depends on the repetition of monomers which transform it into the elastomer, and when it enters into an aquatic environment, water passes over PDMS and helps with the absorption of hydrophobic organic contaminants on the surface of polymers. The octanol-water partition coefficient is a defining parameter to deal with these hydrophobic interactions. For example, the chemical's ability to diffuse into the polymers PDMS and Polyethylene is governed by Kow.

The microplastics when released into the environment they have the absorption capacity and other persistent pollutants can get absorbed into these microplastics which make situation even worse therefore, it is necessary to have a model to know the diffusive nature of chemicals so that its risk potential could be measured, and the manufacturing of these chemicals could be stopped or improved.

3.2.3 Air-Water Partition Coefficient (logKaw)

Comprehensive information of the physical and chemical properties of emerging pollutants is required for the prediction and estimation of the fate of environmental contaminants. In this context, a strong chemo dynamic property solubility is requisite for determining pollutants' concentration and their minimization from environmental media. Similarly, the air-to-water partitioning is the ratio of a concentration of a in the air to the water phase, given that the temperature is constant; this is related to the Henry's Law constant (HLC) when it is related to vapour pressure data. Therefore, Henry's Law constant is the same as air water partition coefficient and is measured using compounds' solubility. The HLC data is required for various purposes, and one of them is its use for the development of transport models that elaborate on the movement of contaminants in the different phases of the environment. Like octanol-water partition coefficients, the data for air-water partition coefficients are available for a large set of compounds as their values are easy to determine experimentally. Kaw explains specific interactions such as hydrogen bonding, and when various organic pollutants diffuse into the polymers, this parameter governs the distribution of chemicals covering their hydrogen interactions.

3.3 EPI SuiteTM Software

The Estimation Program Interface Suite™ (EPI Suite™) is a window-based program developed for the estimation of properties (physical/chemical) and the fate of organic compounds by EPA and Syracuse Research Corp. (SRC). This program helps determine the chemical's properties, such as vapor pressure, melting and boiling point, and bioaccumulation capacity. Moreover, the fate of the chemicals across different environmental parts can also be evaluated using this program. For instance, the movement of chemicals from the atmosphere into the water or soil or vice versa.
EPI Suite™ has different input modules such as AOPWIN™, KOWWIN™, BIOWIN™, HYDROWIN™, HENRYWIN™, AEROWIN™, and ECOSAR™, etc.

I used EPI Suite™ to collect data on chemicals regarding Kow and Kaw using modules KOWWIN and HENRYWIN, respectively. This program utilizes the constant fragment technique for Kow, where the particle is divided into fragments, and then the coefficient values for each fragment are added to give the estimated value of Kow.

One hundred ninety-eight chemicals for which experimental values for diffusivity were available in the literature, and among them, 124 ASDs were available from the database. Therefore, my data shrink to 124 chemicals from 198. On the other

hand, some experiment values were missing for log Kow and logKaw. Therefore, I used the ASM model (Poole et al., 2013), (Zhao & Abraham, 2005) to calculate the log Kow values for the remaining chemicals.

$$log\ Kow\ =\ 0.088\ +\ 0.562E\ -\ 1.054S\ +\ 0.034A\ -\ 3.460B\ +$$
$$3.814V$$

$$Eq.\,3.2$$

$$log\ Kaw\ =\ -0.994\ +\ 0.577E\ +\ 2.549S\ +\ 3.813A\ +\ 4.841B$$
$$-\ 0.869V \qquad\qquad Eq.\,3.3$$

The experimental value for Henry Law Constant is taken from HENRYWIN which is then divided by the value of gas constant and Temperature to convert in to air-water partition coefficients.

$$K_{aw} = \frac{HLC}{RT} \qquad\qquad Eq.\ 3.4$$

Where R = gas constant and T = Temperature

3.4 Statistical Analysis

Various statistical analysis was performed, including Pearson Correlation (PC), Principal Component Analysis (PCA), and multiple linear regression (MLR) using RStudio (version 1.4.1106) and XLSTAT (XLSTAT, 2020). MLR was used to develop pp-LFER and a two-parameter LFER model. MLR was performed to examine the optimum number of parameters required to build the model using dependent and independent descriptors. In this case, diffusion coefficients of PDMS (logDPDMS) and LDPE (logDPE) were the dependent property, and LFER variables such as E, S, A, B, V, L, log Kow and logKaw were independent. Changes in independent descriptors bring changes in dependent property.

MLR was used to develop a model and statistical analysis such as variance Inflation Factor (VIF), and Akaike Information Criterion (AIC) was used to determine the significant descriptors that best describe the dependent property. In MLR, the variables were picked to develop an optimum predictive model based on the maximum R2adj value, and minimum root mean squared error (RMSE) value. Principal Component Analysis was used to analyze the chemical space and to minimize data

redundancy. It was also run to determine the variance in the data and to know the contribution of each variable in explaining information. Pearson correlation was performed to determine the relationship and redundancy between each variable.

3.5. Model Validation

To assess the performance of developed models and to compare and select the best predictive model, the OECD guidelines (OECD, 2007) were followed. Internal and external validation methods were employed, such as "leave-one-out cross-validation (LOOCV), k-fold validation and bootstrapping" (Liu et al., 2016). Cross-validation tests such as leave one out and the bootstrap method (n=1000) were used to evaluate the robustness of models. External validation was done by splitting the data set into a training set and a test in an 80:20 ratio. All the statistical parameters, such as Mean Absolute Error (MAE), RMSE and R^2, sometimes called independent indicators, are used for the assessment of validation of models.

4. RESULTS AND DISCUSSION

4.1 Recreation and Validation of Abraham Solvation Model

The Abraham Solvation Models were created for both microplastics PDMS and LDPE. In his paper Zhu et al. (2020) developed six parameter pp-LFER model to predict the diffusivity of chemicals into the Low-Density Polyethylene. However, there is now work done on the development of pp-LFER model for the PDMS. I developed pp-LFER model for the PDMS and recreated solvation model for LDPE.

4.1.1 Development of ASM for PDMS

As mentioned earlier in section 3.1 the data was acquired from the Belle (2018) paper, overall, the chemicals were 197 but after careful curation and organization the chemicals shrank to 124.

The multiple linear regression was run on the four variants of ASDs as described above ESABV, ESABL, SABVL, and SABL. The results of Abraham Solvation Models are shown in table 4.1.

Table 4.1 The four variations of ASMs ($logD_{PDMS}$)

Model Name	R^2	RMSE	R^2_{Adj}
ESABV	0.82	0.45	0.81
ESABL	0.82	0.44	0.816
SABVL	0.817	0.45	0.81
SABL	0.817	0.45	0.81

The ESABL model for the PDMS polymer performed well and stood out as the best fit model with high coefficient correlation (R^2) and lower value for RMSE after running multiple regression analysis. All the Abraham Parameters are used to explain the diffusivity of organic chemicals into PDMS except V. All the parameters of Abraham are significant in explaining the variance in response variable.
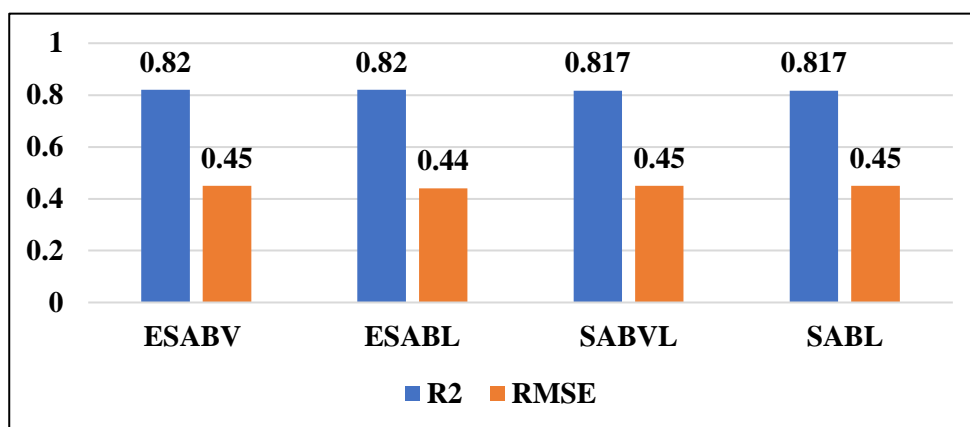
Figure 4.1 Bar plot representing the statistics of four variations of ASMs. Results for all variants of Abraham are similar but ESABL model represents minimum error

In figure 4.1, the y-axis represents the values of root mean squared error and R^2, and the x-axis shows the variations of ASMs. On the basis of R^2 and RMSE value the best model is ESABL with least error value of 0.44.

The equation for ESABL model is presented as:

logD$_{PDMS}$ = -9.30($\pm$0.12)+ 0.19($\pm$0.09)**E** -0.29 ($\pm$ 0.16)**S** -1.42 ($\pm$0.43)**A** - 1.71($\pm$0.14)**B** - 0.07($\pm$0.01)**L**   *Eq. 4.1*

n= 124, R^2 = 0.82,   RMSE =0.44

A standardized regression coefficient analysis was done to know the contribution of each parameter. As each descriptor is measured in different units and have different
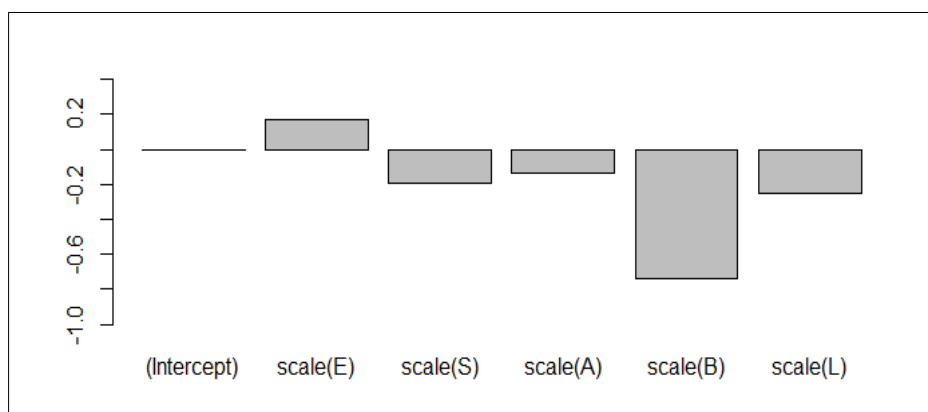
 Figure 4.2 A graph represents the results of regression coefficients. As shown above B parameter have significant contribution in explaining information related to diffusion coefficient.

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impacts on the property therefore to know the contribution of each descriptor its units are neutralized by standardizing the regression coefficients. The B descriptor contributes more towards explaining information followed by L and then S and E displayed in figure 4.2. y-intercept was made zero to avoid its intervention and to solely know solely about the contribution of independent descriptors.

Sometimes, it happens that similar information is explained by each variable, or two variables are highly correlated with each other. To avoid redundancy and overlapping of information a correlation analysis was done. A Pearson Correlation was done using RStudio.
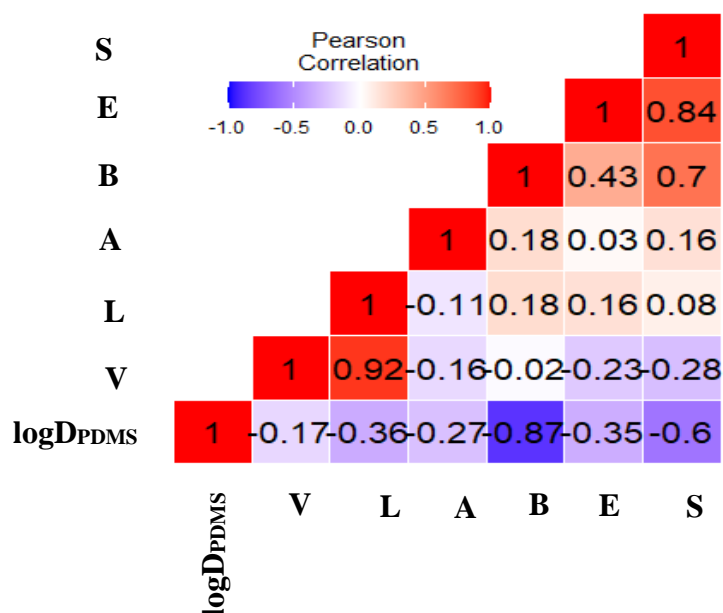
Figure 4.3 Pearson Correlation depicting that two parameters are not highly correlated with each other for instance B descriptor and L descriptor, the R value is 0.18 which represent that both are not highly correlated with each other.

4.1.1.1 Best Predictive Model

To determine the best predictive model among the four variants of Abraham Solvation Model developed for the PDMS, Akaike Information Criterion (AIC) analysis was done. AIC is a mathematical technique for evaluating that how much a model performs well and fits for the dataset from it was generated. Statistically, it determines that which model is best for the data by comparing different models generated from same dataset. Akaike Information Criterion calculations depend on the

number of independent variables that are required to build model and maximum estimation ability of the model i.e., how well a model reproduces data (Bevans, 2022). Therefore, AIC analysis was carried out to select the best model among the four-model developed using Abraham descriptors.

Table 4.2 Akaike Information Criteria analysis was done for Abraham Model. Less value of AIC represents the best model.

Model	AIC
E.S.A.B.L	159.25
S.A.B.L	161.55
E.S.A.B.V	162.78
S.A.B.V.L	163.61

The least value of AIC is 159.25 shown in table 4.2 which is for ESABL i.e., ESABL model has good predictive power. It was also shown by the regression analysis by the high R^2 value and low RMSE 0.44 from the other models.

4.1.2 Recreation of ASM for Polyethylene

Similarly, the ASM models were recreated for Polyethylene polymer. Pearson correlation analysis was done on the data set to assess the correlation of Abraham descriptors with each other and with the independent variable, $logD_{PE}$. If the correlation between the two independent parameters is high, it means that both variables explain some information. The model created by these variables is not suited for prediction because it may happen that variables are explaining the same type of information, which inflates results. A perfect model has zero biasness and variance and follows the principle of parsimony. Therefore, to analyze the contribution of each variable and their correlation with each other, I performed a Pearson correlation analysis. Figure 4.4 demonstrate the results of Pearson Correlation analysis among the independent

variables. The two independent variables, for instance, V and S, represent the high value
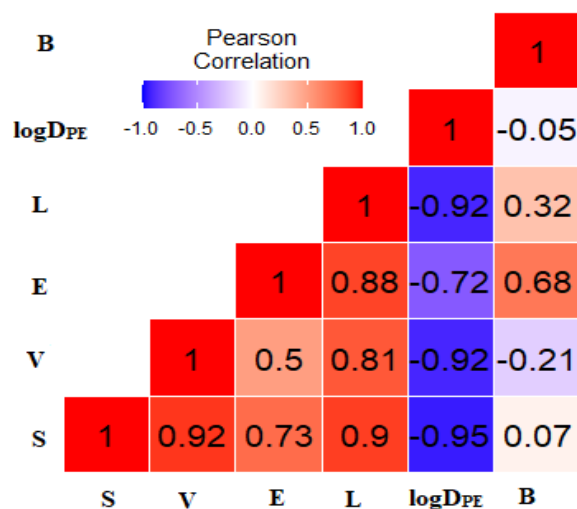
Figure 4.4 Pearson correlation. Figure demonstrates the correlation among independent variables and with dependent variable. The negative value presents the negative correlation among variables. Red portion indicates positive correlation higher the value depicts high correlation among variables.

of r (0.92) demonstrates that both are highly correlated and explain each other very well. When these two descriptors are used to make a model, it may inflate the results for other reasons, not only by explaining the property under discussion, such as logDPE. Moreover, in figure 4.4, dependent property logDPE shows a high correlation with each independent descriptor, which explains the property of interest well. Therefore, Variance Inflation Factor (VIF) analysis is done to avoid inflation of results and remove redundancy.

For polyethene, the values for the A parameter were '0', and the software considered these values as 'NA' and did not count it in the statistical measures; therefore, I removed the A parameter and ran a regression analysis on other parameters. The statistical results were promising, as shown in table 4.3; almost all models gave good results with a high R2 value of 0.95. All models gave the same results with minimum error. It is challenging to choose the best model among these four. On further evaluation for choosing the best model, Variance Inflation Factor (VIF) values were calculated, and the cut-off value was set as 10. The values greater than 10 represent that the particular predictor variable overlaps with another variable, and the variables also explain the noise, which affects the model's explanatory power. Therefore, on careful analysis using VIF criteria, V and E were two significant parameters in explaining information.

In the ESBV model, the E and V parameters were significant, whereas the *p-value* of B was greater than 0.05; therefore, we eliminated the non-significant parameters and re-ran the regression.

Table 4.3 Different variations of Abraham Solvation Model for Polyethylene

Model Name	R^2	RMSE	R^2_{Adj}
ESBV	0.95	0.10	0.94
ESBL	0.95	0.10	0.94
SBVL	0.95	0.10	0.95
SBL	0.95	0.10	0.94
VE	0.94	0.10	0.94

Regression analysis was performed using different variation of Abraham descriptors. The VE model was added after VIF evaluation. The VIF values of these two parameters were less than ten and were not overlapping with each other therefore these two parameters were selected to develop model.

$$\textbf{logD}_{PE} = -10.21(\pm 0.09) -0.27(\pm 0.03)\textbf{E} -1.19(\pm 0.06)\textbf{V} \qquad Eq.\ 4.2$$

n= 54, $R^2 = 0.94$,   RMSE= 0.10

Table 4.4 Variance Inflation Factor (VIF) representing values for different parameters of different model

Model Name	E	S	B	V	L
ESBV	15.8	19.7	8.9	14.4	
ESBL	29.6	8.9	9.3		9.3
SBVL		10.4	4.32	19.8	10.4
SBL		6.8	1.5		7.5
VE	1.3			1.3	

4.2 Justification, Formulation, and Validation of Partition models (PMs) for logD$_{PDMS}$ and logD$_{PE}$ estimation

4.2.1 Justification of Two Parameter Model logK$_{ow}$ and logK$_{aw}$ for PDMS Model

It was hypothesized that the new two-parameter model would have comparable predictive ability to the ASMs. To check our hypothesis that the linear free energy two parameters logKow and logKaw would have comparable predictions, I thoroughly analyze the information present in the Abraham Solvation descriptors (ASDs) of the datasets of the ASMs. In the previous section, it was analyzed that a minimum of five dimensions are required to demonstrate the variability in the Abraham Solvation Models. Principal Component Analysis was done to further investigate the spread of data variability, and results described that where the five dimensions of Abraham represent the information, similar information is represented by the two-parameter model. The two descriptors logKow and logKaw are used to represent similar information in two dimensions. The selection for new variables was made on the basis of these considerations the parameter should (i) be easily accessible, (ii) have simple chemical interpretation, (iii) have more extensive databases that could be determined experimentally or estimated computationally by simple and cost-effective methods (iv) be able to encompass all the intermolecular interactions and the free energy changes during the transfer of the solute molecules (v) have ability to explain the mechanism to a considerable extent physically as well as thermodynamically.

The partition coefficients Kow and Kaw fit best on the given selection criteria. Hence to prove the suitability of these two parameters, PCA was run, and as a result, a Correlation circle, Scree plot and dimensionality plot were obtained. According to the Scree plot given in figure 4.5, (a) approximately 78 per cent of the variability is explained in the first two dimensions. Further correlation circle represents that most of the variation is explained by the log Kaw and less information is covered by the logKow parameter; however, collectively, both parameters cover specific and non-specific interactions.

(a)

(b)

(c)

(d)
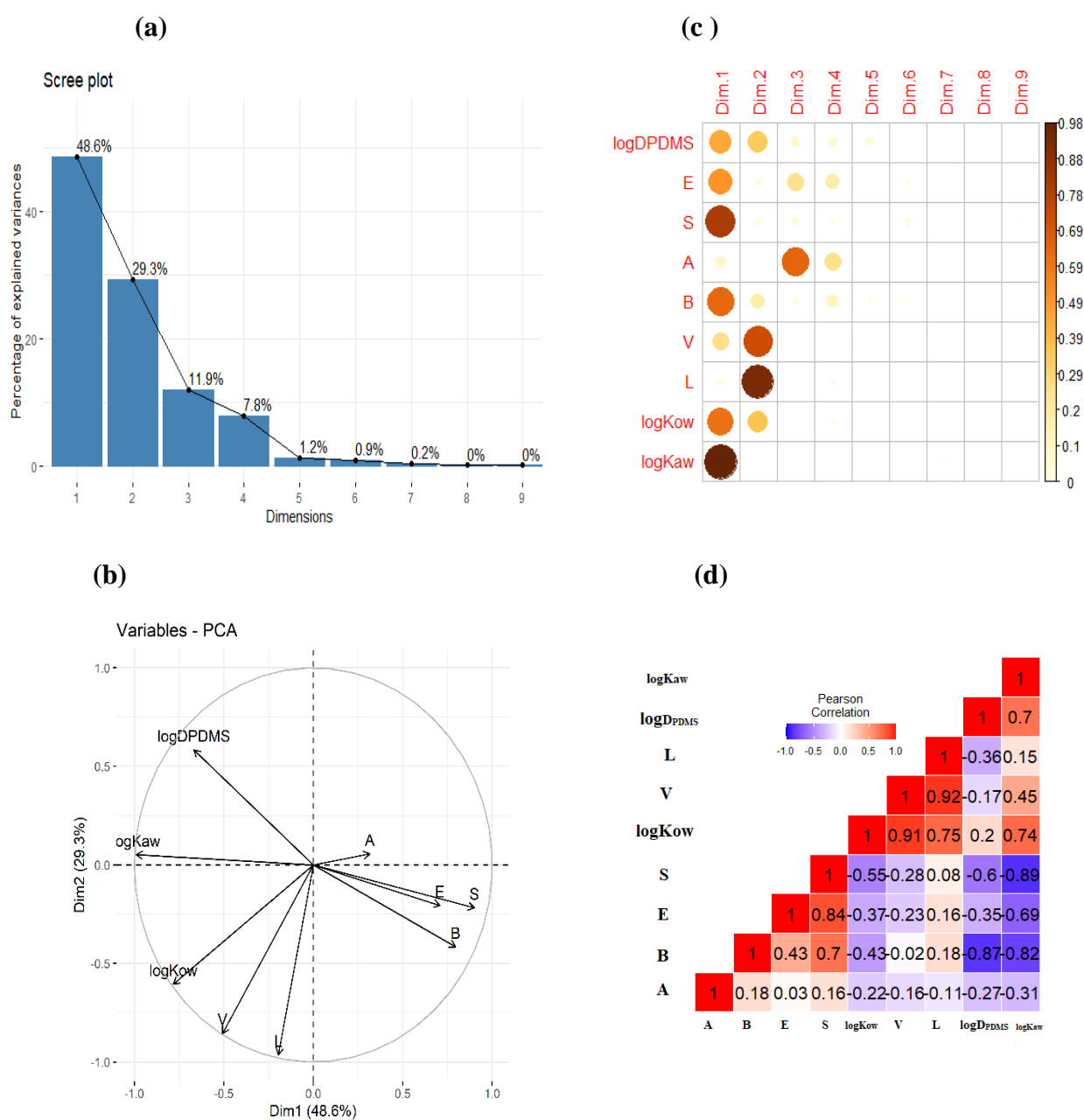
Figure 4.5. Above figures shows the results of the statistical analysis ran on the PDMS dataset. It represents the dimensionality analysis of PMs data. Upper panels represent the results of PCA ran on 643×4 matrix, [E, S, A, B, LV] of ASM descriptors used to estimate $logD_{PDMS}$ values. (a) It represents the scree plot of eigen values which demonstrate the amount of information explained by each component. (b) The PCA correlation circle shows the quality of representation and relationship among the variables in first two dimensions. The angle between the arrows shows the correlation between the ASDs. The quality of representation of a parameter is proportional to the length of arrow lines. (c) It shows the distribution of data into 8 dimensions obtained by the PCA of 643×8 matrix [E, S, A, B, V, $logK_{ow,}$ $logK_{aw}$, $logD_{PDMS}$]. Size of the circle and color intensity are proportional to the quality of representation of a parameter. (d) represents the correlation matrix correlogram obtained from Pearson correlation analysis. Red color is the representation of positive correlation while blue color represents the negative correlation between each pair of variables. The values of r (correlation coefficient) showing the magnitude of correlation.

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Additionally, in correlation circle figure 4.5 (b), the logKaw and logKow arrows touch the circle, which indicates that these parameters cover maximum intermolecular interactions to explain the variation in the dependent property. The Pearson Correlation analysis was also carried out using RStudio to determine the relationship between variables and their strengths. The correlation analysis for the whole dataset shows that Kaw and Kow capture the crucial intermolecular interactions, otherwise captured in the ASDs, to express the diffusivity of organic pollutants into PDMS. The correlation between logKow and logKaw are separated from each other (r = 0.74), which depicts that much of the information will be covered by these two parameters.

4.2.2 Justification of Two Parameter Model logK$_{ow}$ and logK$_{aw}$ for Polyethylene Model

A similar statistical analysis was done the determination the suitability of a two-parameter for the polyethene model. These analysis results show that the two-parameter model can be developed to explain the diffusivity of organic substances into polymers.

The Scree plot in figure 4.6 (a) represents that more than 90 per cent of the variance is explained in the first two dimensions. The arrow length of two parameters, logKow and logKaw, touch the circle, which means they explain maximum intermolecular interactions, which ASDs otherwise explain. Similar is endorsed by dimensionality analysis representing that complete information is explained in the first two dimensions.
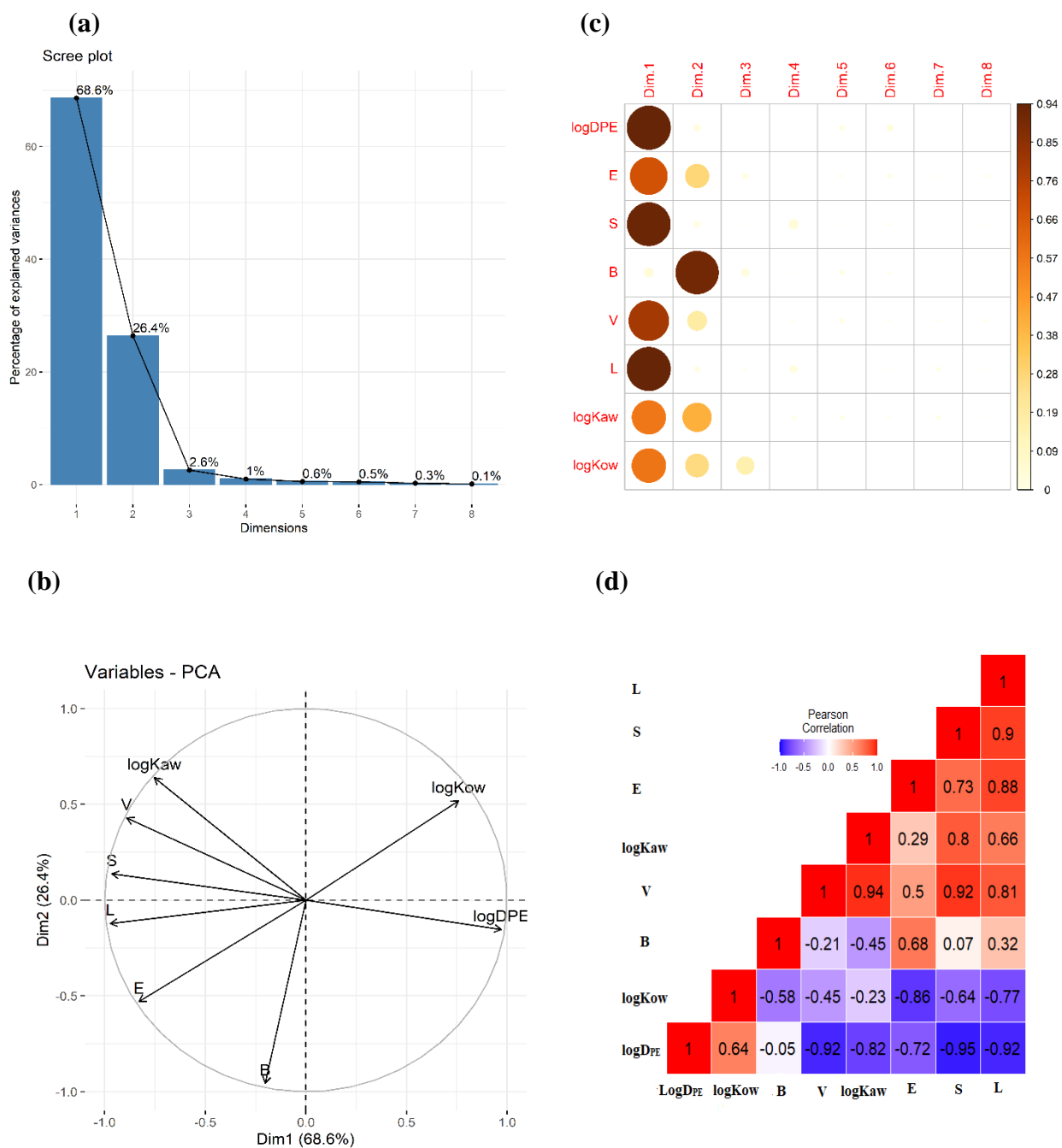
Figure 4.6. Above figures shows the results of the statistical analysis ran on the Polyethylene dataset. It represents the dimensionality analysis of PMs data. Upper panels represent the results of PCA ran on 643×4 matrix, [E, S, B, L,V] of ASM descriptors used to estimate $logD_{PE}$ values. (a) It represents the scree plot of eigen values which demonstrate the amount of information explained by each component. (b) The correlation circle shows the quality of representation and relationship among the variables in first two dimensions. The angle between the arrows shows the correlation between the ASDs. The quality of representation of a parameter is proportional to the length of arrow lines. (c) It shows the distribution of data into 8 dimensions obtained by the PCA of 643×8 matrix [E, S, A, B, V, $logK_{ow}$, $logK_{aw}$, $logD_{PE}$]. Size of the circle and color intensity are proportional to the quality of representation of a parameter. (d) represents the correlogram of the correlation matrix, obtained from Pearson correlation analysis. Red color is the representation of positive correlation while blue color represents the negative correlation between each pair of variables. The values of r (correlation coefficient) showing the magnitude of correlation.

4.3 Formulation of Two-parameter model

The regression analysis was run to develop two parameter models for both polymers Polydimethylsiloxanes and Polyethylene. The MLR results were satisfactory and most of the variance is explained by two parameters.

Two parameter- Linear Free Energy Relationship Model (logD$_{PDMS}$)

$$logDPDMS = -9.14(\pm 0.14) - 0.16\,(\pm0.017)\mathbf{logK_{ow}} + 0.32(\pm0.02)\mathbf{logK_{aw}} \quad \textit{Eq. 4.3}$$

n= 124, R^2= 0.70, RMSE = 0.57, R^2$_{Adj}$ = 0.69

Standardized coefficient analysis was taken to determine the contribution of each parameter by keeping intercept zero.
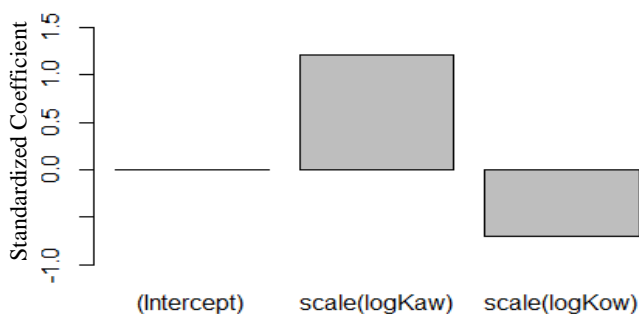
Figure4.7 Standardized Coefficient graph for logD$_{PDMS}$ logKaw explains more intermolecular interactions.

Two parameter- Linear Free Energy Relationship Model for low density Polyethylene

LogD$_{PE}$ = -10.72 ($\pm$0.12) - 0.27($\pm$0.018)**logKaw** + 0.21($\pm$0.021)**logKow** *Eq. 4.4*

R^2 = 0.89, RMSE = 0.15, R^2$_{Adj}$ = 0.88

Standardized coefficient analysis was taken to determine the contribution of each parameter by keeping intercept zero.
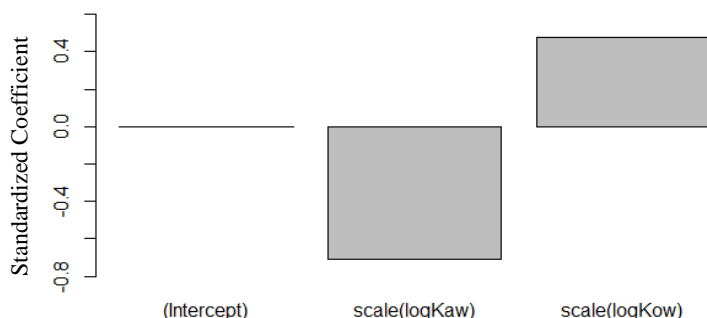
Figure 4.8 Standardized Coefficient for Polyethylene representing that logKaw has higher contribution in explaining information than logKow

Table 4.5 This table represent the regression results in the form of R^2, RMSE and R^2_{Adj}

Model Name	R^2	RMSE	R^2_{Adj}
2p-LFER Model ($logD_{PDMS}$) logKow +logKaw	0.7023	0.57	0.697
2p-LFER ($logD_{PE}$) logKow + log Kaw	0.89	0.148	0.884

The regression analysis was run on both datasets for PDMS and Polyethylene, and the results are depicted in table 4.5, which represent that the predictive ability of the two-parameter PDMS model is 70 per cent, as represented by the R2 value. The RMSE value of the model is way too high, which is 0.57; the high value of prediction error means the model is not suitable for the prediction. However, the adjusted R2 value is concomitant with the regression coefficient value (R2).

4.4 Model Validation and Assessment

The developed models are internally cross-validated to assess the model's predictive ability. Cross-validation is a resampling method to evaluate the model's true

prediction error to avoid overfitting (Kohavi, 1995). After the selection of the best Abraham solvation model and the development of two-parameter diffusivity models for the PDMS and Polyethylene, cross-validation was carried out. Leave-One-Out Cross-validation (LOOCV), K-fold test, repeated K-fold test (r=3) and Bootstrap validation tests were performed on the selected models using RStudio software. Each test dataset was randomly split into two training, test sets, and regression. Moreover, regression diagnostics were applied to identify the applicability domain of models using influential points.

The model is internally cross-validated using different model assessment approaches such as Leave one out, K-fold, and bootstrapping approaches. My model depicts good agreement between the training and test set models.

Leave-One-Out Cross Validation (LOOCV)

Leave-one-out cross-validation is a process where one observation from the whole dataset is excluded, and regression is performed on the remaining data. Likewise, the process is repeated with the exclusion of one different observation every time the analysis is performed. This process is time taking and is preferred for short datasets. The diagnosis indicators are R2, and root means square error and the mean absolute error.

K-fold Validation

The dataset is divided into k-folds or k groups of equal sizes in K-Fold validation. For validation, the model is trained on k-1 folds or groups. This process is repeated K times, and a different fold is used each time (Kumar, 2021). In this K-fold test, K =3 is selected for the validation and evaluation of models.

Bootstrapping

In bootstrapping algorithm, the software randomly resamples the dataset each time and analyses are performed on the selected data set (Kumar, 2021). In this work, bootstrapping was carried out as n=1000 on the R program.

This table 4.6 represents that our training sets and datasets statistics are more or less the same, which validates that these models could be used for predictive purposes.

Table 4.6 The table represents statistical diagnostics for different validation approaches where R^2 represents the regression coefficient, MAE represents the mean absolute error and RMSE represents the root mean square error

Model	Model Validation								
	Leave one out approach			K-fold Approach Rep= 3 times			Bootstrap Approach Rep=1000		
	R^2	RMSE	MAE	R^2	RMSE	MAE	R^2	RMSE	MAE
ESABL	0.795	0.46	0.31	0.848	0.44	0.31	0.803	0.478	0.320
2p-LFER (PDMS)	0.688	0.57	0.42	0.723	0.56	0.42	0.704	0.580	0.42
2p- LFER (LDPE)	0.87	0.15	0.12	0.90	0.15	0.12	0.87	0.16	0.13

Cross-validation was performed on all the selected models. The Abraham Solvation Model ESABL for predicting the diffusivity of organic chemicals into PDMS approximately shows the value of R2 and the RMSE same as the developed model, and it shows the robustness of the model. The validation results for the two-parameter model for PDMS are almost the same as the diagnostic parameters for the developed model, but the value of R2 is low as well as the value of RMSE and MAE is high.

The cross-validation results for all the validation tests for the two-parameter LDPE model represent the regression coefficient's excellent value and lower values for the prediction error RMSE and MAE.

5. MASS TRANSFER COEFFICIENT MODEL (MTC)

5.1 Mass Transfer Coefficient Model

Mass Transfer Coefficient models are based on mass solute transfer in distinct phases or environment regions. The MTC is also expressed through (k) and is usually taken as the velocity of a solute moving through some environment and measured in cms-1. The MTC (k) is equal to D/δ, and D represents the diffusivity and δ is an adequate thickness of a specific phase (Huckins *et al*. 2006).

Mass Transfer Coefficient models are considered as the fluxes through various phases and are the proportionality constant between the flux and the effective concentration; therefore, also known as the overall conductivity, which is represented by k_0.

Similarly, 1/ko is represented as the transport resistance, the sum of the mass transfer resistance for the succeeding phases (*Iw, Ib, Im*) (Huckins *et al*. 2006). .

$$I_o = \ I_w + I_b + I_m \qquad\qquad Eq.\ 5.1$$

Where I_0 = Impedance

I_w = Impedance for Water Boundary Layer

I_b = Impedance for biofilm

I_m = Impedance for the membrane

Correspondingly, $\dfrac{1}{k_0}$ is also known as transport resistance which is equal to impedance. It is written as:

$$\frac{1}{k_0} = \ \frac{1}{k_w} + \ \frac{1}{kb\ Kbw} + \frac{1}{kmKmw} \qquad\qquad Eq.\ 5.2$$

Eq. 5.2 represents that mass transfer resistances are additive property and higher the partition coefficients of K_{mw} and K_{bw} reduce the transport resistance in the respective phases (Huckins *et al*. 2006). As given above the MTC (k) is also equal to D/δ, by incorporating the value of k the final equation becomes as:

$$\frac{1}{k_0} = \frac{\delta_w}{D_w} + \frac{\delta b}{Db\ Kbw} + \frac{\delta w}{DmKmw} \qquad \qquad Eq.\ 5.3$$

Where,

δ = thickness of a phase

D_m = Diffusion Coefficient

The thickness of each phase is directly related to the resistance to mass transfer. Therefore, the greater the thickness of the phase the larger the resistance to solute transfer.

5.2 Leaching Time

Leaching is a process of transfer of mass that occurs by excerpting a substance from a solid substance that has come into touch with a solvent. The desired constituents diffuse into the solvent from its natural solid form ("Chapter 2: General Principles for the Leaching and Extraction of Materials," 1997).

The leaching process occurs when a liquid or solvent from the bulk solution comes in contact with the solid phase and diffuses into the solid. The solute from the solid leaches into the solvent, and sometimes the solute diffuses from the solvent mixture into the solid. However, when a solute is present on the surface of an insoluble solid and the solute is precisely washed off by the solvent, it is normally known as elution or elutriation. Leaching is the mass transfer of a solute into a solvent when a solvent comes in contact with a solid. Millions of chemicals are discharged into the environment on a daily basis ("Chapter 2: General Principles for the Leaching and Extraction of Materials," 1997). Among these are widely used microplastics which are released into the environmental compartments as microbeads, and sometimes these microplastics are released into the environment as a consequence of fragmentation and degradation of larger plastics.

These microplastics are widely available in nature and present in different sizes. These microplastics have the potential to sorb organic pollutants and then release them into the environment. Therefore, these microplastics are of great concern as they act as a transport vector for organic compounds.

It is necessary to calculate the leaching potential of organic pollutants from these polymers, such as PDMS and Polyethylene when they come into contact with them. Polyethene and PDMS have numerous applications; therefore, their broader discharge into the environment raises health issues. These polymers act as a carrier, and when these reach the body of animals or human beings, these organic pollutants leach into the body and cause damage.

5.2.1 Leaching time as a function of size of polymers

The leaching time of solute particles depends on the mass transfer potential of a substance which is affected by the size of the polymers. The leaching time of the polymer is affected by the size and nature of the polymers. Different size polymers, such as microplastics, standard plastics and Nano plastics, have different capacities to leach organic chemicals. Therefore, I have calculated the transport resistance of organic chemicals in different plastic media such as microplastics, Nano plastic and normal polymer sizes. The resistance for both properties, logDPDMS and logDPE, is calculated using the partitioning coefficients and diffusion coefficients of both properties. For the partition coefficients data, I took it form online database UFZ-LSER.

$$\frac{1}{k_0} = \frac{\delta_m}{D_m K_{mw}}$$

$$\frac{1}{k_0} = \frac{0.000005}{9.33E-11(4.17E+03)}$$

$$\frac{1}{k_0} = 1.29E+01$$

$$LT_{MP} = 1.29E+01(0.000005)$$

$$LT_{MP} = 6.43E-05 \text{ (sec)}$$
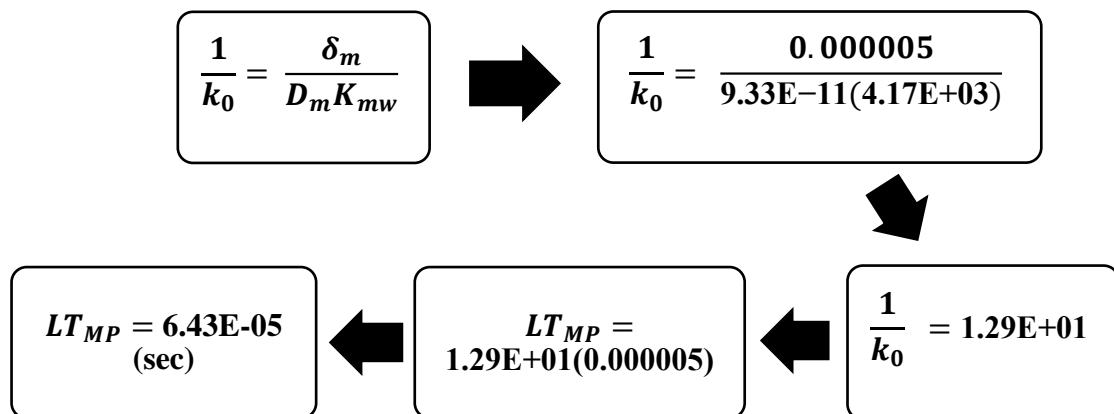
Figure 5.1 This flow chart represent the process of calculation of leaching time. 1/ko represents the resistance and its unit is s/m. To calculate time thickness is multiplied with the Resistance.

34
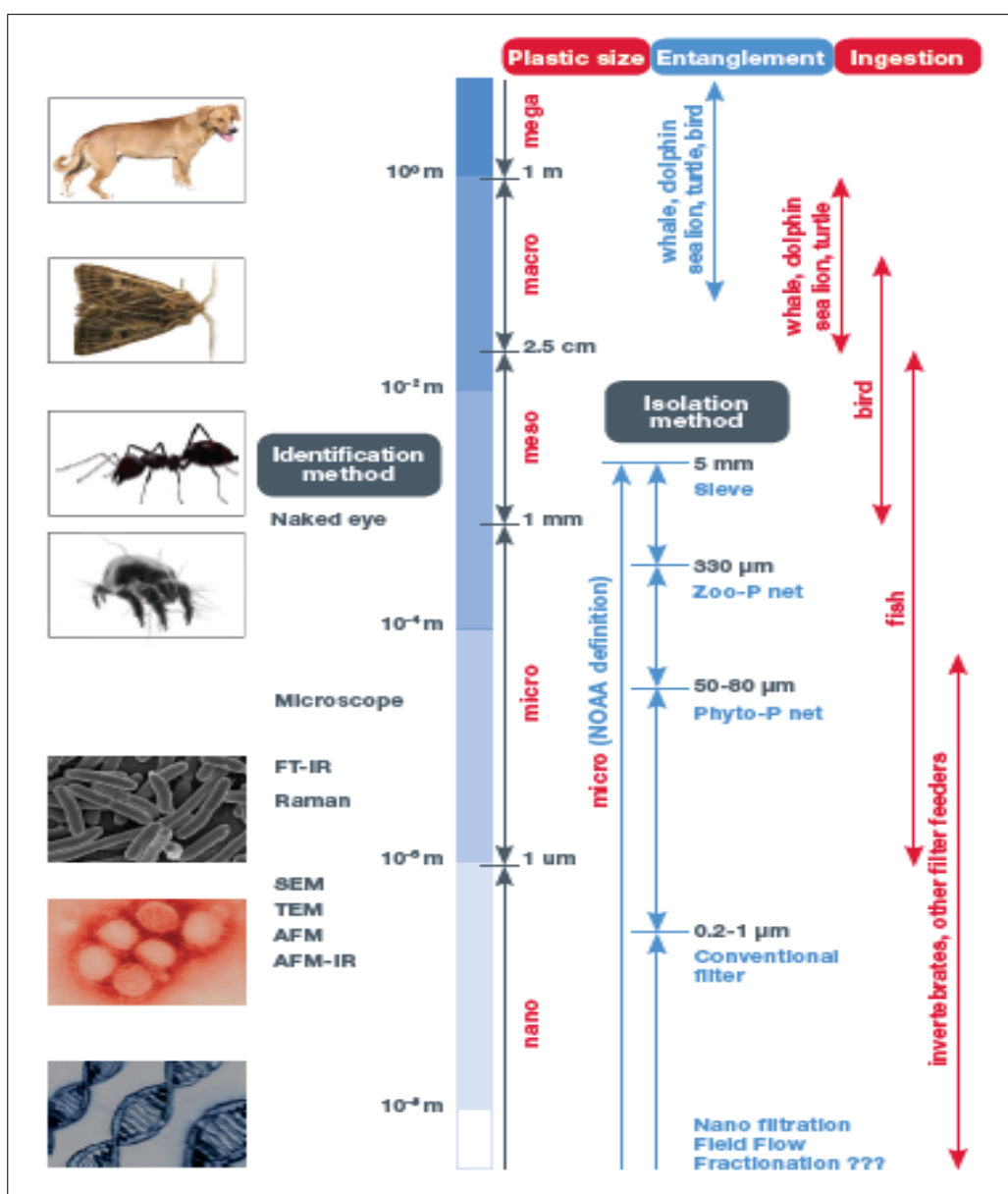
Figure 5.2 This figure depicts different ranges of polymers. (Microplastics in the ocean, GESAMP)

I took the organic chemicals from dataset that I have curated for the model development. The thicknesses of various plastic sizes are taken from the literature. The value of thickness for micro plastic is taken as the average of range between 1μm -1mm (Microplastics in the ocean, GESAMP) given in figure 5.2 whereas the chemical range for Nanoplastic is taken from 1nm - 1μm (Gigault et al., 2018). For calculation of impedance for plastic polymers I used variation of *eq.7* to calculate the mass transfer potential. The process for the calculation of leaching time is demonstrated in figure 5.1.

$$\frac{1}{k_0} = \frac{\delta w}{DmKmw} \qquad\qquad Eq.\ 5.4$$

The graph for PDMS in figure 5.3 (above) represents that in normal plastics
naphthalene leaches out 2 orders of magnitude quickly as compared to the leaching
time in Microplastic and 4 orders of magnitude faster than in Nanoplastic. Organic
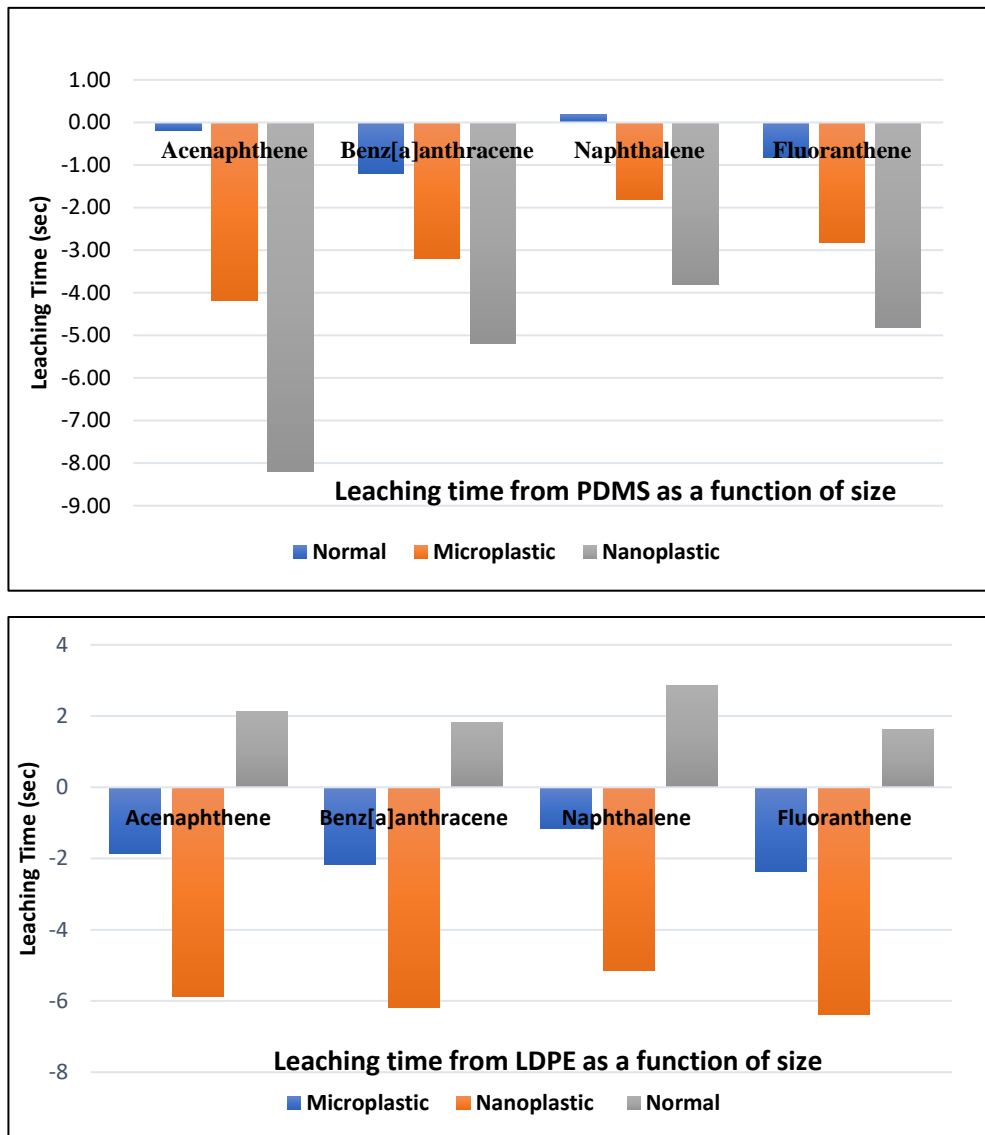
**Figure 5.3 Leaching time of four organic chemicals is represented as a
function of size. Above figure represents the leaching time from PDMS. Below
represents the leaching time from LDPE as a function of size.**

chemicals leach out slowest in normal plastics and then little quicker in microplastic
and followed by microplastics and then more in Nanoplastic.

The leaching time of naphthalene from LDPE represents that it leaches out 4 degrees faster in microplastic than in normal plastics and 8 orders of magnitude faster in nano plastics as compared to normal microplastics. The organic chemicals leach out faster in nano plastics, followed by microplastics and normal plastics.

5.2.2 Leaching time as a function of Nature
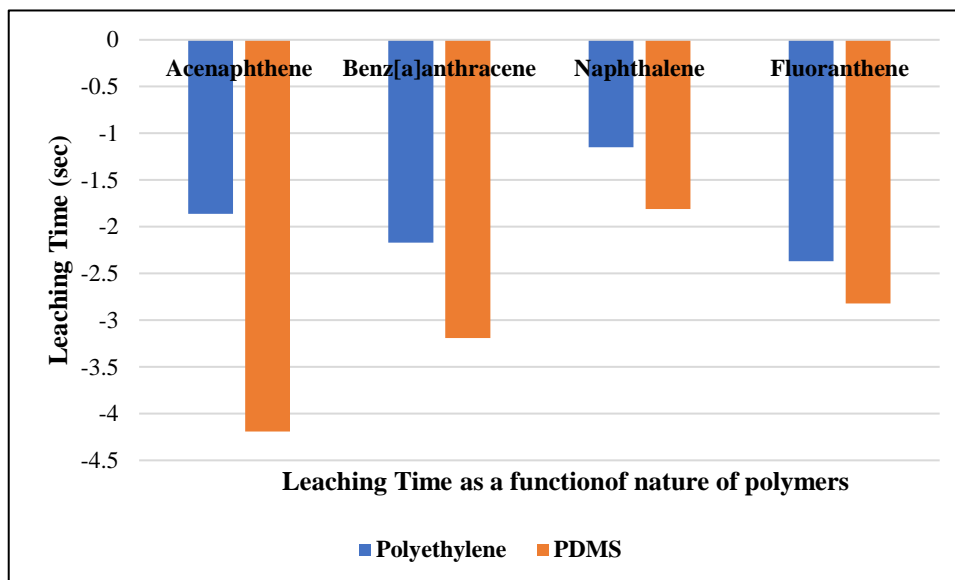
Figure 5.4 Cluster graph represents the leaching time of organic chemicals as a function of nature of polymers.

The leaching time of naphthalene from LDPE represents that it leaches out 4 degrees faster in microplastic than in normal plastics and 8 orders of magnitude faster in nano plastics as compared to normal microplastics. The organic chemicals leach out faster in nano plastics, followed by microplastics and normal plastics.

6. CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

Several approaches are used to determine the diffusion coefficients of polymers using experimental measures, but fewer simulation methods are developed using QSPR and LFER methods. The two-parameter models are developed using descriptors logKaw and Kow, which represent a good correlation with the Abraham Solvation model. The 2p-model for PDMS polymer depicts satisfactory results with an R2 value of 0.70 which means that the models explain 70 per cent of variations. However, the high value of RMSE makes the model unsatisfactory for the predictions. The Abraham model ESABL explains 82 per cent of variation with root mean square error less than 0.5. The PDMS 2p-LFER model cannot be used for predictive purposes. In contrast, the predictive power of the Polyethylene model is high and explains 90% of the information. Dimensionality analysis for both polymers demonstrates that most of the information is explained in two dimensions, and that is why the Abraham model can be reduced to a two-parameter model covering most of the information by two descriptors. The statistical diagnostics elaborated in *Eq. 4.4* for LDPE demonstrates that it is a good alternative for experimental techniques.

Moreover, these developed models give mechanistic insights into the chemicals, which means how they will end up in the environment. The Henry Law Constant and octanol-water partition coefficient describe the compounds' volatility or non-volatility, hydrophobicity, and hydrophilicity. The model can depict the values of diffusivity of PDMS and polyethene for organic pollutants that fall in the domain of applicability for the classes of compounds which were used to develop models. The model is not suitable for the determination of ionizable species or the chemicals that react through the specific mechanism. However, the predictive ability and the application domain of both parameters can be improved using large datasets. These models are not suitable for the prediction of polar compounds and polar organic compounds. These models can be integrated into the EPI SuiteTM software to predict the diffusivity of organic pollutants into PDMS and Polyethylene.

On the other hand, the mass transfer equation is used for calculating the leaching time for both polymers, representing that Naphthalene in Polyethylene leaches faster than in PDMS. The thickness of the polymers is directly related to the mass resistance;

therefore, when thickness increases, the resistance increases, and the organic molecules face difficulty diffusing into the polymers. Thus, according to the nature of the polymers and size, the leaching time of the organic pollutants differs. On the whole, the leaching time of organic pollutants from PDMS is greater than the leaching time from Polyethylene, which means that compounds leach out faster in Polyethylene than in PDMS polymer.

6.2 Recommendation

The estimated Program Interface developed by US Environmental Protection Agency and Syracuse Research Cooperation contains various modules for the prediction of toxicity and fate of a large number of compounds whose experimental data is not available. The two-parameter models are developed on the basis of logKow and logKaw values taken from the EPI Suite, and the model gives good statistics for the diffusivity of chemicals into LDPE with minimum error. The model can be integrated into the EPISuite software for the estimation of the diffusivity of organic compounds; however, the logDPDMS statistics were not good enough to integrate the model into EPISuite software.

Furthermore, new descriptors need to be evaluated for modelling the diffusivity of organic chemicals into PDMS, as these two parameters cannot describe the diffusion coefficients for the diverse set of organic compounds. Moreover, more experimental data are required for Polyethylene as very few numbers of chemicals with experimental values were available to wider the applicability domain.

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LIST OF CHEMICALS

Table 1 Abraham Solvation Descriptors for PDMS

Name	E	S	A	B	V
Acenaphthene	1.6	1.05	0	0.22	1.2586
Acenaphthylene	1.75	1.14	0	0.26	1.2156
Anthracene	2.29	1.34	0	0.28	1.4544
Benz[a]anthracene	2.99	1.7	0	0.35	1.8234
Benzo[a]pyrene	3.63	1.98	0	0.44	1.9536
Benzo[ghi]perylene	4.07	1.9	0	0.45	2.0838
Chrysene	3.03	1.73	0	0.33	1.8234
Dibenz[ah]anthracene	4	2.04	0	0.44	2.1924
Fluoranthene	2.38	1.55	0	0.24	1.5846
Fluorene	1.59	1.06	0	0.25	1.3565
Indeno[1,2,3-cd]pyrene	3.61	1.93	0	0.42	2.0838
Naphthalene	1.34	0.92	0	0.2	1.0854
Phenanthrene	2.06	1.29	0	0.26	1.4544
Pyrene	2.81	1.71	0	0.28	1.5846
Benzene	0.61	0.52	0	0.14	0.7164
n-Butylbenzene	0.6	0.51	0	0.15	1.28
Chlorobenzene	0.72	0.65	0	0.07	0.8388
2-Chlorotoluene	0.76	0.65	0	0.07	0.9797
1,3-Dichlorobenzene	0.85	0.73	0	0.02	0.9612
1,2-Dichlorobenzene	0.87	0.78	0	0.04	0.9612
m-Xylene	0.62	0.52	0	0.16	0.9982
Isopropylbenzene	0.6	0.49	0	0.16	1.1391
sec-Butylbenzene	0.6	0.48	0	0.16	1.28
n-Propylbenzene	0.6	0.5	0	0.15	1.1391
tert-Butylbenzene	0.62	0.49	0	0.16	1.28
1,3,5-Trichlorobenzene	0.98	0.73	0	0	1.0836
1,2,3-Trimethylbenzene	0.73	0.61	0	0.19	1.1391
1,2,4-Trimethylbenzene	0.68	0.56	0	0.19	1.1391
hexachloro-1,3-butadiene	1.02	0.44	0	0.15	1.3206
2-isopropyltoluene	0.67	0.53	0	0.19	1.28
1,2-Dibromoethane	0.75	0.76	0.1	0.17	0.7404
1,1,1,2-Tetrachloroethane	0.54	0.63	0.1	0.08	0.88
1,1,2-Trichloroethane	0.5	0.68	0.13	0.08	0.7576
Ethylbenzene	0.61	0.51	0	0.15	0.9982
Bromodichloromethane	0.59	0.69	0.1	0.04	0.6693
Chlorodibromomethane	0.78	0.68	0.12	0.1	0.7219

Tribromomethane	0.97	0.68	0.15	0.06	0.7745
1,2-Dibromo-3-chloropropane	0.73	0.88	0	0.14	1.0037
1,2-Dichloropropane	0.37	0.63	0	0.17	0.7761
1,2,3-Trichloropropane	0.55	0.65	0.03	0.31	0.8985
trans-1,3-Dichloropropene	0.49	0.86	0	0.06	0.7331
Styrene	0.85	0.65	0	0.16	0.9552
Tetrachloroethene	0.64	0.44	0	0	0.837
Toluene	0.6	0.52	0	0.14	0.8573
1,2,4-Trichlorobenzene	0.98	0.81	0	0	1.0836
Trichloroethene	0.52	0.37	0.08	0.03	0.7146
BDE 153	3.09	1.54	0	0.52	2.4329
BDE 154	3.09	1.5	0	0.53	2.4329
n-Decane	0	0	0	0	1.5176
n-Undecane	0	0	0	0	1.6585
n-Dodecane	0	0	0	0	1.7994
n-Tridecane	0	0	0	0	1.9403
n-Tetradecane	0	0	0	0	2.0812
n-Pentadecane	0	0	0	0	2.2221
n-Hexadecane	0	0	0	0	2.363
n-Heptadecane	0	0	0	0	2.5039
n-Octadecane	0	0	0	0	2.6448
n-Nonadecane	0	0	0	0	2.7857
n-Eicosane	0	0	0	0	2.9266
n-heinecosane	0	0	0	0	3.0675
n-Docosane	0	0	0	0	3.2084
n-Tricosane	0	0	0	0	3.3493
n-Tetracosane	0	0	0	0	3.4902
n-Pentacosane	0	0	0	0	3.6311
n-Hexacosane	0	0	0	0	3.772
n-Heptacosane	0	0	0	0	3.9129
n-Octacosane	0	0	0	0	4.0538
n-Nonacosane	0	0	0	0	4.1947
Triacontane	0	0	0	0	4.3356
n-Heinetriacontane	0	0	0	0	4.4765
n-Dotriacontane	0	0	0	0	4.6174
Tritriacontane	0	0	0	0	4.7583
Tetratriacontane	0	0	0	0	4.8992
n-Pentatriacontane	0	0	0	0	5.0401
n-Hexatriacontane	0	0	0	0	5.181
n-Heptatriacontane	0	0	0	0	5.3219
Atrazine	1.22	1.29	0.17	1.01	1.6196
Azoxystrobin	2.59	2.01	0	2.3	2.9165
Bromophos-ethyl	1.51	1.26	0	0.71	2.244
Bromophos	1.51	1.51	0	0.46	1.9622
1-naphthyl N-methylcarbamate	1.51	1.67	0.22	0.79	1.5414

carbofuran	0.92	1.08	0.21	1.1	1.6861
Chlorpropham	0.95	1.25	0.29	0.52	1.5766
Chlorpyrifos	1.59	0.92	0	1.01	2.1503
N,N-Diethyl-3-methylbenzamide	0.96	1.4	0	1.02	1.6773
Disulfoton	1.25	0.86	0	1.03	2.0483
Ethion	1.35	1.66	0	1.25	2.6747
Ethofumesate	1.03	1.26	0	1.21	2.0511
Fenpropathrin	1.73	1.91	0	0.68	2.7715
Fenthion	1.33	1.73	0	0.67	1.9877
Fenvalerate	2.2	2.5	0	1.2	3.1876
Hexachlorobenzene	1.49	0.99	0	0	1.4508
Irgarol	1.69	1.39	0.26	1.08	1.9748
Malathion	0.69	1.84	0	1.18	2.3154
Metazachlor	1.8	1.73	0	1.23	2.0865
3(4-Bromophenyl)-1-methyl-1-methoxyurea	1.39	1.62	0.36	0.81	1.5881
Metolachlor	1.11	1.53	0	1.25	2.2811
Mevinphos	0.29	1.36	0	1.16	1.5657
Paraoxon-ethyl	1.11	1.72	0	1.2	1.8936
Parathion	1.44	0.93	0	1.04	1.9984
Parathion-methyl	1.44	1.2	0	0.96	1.7166
Pendimethalin	1.39	1.39	0.16	0.71	2.1509
Permethrin	2.05	1.42	0	0.88	2.8186
Prometryn	1.43	1.23	0.17	1.01	1.9425
Propazine	1.19	1.26	0.13	1.05	1.7605
Propham	0.9	1.25	0.37	0.64	1.4542
Simazine	1.25	1.32	0.18	0.98	1.4787
Terbutryn	1.43	1.23	0.12	0.99	1.9425
Terbuthylazine	1.19	1.26	0.14	0.91	1.7605
Galaxolide	1.09	1.15	0	0.63	2.2487
1-tert-butyl-3,5-dinitro-2-methoxy-4-methylbenzene	1.19	1.72	0	0.7	1.9689
Musk xylene	1.42	2.18	0	0.63	2.0844
9-Nitroanthracene	2.47	1.73	0	0.53	1.6286
1-Nitronaphthalene	1.6	1.59	0	0.29	1.2596
2-Nitronaphthalene	1.6	1.5	0	0.27	1.2596
1-Nitropyrene	2.81	2.07	0	0.33	1.7588
Tri-n-butyl phosphate	-0.1	0.71	0	1.26	2.2388
triphenyl phosphate	1.83	1.66	0	1.1	2.3714
tricresyl phosphate	1.73	1.63	0	0.94	2.7941
Tri-m-cresylphosphate	1.61	1.82	0	1.1	2.7941
2-Hydroxy-4-methoxybenzophenone	1.65	1.63	0	0.62	1.7391
2-Hydroxybenzophenone	1.54	1.46	0	0.46	1.5395
4-Nonylphenol	0.77	0.88	0.55	0.36	2.0432
Triclosan	1.73	1.55	0.47	0.45	1.8088

Table 2 Abraham Solvation Descriptors for LDPE

Name	E	S	B	V	L
Indeno[1,2,3-cd]pyrene	3.61	1.93	0.42	2.0838	12.699
Naphthalene	1.34	0.92	0.2	1.0854	5.161
Acenaphthene	1.6	1.05	0.22	1.2586	6.469
Acenaphthylene	1.75	1.14	0.26	1.2156	6.175
Fluorene	1.59	1.06	0.25	1.3565	6.922
Anthracene	2.29	1.34	0.28	1.4544	7.568
Phenanthrene	2.06	1.29	0.26	1.4544	7.632
Fluoranthene	2.38	1.55	0.24	1.5846	8.827
Pyrene	2.81	1.71	0.28	1.5846	8.833
Benz[a]anthracene	2.99	1.7	0.35	1.8234	10.291
Chrysene	3.03	1.73	0.33	1.8234	10.334
Benz[b]fluoranthene	3.19	1.82	0.4	1.9536	11.632
Benzo[ghi]perylene	4.07	1.9	0.45	2.0838	13.264
Dibenz[ah]anthracene	4	2.04	0.44	2.1924	12.96
PCB 4	1.6	1.22	0.2	1.569	6.815
PCB 14	1.65	1.18	0.16	1.569	7.365
PCB 18	1.75	1.35	0.17	1.6914	7.48
PCB 28	1.76	1.33	0.15	1.6914	7.904
PCB 29	1.77	1.33	0.15	1.6914	7.722
PCB 30	1.74	1.35	0.17	1.6914	7.39
PCB 31	1.77	1.33	0.15	1.6914	7.862
PCB 44	1.9	1.48	0.15	1.8138	8.312
PCB 47	1.88	1.48	0.15	1.8138	8.227
PCB 49	1.89	1.48	0.15	1.8138	8.186
PCB 50	1.86	1.48	0.15	1.8138	7.854
PCB 52	1.9	1.48	0.15	1.8138	8.144
PCB 56	1.92	1.46	0.13	1.8138	8.842
PCB 66	1.91	1.46	0.13	1.8138	8.716
PCB 74	1.91	1.46	0.13	1.8138	8.583
PCB 85	2.03	1.61	0.13	1.9362	9.092
PCB 87	2.04	1.61	0.13	1.9362	9.051
PCB 97	2.04	1.61	0.13	1.9362	9.033
PCB 99	2.03	1.61	0.13	1.9362	8.91
PCB 101	2.04	1.61	0.13	1.9362	8.868
PCB 104	1.98	1.61	0.13	1.9362	8.244
PCB 105	2.04	1.59	0.11	1.9362	9.594
PCB 110	2.04	1.61	0.13	1.9362	9.161
PCB 118	2.06	1.59	0.11	1.9362	9.396
PCB 128	2.18	1.74	0.11	2.0586	9.957
PCB 137	2.18	1.74	0.11	2.0586	9.712
PCB 138	2.18	1.74	0.11	2.0586	9.772

PCB 141	2.19	1.74	0.11	2.0586	9.67
PCB 145	2.13	1.74	0.11	2.0586	8.928
PCB 149	2.16	1.74	0.11	2.0586	9.352
PCB 151	2.17	1.74	0.11	2.0586	9.142
PCB 153	2.18	1.74	0.11	2.0586	9.587
PCB 155	2.12	1.74	0.11	2.0586	8.715
PCB 156	2.21	1.72	0.09	2.0586	10.2
PCB 170	2.33	1.87	0.09	2.181	10.577
PCB 180	2.29	1.87	0.09	2.181	10.415
PCB 187	2.31	1.87	0.09	2.181	9.864
PCB 194	2.48	2	0.06	2.3034	11.186
PCB 204	2.52	2	0.06	2.3034	10.143
Hexachlorobenzene	1.49	0.99	0	1.4508	7.39

Table 3 Diffusion Coefficient, Partition Coefficient, Thicknesses and Leaching time of some of the organic chemicals from PDMS polymer

Name of Chemicals	$\log D_{PDMS}$ $(m^2 s^{-1})$	D_{PDMS} $(m^2 s^{-1})$	K_{PDMS-W}	Thickness macroplastic (m)	Thickness microplastic (m)	Thickness nanoplastic (m)	Normal	Microplastic	Nanoplastic
Acenaphthene	-10.03	9.33E-11	4.17E+03	5.00E-04	5.00E-06	5.00E-08	-0.19	-4.19	-8.19
Benz[a]anthracene	-10.73	1.86E-11	2.09E+05	5.00E-04	5.00E-06	5.00E-08	-1.19	-3.19	-5.19
Naphthalene	-9.82	1.51E-10	1.07E+03	5.00E-04	5.00E-06	5.00E-08	0.19	-1.81	-3.81
Fluoranthene	-10.4	3.98E-11	4.17E+04	5.00E-04	5.00E-06	5.00E-08	-0.82	-2.82	-4.82
Benzo[ghi]perylene	-10.98	1.05E-11	3.16E+05	5.00E-04	5.00E-06	5.00E-08	-1.12	-3.12	-5.12
Styrene	-9.71	1.95E-10	7.24E+02	5.00E-04	5.00E-06	5.00E-08	0.25	-1.75	-3.75
Toluene	-9.56	2.75E-10	2.57E+02	5.00E-04	5.00E-06	5.00E-08	0.55	-1.45	-3.45
m-Xylene	-9.68	2.09E-10	8.91E+02	5.00E-04	5.00E-06	5.00E-08	0.13	-1.87	-3.87
Ethylbenzene	-9.75	1.78E-10	5.13E+02	5.00E-04	5.00E-06	5.00E-08	0.44	-1.56	-3.56
Benzene	-9.4	3.98E-10	1.10E+02	5.00E-04	5.00E-06	5.00E-08	0.76	-1.24	-3.24

Table 4 Diffusion Coefficient, Partition Coefficient, Thicknesses and Leaching time of some of the organic chemicals from PE polymer

Name of Chemicals	$\log D_{PE}(m^2 s^{-1})$	D_{PE} $(m^2 s^{-1})$	K_{PE}	Thickness macro (m)	Thickness microplastic (m)	Thickness nanoplastic(m)	Normal	Microplastic	Nanoplastic
Acenaphthene	-12.36	4.37E-13	4.17E+03	5.00E-04	5.00E-06	5.00E-08	2.14	-1.86	-5.86
Benz[a]anthracene	-14.16	6.92E-15	5.37E+05	5.00E-04	5.00E-06	5.00E-08	1.83	-2.17	-6.17
Naphthalene	-12.26	5.50E-13	6.46E+02	5.00E-04	5.00E-06	5.00E-08	2.85	-1.15	-5.15
Fluoranthene	-13.16	6.92E-14	8.51E+04	5.00E-04	5.00E-06	5.00E-08	1.63	-2.37	-6.37
PCB 28	-12.75	1.78E-13	2.51E+05	5.00E-04	5.00E-06	5.00E-08	0.75	-3.25	-7.25
PCB 156	-13.04	9.12E-14	9.12E+06	5.00E-04	5.00E-06	5.00E-08	-0.52	-4.52	-8.52
Phenanthrene	-12.61	2.45E-13	1.66E+04	5.00E-04	5.00E-06	5.00E-08	1.79	-2.21	-6.21
Pyrene	-13.28	5.25E-14	1.26E+05	5.00E-04	5.00E-06	5.00E-08	1.58	-2.42	-6.42
Chrysene	-13.28	5.25E-14	6.03E+05	5.00E-04	5.00E-06	5.00E-08	0.9	-3.1	-7.1
PCB 105	-12.91	1.23E-13	2.75E+06	5.00E-04	5.00E-06	5.00E-08	-0.13	-4.13	-8.13
PCB 153	-13.04	9.12E-14	6.46E+06	5.00E-04	5.00E-06	5.00E-08	-0.37	-4.37	-8.37