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Master's Thesis

**Sorption of polycyclic aromatic hydrocarbons (PAHs) on  
microplastics in the freshwater, brackish, and saline  
environments**

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## ABSTRACT

This study aims to examine the sorption behavior of polycyclic aromatic hydrocarbons (PAHs) on microplastics in the freshwater, brackish, and saline environments. Batch adsorption experiments were conducted (1) to compare the sorption behaviors of PAHs on microplastics; (2) to determine to which kind of microplastic PAHs have more affinity to; (3) to know the effect of changing salinity on the sorption behaviors of PAHs on microplastics; and (4) to determine the effect of the co-existence of different microplastics on the sorption of PAHs. Phenanthrene was used as the model PAH and polyethylene (PE) and polystyrene (PS) were used as the model microplastics. The sorption equilibrium of phenanthrene on PE and PS was reached within 5 minutes of contact time and that PE had greater sorption capabilities than PS. Additionally, the results best fitted the linear isotherm model (with non-zero intercept). Partition coefficient  $K$  of PE were higher by around 30 to 40 times to PS. This difference can be explained by the fact that PE is a rubbery polymer and has specific surface area three times greater than that of PS, a glassy polymer. Furthermore, PE and PS may have an interaction with each other as the composite additive model did not work out. Aggregation may have occurred between the PE and PS particles as aggregation can decrease the SSA, which in turn, decreases the sorption capabilities of the sorbent. The possible main sorption mechanisms are hydrophobic interactions and van der Waals forces. Furthermore, more phenanthrene is sorbed on PS and PE in more saline environments possibly due to the salting-out effect. Since the marine environment is the ultimate sink for both microplastics and PAHs, this may pose a risk on the organisms living in there. Additionally, PE is one of the most found and widely used plastic so disposal and handling of PE must be properly managed in the future as it can store more PAHs.

**Keywords:** Sorption, polycyclic aromatic hydrocarbons, microplastics, freshwater, brackish, saline, phenanthrene, polyethylene, polystyrene, linear isotherm model, hydrophobic interactions, van der Waals forces, salting-out effect

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## **LIST OF ABBREVIATIONS**

BET – Brunauer, Emmett, and Teller

HDPE – High density polyethylene

HPLC – High Performance Liquid Chromatography

LDPE – Low density polyethylene

LOD – Limit of detection

MPs – Microplastics

PAHs – Polycyclic aromatic hydrocarbons

PE – polyethylene

PET – Polyethylene terephthalate

PHE – Phenanthrene

PMMA – Poly(methyl methacrylate)

POPs – Persistent organic pollutants

PP – Polypropylene

PS – Polystyrene

PSU – practical salinity scale unit

PTFE – Polytetrafluoroethylene

PU – Polyurethane

PVA – Polyvinyl alcohol

PVC – Polyvinyl chloride

SSA – Specific surface area

US EPA – United States Environmental Protection Agency

UV – Ultraviolet

## **Chapter I**

### **INTRODUCTION**

#### **1.1. Research background**

Around 75 to 90% of the plastic debris and most of the persistent organic pollutants (POPs) found in marine environment are from land-based sources, especially in coastal regions near industrial areas and cities [1–6]. Furthermore, numerous megacities and settlements around the world are situated near coastal zones [7]. Mismanaged plastic wastes dumped directly and indirectly from anthropogenic activities inland heavily impact many water bodies, not only coastal areas, but also rivers, lakes, and estuaries. Plastics that are exposed to various environments are degraded into microplastics through long periods of time. Here, microplastics are the plastics that are less than 5 mm in size [8–14].

Aside from being an unattractive sight in the environment, plastics and microplastics have far more severe dangers that it can impose on the wildlife. Physically, some studies indicate that plastics can cause digestive tract blockages and internal injuries to the organisms that ingest them. Blockages can cause reduced food consumption and starvation. Filter feeders also had reduced filtering activity and photosynthesis of planktons were interfered due to microplastics [15–17]. Microplastics also cause severe developmental effects on sea urchin embryos [18]. Potential of microplastic bioaccumulation was also observed by Murray and Cowie (2011) [19] when they fed polypropylene strands to small lobsters and, in turn, let fishes ingest these lobsters. They observed that the microplastic strands were ingested but not excreted by the fishes [17].

Microplastics are also observed to sorb and carry POPs in the environment, and pose the potential to be more harmful when ingested by organisms due to the added toxicity by the sorbed pollutant [16, 20]. POPs are contaminants of concern due to their persistence, toxicity, tendency to bioaccumulate, and susceptibility for transportation in long distances [21]. Various studies have found POPs on the surfaces of microplastics such as antibiotics, polychlorinated biphenyls, organochlorine pesticides, and polycyclic aromatic hydrocarbons [16, 22–25].

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds that have three or more fused benzene rings and are ubiquitous in the environment due to their regular

emission in the environment [26–30]. They are of environmental concern due to their high carcinogenic and mutagenic properties, long environmental persistence, wide distribution and transportation, poor biodegradation, and the risk to bioaccumulate and biomagnify in food chains [26–30]. PAHs are mostly colorless, white, or pale-yellow solids that are naturally found together as mixtures of two or more compounds (e.g., soot) [26–30]. Generally, they also have high melting and boiling points, low vapor pressure, and very low aqueous solubility (hydrophobic); but they are highly soluble to organic solvents because they are highly lipophilic [26–30]. PAHs found in the environment are usually from the incomplete combustion of fuels and crude oil spills [27, 29]. After PAHs are emitted in the atmosphere, it reaches the marine and terrestrial environments through wet (e.g., rain and snow) and dry deposition. Those PAHs on the soil and land are transported to the marine environment through surface runoff, making the marine environment a sink of PAHs [27, 30]. Total PAH concentrations of up to 0.069 ppm are found in urban runoff waters [31] and up to 146 ppm in seawater during oil spill events [32].

Many studies have reported sorption of PAHs on microplastics as observed in field samples [22, 33, 34] and laboratory experiments [6, 35–37], and they can act as storage and sinks for these pollutants [25, 38–41]. This can pose a problem in the environment as these microplastics can be vessels for contaminant transport. Re-emission or secondary emission may occur when the concentration of the contaminants is lower in the surrounding water than what is sorbed on other materials, such as microplastics [42]. Furthermore, microplastics can also be ingested by organisms and consequently, the sorbed pollutants may result to various levels of toxicities to the organisms [43, 44].

There are limited studies on the effect of salinity changes on the sorption of PAHs on microplastics, which can be observed from the disposal of plastics from the terrestrial to the marine environment. Also, experiments conducted are usually done using separate microplastic setups [6, 35–37]. Plastics do not occur alone in the environment and the co-existence of different kinds of microplastics may have an effect on their sorption of PAHs.

The presence of plastics in the environment is continuously rising throughout the years [3, 45]. Plastics are used almost everywhere, especially in single-use packaging, which is why it has a large volume of production. As of 2015, around 6,300 million metric tons of plastic waste have been generated and only about 9% were recycled, 12% were

incinerated, and the remaining 79% were discarded into landfills or directly into the environment [45]. Microplastics can be a sink and storage of PAHs which can cause great harm to the organisms that ingest them [46]. Additionally, microplastics can be vectors for PAH transport to places that have low PAH concentrations in the surrounding water through re-emission [47]. Due to the rapid usage and disposal of plastic wastes and the continuous emission and deposition of PAHs due to anthropogenic activity, it is important to study their interaction with each other.

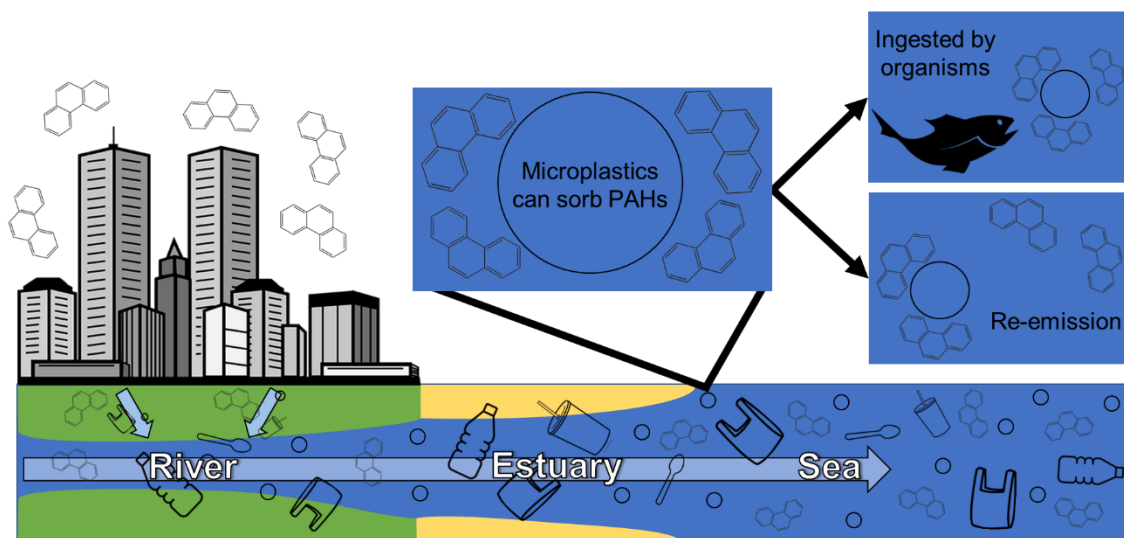


Figure 1-1. Schematic diagram for how PAHs and microplastics from anthropogenic activity can pose a threat in the freshwater, brackish, and saline environments.

## 1.2. Objectives

The objectives of this research are set to be:

1. To compare the sorption behaviors of PAHs on microplastics
2. To determine to which kind of microplastic PAHs have more affinity to
3. To know the effect of changing salinity on the sorption behaviors of PAHs on microplastics
4. To determine the effect of the co-existence of different microplastics on the sorption of PAHs

## 1.3. Significance of the study

With the increasing and constant disposal and emission of plastics and PAHs, it is important to study how they would interact with each other. Plastics that have been disposed in the environment a long time ago may have been degraded into microplastics and these microplastics are found to be more capable in sorbing more PAHs than larger-

sized plastics due to an increase in surface area [48]. Microplastics can act as storage for the PAHs which can be transported in further distances [17]; deposited at the sediments which may reduce degradation of PAHs and be the source of re-emission in the future [49]; or ingested by organisms [43, 44]. Therefore, sorption of PAHs onto microplastics would be an environmental concern. Understanding the mechanisms of the sorption of PAHs to microplastics may help with comprehending how they interact in the natural environment. Since microplastic research is still relatively new and still has a lot of gaps and many researchers still lack consensus and standards in various concepts and methodologies [50, 51], shedding light on the sorption behavior of microplastics and PAHs, which is another pollutant that receives attention due to its harmful effects on organisms, can add to the growing knowledge of this emerging pollutant, microplastics.

#### **1.4. Structure of the thesis**

This thesis comprises six chapters. Chapter one presents the background of the research, objectives, and significance of this study. Also included in this chapter is the structure of the thesis. Chapter two describes major sources, formation, transport and fate, and the occurrence of both PAHs and microplastics in the environment. Previous field studies and laboratory experiments regarding the sorption of PAHs onto microplastics and its mechanisms are reviewed. Current study on the adsorption isotherm models applied are also part of this chapter. Chapter three includes the description of the model PAH and microplastic materials chosen for the study as well as the other materials needed to conduct the experiments. Experimental setup, design, and procedure and analytical methods used are also explained here. Chapter four shows the results obtained from the experiments such as the effect of contact time on the sorption of phenanthrene onto microplastics and the sorption behavior of phenanthrene to PE and PS. Chapter five discusses the possible mechanisms involved in the sorption of phenanthrene on the microplastics with the effects of salinity on the sorption behavior. The affinity of different kinds of microplastics to phenanthrene is also discussed together with the adsorption isotherm model that best describes the sorption behavior. Chapter six summarizes the research findings. It also includes recommendations for further improvement of research and future work.

## **Chapter II**

### **REVIEW OF RELATED LITERATURE**

This chapter is divided into four sections. The first section is the in depth review on the fate of microplastics while the second section is the comprehensive description of PAHs. The third section is a review on the sorption of PAHs on microplastics such as field occurrence of sorbed PAHs onto microplastics and laboratory experiments. Possible mechanisms and factors affecting sorption capability are also presented in this section. The fourth section describes the different adsorption isotherm models that are applied in this study.

#### **2.1. Microplastics**

##### **2.1.1. General description**

The presence of plastics in the environment is a growing environmental concern in the contemporary times. Plastics are everywhere; they are used in packaging (mostly single-use), construction, vehicles, electronics, and many more. Due to the durability, versatility, and low production cost of plastics, it is widely used by many. Most of the time, the robustness of the plastics exceeds their product lifetime or service life such that plastics are usually discarded after their usage and they persist in the environment due to their resistance to degradation [45, 52–54]. Their high stability and durability make the degradation very slow [55]. Production of plastics rapidly grows throughout the years. As of 2015, around 6,300 million metric tons of plastic waste has been generated and only about 9% was recycled, 12% was incinerated, and the remaining 79% was discarded into landfills or directly into the environment (Figure 2-1) [45].

Mismanaged plastic wastes are exposed to various environments which drive their degradation into microplastics through long periods of time. Microplastics (MPs) are plastics that are less than 5 mm [8–14]. Although, there is no clear agreement yet on the size range of MPs, e.g., some consider MPs to be less than 1 mm [56] and less than 2 mm [57]. There are also variations on the lower limit, for example, some researchers use 0.1  $\mu\text{m}$  [11, 46], 1 nm [9], 0.3 mm (due to the usage of zooplankton nets with mesh size of 333  $\mu\text{m}$ ) [8], or 0.5 mm (due to technical difficulties in the analysis of plastics smaller than 0.5 mm) [53, 58].

Due to their small size, marine organisms tend to ingest them, which in turn causes the accumulation of MPs in their digestive tracts. This will cause internal blockages in their digestive systems which will affect their intake of food and nutrients needed for their growth and development [13]. Studies also found out that MPs affect the photosynthesis of some algal species that attach to them due to the blockage of light and air [59]. An experiment also demonstrated the trophic transfer of MPs. Mussels with MPs were fed to fishes and crabs and results showed that the gastrointestinal tracts of the fishes and crabs contained MPs. After 10 days, depuration of MPs happened, and the gastrointestinal tracts of the predators used were clear of MPs which may indicate that transfer of MPs to higher trophic levels may be improbable, however, the ingestion of MPs is still a concerning issue for future studies [60]. Microplastics were also known to adsorb pollutants from the surrounding water. When ingested, the adsorbed pollutants and inherent additives may result to various levels of toxicities depending on the kind of contaminant, and these can be harmful to organisms [43, 44].

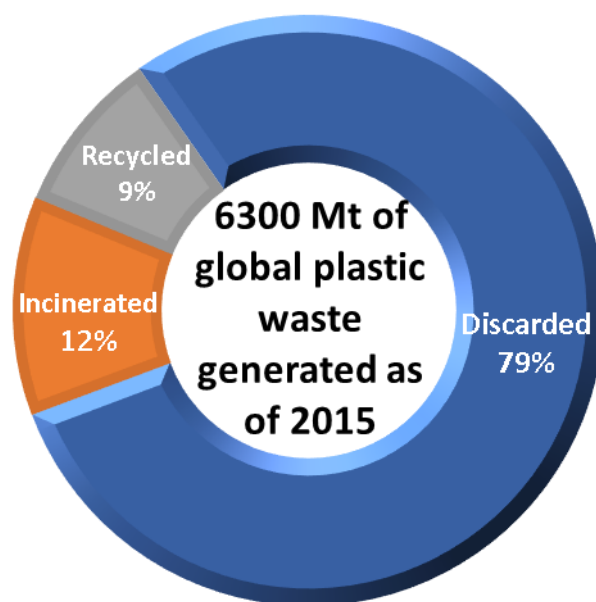


Figure 2-1. Amount of plastic waste generated as of 2015 and the percentage of it that is recycled, incinerated, and discarded. Data obtained from [45]

### 2.1.2. Formation of microplastics

There are two types of microplastics found in the environment based on their formation: primary and secondary. Primary MPs are microplastics that are manufactured in small sizes before being released in the environment. Examples of these are abrasives

from personal care products and cleaning products. Secondary MPs, on the other hand, are created from the weathering and degradation into smaller sizes from larger-sized plastics [8, 9, 11, 58].

Degradation is the process where the plastics are changed chemically or physically which significantly reduces their average molecular weight. Four main processes are involved in the natural degradation of plastics: photodegradation, thermooxidative degradation, mechanical abrasion, and biodegradation (Figure 2-2). Usually, the initial and the fastest and most effective degradation of plastics is the photodegradation or photooxidative degradation due to the exposure to ultraviolet (UV) radiation. Incorporation of oxygen atoms into the plastic polymers, initiated by the exposure to UV rays, forms oxygen-rich functional groups which embrittles and weakens the plastic. The plastics are now more susceptible to fragmentation by mechanical abrasion caused by waves, sand, or other materials due to its weakened surface and structure. Biofilm, algal mats, and colony of invertebrates can also form on the surface of plastics which causes biofouling. Addition of these organisms on the surface of plastic causes it to sink and accumulate in the benthic environment. Exposure to UV radiation may also decrease due to biofouling and other degradation processes may be more significant at this stage, such as thermooxidative degradation and mechanical abrasion [11, 55, 61, 62]. Thermooxidative degradation involves formation of oxygen-rich functional groups which weakens the polymer chains, initiated by moderate temperatures. It can also be described as the slow oxidative breakdown that occurs at moderate temperatures [61, 63]. Natural biodegradation of common plastics is rare and is tremendously slow as microbial species that can metabolize polymers are rarely found in the environment. Even photodegraded, thermooxidatively degraded, and mechanically abraded MPs are not guaranteed to increase susceptibility to biodegradation. The process of plastic degradation may take more than 50 years or even longer in aquatic environments due to relatively lower temperature and oxygen concentration than in the terrestrial environment as plastics on land are exposed in air [55, 61].

### **2.1.3. Sources, transport, and fate of microplastics**

Around 75 to 90% of the plastic debris found in the marine environment are from land-based sources. One of the largest land-based sources of marine plastic debris are

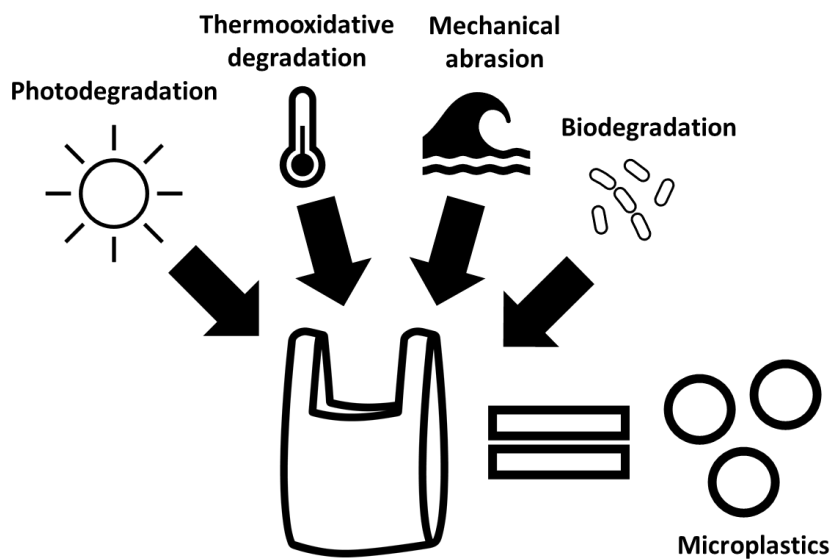


Figure 2-2. Schematic diagram of the four main processes of natural degradation of plastics in the environment. Out of these four, biodegradation is the rarest while photodegradation is the fastest and the most effective.

from sewage and storm water, especially in coastal regions near industrial areas and cities [1–5]. Rivers are also considered as the major pathway for plastic debris to enter the marine environment because rivers contribute 80 to 94% of the total plastic load of the seas. An estimated amount of 1.15 to 2.41 million metric tons of plastic waste from rivers enter the ocean annually [64]. The largest volume of plastic debris observed at river mouths are during rainy seasons when there are huge amounts of floodwater discharge from upstream sources [65]. After plastics and microplastics enter different bodies of water, four transport processes may occur: beaching, surface drifting, water column suspension, and bottom settling (Figure 2-3) which is mainly affected by the density of the plastic [64–66].

Many of the common plastics used and produced nowadays are buoyant and float on the surface of oceans, seas, and other bodies of water. Table 2-1 summarizes the density (in  $\text{g/cm}^3$ ) of the common plastics used today. As for comparison, the density of freshwater is around  $1.00 \text{ g/cm}^3$  while the density of seawater is about  $1.03 \text{ g/cm}^3$  (in standard ambient temperature and pressure) [65]. The plastics that are floating on the surfaces are mainly transported through wind forces, surface currents, and geostrophic circulation. The plastic debris will passively float until deposited to shores and beach, which is called beaching, or be trapped in subtropical convergence zones, as seen from the western and eastern garbage patches in the North Pacific Ocean. Surveys by Moore

et al. (2001) in the North Pacific Ocean eastern garbage patch reported around 334,271 pieces/km<sup>2</sup> of plastic while Law et al. (2010) reported around 1,069 to 580,000 pieces/km<sup>2</sup> of plastic in the western North Atlantic Ocean and Caribbean Sea subtropical convergence zones [64, 65]. Microplastics were also found in the Arctic and Antarctica which are very far from the production and use of plastics [67].

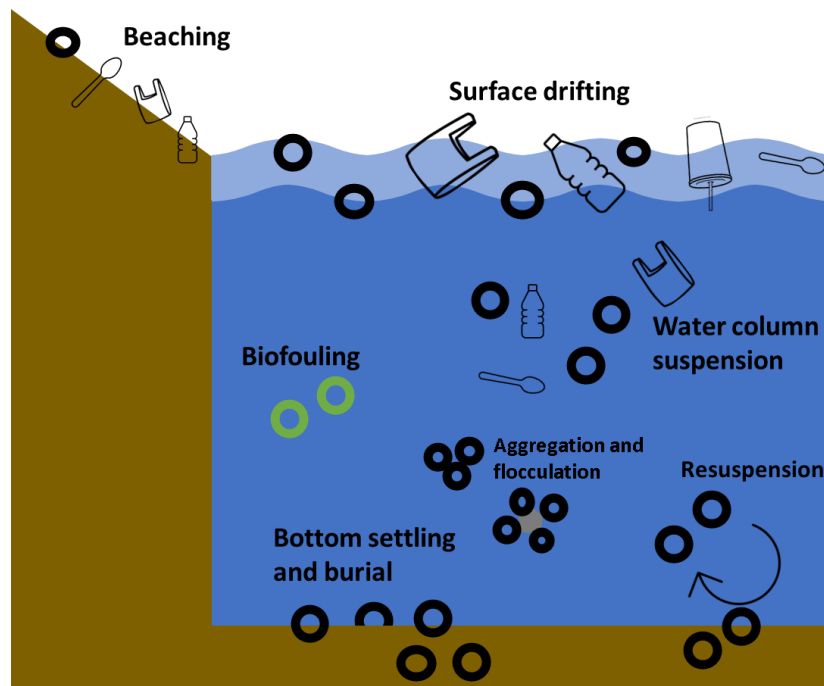


Figure 2-3. Schematic diagram of the transportation and fate of plastics and microplastics in the environment

Plastics and microplastics that have neutral density with the surrounding water tend to be suspended in the water column (subsurface to deep water). The plastics are mixed and moved from the surface to the deep water or vice versa through advection and turbulent mixing forces. Size and shape of plastics are important factors that determine the velocity at which the plastics are mixed and transported along the water column. Microplastics and smaller-sized plastics can act as colloidal particles and are most likely to be suspended in the water column. Fibrous-shaped plastics have the lowest velocity when affected by turbulent mixing, followed by sheets and particles. Originally buoyant plastic may also sink and be suspended in the water column when its physical properties change through processes such as degradation, biofouling, flocculation, and aggregation. Biofouling occurs when the plastic accumulates biofilms, or when its surface is colonized by algae and invertebrates. This can increase the overall density of the plastic causing it to sink. Plastics that have greater density than the surrounding water will settle to the

benthic environment. Non-buoyant plastic will naturally sink and settle at the bottom of the sea, oceans, or freshwater bodies. Microplastics were also observed to have the tendency to aggregate and flocculate with organic and inorganic matter [11, 64, 65]. An experiment by Long et al. (2015) found that microplastics that aggregated with other particles have settling rates of hundred meters per day compared with microplastics that were not aggregated (less than 4 mm/day). Microplastics incorporated with aggregates increase their density as well as their settling rates [64, 65]. Microplastics that have settled at seafloor and other benthic environments may be buried due to the constant deposition of sediments and other matter or may be resuspended predominantly due to storm events and storm-induced currents. In estuaries, tidal currents are the main forces that drives the resuspension of sediments and microplastics from the benthic environment [65].

*Table 2-1. Density of the commonly used plastics today. Data adapted from [46, 68]*

<b>Plastic</b>	<b>Density (g/cm<sup>3</sup>)</b>
High density polyethylene (HDPE)	0.94–0.97
Low density polyethylene (LDPE)	0.91-0.93
Polypropylene (PP, atactic)	0.85-0.94
Polyethylene terephthalate (PET)	1.34-1.45
Polytetrafluoroethylene (PTFE)	2.2
Polyvinyl alcohol (PVA)	1.19-1.31
Polyvinyl chloride (PVC)	1.16-1.58
Polypropylene (PP, isotactic)	0.92
Polystyrene (PS)	1.04-1.10
Polyurethane (PU)	1.2
Poly(methyl methacrylate) (PMMA)	1.18
Polyamide (Nylon 6,6)	1.13-1.15

#### **2.1.4. Occurrence of microplastics in the environment**

Multiple studies have been done for the quantification of microplastics in the marine environment. Some examples of these studies indicate the concentrations of microplastics ranges from  $10^{-5}$  to  $10^5$  particles/m<sup>3</sup> in seawater worldwide (North Pacific South Equatorial counter current and Geoje Island, Korea, respectively); while

concentration ranges from 10 to  $10^{3.5}$  particles/kg dry weight in subtidal sediments worldwide (Southern Baltic Sea and Industrial Harbor, Sweden, respectively) [69]. Other studies concerning the concentrations of microplastics from other areas are done in Beibu Gulf, China coastline sediments (5,020 to 8720 particles/kg dry weight of sediments) [70], in the Norwegian Continental Shelf (20 to 90 mg/kg dry weight of sediments) [71], and in Alang-Sosiya ship-breaking yard, India (81.43 mg/kg dry weight of sediments) [72]. A lot of researchers have contributed to the knowledge of the distribution of microplastics worldwide, however, there is still no standard unit of quantification of the concentration of microplastics found which makes comparison between studies challenging [14]. Table 2.2 summarizes some of the microplastic concentrations found in different places and environmental compartments. Polyethylene and polystyrene are among the most common types of microplastics found in the environment.

## **2.2. Polycyclic aromatic hydrocarbons (PAHs)**

### **2.2.1. General description**

Polycyclic aromatic hydrocarbons (PAHs), a class of hydrophobic organic contaminants, are a group of compounds that have three or more fused benzene rings and are ubiquitous in the environment due to their regular emission to the environment. They are of environmental concern due to their carcinogenic and mutagenic properties, long environmental persistence, wide distribution and transportation, poor biodegradation, and the risk to bioaccumulate and biomagnify in food chains. PAHs are mostly colorless, white, or pale-yellow solids that are naturally found together as mixtures of two or more compounds (e.g., soot). Generally, they also have high melting and boiling points, low vapor pressure, and very low aqueous solubility; but they are highly soluble to organic solvents because they are highly lipophilic [26–29].

Studies have found that PAHs have moderate to acute toxicity to aquatic life and birds. Tumors and problems in reproduction, development, and immunity are some of the severe effects PAHs can cause on organisms. Laboratory studies discovered that animals exposed to PAHs over long periods of time can develop lung cancer, stomach cancer and skin cancer depending on the mode of contact. PAHs can also be dangerous to humans, not only to animals. The United States Environmental Protection Agency (US EPA) have classified seven PAHs that can potentially cause cancer to humans if exposed in high

concentrations or in long periods of time: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a)anthracene, and indeno(1,2,3-cd)pyrene [27].

Table 2-2. Summary of some of the plastic concentrations found in different parts of the world.

Location	Plastic concentration	Sample type	Plastic composition	Reference
Belgium coastal zone	390 particles/kg	Subtidal sediments	Nylon, PVA, PP, PE, PS	[73]
Caribbean Sea	1414 pieces/km <sup>3</sup>	Seawater	PE, PP	[74]
Heungnam Beach, South Korea	473 particles/m <sup>2</sup>	Beach sediment	PS	[14]
Antua River, Portugal	18-629 items/kg dry	Sediments	PP, PE, PS, PET	[75]
Wushan county of Gansu Province	360-1320 items/kg dry	Sediments	PE, PVC, PS	[75]
Soya Island, South Korea	46,334 items/m <sup>2</sup>	Surface water	PS, PP, PE	[14]
Japanese Sea	1.72 million items/km <sup>2</sup>	Surface water	NA	[14]
Three Gorges Reservoir, China	3407.7 x 10 <sup>3</sup> to 13,617.5 x 10 <sup>3</sup> particles/m <sup>3</sup>	Surface water	PP, PE, PS	[76]
Urban river of Wuhan, China	2516.7 to 2933 particles/m <sup>3</sup>	Surface water	PET, PP, PE, nylon, PS	[76]

\*Polyvinyl alcohol (PVA), Polypropylene (PP), Polyethylene (PE), Polystyrene (PS), Polyethylene terephthalate (PET), Polyvinyl chloride (PVC), Not available (NA)

### **2.2.2. Sources and formation of PAHs**

There are three types of PAHs: pyrogenic, petrogenic, and biological, which corresponds to their major sources in the environment. Pyrogenic PAHs are created during pyrolysis; it is the process when organic substances undergo high temperatures (around 350°C to more than 1200°C) with low to no oxygen conditions. Examples of pyrolytic processes that create pyrogenic PAHs are thermal cracking of petroleum residuals, distillation of coal into coke and coal tar, volcanic eruptions, and incomplete combustion of motor fuel from car engines, wood from forest fires, and cigarettes. They are usually found in great concentrations near urban areas [27].

PAHs that are made through lower temperatures (100°C to 150°C) in diagenetic processes that encompasses millions of years are called petrogenic PAHs. Usage and transportation of crude oils and petroleum products add their concentration in environment. Oil spills, storage tank leakages, erosion of sedimentary rocks containing fossil fuels, and small releases of gasoline and motor oil are some of their pathways to the surroundings [27].

Lastly, biological PAHs are produced by certain plants, bacteria, and algae or degradation of vegetative matter although this type of PAH is not well-known. Based on the examples mentioned, PAHs are seen to be synthesized both naturally and anthropogenically which further proves their ubiquity in the environment. Pyrogenic PAHs from anthropogenic activities are said to be the largest contributor of PAHs in the environment with their input concentrations varying due to seasonal changes and industrialization [27, 29].

### **2.2.3. Transport and fate of PAHs**

PAHs are established to be produced from plentiful sources and these enter the marine environment through wet and dry atmospheric deposition, run-off and river effluents, spillage of fossil fuels, and industrial wastewater sewages (Figure 2-4) [27, 29, 77, 78]. Incomplete combustion emits the most PAHs. These PAHs go to atmosphere and tend to attach to particulates due to their low vapor pressures and they can be deposited to the coastal, marine, and terrestrial environments through dry deposition (settling) or wet deposition (precipitation in the form of ice or rain). Those PAHs that have settled on

land can be deposited in the marine environment through surface runoff. The marine environment is usually the ultimate sink and storage of PAHs [29].

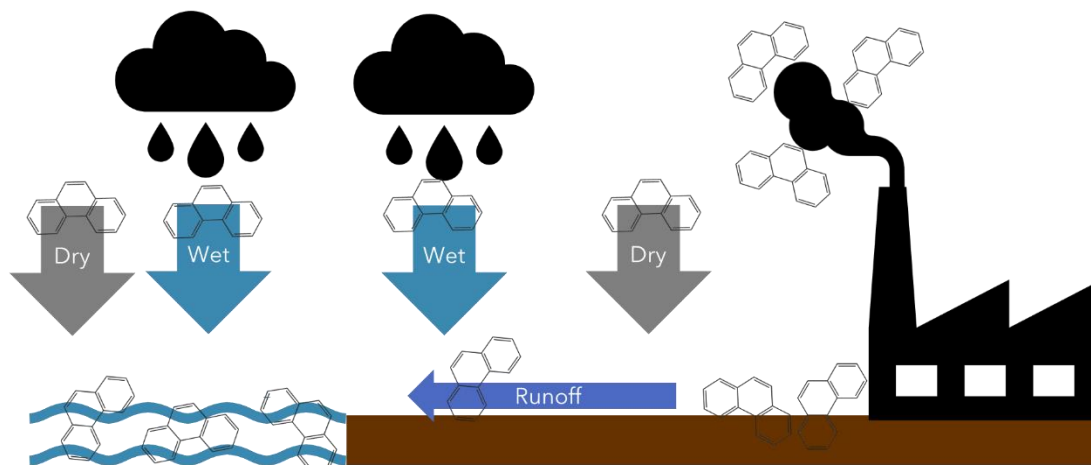


Figure 2-4. Schematic diagram for the emission and deposition of PAHs in the environment.

Melting of snow can also add PAHs to the marine environment as ice is an important accumulator of pollutants [79]. The amount of atmospheric PAH that will enter the marine environment depends on the volume of precipitation [80, 81], ambient temperature [82], and intensity of solar radiation. Ambient temperature affects the evaporation of PAHs from the water [82] while ultraviolet light from the solar radiation causes photodegradation of the PAHs coming from the atmosphere [83].

Upon entering the water column from different sources, PAHs will sorb to suspended particles due to their hydrophobicity, and eventually, these pollutants will settle and accumulate in the bottom sediments. Once the PAHs are assimilated into the sediments, they are mostly immobile as they are non-polar which prevents them from dissolving back into the water [27, 29]. PAHs incorporated in sediments can also persist in longer times than free molecules in air or water. Photolysis of PAHs in water is only effective on the upper few centimeters of the water column. PAHs are also considered persistent in anaerobic conditions which indicates that there is low biodegradation of PAHs in sediments. The calculated half-lives of phenanthrene, a kind of PAH, in water and sediments are 12-42 days and 420-1250 days, respectively [84]. Unless other factors occur that will cause their re-emission into the water column, such as sediment resuspension due to natural (storms, waves, and currents) or man-made events (dredging) [85] or change in concentration in the surrounding water over time which disturbs the

equilibrium of the amount of PAHs between sediment and water [42, 86–89], sediments and other particles, such as microplastics, can be a sink and storage for these contaminants.

#### **2.2.4. Occurrence of PAHs in the environment**

Many researches have been conducted for the quantification of PAHs in the marine environment. Some examples are concentrations of PAHs in the sediments collected from the coast of Chiba, Japan (8 to 18 µg/kg dry weight) [90], surface sediments around coastal areas from England and Wales (6 to 43,470 µg/kg dry weight) [91], urban runoff waters in the United States (69 µg/L) [31], estuarine sediments from Gironde Estuary, France (1,000 to 2,000 ng/g dry weight) [92], sediments from the Black Sea (200 to 1,250 ng/g dry weight) [93], sediments from the lagoon in Cotonou, Benin, Africa (25 to 1,450 ng/g dry weight) [94], coastal seawater from Bohai Bay, China (48 to 607 ng/L) [95], seawater after the Deepwater Horizon Oil Spill event in the Gulf of Mexico (146,000 µg/L) [32], and seawater from Cadiz Bay, Spain (266 to 377 ng/L) [96]. Sources of the PAHs from the examples above differ from case-to-case. Those from sediments in Chiba, Japan and England and Wales are predominantly pyrogenic while those sediments from Gironde Estuary, Black Sea shelf, and lagoon in Cotonou in Africa and water from urban runoff in the United States, Bohai Bay, and Cadiz Bay are mostly from petrogenic sources [31, 90–96]. PAHs in the surrounding water is usually lesser in concentration compared to those in sorbed in particulate matter. Table 2-3 summarizes some of the PAHs concentration found in the environment.

### **2.3. Sorption of PAHs on microplastics**

#### **2.3.1. Field occurrence**

Many studies have reported sorption of PAHs on microplastics taken from the field in the sediments, seawater, and freshwater environments. Frias et al. (2010) collected microplastics from Cresmina and Fonte da Telha, two beaches in the Portuguese Coast. Total PAHs concentrations of the plastics ranged from 0.2 to 319.2 ng/g with phenanthrene, pyrene, and fluoranthene being the PAHs with highest concentrations [22]. Hirai et al. (2011) studied the concentration of organic contaminants sorbed to microplastics from open oceans and seas (Pacific Ocean and Caribbean Sea) and urban (Odaiba, Tokyo, Japan; Kugenuma, Kanagawa, Japan; and Seal Beach, USA) and rural

beaches (Marbella Beach, Costa Rica and Thinh Long, Tonking Bay, Vietnam). The polyethylene gathered from the urban beach of Kugenuma, Kanagawa, Japan has the highest concentration of total PAHs concentration (9,297 ng/g). In general, they reported that higher concentrations of PAHs are found in plastics found in urban beaches [33]. Camacho et al. (2019) studied the concentrations of organic pollutants in microplastics from Canary Islands beaches. They also reported that PAHs are the contaminants with the highest concentration (52.0 to 17,068.7 ng/g) [34]. Table 2-4 summarizes some of the studies that observed microplastics from field samples sorbing PAHs.

Table 2-3. Summary of some of the PAH concentrations found in different parts of the world.

Location	Sample type	PAH concentration	Reference
Coast of Chiba, Japan	Sediments	8-18 µg/kg dry	[90]
Coastal areas from England and Wales	Sediments	6-43,470 µg/kg dry	[91]
Urban runoff waters in the United States	Surface water	69 µg/L	[31]
Gironde Estuary, France	Sediments	1000-2000 ng/g dry	[92]
Black Sea	Sediments	200-1250 ng/g dry	[93]
Lagoon in Cotonou, Benin, Africa	Sediments	25-1450 ng/g dry	[94]
Bohai Bay, China	Seawater	48-607 ng/L	[95]
Gulf of Mexico oil spill event	Seawater	146,000 µg/L	[32]
Cadiz Bay, Spain	Seawater	266-377 ng/L	[96]
Storm water in the United States	Surface water	0.6-6.1 µg/L	[37]
Petroleum wastewater in Shandong Province, China	Surface water	7.6-9.9 µg/L	[97]

These are the examples that demonstrate that PAHs sorb to microplastics in the natural environment. However, there are still no standardized sampling, handling, analysis, cleaning and separation, and contaminant extraction techniques for the microplastics in the environment, and researchers use different methodologies which make it difficult to compare data and results obtained. [51, 68, 98–100].

*Table 2-4. Summary of some of the studies showing that PAHs sorb to microplastics from field samples.*

<b>Location</b>	<b>Sorbed PAH concentration</b>	<b>Reference</b>
Cresmina and Fonte da Telha beaches, Portugal	0.2 to 319.2 ng/g	[22]
Kugenuma, Kanagawa, Japan	9297 ng/g	[33]
Canary Islands beaches	52.0-17,068.7 ng/g	[34]
Ponta da Praia, Brazil	386-1996 ng/g	[101]
North Atlantic gyre	11.2-172 ng/g	[23]
Indonesian Cilacap coast	153-2000 ng/g	[23]
Lake Biwa and Osaka Bay, Japan	1730-27,100 ng/g dry	[102]

### **2.3.2. Sorption experiments**

Some studies have already been done to analyze the sorption of PAHs on different kinds of microplastics. Teuten et al. (2007) tested the sorption of phenanthrene, a kind of PAH, to PE, PP, and PVC microplastics in natural seawater, and the results showed that PE had greater partition coefficient ( $K_d$  values) (around 20 times) than PVC and PP. PVC had the smallest  $K_d$  value [37]. Rochman et al. (2013) conducted an experiment to compare the sorption of PS to PET, HDPE, PVC, LDPE, and PP. They deployed virgin microplastics in San Diego Bay and measured sorbed PAH concentrations for a year. They found that PS, HDPE, and LDPE sorbed similar amounts of PAHs but sorbed more PAHs than PET, PVC, and PP. However, PS sorbed 8-200 times greater concentrations of PAHs than HDPE and LDPE in less than a month [39]. Bakir et al. (2014) studied the sorption of phenanthrene to PE and PVC microplastics in estuarine conditions and found that PE sorbed more phenanthrene than PVC using natural diluted saline water (0, 8.8,

17.5, 26.3, and 35 psu (practical salinity scale unit)) [6]. Another study done by Lee et al. (2014) stated that PS sorbed more PAHs than PE and PP in synthetic seawater environment [103]. On the other hand, O'Connor and Hendriks (2016) discussed that organic contaminants, especially PAHs, are more attracted to LDPE and HDPE than PP, PVC, and PS. PVC and PS had the least PAH sorption capabilities in their study [104]. Wang et al. (2018) compared the sorption of phenanthrene to PE and nylon and results showed that PE had higher sorption capabilities than nylon in synthetic seawater [35]. An experiment on the sorption of phenanthrene on PE, PS, and PVC using synthetic freshwater was done by Wang and Wang (2018), and they stated that the order of sorption capabilities was PE > PS > PVC [105]. Wang et al. (2019) tested the sorption of PAHs on HDPE, PS, LDPE, and PVC microplastics in synthetic freshwater, and the sorption order was HDPE > PS > LDPE > PVC [106]. Wang et al. (2020) also discussed that PE had greater K<sub>d</sub> values than PS, PVC, and PP by around 3 to 20,000 times [48]. The different studies had varying results, but PE and PS had the highest sorption capacities in many of the experiments. However, there are still disagreements whether PE or PS had the greater sorption capability.

Table 2-5. Summary of the experimental studies on the sorption of PAHs to microplastics

Order of sorption capabilities	Sorbate	Background solution/environment	Reference
PE > PP > PVC	Phenanthrene	Natural seawater	[37]
PS > HDPE ≈ LDPE > PET ≈ PVC ≈ PP	PAHs	San Diego Bay seawater	[39]
PE > PVC	Phenanthrene	Natural diluted seawater	[6]
PS > PE > PP	PAHs	Synthetic seawater	[103]
LDPE ≈ HDPE ≥ PP > PVC ≈ PS	PAHs	Synthetic seawater	[104]
PE > nylon	Phenanthrene	Synthetic seawater	[35]
PE > PS > PVC	Phenanthrene	Synthetic freshwater	[105]
HDPE > PS > LDPE > PVC	PAHs	Synthetic freshwater	[106]

### **2.3.3. Mechanisms of sorption of PAHs on microplastics**

Sorption of PAHs on microplastics are mainly governed by hydrophobic partitioning interaction,  $\pi$ - $\pi$  interaction, and van der Waals forces [48].

#### **2.3.3.1. Van der Waals forces**

Van der Waals forces are weak intermolecular forces that do not affect nor is not affected by the structure of the molecules. It is attractive or repulsive depending on the distance between interacting molecules [107]. These are forces experienced by most molecules. There are three types of van der Waals forces: Keesom forces (where two dipoles interact with each other), Debye forces (where a permanent dipole induces a temporary dipole on another molecule without dipoles), and London dispersion forces (where two molecules with no dipole moments are attracted with each other due to random fluctuations on their electron clouds that lead to temporary charge redistribution) [108]. Guo et al. (2012) mentioned that PE is aliphatic such that it only has C-H bonds and has no functional groups, so other attractive interactions cannot occur between PE and hydrophobic organic compounds (HOCs). Van der Waals forces may be one of the main mechanisms that govern the sorption of HOCs, such PAHs, to PE [109].

#### **2.3.3.2. Hydrophobic interactions**

Hydrophobic interactions or the hydrophobic effect occurs when nonpolar molecules, such as PAHs, tend to aggregate together instead of dissolving in the surrounding water due to the fact that the dipole-dipole bondings of water molecules are stronger and more favorable than the van der Waals forces acting between nonpolar molecules and water molecules [110]. This process is effectively characterized by the linear sorption isotherm model [48]. Studies by Teuten et al. (2007), Bakir et al. (2014), and Wang and Wang (2018a) compared the sorption capability of phenanthrene on PE and PVC, and they found that PE had greater sorption capacity of phenanthrene than PVC, a polar polymer [6, 37, 105]. Another study by Nabetani et al. (2017) indicated that the sorption of PFCs (perfluorinated compounds) and PAHs on microplastics are dominated by hydrophobic effects. It is because the ratio of the chemical concentration on microplastics to dissolved phase in the surrounding waters of Lake Biwa and Osaka Bay

increases as octanol/water partition coefficient ( $\log K_{ow}$ ) of the contaminants, a parameter to measure hydrophobicity [111], increases [102]. Wang and Wang (2018b) also compared the sorption of pyrene, another kind of PAH, to PE, PS, and PVC, and the order of sorption based on their results was  $PE > PS > PVC$  [112].

### **2.3.3.3. $\pi$ - $\pi$ interactions**

Sorption of PAHs to microplastics are also governed by  $\pi$ - $\pi$  interactions, which are bonds that occur between aromatic compounds. Velzeboer et al. (2014) discovered that polychlorinated biphenyls (PCBs) and PAHs have stronger sorption affinity to polystyrene (PS) than to PE due to its higher aromaticity. PS has a phenyl functional group where  $\pi$ - $\pi$  interactions with PCBs and PAHs can occur [24]. Huffer et al. (2016) studied the sorption of different organic compounds (n-Hexane, cyclohexane, benzene, toluene, chlorobenzene, ethylbenzoate, and naphthalene) to different kinds of microplastics (PE, PS, PVC, and polyamide or PA) and found that PS had the highest sorption affinity which may be due to  $\pi$ - $\pi$  interactions [113].

## **2.3.4. Factors affecting sorption of PAHs on microplastics**

### **2.3.4.1. Effect of kind of plastic**

The kind of MP may affect the sorption of PAHs as they have different inherent properties. Polymers that are in a rubbery state tend to sorb more contaminants than those in glassy states. Polymers are usually semi-crystalline; they have both crystalline (chains are more ordered) and amorphous (disordered chains) regions. Amorphous regions are in rubbery states when their glass transition temperature  $T_g$  is below room temperature, such as PE ( $T_g$  of  $-125^\circ\text{C}$ ). Otherwise, they are in a glassy state when their  $T_g$  is above room temperature, such as PS ( $90 - 110^\circ\text{C}$ ). When heat is applied to plastics above their  $T_g$ , they transition from glassy to rubbery polymers. Table 2-6 summarizes the  $T_g$  of selected plastics. Glassy polymers have lower sorption levels than rubbery polymers. Polymers that are in a glassy state have denser structures with higher cohesive forces between polymer chains which restricts movement. Entrance of contaminants is difficult due to this and adsorption is the main mechanism of sorption to them. Polymers that are in rubbery states have more free volume due to polymer chains having more mobility and flexibility so contaminants can enter more easily. Absorption mainly happens to these

polymers. Studies also show that organic contaminants have more affinity with rubbery polymers [11, 48, 114–117]. Wang et. al (2019) reported that the order of sorption ability of microplastics to phenanthrene, nitrobenzene, and naphthalene was HDPE > PS > LDPE > PVC and HDPE is in a more rubbery state than PS [106]. However, different plastics also have different functional groups. As mentioned earlier, PS have phenyl groups which makes it more sorptive to aromatic compounds due to  $\pi$ - $\pi$  interactions [113].

*Table 2-6. Glass transition temperatures of selected plastics. Data adapted from [11, 46]*

<b>Plastic</b>	<b>T<sub>g</sub> (°C)</b>
High density polyethylene (HDPE)	-125
Low density polyethylene (LDPE)	-130
Polypropylene (PP, atactic)	-20-0
Polyethylene terephthalate (PET)	70-80
Polytetrafluoroethylene (PTFE)	120-130
Polyvinyl alcohol (PVA)	80-90
Polyvinyl chloride (PVC)	65-87
Polypropylene (PP, isotactic)	100
Polystyrene (PS)	90-110
Polyurethane (PU)	120-160
Poly(methyl methacrylate) (PMMA)	85-105
Polyamide (Nylon 6,6)	47-60

#### **2.3.4.2. Effect of specific surface area**

Specific surface area (SSA) is the part of the total surface area of a sorbent that is available for sorption. SSA increases when the material is more porous [118]. Following this definition, the greater the SSA of a plastic, the greater its sorption capability. Teuten et al. (2007) obtained the SSA of PE, PP, and PVC and found that PE had SSA values 4 times greater than that of PP and PVC and that the K<sub>d</sub> of PE for phenanthrene was around 20 times greater than that of PVC and PP [37]. Wang and Wang (2018a) studied the SSA of PE, PS, and PVC and discovered that the SSA of PE was greater by 3 times to both PS and PVC. The Langmuir K of PE for phenanthrene was larger by 2 and 5 times than PS and PVC, respectively [105]. Another experiment of Wang and Wang (2018b) obtained

the SSA of PE, PS, and PVC and results showed that PE had higher SSA values (around 3 times) than PS and PVC and the Langmuir K values of PE for pyrene were 3 times higher than that of PS and PVC [112, 115]. On the other hand, Wang et al. (2019) studied the SSA of HDPE, LDPE, PVC, PP, and PS micro- and mesoplastics (plastics with sizes between 5 to 20 mm) and found that PVC and PP microplastics had SSA values greater than the other plastics (around 3 times). However, HDPE still had greater K<sub>d</sub> values [106].

#### **2.3.4.3. Effect of salinity**

Increasing salinity of the water can affect the sorption of contaminants to microplastics due to salting-out effect. When strong electrolytes are added into the water, these create solvation shells from the added ions which decreases the free water molecules that can interact with other nonelectrolytes and weak electrolytes, and in turn, decrease their solubility with water. Lesser water molecules are available to interact with the weak and nonelectrolytes [119]. Most PAHs are said to have higher log K<sub>d</sub> in seawater than in freshwater [120, 121]. Organic compounds are said to be less soluble as salinity increases [122]. However, Bakir et al. (2014) argued that salinity had no significant effect on the sorption capacity and desorption rates of phenanthrene on PVC and PE [6]. Liu et al. (2016) compared the experimental data they obtained for the sorption of PAHs to PS (freshwater) to the data obtained by Lee et al. (2014) (seawater). They observed that the K<sub>d</sub> values they obtained under freshwater condition were lower than that of Lee et al. (2014) under seawater condition [103, 123].

#### **2.3.4.4. Effect of size**

Usually, decrease of the particle size, increases the SSA of a sorbent which in turn would increase the sorption capacity [48]. Also, between two similar materials of the same amount, greater SSA can be observed on the more finely divided material [118]. Liu et al. (2016) compared the sorption capabilities of PAHs to aggregated and non-aggregated 70 nm PS particles and found that aggregation did not have an effect on the sorption capabilities [123]. Meanwhile, Wang et al. (2019) tested the sorption behaviors of phenanthrene to micro- and mesoplastics and found that microplastics sorbed greater concentrations of phenanthrene and had greater SSA values [106]. Wang et al. (2019), on the other hand, conducted experiments on the sorption of phenanthrene to PS particles

with the sizes from 50 nm to 170  $\mu\text{m}$ , and results exhibited that 50 nm-sized PS had lesser  $K_d$  values than 235 nm-sized PS due to aggregation. Aggregation of the smaller PS may have decreased its SSA [36].

## 2.4. Adsorption isotherm models

The three most commonly used isotherm models are linear, Freundlich, and Langmuir isotherm models due to their relative mathematical simplicity and reasonable accuracy [124, 125]. Each of the adsorption isotherm models are described below. The criteria used by past researchers on which isotherm model is the best are when the equilibrium data and the isotherm function have a good fit (high  $R^2$  value) and that the other calculated values (maximum adsorption capacity, etc.) should have realistic values [126].

### 2.4.1. Linear isotherm model

The linear isotherm model is described by Eq. 2-1.

$$q_e = K C_e \quad (\text{Eq. 2 - 1})$$

where:  $q_e$  = sorbed sorbate concentration at equilibrium ( $\mu\text{g/g}$ )  
 $K$  = partition coefficient (L/g)  
 $C_e$  = amount of sorbate at the bulk solution at equilibrium ( $\mu\text{g/L}$ )

Hydrophobic interactions and van der Waals partition processes were better described by using linear isotherm model [48, 127]. Guo et al. (2012) described the sorption of phenanthrene to PE to be highly linear but not to PS which indicates that the main sorption mechanism in PE is hydrophobic partitioning and other processes may have occurred to PS such as  $\pi$ - $\pi$  interactions [109]. Additionally, Wang et al. (2019) stated that the sorption of phenanthrene to PS was linear ( $R^2 = 0.999$ ) due to hydrophobic partitioning [36]. Usually, sorption of organic compounds to rubbery polymers are better described using linear isotherm which indicates that the sorption happens in the bulk of the polymer rather than on the surface only [106, 113, 128]. However, a study by Zhao et al. (2020) indicated that the sorption of PAHs to PS, a glassy polymer, had better fitting to the linear isotherm ( $R^2 > 0.946$ ).

#### 2.4.2. Freundlich isotherm model

The equation for the Freundlich isotherm model is shown in Eq. 2-2. The linearized form of the Freundlich isotherm is on Eq. 2-3. The Freundlich isotherm will reduce to the linear isotherm model when  $n = 1$  [127]. On the other hand, the heterogeneity of the sorbent increases as  $n$  decreases [6].

$$qe = KfCe^{\frac{1}{n}} \quad (\text{Eq. 2 - 2})$$

$$\log qe = \log Kf + \frac{1}{n} \log Ce \quad (\text{Eq. 2 - 3})$$

where:  $qe$  = sorbed sorbate concentration at equilibrium ( $\mu\text{g/g}$ )  
 $Kf$  = Freundlich constant or the adsorption capacity ( $\mu\text{gL}^{1/n}/\mu\text{g}^{1/n}$ )  
 $1/n$  = intensity of adsorption or the heterogeneity of the surface (unitless)  
 $Ce$  = amount of sorbate at the bulk solution at equilibrium ( $\mu\text{g/L}$ )

The Freundlich isotherm model is used to represent the multilayer adsorption on the heterogenous surface of the sorbent. The surface of a sorbent is said to heterogeneous when there are large quantities sorption sites (that are energetically inequivalent) simultaneously acting [129–131]. Wang et al. (2019) found that the sorption of phenanthrene to HDPE, LDPE, PVC, PP, and PS fitted better when Freundlich isotherm model ( $R^2 > 0.954$ ) was used compared to the linear isotherm model ( $R^2 > 0.889$ ) [106].

#### 2.4.3. Langmuir isotherm model

Langmuir isotherm model is defined by Eq. 2-4. There are five types of linearized Langmuir isotherm models as written in Eq. 2-5 to 2-9.

$$qe = \frac{Cebqm}{1 + Ceb} \quad (\text{Eq. 2 - 4})$$

$$\text{Langmuir I: } \frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{bqm} \quad (\text{Eq. 2 - 5})$$

$$\text{Langmuir II: } \frac{1}{qe} = \frac{1}{bqm} \frac{1}{Ce} + \frac{1}{qm} \quad (\text{Eq. 2 - 6})$$

$$\text{Langmuir III: } qe = qm - \frac{1}{b} \frac{qe}{Ce} \quad (\text{Eq. 2 - 7})$$

$$\text{Langmuir IV: } \frac{qe}{Ce} = bqm - bqe \quad (\text{Eq. 2 - 8})$$

$$\text{Langmuir V: } \frac{1}{Ce} = bqm \frac{1}{qe} - b \quad (\text{Eq. 2 - 9})$$

where:  $qe$  = sorbed sorbate concentration at equilibrium ( $\mu\text{g/g}$ )  
 $Ce$  = amount of sorbate at the bulk solution at equilibrium ( $\mu\text{g/L}$ )  
 $qm$  = maximum adsorption capacity ( $\mu\text{g/g}$ )  
 $b$  = adsorption equilibrium constant or the affinity of the binding sites to the sorbate ( $\text{L}/\mu\text{g}$ )

The Langmuir isotherm model describes the monolayer adsorption on a homogeneous sorbent surface [124]. The main assumptions of the Langmuir isotherm are each active adsorption site only interacts with one adsorbate molecule; the adsorption sites have definite localized sites and are finite, homogeneous, well-distributed, and energetically equivalent; and the interaction between adsorbate molecules are negligible [118, 127, 129, 132]. Wang and Wang (2018a) indicated that sorption of pyrene on PE, PS, and PVC was better described by the Langmuir isotherm ( $R^2 > 0.99$ ) than the other isotherm models used (Freundlich, Tempkin, Dubinin-Radushkevich, and Redlich-Petersen) [112]. Another study by Wang and Wang (2018b) used the linear, Freundlich, and Langmuir isotherm models to fit the sorption data of phenanthrene on PS, PVC, and PE. The results were that Langmuir isotherm had better fitting for the sorption behaviors ( $R^2 > 0.9957$ ) than linear ( $R^2 > 0.9352$ ) and Freundlich ( $R^2 > 0.9775$ ) [105]. Zhao et al. (2020) studied the sorption of PAHs on polyurethane (PU), a polar polymer with benzene rings, and found out that Langmuir isotherm fit the data better which may indicate that  $\pi$ - $\pi$  Electron-Donor-Acceptor interaction occurred on the sorption of PU and the PAHs. This may show that only one molecule of the PAHs adsorbed on each adsorption site of PU [133].

## Chapter III

### MATERIALS AND METHODS

In this chapter, the experimental methodology, analyses, and the materials used to conduct the experiments are described. At first, the model PAH and microplastic materials chosen for this study are explained together with the other materials used for the experiments. Then, the experimental setup is presented with special reference to the experimental design used to determine the effect of phenanthrene contact time with the microplastics and the sorption behavior of the model PAH to the model microplastics. Lastly, the analyses, i.e., High Performance Liquid Chromatography (HPLC) analysis and BET analysis, are presented. All the experiments were conducted at the Geosphere Environment Systems Laboratory, University of Tokyo Kashiwa Campus; the HPLC analysis at the Environmental Science Center, University of Tokyo Kashiwa Campus; and the BET analysis at the Otomo Laboratory, University of Tokyo Kashiwa Campus.

### 3.1. Materials

#### 3.1.1. Description of the model materials

Phenanthrene (PHE,  $C_{14}H_{10}$ ) is a kind of polycyclic aromatic hydrocarbon (PAH) with three angularly bonded benzene rings (Figure 3-1). This is chosen as the model PAH as it is one of the simplest PAHs according to the International Agency for Research on Cancer [27]. Like all other PAHs, it is highly hydrophobic.

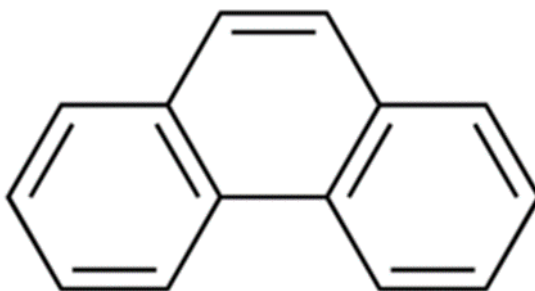


Figure 3-1. Chemical structure of phenanthrene

Polystyrene (PS,  $(C_8H_8)_n$ ) and polyethylene (PE,  $(C_2H_4)_n$ ) are used as the model microplastics as they are the most found and widely used kinds of plastics [10, 14, 20, 45, 134]. Previous studies have also noted their high sorption capacity of PAHs compared with other types of plastics [105, 106, 109, 135]. Plastics are polymers and are commonly

composed of long chains of repeating hydrocarbon monomers. PE is composed of ethylene monomers while PS is composed of styrene monomers (Figure 3-2) [136, 137].

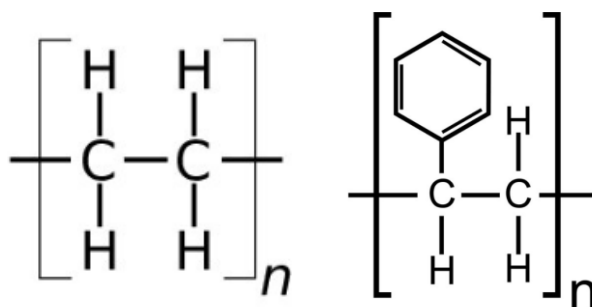


Figure 3-2. Chemical structure of polyethylene (left) and polystyrene (right)

### 3.1.2. Materials for the experiment

Milli-Q water was used as the representative freshwater background solution (0 parts per thousand), and sea salts (Sigma-Aldrich) were used for preparing the synthetic brackish (17.5 parts per thousand) and seawater (35 parts per thousand) background solutions. Freshwater has a salinity range of 0-0.5 parts per thousand while brackish water, 0.5-30 parts per thousand and saline water 30-50 parts per thousand, with an average of 35 parts per thousand [138].

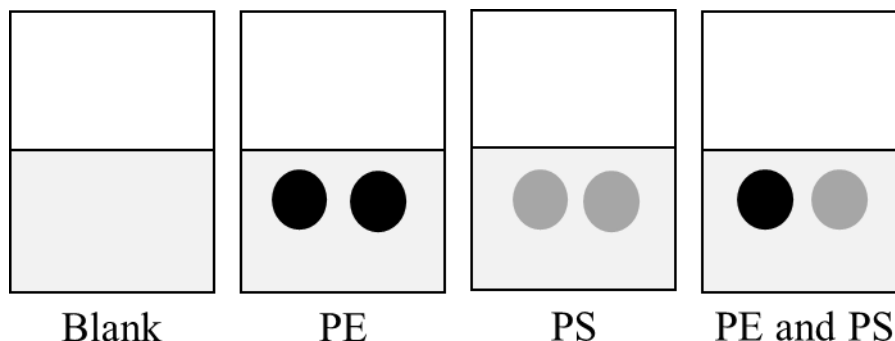
Analytical standard phenanthrene (Supelco) and  $\geq 99.9\%$  purity acetonitrile (Sigma-Aldrich) were used to create the phenanthrene stock solutions for spiking the background solutions. The acetonitrile was also used as the eluent for the HPLC analysis. Acetonitrile is widely used in chromatographic separations due to its low chemical reactivity, high miscibility with water mixtures, low viscosity, and low UV cut-off [139]. PS and PE (GoodFellow) with 3 mm average granular size were used for the model MPs.

The phenanthrene stock solutions were stored in brown borosilicate reagent bottles with PTFE-lined caps and in the dark at 4°C to avoid degradation [36, 106, 123]. PTFE and borosilicate glass are better materials for working with PAHs to prevent loss of reagents through container leaching [140, 141].

### 3.2. Experimental setup

Four setups were prepared to study the sorption behavior of phenanthrene onto the microplastics – blank, PE-only, PS-only, and PS and PE setups (Figure 3-2). Amber vials were used on all setups to avoid photodegradation [83]. All experiments were done

using a water-filled shaking bath (Yamato BW 200 model) to achieve constant stirring speed (125 rpm) and temperature (standard ambient temperature, 25°C) throughout the duration of the experiments.



*Figure 3-2. Schematic diagram for the experimental setups*

### **3.3. Experimental design**

#### **3.3.1. Effect of contact time**

To determine the effect of contact time to the sorption of phenanthrene to PS and PE, each of the four setups were spiked with the same initial phenanthrene concentration of 5 ppm and a group of setups were prepared for sampling at time intervals of 5, 10, 15, 20, 25, and 30 minutes. A total of 24 setups were prepared per run to test the effect of contact time. The samples of the liquid phase were analyzed and the concentration of phenanthrene in each time interval were compared. The data obtained,  $C_e$  ( $\mu\text{g/L}$ , amount of phenanthrene not sorbed by the microplastics in the liquid phase) were used to calculate  $q_t$ , which is the amount of solute sorbed per mass of sorbent ( $\mu\text{g/g}$ ).

#### **3.3.2. Sorption behavior of phenanthrene to PE and PS**

To observe the sorption behavior of phenanthrene to both PE and PS, each of the four setups were spiked with varying initial phenanthrene concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1, 2.5, 3.5, 4, 5, 6, and 7 ppm. A total of 52 setups were prepared per run to test the sorption behavior of phenanthrene to PE and PS. After sampling and analysis, the phenanthrene concentrations were compared. The data obtained,  $C_e$  ( $\mu\text{g/L}$ , amount of phenanthrene not sorbed by the microplastics in the liquid phase at equilibrium) were used to calculate  $q_e$ , which is the amount of solute sorbed per mass of sorbent at equilibrium ( $\mu\text{g/g}$ ).

### 3.4. Experimental procedure

Before conducting batch adsorption experiments, the plastics were each weighed. Then, amber vials with 10 mL of background solutions were prepared. These were then spiked with the phenanthrene stock solution to the designed initial phenanthrene concentration. The microplastics were placed in the vials of each setup. The vials were continuously shaken in the water bath and 1 mL samples were taken from the background solution at the designated time intervals to be analyzed by using HPLC. Data obtained from the HPLC analysis were then used to calculate and fit the results on different adsorption isotherms. Sorption behavior were determined from the results. All the experiments were replicated twice, and the results were averaged.

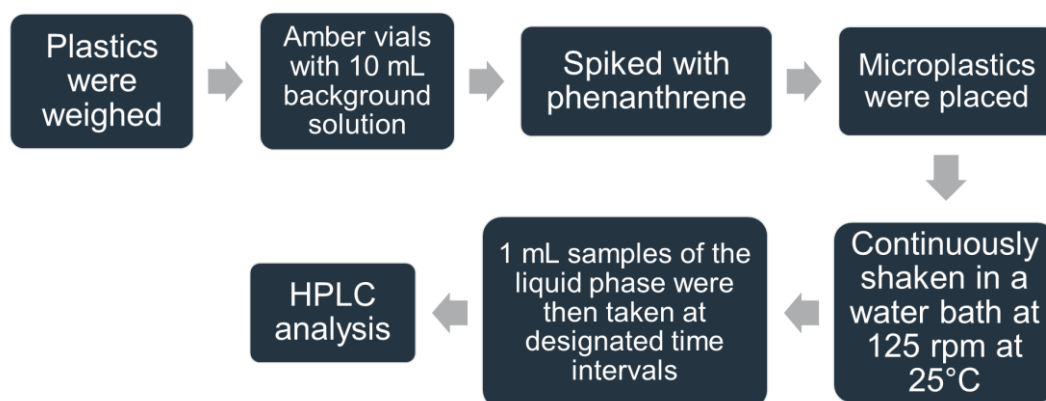


Figure 3-3. Flowchart of the experimental procedure

### 3.5. Analytical methods

#### 3.5.1. HPLC analysis

The liquid samples obtained from the background solutions were analyzed using HPLC. The HPLC system with fluorescence detector and C18 column was utilized for the analysis of the concentration of phenanthrene. PAHs are strongly fluorescent and fluorescence detectors are demonstrated to be more sensitive and provides limit of detections (LODs) 95-100 times lower than that of UV detectors [142].

The JASCO International HPLC system was used with the following components: intelligent fluorescence detector (FP-2020 Plus), intelligent HPLC pump (PU-2080 Plus), line degasser (DG-2080-53), intelligent autosampler (AS-2055 Plus), intelligent column oven (CO-2065 Plus), and reversed-phase C18 column (YMC-Triart C18 model, column size: 250 x 4.6 mm, particle size: 5  $\mu$ m, pore size: 12 nm). JASCO ChromNAV ver.

1.16.02 software program was used to quantify the phenanthrene concentration from the liquid samples.

Reversed-phase liquid chromatography is usually used for separation of hydrophobic compounds and C18 column is an efficient stationary phase as it is the most hydrophobic [143]. Optimized analysis conditions used in HPLC analysis were 246/370 nm excitation/emission wavelengths, 100% acetonitrile as the mobile phase, 1 mL/min flow rate, 40°C column oven temperature, isocratic elution, and 10 µL injection volume. The eluent was degassed using an ultrasonic bath for around 30 minutes at 22-25°C before usage to minimize the interference of gas bubbles in the detector. Phenanthrene standards were prepared using acetonitrile and concentrations from 0.001 to 7 ppm were used for the determination of the calibration curve and LOD.

### 3.5.2. BET analysis

BET analysis was used to determine the specific surface area (SSA) of microplastics. SSA is defined as the portion of the total surface area of an adsorbent that is available for adsorption [118]. The BET analysis was based on the Brunauer, Emmett, and Teller (BET) theoretical isotherm equation (Eq. 3-1) which was developed to estimate the number of adsorbate molecules required to cover the adsorbent surface in multimolecular layers. This is best applied in the adsorption equilibrium of gas-solid systems and this is commonly used to quantify the surface area of an adsorbent from nitrogen adsorption data [126, 127, 144].

$$\frac{1}{Q \left( \frac{P}{P^0} - 1 \right)} = \frac{(C - 1) \frac{P}{P^0}}{C Q_m} + \frac{1}{C Q_m} \quad (\text{Eq. 3 - 1})$$

where: P = equilibrium pressure of the gas  
P<sup>0</sup> = saturation pressure of the gas  
Q = amount of gas adsorbed  
Q<sub>m</sub> = monolayer capacity of the adsorbed gas on the solid  
C = BET constant

The specific surface area (Eq. 3-3) is calculated from the total surface area (Eq. 3-2) of the adsorbent which can be obtained from the Q<sub>m</sub> from the BET equation [144].

$$S_t = \frac{Q_m N s}{V} \quad (\text{Eq. 3 - 2})$$

where:  $S_t$  = total surface area of the adsorbent  
 $N$  = Avogadro's number  
 $s$  = cross-sectional area of the adsorbate gas  
 $V$  = molar volume of the adsorbate gas

$$S_{BET} = \frac{S_t}{a} \quad (\text{Eq. 3 - 3})$$

Where:  $a$  = mass of the adsorbent  
 $S_{BET}$  = specific surface area

The BET analysis was conducted using the NOVA 2200e Surface Area & Pore Size Analyzer with  $N_2$  as the adsorbate gas. Usually, the analysis is done using  $N_2$  at its boiling temperature of 77 K. The microplastics used in this study were first degassed under high vacuum conditions using an inert gas ( $N_2$ ) at 25°C for 2 hours to remove impurities and to prevent altering the surface properties of both PS and PE [145]. Quantachrome software was then used to analyze and calculate the results.

## Chapter IV

### RESULTS

This chapter is divided into three sections. In the first section, the results from the effect of contact time on the sorption of phenanthrene are described. In the second section, the sorption behaviors of phenanthrene to both PE and PS are presented. Then, in the third section, the specific surface areas of PS and PE obtained from the BET analysis are shown.

#### 4.1. Effect of contact time on the sorption of phenanthrene

To test the effect of contact time of phenanthrene with PS and PE on the sorption in freshwater, brackish, and saline environments, samples of the liquid phase (taken at designated time intervals as discussed in chapter three) from each of the four setups were analyzed using HPLC. The experiment was duplicated, and the obtained results were averaged. The results were summarized in Figure 4-1.

It was observed that the sorption equilibrium of phenanthrene to both PS and PE in all environments studied (freshwater, brackish, and saline) was reached within 5 minutes of contact time.

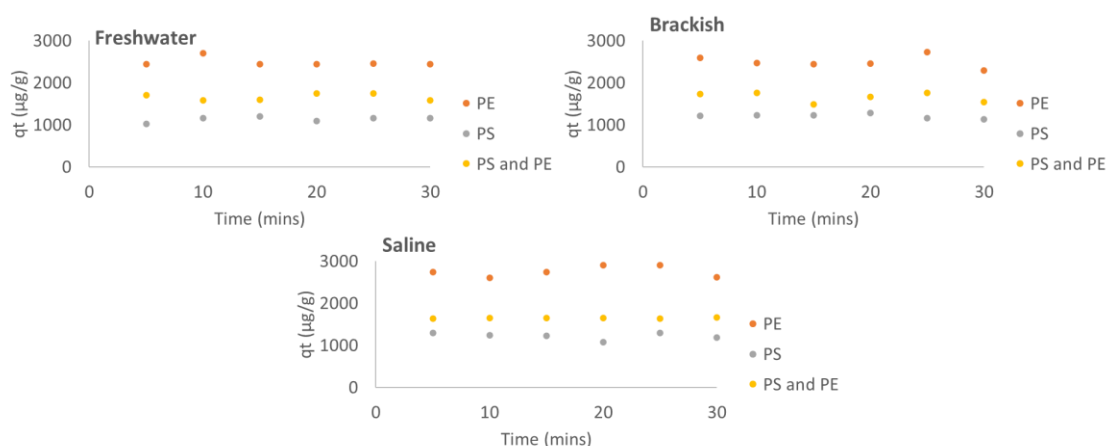


Figure 4-1. Effect of contact time on the sorption of phenanthrene on PS and PE in the three environments studied. qt = amount of solute sorbed per mass of sorbent (µg/g)

#### 4.2. Sorption behavior of phenanthrene to PE and PS

To investigate the sorption behavior of phenanthrene to both PE and PS in freshwater, brackish, and saline environment, the background solution was spiked with varying initial concentrations of phenanthrene as discussed in chapter three. The solution

was then sampled and was analyzed using HPLC. The experiment was duplicated, and the obtained results were averaged. The results were summarized in Figure 4-2. Figure 4-3 was shown to better compare the sorption capabilities of PE and PS in each environment studied.

From the results, PE-only setups showed greater sorption capability than PS-only and PS and PE setups in all of the environments studied (freshwater, brackish water, and saline water) while PS-only setups had the least sorption capability among the other setups (Figure 4-2). Furthermore, both PE and PS demonstrated greater sorption capability in the saline environment than in the brackish and freshwater environment, and the environment which induced the least sorption capability for both PE and PS is the freshwater environment (Figure 4-3). As summary, the order of sorption capabilities for the setups is: PE-only > PE and PS > PS-only, while the order of sorption capabilities of PS and PE in the three environments studied is saline water > brackish water > freshwater.

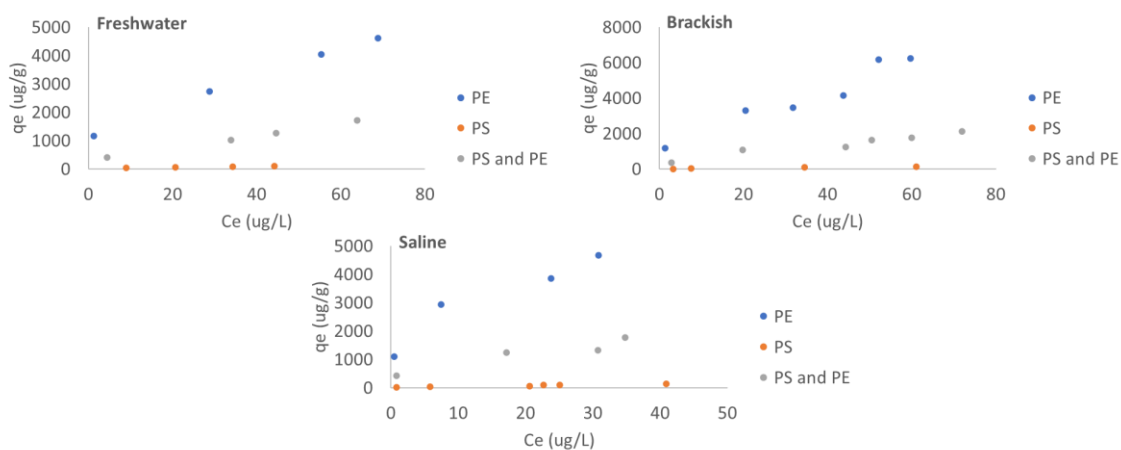


Figure 4-2. Sorption behavior of PHE to PS and PE in the three environments studied.  $q_e$  = sorbed sorbate concentration at equilibrium (ug/g),  $C_e$  = amount of sorbate at the bulk solution at equilibrium (ug/L)

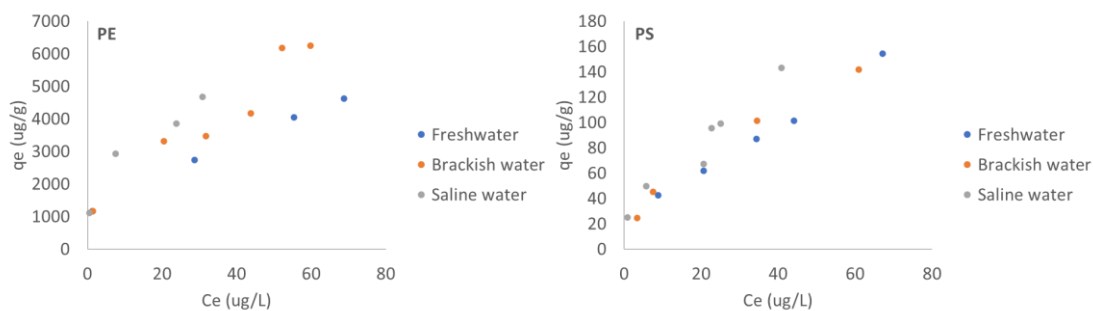


Figure 4-3. Sorption behavior of phenanthrene on PE and PS in the freshwater, brackish, and saline environments.  $q_e$  = sorbed sorbate concentration at equilibrium (ug/g),  $C_e$  = amount of sorbate at the bulk solution at equilibrium (ug/L)

### 4.3. Specific surface area of PE and PS

The results from analyzing specific surface areas (SSA) obtained are summarized in Table 4-. From the results, PE has 3 times greater SSA than PS.

*Table 4-1. Specific surface area of PE and PS*

<b>Microplastic</b>	<b>Specific surface area (m<sup>2</sup>/g)</b>
Polyethylene	0.759
Polystyrene	0.258

## Chapter V

### DISCUSSION

This chapter is divided into four sections. The first section discusses the fitting of the sorption data into the linear, Freundlich, and the Langmuir isotherm models. The second section includes the in depth discussion on the mechanism of sorption of phenanthrene to PE and PS. The third section discusses how the knowledge gained in this study can be applied in the natural setting. Lastly, the fourth section is about the scope and limitations of this study.

#### 5.1. Adsorption isotherms

Results and data obtained from the experiments were fitted into linear, Freundlich, and Langmuir isotherm models. The equation used for the linear isotherm model is shown in Eq. 5-1. Using linear regression, K values of the linear isotherm model were obtained (Table 5-1). High  $R^2$  values ( $R^2 \geq 0.908$ ) were observed in this model and PE had higher K values by around 30 to 40 times to PS.

$$qe = KCe \quad (\text{Eq. 5 - 1})$$

where:  $qe$  = sorbed sorbate concentration at equilibrium ( $\mu\text{g/g}$ )

$K$  = partition coefficient ( $\text{L/g}$ )

$Ce$  = amount of sorbate at the bulk solution at equilibrium ( $\mu\text{g/L}$ )

Intercepts were obtained after fitting the data in the linear isotherm. This may mean that the intercept is the amount of phenanthrene PE or PS can sorb at once as none is left in the liquid phase at equilibrium. Concentrations after the intercept may be sorbed at increments following the linear isotherm model. This may be due to the fact that PE is a rubbery polymer, and that and rubbery polymers have more free volume due to polymer chains having more mobility and flexibility which makes phenanthrene enter into the bulk structure more easily. PS, on the other hand, is a glassy polymer, which means that PS have denser structures that have higher cohesive forces between polymer chains and restrict movement [11, 48, 114–117]. Due to these characteristics, phenanthrene cannot enter the PS structure easily. Since the linear isotherm represents sorption by hydrophobic

interactions and van der Waals forces [48, 127] and sorption of the sorbate happens not only on the surface but also at the bulk of the polymer [106, 113, 128], the intercepts may indicate that PE can sorb around 1000  $\mu\text{g}$  of phenanthrene per gram of PE until all sites of sorption inside the bulk of the polymer are filled (absorption). The increments of phenanthrene sorbed after this concentration may be due to the adsorption on the surface of PE and by following the definition of hydrophobic interactions, phenanthrene molecules may interact with each other on the surface as phenanthrene is a hydrophobic compound. PS, on the other hand, can absorb 30  $\mu\text{g}$  of phenanthrene per gram of PS before adsorption happens which is a lot lesser than that of PE.

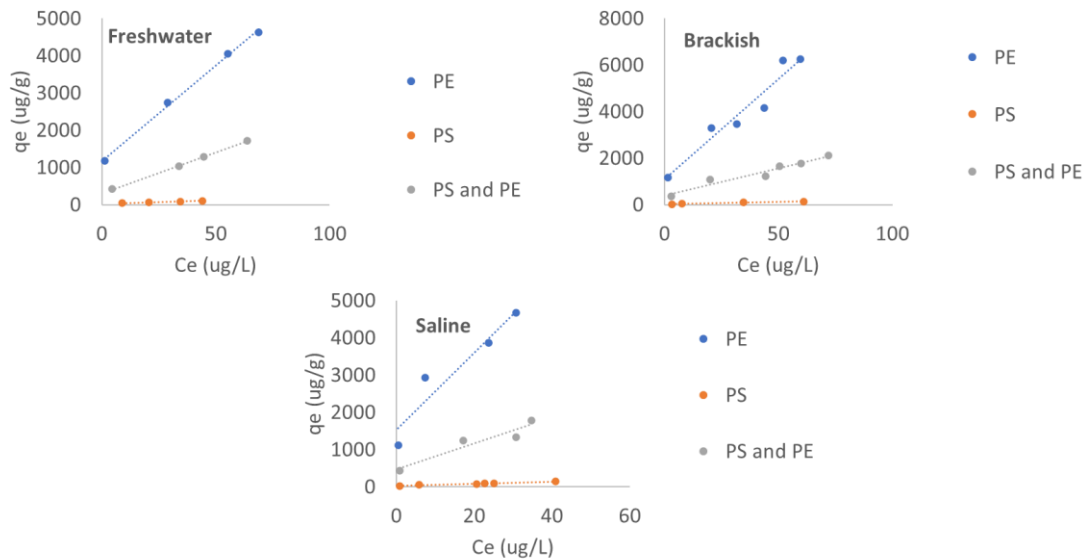


Figure 5-1. Fitting of the sorption data using linear isotherm model.  $q_e$  = sorbed sorbate concentration at equilibrium ( $\mu\text{g/g}$ ),  $C_e$  = amount of sorbate at the bulk solution at equilibrium ( $\mu\text{g/L}$ )

Table 5-1.  $K$ , intercept, and  $R^2$  values obtained using linear regression for the linear isotherm model.

	Freshwater			Brackish water			Saline water		
Linear	PE	PS	PE and PS	PE	PS	PE and PS	PE	PS	PE and PS
$K$	51.2	1.69	21.8	86.3	1.98	23.4	103.6	2.829	34.6
Intercept	1170	27.6	309	1080	25.6	393	1520	25.3	473
$R^2$	0.997	0.998	0.999	0.936	0.982	0.945	0.910	0.955	0.908

The linearized equation used for the Freundlich isotherm model is shown in Eq. 5-2. Values for  $\log q_e$  and  $\log C_e$  are plotted in Figure 5-2. Using linear regression,  $K_f$  and  $1/n$  values of the Freundlich isotherm model were obtained (Table 5-2). High  $R^2$  values were also obtained in some points in this model ( $0.970 \geq R^2 \geq 0.478$ ) but Linear isotherm still had higher  $R^2$ .

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (\text{Eq. 5 - 2})$$

where:  $K_f$  = Freundlich constant or the adsorption capacity ( $\mu\text{gL}^{1/n}/\text{g}\mu\text{g}^{1/n}$ )  
 $1/n$  = intensity of adsorption or the heterogeneity of the surface (unitless)

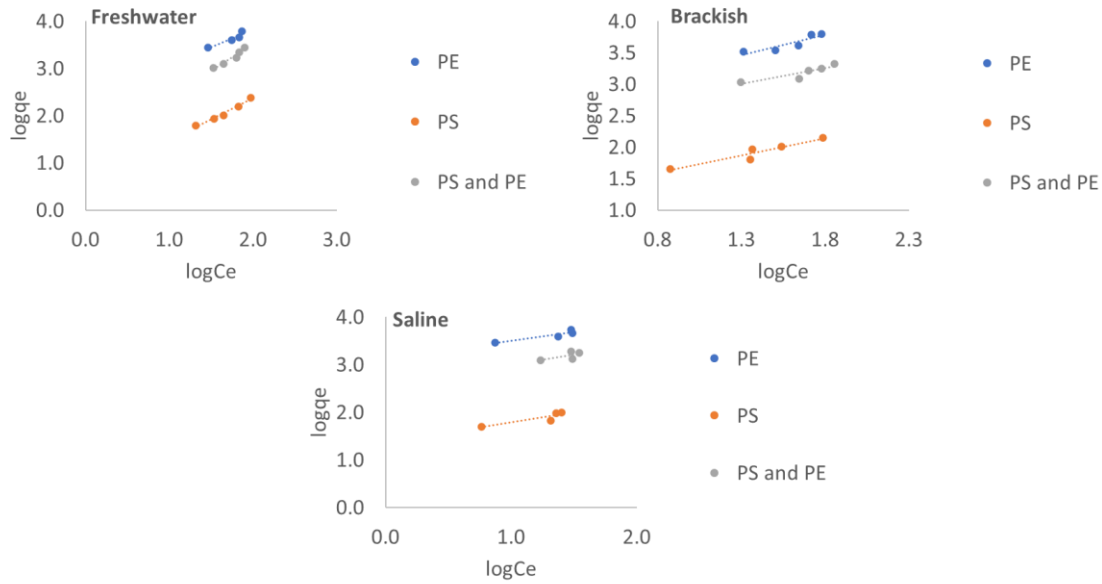


Figure 5-2. Fitting of the sorption data using the Freundlich isotherm model

Table 5-2.  $K_f$ ,  $n$ , and  $R^2$  values obtained using linear regression for the Freundlich isotherm model.

	Freshwater		Brackish water			Saline water			
Freundlich	PE	PS	PE	PE	PS	PE	PE	PS	PE
			and PS			and PS			and PS
<i>Kf</i>	221	3.86	17.7	426	14.5	228	1370	23.3	342
<i>1/n</i>	0.742	0.890	1.14	0.644	0.547	0.498	0.367	0.421	0.455
<b>R<sup>2</sup></b>	0.902	0.970	0.941	0.811	0.908	0.818	0.823	0.799	0.478

Lastly, the data were fitted using five types of the linearized Langmuir isotherm model. The equations of these types, i.e., Langmuir I to V, are shown in Eq. 5-3, to 5-7. X and Y axes for the cross-plots differ depending on the linearization of the Langmuir equation (Figures 5-3 to 5-7). Linear regression was used to obtain the  $qm$  and  $b$  values (Tables 5-3 to 5-7). Some of the  $R^2$  values were high, however, in many instances, very low  $R^2$  values ( $0.999 \geq R^2 \geq 0.108$ ) were observed compared to Linear and Freundlich isotherms. Some negative  $qm$  and  $b$  values were also seen from the results which are not possible because PE and PS cannot be desorbing phenanthrene before sorption.

$$\text{Langmuir I: } \frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{bqm} \quad (\text{Eq. 5 - 3})$$

$$\text{Langmuir II: } \frac{1}{qe} = \frac{1}{bqm} \frac{1}{Ce} + \frac{1}{qm} \quad (\text{Eq. 5 - 4})$$

$$\text{Langmuir III: } qe = qm - \frac{1}{b} \frac{qe}{Ce} \quad (\text{Eq. 5 - 5})$$

$$\text{Langmuir IV: } \frac{qe}{Ce} = bqm - bqe \quad (\text{Eq. 5 - 6})$$

$$\text{Langmuir V: } \frac{1}{Ce} = bqm \frac{1}{qe} - b \quad (\text{Eq. 5 - 7})$$

where:  $qm$  = maximum adsorption capacity ( $\mu\text{g/g}$ )  
 $b$  = adsorption equilibrium constant or the affinity of the binding sites to the sorbate ( $\text{L}/\mu\text{g}$ )

The criteria used by past researchers to choose which isotherm model best fits the data are high  $R^2$  value and that the calculated parameters (maximum adsorption capacity, etc.) should be realistic [126]. Out of the three adsorption isotherm models used in this study, the data best fitted the linear isotherm model due to higher  $R^2$  values ( $R^2 \geq 0.908$ ). Partition coefficient  $K$  and other values from the linear isotherm will be used in the further parts of discussion in this study.

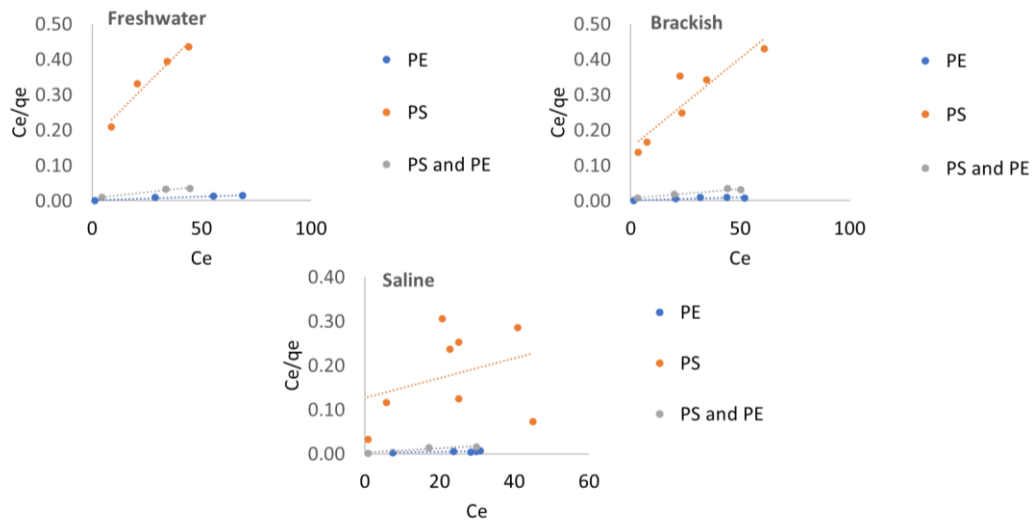


Figure 5-3. Fitting of the sorption data using the Langmuir I isotherm model.

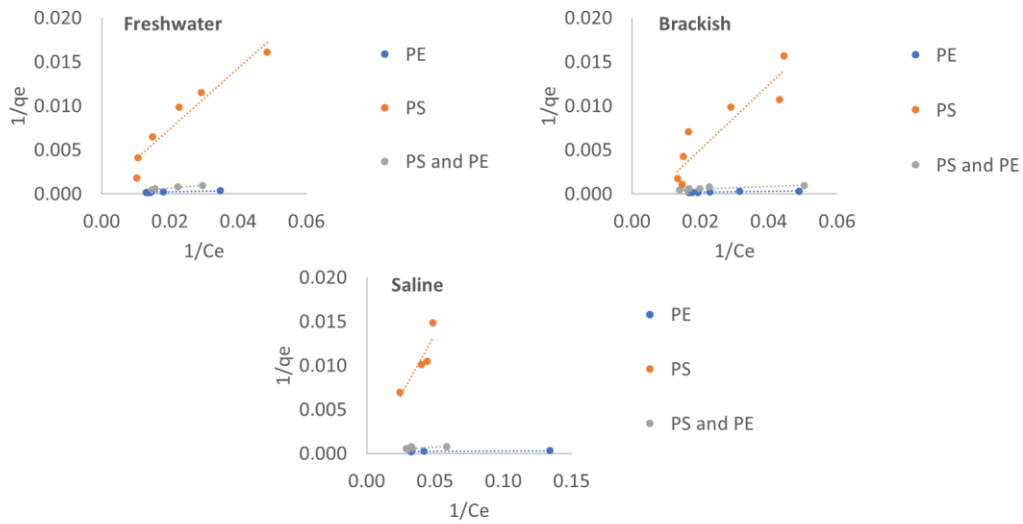


Figure 5-4. Fitting of the sorption data using the Langmuir II isotherm model

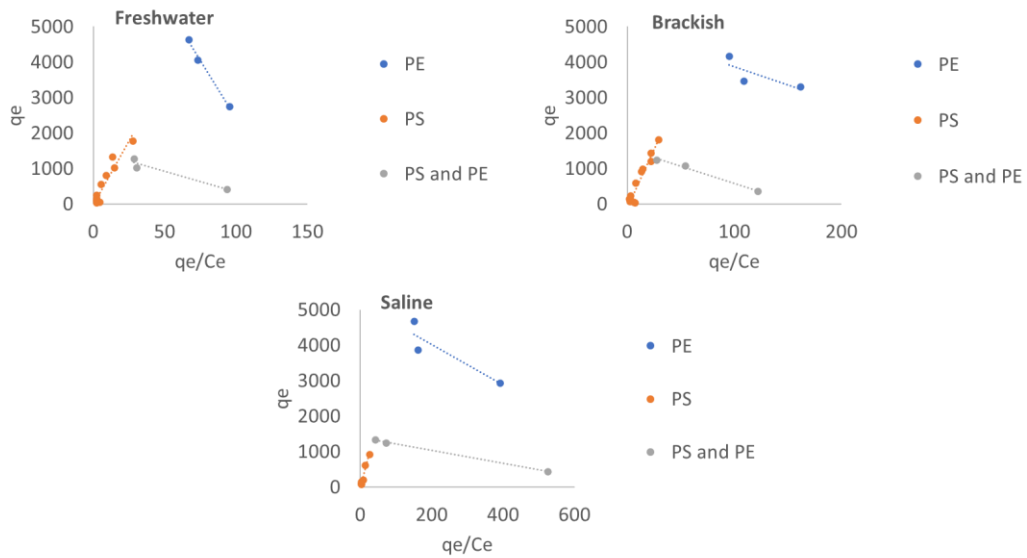


Figure 5-5. Fitting of the sorption data using the Langmuir III isotherm model

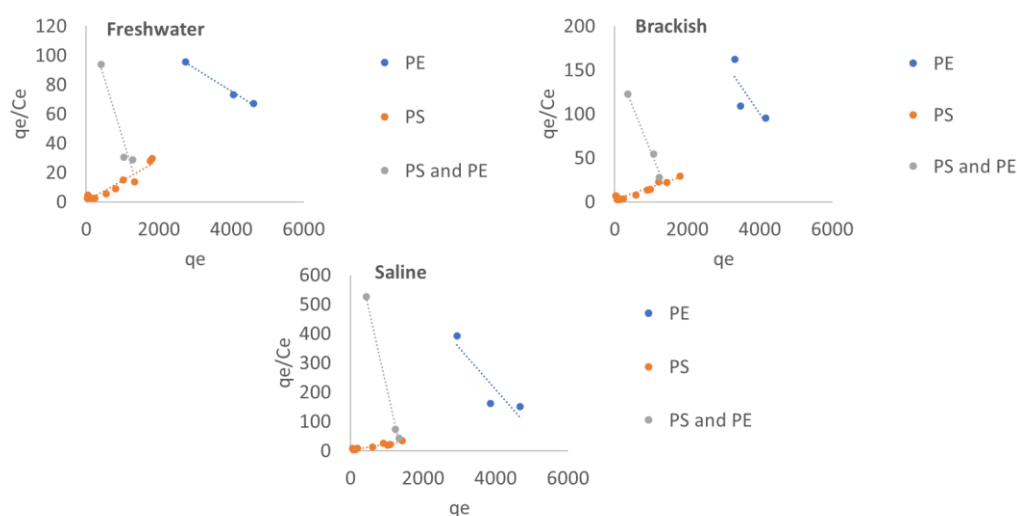


Figure 5-6. Fitting of the sorption data using the Langmuir IV isotherm model

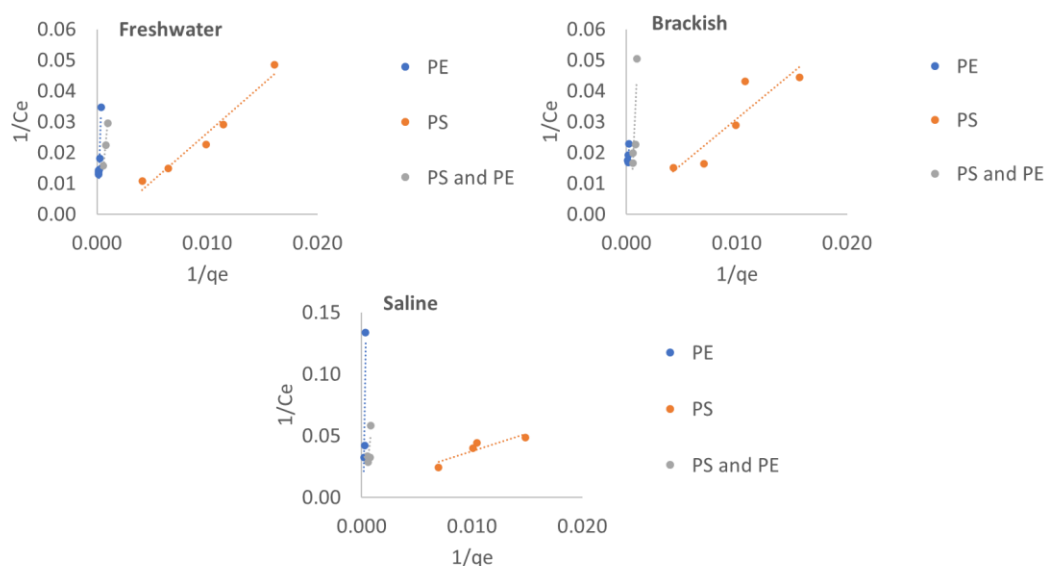


Figure 5-7. Fitting of the sorption data using the Langmuir V isotherm model

Table 5-3.  $q_m$ ,  $b$ , and  $R^2$  values obtained using linear regression for the Langmuir I isotherm model.

Langmuir I	Freshwater		Brackish water			Saline water		
	PE	PS	PE and PS	PE	PS	PE and PS	PE	PS and PS
$q_m$	5020	161	1670	6170	200	1840	7520	435
$b$	0.0850	0.0354	0.0698	0.0721	0.0330	0.0732	0.0756	0.0182
$R^2$	0.919	0.949	0.965	0.782	0.836	0.919	0.596	0.108

Table 5-4. qm, b, and R<sup>2</sup> values obtained using linear regression for the Langmuir II isotherm model.

Langmuir II	Freshwater			Brackish water			Saline water		
	PE	PS	PE and PS	PE	PS	PE and PS	PE	PS	PE and PS
qm	21300	2000	41700	12300	-435	2940	5260	-2500	3330
b	0.00503	0.00145	0.000735	0.0159	-0.00625	0.0275	0.171	-0.00143	0.0342
R <sup>2</sup>	0.903	0.926	0.957	0.746	0.831	0.707	0.929	0.819	0.510

Table 5-5. qm, b, and R<sup>2</sup> values obtained using linear regression for the Langmuir III isotherm model.

Langmuir III	Freshwater			Brackish water			Saline water		
	PE	PS	PE and PS	PE	PS	PE and PS	PE	PS	PE and PS
qm	8890	-30.8	1500	4890	-116	1540	5180	-34.7	1390
b	-0.0155	0.0139	-0.0864	-0.0983	0.0152	-0.105	-0.174	0.0265	-0.547
R <sup>2</sup>	0.991	0.906	0.932	0.616	0.930	0.988	0.817	0.957	0.998

Table 5-6. qm, b, and R<sup>2</sup> values obtained using linear regression for the Langmuir IV isotherm model.

Langmuir IV	Freshwater			Brackish water			Saline water		
	PE	PS	PE and PS	PE	PS	PE and PS	PE	PS	PE and PS
qm	8950	-55.6	1540	5660	-168	1550	5480	-142	1390
b	0.0153	-0.0138	0.0805	0.0606	-0.0141	0.103	0.142	-0.0201	0.546
R <sup>2</sup>	0.991	0.926	0.932	0.616	0.931	0.988	0.817	0.909	0.998

Table 5-7. qm, b, and R<sup>2</sup> values obtained using linear regression for the Langmuir V isotherm model.

Langmuir V	Freshwater			Brackish water			Saline water		
	PE	PS	PE and PS	PE	PS	PE and PS	PE	PS	PE and PS
qm	34500	629	6630	-5150	-1970	2640	5300	-352	8160
b	0.00280	0.00500	0.00540	-0.0101	-0.00150	0.0298	0.158	-0.00830	0.00870
R <sup>2</sup>	0.903	0.964	0.999	0.825	0.812	0.740	0.929	0.819	0.509

## 5.2. Sorption mechanisms of phenanthrene on PE and PS

Based on the results, phenanthrene had greater sorption affinity to PE than PS with higher K values by around 30 to 40 times to PS. Few studies suggested that PS should have greater sorption capacity than PE because of  $\pi$ - $\pi$  interactions, which is the attractive force that occurs between aromatic molecules, between the phenyl functional group of PS and the benzene rings of phenanthrene [24, 113]. However, from the results of this study, PE has more sorptive capacity than PS. This may indicate that the mechanism of sorption for both PS and PE is hydrophobic interactions and van der Waals forces.

PE has SSA values of three times greater than that of PS which means that PE has more available sorption sites for phenanthrene while the K values of PE and PS differ by around 30 to 40 times. This can be explained by the fact that PE is a rubbery polymer and PS is a glassy polymer. Rubbery polymers have more free volume because its polymer chains have more mobility and flexibility. Phenanthrene can enter the bulk structure of PE more easily. Glassy polymers have denser structures that have higher cohesive forces between its polymer chains which restricts movement that makes the penetration of phenanthrene into inside of the PS polymer harder [11, 48, 114–117]. This is in accordance with previous studies. Wang et al. (2019) studied the sorption capabilities of HDPE, LDPE, PS, PVC and found that HDPE sorbs more than PS as it is a rubbery polymer [106]. Furthermore, BET analysis of SSA was developed to estimate the number of adsorbate molecules required to cover the adsorbent surface in multimolecular layers [126, 127, 144]. This does not consider the free volume inside of the bulk of the polymers.

Sorption equilibrium of phenanthrene on both PE and PS in all environments studied was reached within 5 minutes of contact time. This may be due to hydrophobic interactions (low solubility of phenanthrene in water). Since phenanthrene is hydrophobic, it tends to partition into phases that are also hydrophobic such as, PE and PS.

More phenanthrene is sorbed in saline environments. Increase in salinity increases the sorption capability of both PS and PE. Partition coefficient K and salinity (parts per thousand) were plotted against each other and it was observed that K increases linearly as salinity increases (Figure 5-8). This may be due to the salting-out effect. An increase in salt concentration in the aqueous phase decreases the solubility of organic compounds as the salt attaches to the water molecules – leaving lesser room for organic compounds to attach to the water molecules [119, 122]. The results obtained in this study were

different from the study of Bakir et al. (2014). They concluded that salinity had no effect on the sorption capacity of phenanthrene on PVC and PE [6]. However, based on the results obtained in this study, salinity had an effect on the sorption behavior and the order of sorption is saline > brackish > freshwater.

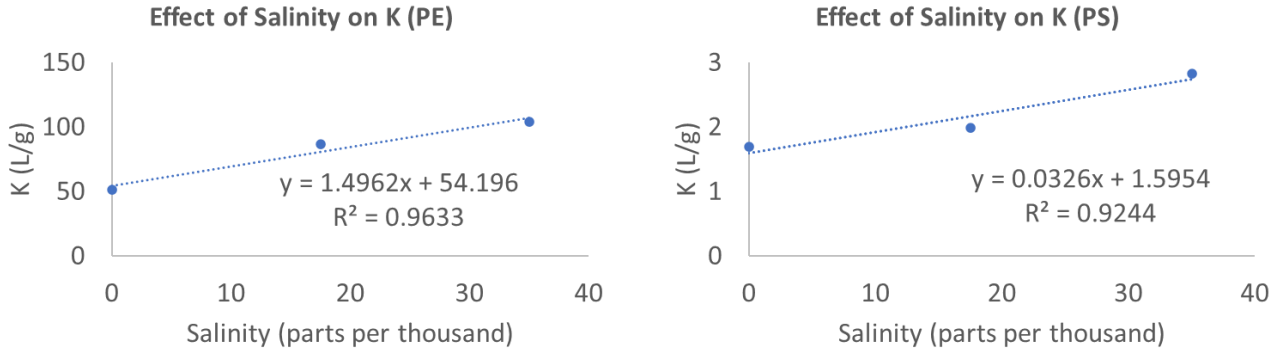


Figure 5-8. Effect of salinity on the partition coefficient K of PE (right) and PS (left)

The interaction of PE and PS was also checked. Using the experimental  $C_e$  values obtained from PS and PE setups and the K values obtained from PE-only and PS-only setups,  $q_e$  for the combined setup were obtained through the composite additive model (Eq. 5-8). Partition coefficient K is a constant value for each sorbent in this study and  $q_e$  is the sorbed amount of phenanthrene at equilibrium. The calculated  $q_e$  were then compared with the experimental  $q_e$  of PE and PS setups. The results are summarized in Figure 5.9. The calculated values and the experimental values have values that are quite different (i.e., the experimental values are lesser than the calculated values). This indicates that PE and PS may have an interaction with each other. Aggregation may have occurred between the PE and PS particles as aggregation can decrease the SSA, which in turn, decreases the sorption capabilities of the sorbent [36].

$$q_{e_{PSPEcalc}} = (K_{PE}C_{e_{PSPEexp}} + I_{PE}) \frac{M_{PE}}{M_{PE} + M_{PS}} + (K_{PS}C_{e_{PSPEexp}} + I_{PS}) \frac{M_{PS}}{M_{PS} + M_{PE}} \quad (\text{Eq. 5 - 8})$$

where:  $q_{e_{PSPEcalc}}$  = calculate  $q_e$  of PS and PE setup  
 $K_{PE}$  = partition coefficient of PE from this study  
 $C_{e_{PSPEexp}}$  = experimental  $C_e$  value of PS and PE setup  
 $I_{PE}$  = intercept from the Linear isotherm of PE from this study

$M_{PE}$  = mass of PE

$K_{PS}$  = partition coefficient of PS from this study

$C_{PSPEexp}$  = experimental  $C_e$  value of PS and PE setup

$I_{PS}$  = intercept from the Linear isotherm of PS from this study

$M_{PS}$  = mass of PS

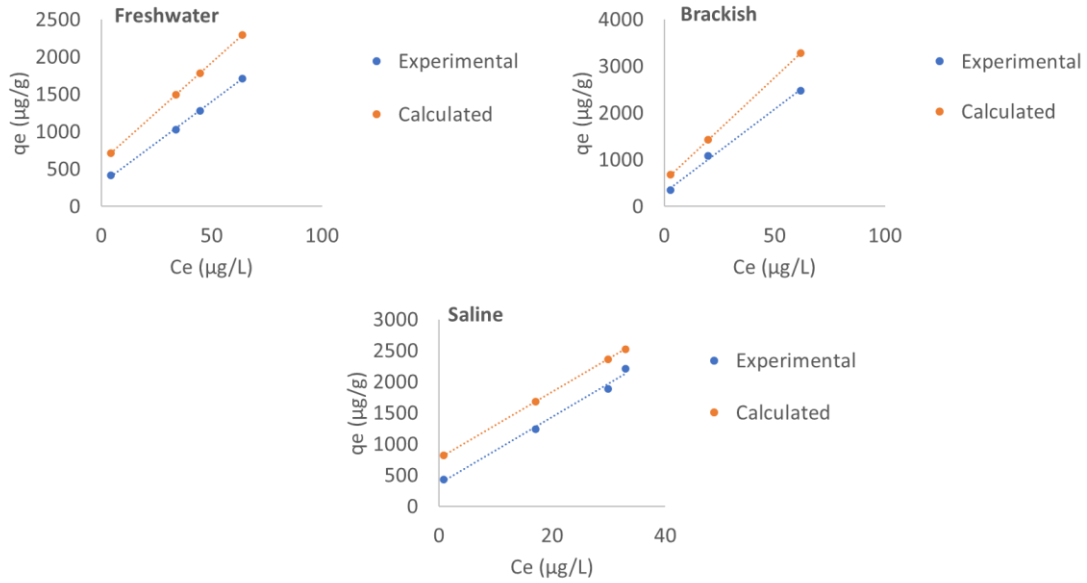


Figure 5-9. Comparison of the calculated  $q_e$  and  $C_e$  of PE and PS setups to check the interaction of the microplastics.

### 5.3. Possible application to the natural environment

This study considered the sorption of phenanthrene on PE and PS in water salinities of 0, 17.5, and 35 parts per thousand (freshwater, brackish, and saline, respectively) at 25°C. This is around the average ocean surface temperature for the tropics and the results from this study can be applied to the marine environment in the tropics [146]. From the freshwater down to the saline environment, sorption of phenanthrene on PE and PS increases. Since the marine environment is the ultimate sink for both microplastics and PAHs, this result is very vital to take note of. The microplastics with sorbed PAHs can be ingested by marine organisms and it is well-known that PAHs can have carcinogenic and mutagenic effects on these organisms [27]. These microplastics can also be a vector for transport to places with lesser amounts of PAHs in the surrounding water. Sorbed PAHs can be re-emitted back into the seawater. Re-emission of PAHs back into the water column can happen through particle resuspension due to natural (storms, waves, and currents) or man-made events (dredging) [85] or through change in

concentration in the surrounding water which disturbs the equilibrium between the amount of PAHs in solid and liquid phase [42, 86–89].

Since more sorption of PAHs on the microplastics occurred in the saline environment than in the brackish environment from the results of this study, movement and transport of microplastics from the saline to the brackish environments (e.g., estuaries) may cause slight release of sorbed PAHs due to decrease in sorption capabilities. Furthermore, estuaries are well-known to be filters and accumulators of various kinds of contaminants [147–151]. Some studies report estuaries as sinks for pollutants, such as polycyclic aromatic hydrocarbons (PAHs) [94, 152, 153] and microplastics [154–156].

PE is one of the most found and widely used plastic [10, 14, 20, 45, 134]. It has around 116 million metric tons of production worldwide as of 2015 compared with PS that only had 25 million metric tons [45]. The waste PE generated last 2015 was around 57 million metric tons while PS was around 17 million metric tons [45]. PE had the greater sorption capacity with respect to phenanthrene than that of PS which means that disposal and handling of PE must be properly managed in the future as it can store more PAHs.

#### **5.4. Scope and limitations of the study**

This research aims to know the sorption behavior of PAHs onto microplastics through the use of model materials, phenanthrene, polystyrene, and polyethylene. This study is limited to the use of spherical pristine polystyrene and polyethylene with a 3 mm average granular size. Plastics that have been degraded in the environment were not used. The effect of different shapes, sizes, and degree of degradation on sorption behavior were not studied.

Synthetic seawater, brackish water, and freshwater were used in this study by mixing Milli-Q water and sea salts obtained from Sigma-Aldrich in concentrations of 0, 17.5, and 35 parts per thousand, respectively. Natural seawater, brackish water, and freshwater were not used in this study. The effects of the other components of natural water (organic matter content, sediments, etc.) on the sorption behavior were not measured.

The limitations of this study are that the experiments were done in a controlled environment inside a laboratory and the batch adsorption experiments were only done in standard ambient temperature (25°C) and at constant shaking (125 rpm) using a water-

filled shaking bath. The effect of the change in temperature and shaking speed to the sorption capability were not considered.

## Chapter VI

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1. Conclusions

In this study, the sorption behavior of polycyclic aromatic hydrocarbons (PAHs) on microplastics in the freshwater, brackish, and saline environments were examined. Phenanthrene, polyethylene (PE), and polystyrene (PS) were the model materials that were used to represent PAHs and microplastics. After conducting batch adsorption experiments, the results were that PE had the greater sorption capability of phenanthrene than PS (around 30 to 40 times larger partition coefficient  $K$  values) and the main mechanism of sorption was estimated to be hydrophobic interactions and van der Waals forces. The sorption equilibrium in all the environments studied was reached within 5 minutes of contact time. The sorption equilibrium data best fit the linear isotherm model (with non-zero intercept). Additionally, as salinity increases, the sorption capabilities of both PE and PS increases as well possibly due to the salting-out effect. Furthermore, PE and PS may have an interaction with each other as the composite additive model did not work out. Aggregation may have occurred between the PE and PS particles as aggregation can decrease the SSA, which in turn, decreases the sorption capabilities of the sorbent.

The specific surface area (SSA) of PE and PS measured by BET analysis showed that PE had three times as large as that of PS. BET Analysis only takes into consideration the surface properties and not the free volume of the sorbent. PE is a rubbery polymer and it has more free volume than PS, a glassy polymer (polymers than have denser polymer chain structures). This is another possible reason for the larger sorption capacity of phenanthrene of PE. Based on the intercepts obtained from the linear isotherm, PE can absorb 1000  $\mu\text{g}$  of phenanthrene per gram of PE until all sites of sorption inside the bulk of the polymer are filled (absorption) and then increments of phenanthrene are sorbed after on the surface. PS, on the other hand, can absorb 30  $\mu\text{g}$  of phenanthrene per gram of PS before all sorption sites inside the polymer are filled up.

The marine environment is the ultimate sink for the PAHs and microplastics. In this study, both PE and PS had the greatest sorption capability in the saline environment. These microplastics can be ingested by organisms which can cause serious health effects and these microplastics can re-emit the sorbed PAHs in places that have lesser

concentrations of PAHs. Proper disposal of PE plastics must be taken care of as PE had the greater sorption capacity.

## **6.2. Recommendations**

For the further improvement of this research, the following recommendations are proposed:

1. Conducting experiments with different temperature and mixing speed

In the natural environment, the temperature is not constant throughout the water column and turbulence and other means of particle movement are variable. These parameters may have an effect on the sorption capacity of PAHs on microplastics as these can affect the solubility of PAHs [157].

2. Usage of other kinds of microplastics

Since many other kinds of plastics exist and are currently used and disposed, they may have different sorption capabilities and mechanisms.

3. Comparison of sorption behavior of different sizes of plastics

Sorption capabilities usually increase when size of sorbents decrease because of an increase in SSA. However, aggregation may occur, and this may affect the sorption capacity of the plastics. This can be important to study as plastics are continuously degrading into even smaller sizes as of now.

4. Studying the sorption capabilities of weathered and degraded microplastics

Pristine microplastics are rare in the environment – most of those found in the environment have been degraded at some degree. Changes on the surface and chemical properties of the plastics and introduction of biofilm may have an effect on the sorption capabilities of the microplastics.

5. Modelling of sorption phenomenon

Through conducting experiments, data can be obtained on how PAHs are sorbed on the microplastics. Modelling can be done to predict the sorption capabilities of the microplastics and be applied in different situations and environments.

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## ANNEX

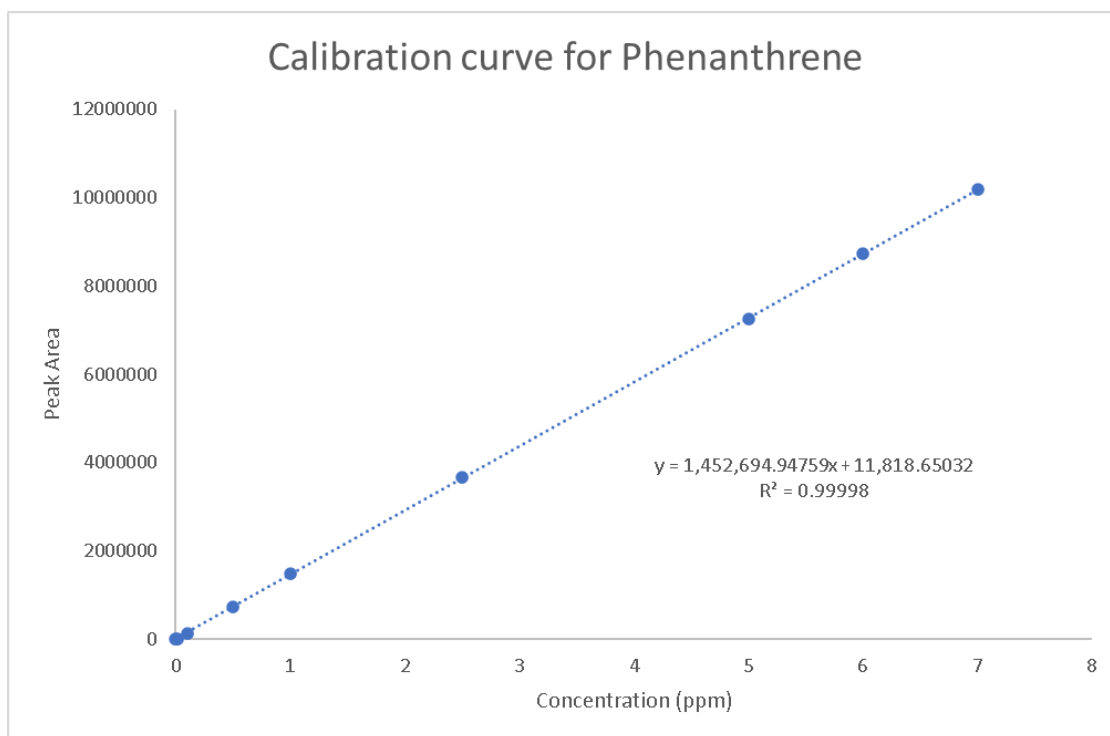


Figure A1. Calibration curve obtained for phenanthrene using HPLC.