

Sorption Behavior of Trace Organic Chemicals on Nanoplastics and their Implications on
Co-contaminant Transport

by

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Abstract

Nanoplastics are plastic fragments less than 1000 nm and are a growing concern within the plastic pollution crisis. They have distinct properties that differ from bulk plastics because of their size, large surface area-to-volume ratio, and their potential to disrupt biological processes once ingested. These particles can be further transported at larger distances and can be carriers for other pollutants via the “Trojan Horse” mechanism. This co-contaminant transport and uptake raise a concern as pollutants bound to nanoplastics can have a larger effect than they would on their own. Hence, understanding the role of nanoplastics as vectors for organic contaminants is crucial for formulating effective strategies to mitigate their adverse effects on aquatic organisms and human health.

This thesis evaluated the adsorption of two different-sized polystyrene nanoplastics (PSNPs) (500 and 20 nm) with various trace organic substances in four types of water matrices. The sorption of plant protection products (glyphosate, methyl parathion), an antidepressant (fluoxetine), a ubiquitous industrial chemical (perfluorooctanoic acid [PFOA]) and a polycyclic aromatic hydrocarbon (phenanthrene) to commercially available polystyrene PSNPs was measured via radiolabeled techniques. The impacts of pH changes, low and high amounts of natural organic matter (NOM), and tertiary-treated wastewater effluent (pre- and post-UV treatment) on sorption were further evaluated.

Based on the calculated sorption coefficients (K_d in L/kg), the sequence of chemicals displaying the highest to lowest sorption affinity towards 20 and 500 nm PSNPs is – fluoxetine > phenanthrene > methyl parathion > PFOA > glyphosate. The sorption of compounds onto PSNPs was impacted by the interactions between the plastics and target chemicals, with cationic (e.g., fluoxetine) and hydrophobic (e.g., phenanthrene) compounds more amenable to sorption. Substances that are negatively charged (i.e., glyphosate) showed poor sorption onto PSNPs due to the electrostatic repulsion between the plastics and the chemical. Although

PFOA has a $\log K_{ow} > 4$, it was found to sorb poorly likely because of its negative charge brought by the ionization of its carboxylic functional group. Overall, 20 nm PSNPs sorb more amounts of chemicals than 500 nm PSNPs suggesting that the ingestion of smaller-sized NPs may be more concerning with regards to the Trojan Horse effect.

The extent of sorption varied based on chemicals and was affected by pH, NOM, and other substances present in treated wastewater effluent (cations, anions). Increasing the pH resulted in more adsorption of fluoxetine and glyphosate in 500 nm PSNPs, while the opposite was observed for PFOA. There were no significant pH-related effects detected in relation to phenanthrene as it was not ionizable. The decrease in sorption was additionally noted in water containing high levels of NOM and in treated wastewater effluent (pre- and post-UV). Although it may be perceived as a positive influence on reducing the availability of chemicals from aqueous environments, the mobility of nanoplastics allows them to cover larger distances and potentially spread contamination to different regions. Their small size also makes them easily digested by a variety of organisms and can subsequently release the contaminants that were initially sorbed.

This thesis has contributed to an enhanced understanding of the sorption mechanisms involving representative organic chemicals on nanoplastics. It also yielded quantitative information (K_d , sorption at various pH conditions) that can hold potential for the development of predictive models to simulate the fate and transport of nanoplastics and their sorbed contaminants across diverse environmental settings. By examining the potentially complex interactions between nanoplastics and pollutants in aquatic environments, researchers can better understand the multipart mechanisms that play to effectively assess their implications for aquatic ecosystem health.

Preface

Afrida Nurain completed this thesis in fulfillment of the requirements related to Master of Science program in the Department of Civil and Environmental Engineering at the University of Alberta. Afrida conducted the experiments and Dr. Maricor Arlos supervised the entirety of this work. All experimental work was completed at the University of Alberta, in the Department of Civil and Environmental Engineering (sample preparation), Department of Biological Sciences (Goss Research Lab - sorption experiments), Department of Chemistry (Veinot Research Lab - Dynamic Light Scattering) and nanoFAB – Fabrication & Characterization Facility (Transmission electron microscopy). A short abstract of the thesis was presented and published for an oral presentation at the 15th International Conference on the Environmental Effects of Nanoparticles and Nanomaterials (ICEENN 2022) and has been accepted for WCW Annual Conference & Exhibition 2023. The project received funding from the Increasing Knowledge of Plastic Pollution Initiative (IKPP) from the Environment and Climate Change Canada.

Dedication

In the realm of thoughts and ink so bright,
This journey does not take like a bird in flight.
Yet Abbu (Dad), with heartfelt cheer,
Your belief has brought me here.
Ammu (Mom), your support like a shining ray,
Help me to find my unique way.

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This thesis is dedicated to my father Late Syed Abdul Halim and my mother Nahin Akter who always believe in me and have the utmost encouragement for higher education abroad.

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I would like to express my profound gratefulness to the Almighty who gives me the ability and strength to complete my research work at the University of Alberta. I express my sincere appreciation for all the support and guidance that I have received during my graduate studies and would have been beyond my reach without them.

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I would like to express my special gratitude to Dr. Greg Goss, Department of Biology, for giving me the support to work in his lab and also a guardian of this project who continuously shared his valuable feedback. His expertise has greatly influenced the direction of the research. I am very much grateful to the Principal Investigator of the project Dr. Jeffrey Farner, Department of Civil and Environmental Engineering for his constructive critique and valuable recommendations that significantly improved the quality of this work, more specifically in the characterization part.

I also would like to mention Dr. Yueyang (Brian) Zhang from the Department of Biology for his assistance in understanding radiolabeled techniques and experiments. I wish to thank Dr. Xuehai Tan from nanoFAB - Fabrication & Characterization Facility for helping me in the TEM of my samples and understanding the explanations. My sincerest thanks to Demi Meier for her assistance in the summer of 2021 with my research work.

I extend my heartfelt thanks to my family, relatives and friends for their unwavering care, patience, and compassion. The encouragement of my mother (Nahin), my brother

(Aaiman) and my beloved husband (Zahid) -- having faith in me was influential in overcoming the challenges and giving emotional support specifically at the time when I lost my dear uncles.

I am grateful to the University of Alberta for providing me with the resources and facilities necessary for conducting this research and a conducive environment for academic growth and learning. Thanks to support me through J. Gordin Kaplan Graduate Student Award for my travel to the International Conference on the Environmental Effects of Nanoparticles and Nanomaterials 2022 in Montreal, QC.

Last of all, I am thankful to all of my Arlos lab members as well as Farner lab members (present and former) for their collective support and encouragement which have been essential in working in a shared lab.

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Chapter 1 – Introduction

1.1 Background

Plastics have been around for over 160 years, with the first type developed in 1862 by dissolving gun cotton (nitrocellulose) in a solvent (mixture of nitric and sulphuric acids) and subsequently moulding this material into other products (Mulder and Knot, 2001). The increase in demand and further advancements in chemical processing technologies led to the mass production of plastics, amassing a worldwide production of 407 million tons in 2015 (Geyer et al., 2017). Modern plastics are inexpensive to produce and have a wide range of properties that are used in a number of applications (Abbasi et al., 2019). Plastic Oceans International, a non-profit organization based in the US, estimated that more than 300 million tons of plastic are produced annually. In 2015, around 6300 Mt of plastic waste was generated, with only 9% being recycled, 12% incinerated, and 79% ending up in landfills or the natural environment (Geyer et al., 2017). High-income countries often produce more waste per capita, but low- to middle-income countries have large amounts of mismanaged waste (i.e., unrecycled). As a result, plastics and plastic debris are ubiquitously found in aquatic and terrestrial environments, and their widespread occurrence has raised concerns regarding their potential for ecological threats (Wang et al., 2019).

Global plastic pollution is further exacerbated by the physical and chemical transformation of plastic debris into micro ($\leq 5 \mu\text{m}$) and nano sizes (1–1000 nm) which are known as micro- and nanoplastics (MNPs) respectively. Most of them decompose very slowly (except for biodegradable plastics) and can accumulate within an organism. This observation is further amplified by a recent study that suggests plastic particles are also present in human blood (Leslie et al., 2022). This is alarming because research conducted on animals and in a laboratory, environment showed that microplastics may have negative effects on human health

(Jung et al., 2022). For example, it has been observed that polystyrene can lead to negative effects on the epithelial cells of the human lungs, including inducing cytotoxicity and inflammation (Dong et al., 2020). Given their potential threat to the ecosystem and human health, no general consensus exists among jurisdictions around the globe regarding plastics management.

1.2 Problem Statement and Hypothesis

In 2019, Canadians consumed a substantial 6,176 kilotons (kt) of plastics in various products, as reported by Statistics Canada (2023). Approximately one-third of plastic packaging within the country comes from single-use plastic food packaging, including items like produce bags, yogurt containers, snack wrappers, and foam food trays (Environment and Climate Change Canada [ECCC], 2023). Alarming data reveals that each year, over 3 million tons of plastic waste are discarded, and approximately 9% undergoes recycling, according to ECCC (2020). Furthermore, the impact of micro/nanoplastic particles (MNPs) extends beyond their lightweight and easy transportability in aquatic environments; these particles can also function as carriers for various chemical compounds. Both these contaminants can permeate in aquatic organisms upon ingestion, subsequently entering the food chain. The adsorption process is influenced by a multitude of factors, including the hydrophobicity of contaminants and plastics, surface area and size of the plastics, environmental conditions (e.g., pH), and the presence of other substances. Overall, the sorption of organic contaminants to MNPs is a complex process influenced by many factors. Understanding the contribution of these factors is important when assessing the environmental fate and potential risks associated with MNPs as vectors of organic contamination.

1.3 Aim and Objectives

The aim of this thesis is to gain an understanding of the sorption behaviour of 5 trace organic chemicals (with a variety of physicochemical properties and uses) on two different-sized (500 and 20 nm) polystyrene (PS) nanoplastics. The substances targeted include plant protection products (glyphosate and methyl parathion), a pharmaceutical compound (antidepressant, fluoxetine), a persistent, mobile, and toxic chemical (perfluorooctanoic acid [PFOA]), and a polycyclic aromatic hydrocarbon that is a byproduct of fossil fuel combustion (phenanthrene). This thesis will address the questions related to the influence of compound and plastic physicochemical properties, pH, presence of natural organic matter (NOM), and influence of other matrices (e.g., wastewater treatment plant effluents) on sorption behaviour. To address the aim of this thesis, the following objectives are formulated:

- i. Examine the impact of sizes of nanoplastics and chemical physicochemical properties on the overall sorption behaviour;
- ii. Investigate the effect of different pH conditions and natural organic matter (NOM) on sorption; and
- iii. Assess the influence of real environmental matrix (i.e., wastewater effluent) on the co-contaminant transport.

1.4 Thesis Outline

The introductory chapter provides background information regarding thesis questions, problem statements, and research aims and objectives. Chapter 2 is a brief review of related and relevant literature and theories, and provides a comprehensive understanding of the history, production, distribution, and disposal of plastic, the current status of plastic pollution, MNP formation, and consequences of co-contamination with other chemical compounds. Chapter 3 presents information about the overall study design, nanoplastic characterization before and after the sorption experiments, nanoplastic sample preparation, and methods employed for

kinetic sorption experiments (pH conditions, NOM, wastewater). It also details quality assurance and data analysis techniques. Chapter 4 outlines the results as provided by descriptive statistics and statistical analysis. It also includes a detailed discussion of the thesis findings followed by Chapter 5 which provides conclusions, study limitations, and evaluation of avenues for future research.

Chapter 2 – Literature Review

2.1 Introduction to Plastics

Plastics are synthetic organic materials with high molecular weights derived from cellulose, coal, natural gas, and crude oil which are manufactured in large quantities through polymerization or polycondensation (Mandal et al., 2020). Documented plastic production began in the mid-19th century and was driven by the needs of the manufacturing industry as in the case of the electric industry in 1907 which demanded plastic insulation. However, it was not until the 1930s that plastics were mass-produced (**Figure 2.1**). In 1862, Alexander Parkes created 'Parkesine', a solvent that could dissolve gun cotton which could then be moulded into various products (Parkes, 1866). Celluloid was invented in 1869 by John Wesley Hyatt for collars and cuffs, but it had several drawbacks like flammability, lack of waterproofing, sunlight damage, and moulding issues (Hochheiser, 1983; Mulder and Knot, 2001). Then, Bakelite, invented in 1907 a phenol-formaldehyde resin which surpassed celluloid in insulation, durability, heat resistance, and mass production suitability (Baekeland, 1909). Plastic production improved after World War I with the creation of different types. PVC was discovered in 1872, but only became commercially produced in the US in the late 1920s (Andrady and Neal, 2009). The mass production of plastics experienced significant growth during the 1940s and 1950s (Thompson et al., 2009) with the introduction of polystyrene, polyethylene, and polypropylene in 1937 (Andrady and Neal, 2009). Improvements in catalysts since 1980 have further improved the production and applications of these polymers.

The majority of plastics consist of organic polymers, with the predominant elements in these polymers being carbon, hydrogen, oxygen, nitrogen, chlorine, and sulfur (Ebbing and Gammon, 2016). Each polymer chain can have several thousand repeating units by polymerization reactions (Hasirci et al., 2011). The process involves two fundamental types of polymerization reactions: addition and condensation (Flory, 1946). The addition is the

formation of polymers from monomers which includes a carbon-carbon double bond by an exothermic addition reaction (Jansen et al., 2016). Polyethylene, Polypropylene, poly (vinyl chloride), and polystyrene are produced through polymerization (Yousif and Hasan, 2015).

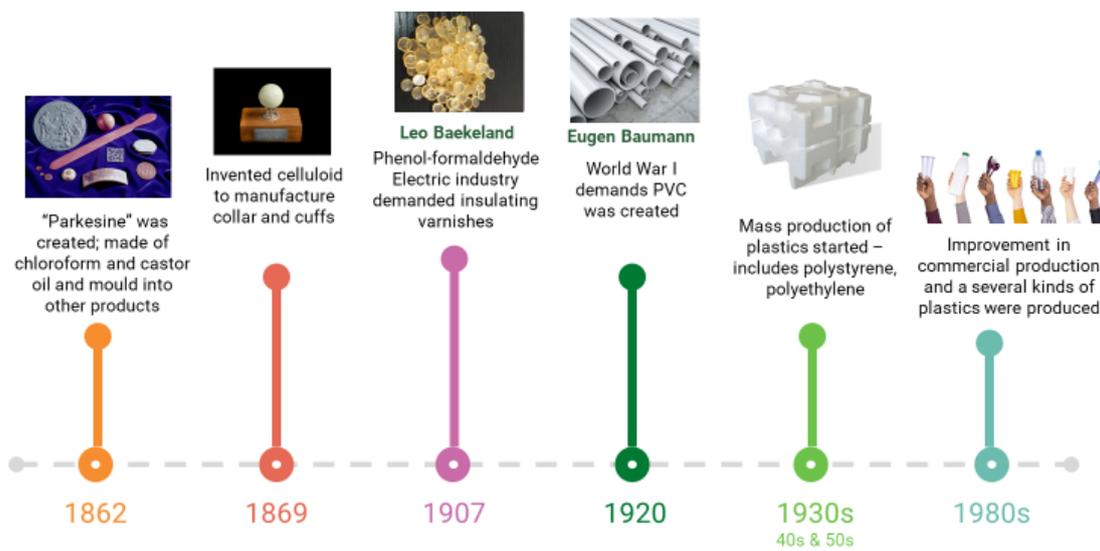


Figure 2.1. History of plastic production beginning in the mid-1800s until the 1980s. Graphics information was taken from Parkes, 1866; Mulder and Knot, 2001; Baekeland, 1909; Andrady and Neal, 2009; Thompson et al., 2009; Andrady and Neal, 2009.

Polymers, owing to their diverse physical attributes, encompass a wide array of functional groups. The process of polymer formation via condensation entails a sequential reaction involving multiple functional groups, often characterized by endothermic behavior that absorbs energy as heat, resulting in the production of byproducts such as water or other small molecules. Polyesters, polyacetals, polycarbonates, and polyamides (PA) are regularly synthesized through condensation reactions. These polymers exhibit several general characteristics: (i) notable chemical resistance; (ii) effective insulation against heat and electricity; (iii) a combination of lightness and varying levels of strength; (iv) diverse processing methods yielding fibers, sheets, foams, and intricate molded components; and (v)

the capacity to augment inherent properties through additives for tailored applications (Ivanov et al., 2001).

2.2 Classification Plastics

Categorized by the chemical structures and temperature responses, plastics can be classified into two primary groups: (i) thermoset and (ii) thermoplastic (Demaid, 1996).

Thermoset plastics exhibit robust qualities like high elastic modulus, durability, and resistance to heat and chemicals due to their dense cross-linking (Asim et al., 2017). Thermosets find prominent use in construction applications encompassing adhesives, sealants, insulation, roofing, flooring, pipes, bridges, cementing, and civil structure rehabilitation (Agarwal and Gupta, 2018). Various thermoset types, such as phenolics, amino plastics, melamine formaldehyde, polyesters, epoxies, and polyurethanes, are available (Crawford and Martin, 2020). In contrast, **thermoplastics** undergo multiple heating and cooling cycles without damage and constitute around 80% of the total plastics consumption (Biron, 2018). Key thermoplastics include polyethylene, low-density polyethylene (LDPE), and high-density polyethylene (HDPE) (Vivaldo-Lima and Saldívar-Guerra, 2013). Within the realm of thermoplastics, two categories emerge: amorphous and crystalline (Demaid, 1996). **Amorphous** plastics lack discernible crystalline structures in X-ray and electron scattering tests but encompass materials like polycarbonate, acrylic, polyethylene terephthalate glycol, acrylonitrile butadiene styrene, and polysulfone (More et al., 2021), often utilized for crafting goggles, medical devices, and kitchen utensils. On the other hand, **crystalline** plastics consist of randomly distributed crystalline units, including short-fibre reinforced plastics (Gradin et al., 1989). Examples of crystalline polymers encompass polyethylene and copolymers, polypropylene, polyesters, and nylons (Cheng and Jin, 2002). A significant disparity between these two plastic classes is that crystalline plastics possess specific melting points while

amorphous ones do not (Rosato, 2003), making crystalline plastics better suited for high-temperature resistant packaging needs.

2.3 General application of plastic products

Plastics have a diverse range of applications spanning across various industries, including packaging, construction, textiles, consumer goods, transportation, electronics, and industrial equipment (Filho et al., 2019). Their incorporation in transportation, construction, and packaging sectors brings about crucial material and energy savings (Andrady and Neal, 2009). Plastic packaging is essential for safeguarding, preserving, storing, and transporting goods. Its attributes, such as durability, lightweight nature, and design flexibility surpass the capabilities of glass and metal (Hedenqvist, 2005), ensuring products remain in excellent condition for consumption and other purposes. Plastics play a pivotal role in supplying and storing clean drinking water as water management gains prominence in urban areas. Within the construction field, plastics find utility in seals, windows, doors, pipes, cables, floor coverings, and insulation (Cousins, 2002) due to their non-corrosive nature and freedom from frequent repainting (Rayner, 1960). The electrical and electronics industry greatly benefits from plastics' insulating and robust properties, as evident in their use in video cassette recorders, CD players, computers, televisions, kitchen appliances, and more. The adaptability of plastics is also a boon for the automotive, aerospace, rail, and marine transportation sectors, where they serve purposes ranging from glazing and wall panels to seating, flooring, and light diffusers. This adaptability is especially valuable for lightweight and cost-effective transportation of both people and products (British Plastics Federation, 2016). Plastics are playing a crucial role in safeguarding goods, enabling efficient construction, enhancing electronics, and offering versatile solutions for transportation needs (Fan and Njuguna, 2016).

2.4 Plastic waste generation – Macroplastics to micro- and nanoplastics (MNPs)

Plastic waste generation is influenced by primary plastic use and its product lifetime. Packaging has a significantly short lifetime, generally ~6 months or less (Geueke et al., 2018). For building and construction, plastic use has an average lifetime of 35 years (Ritchie and Roser, 2018). Among them, packaging is the main producer of plastic waste which is accountable for almost 50% of the world, and of the plastics produced, approximately three-quarters (302 million tons) end up as waste (Geyer et al., 2017). Better solid waste facilities allow developed nations to manage plastic pollution despite them being the highest contributor to plastic pollution. However, developing/low-income countries lack appropriate solid waste management facility and framework and are therefore more impacted by plastic pollution (Nkwachukwu et al., 2013).

Large plastic debris, also called as macroplastics, can affect the aquatic environment and has long been the subject of environmental research due to their impact on wildlife (via ingestion), their habitat (e.g., alteration of seagrass beds, rocky shores), and overall water quality (via accumulation and shoreline washup) (Cole et al., 2011). Small plastics enter the environment directly while larger items often fragment overtime (Barnes et al., 2009; Sul and Costa, 2013), forming another sub-pollutant group called microplastics (MPs).

Microplastics are associated with diverse size-ranges, with different diameters - <10 mm (Graham and Thompson, 2009), <5 mm (Barnes et al., 2009, Betts, 2008), 2–6 mm (Derraik, 2002), <2 mm (Ryan et al., 2009) and <1 mm (Browne et al., 2007, Browne et al., 2010, Claessens et al., 2011). Andrady (2011) recommends adding the word “mesoplastics” to the scientific nomenclature for differentiating between small plastics visible to the human eye versus those only observable via microscope (Cole et al., 2011).

MPs are further sub-classified into: primary and secondary microplastics. Primary MPs are originally produced to be microscopic (Cole et al., 2011) and have been produced for facial cleansers and cosmetics (Zitko and Hanlon, 1991), air-blasting media (Gregory, 1996), and

pharmaceuticals (Patel et al., 2009). Secondary microplastics are represented as small plastic fragments originating from the breakdown or weathering of larger plastic trash (Thompson et al., 2004; Ryan et al., 2009; Cole et al., 2011). The degradation (Figure 2.1) occurs via biodegradation (microorganism-driven), photodegradation (light-driven), thermal degradation (high temperature), thermo-oxidative degradation (chemical breakdown due to high temperature and oxygen exposure), and hydrolysis. A combination of these physical (via abrasion), biological and chemical processes can reduce the structural integrity of microplastics, resulting in further fragmentation (Browne et al., 2007; Cole et al., 2011). These fragments are termed nanoplastics (NPs) and are generally considered more ecotoxicologically important than microplastics because their nano-size has a greater potential to enter and harm living organisms at the cellular level (Patra et al., 2022). A vast majority of NPs are derived through fragmentation (i.e., secondary NPs), but similar to MPs, they are also found in personal care products (Joksimovic et al., 2022), can be discharged directly from textiles/clothing (Landeros et al., 2022), and released in food packaging (e.g., steeping of tea in plastic teabags) (Hernandez et al., 2019). They can enter into different environmental compartments in various ways including from wastewater (Ali et al., 2021) and atmospheric deposition (Bianco and Passananti, 2020).

There is no precise definition of NPs, although there is a general consensus that any plastic from 1 nm to 1 μm (1000 nm) is considered nanoplastics (Gigault et al., 2018). This definition will be used throughout this thesis for consistency. Furthermore, NP distribution in the environment is also complex, and are ubiquitous in aquatic environments. However, challenge on the identification methods continue to hinder the ability to further characterize NPs. Many approaches require different sizes to be separated first (e.g., centrifugal, electrical or gravitational) and then identified via several nanomaterial characterization methods including visualization (via microscopy), nanoparticle distribution, hydrodynamic diameter, and zeta potential. Chemical identification can be further completed via FTIR and Raman

microscopy as examples. The subsequent sections below discuss the distribution of micro- and nanoplastics (MNPs) in freshwater, wastewater, and drinking water systems.

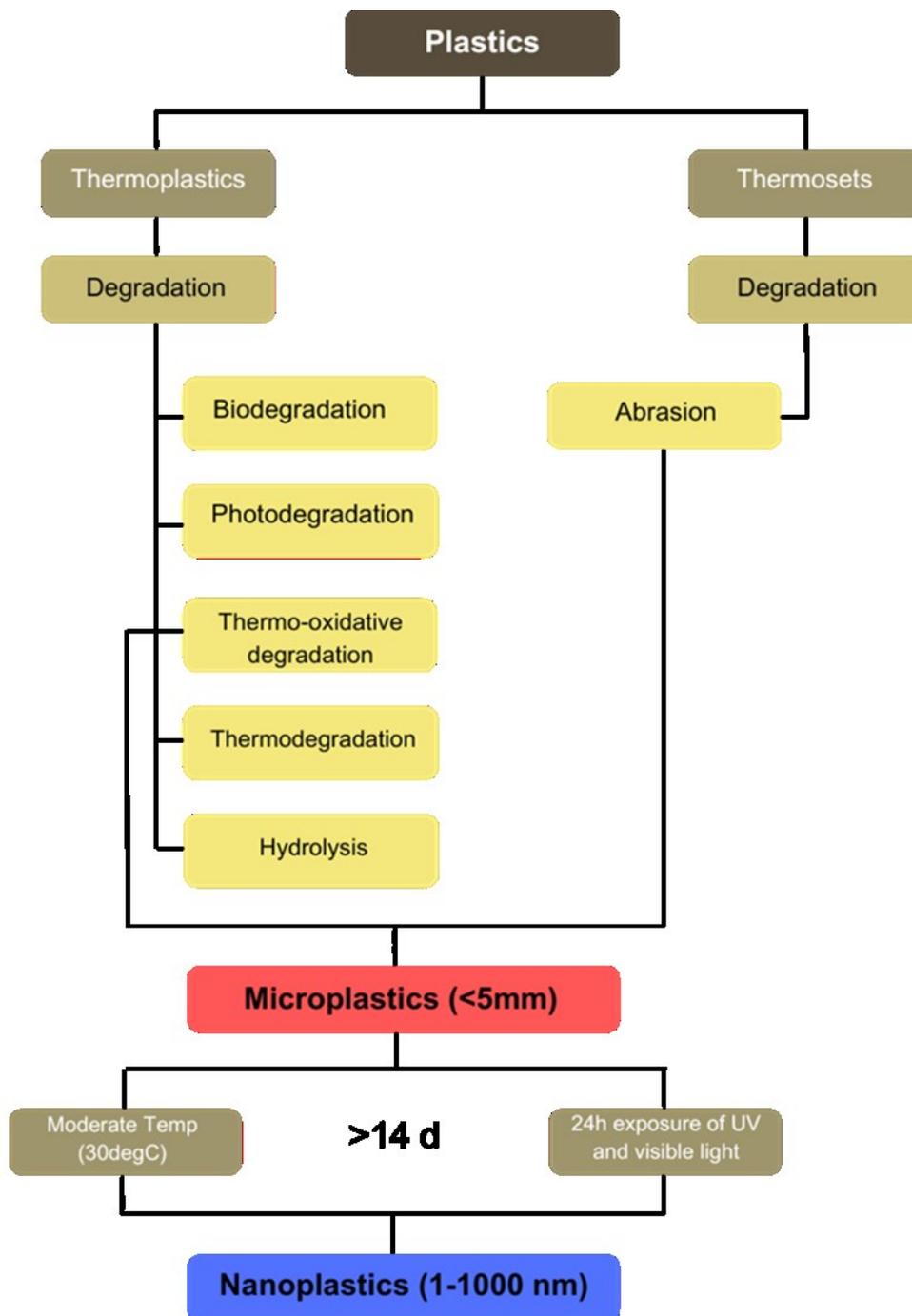


Figure 2.2 Pathway of environmental degradation of “macro” plastics to micro- and nanoplastics (MNPs), often categorized as “secondary” MNPs. MNPs can also be produced as “microscopic” and enter the environment in its original form. Figure adapted from Jiang et al., 2020. Temp = temperature

2.5 Micro- and nanoplastic (MNP) distribution mechanism

According to the data of global total mismanaged plastic waste in 2019, South Asia (~25.26 million tons) has seen more mismanagement than North America (Meijer et al., 2021) (Figure 2.3). Asia is home to most of the rivers that are major contributors to plastic pollution. (Jambeck et al., 2015). Among microplastics, secondary microplastics are the predominant presence in marine ecosystems, primarily attributed to the continuous fragmentation of larger plastic materials (Ajith et al., 2020; Vaid et al., 2021). Non-biodegradable plastics undergo photo-oxidative degradation from UV solar radiation, followed by thermal or chemical degradation in the marine environment (Grassie and Scott, 1988; Shah et al., 2008) and break down to nanoplastics (Jiang et al., 2020). Piperagkas et al., (2019) observed that MP distribution along the beaches is also influenced by their physical characteristics (shape, size) as well as environmental properties such as wind direction (Ajith et al., 2020).

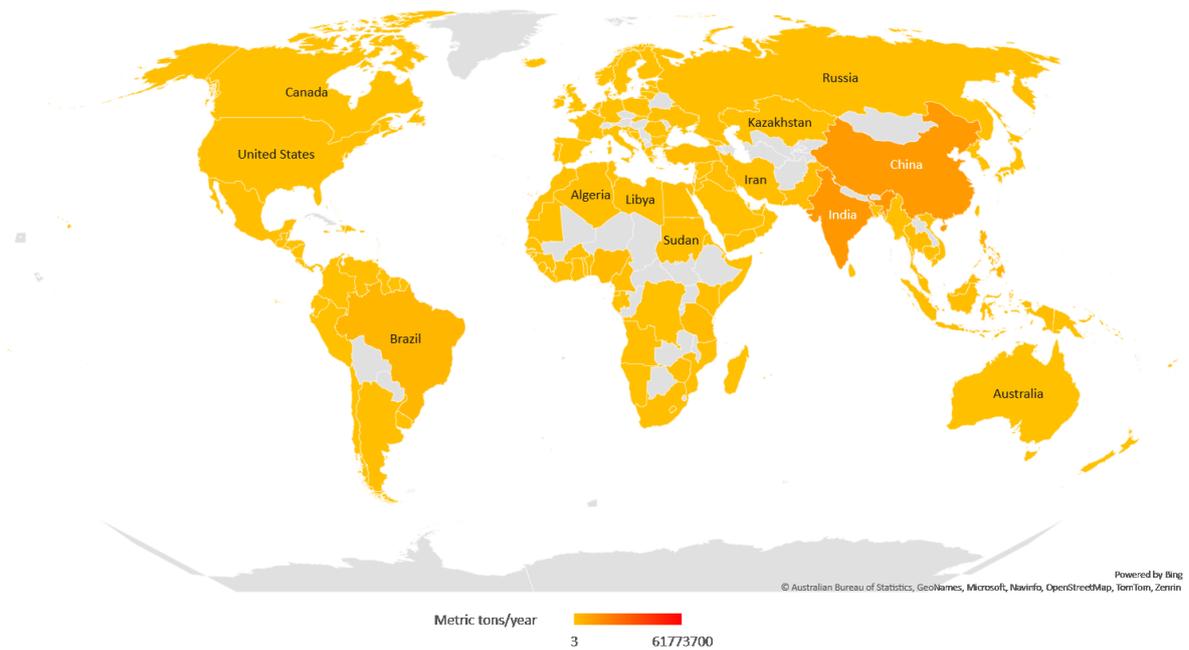


Figure 2.3 Global total mismanaged plastic waste in 2019 (plotted data from Meijer et al., 2021, grey shade means no data available)

The distribution of microplastics in the open ocean is influenced by both their physical and chemical characteristics. Plastic debris, including most synthetic polymers, exhibit buoyancy in water and consequently, they often end up being washed ashore, as discussed by Sul and Costa (2013). However, polymers that are denser than seawater can settle but may still be transported by underlying currents (Sul and Costa, 2013). A significant portion of microplastics originating from terrestrial sources enters the marine environment via rivers and estuaries, a process known as ecocline, as highlighted by Barletta et al. (2019).

Although both MPs and NPs aggregate in the environment, NPs are more susceptible to aggregation and can substantially impact their environmental fate. Particle size, composition, surface modification, electrolyte type, pH, DOM, surfactant, light and microorganisms can have the impact of the aggregation of microplastics (Wang et al., 2021). Due to anthropogenic and natural hydrological conditions plastic particles deposit in the waterbody (D'Avignon et al., 2021).

2.6 Micro- and nanoplastics in freshwater

Microplastics exposure have been shown to have undesirable effects on aquatic organisms including impacts on growth, development, and reproduction such as disrupting hormone levels (Issac and Kandasubramanian, 2021). The mean abundance of microplastics in freshwater was found to be 4.9 particles/m³ globally but the concentration can differ based on the location and the sources of the microplastics. Inadequate data are found on microplastics in developing countries (Eerkes-Medrano et al., 2015). A few examples of microplastic detections in freshwater along with the identification, abundance, composition and other related information are found in the **Table 2.1**.

Table 2.1 Microplastics in freshwater as reported in selected studies. PETE = Polyethylene terephthalate, PP = Polypropylene, PE = Polyethylene, PS = Polystyrene, PVC = Poly Vinyl Chloride, H₂O₂ = hydrogen peroxide, PDAC = Polyallyl diglycol carbonate, FTIR = Fourier transform infrared, SEM = Scanning electron microscope, EDS = Energy dispersive spectroscopy, Visualization = Microscopic findings

Freshwater	Location	Purification method	Separation substrate	Identification method	Mean Abundance (particles/ m ³)	Composition	Reference
Jajroud river	Iran	-	-	Stereomicroscope and FTIR	1.47 ± 0.14 p/m ³	PS, PP	Shekoohiyan and Akbarzadeh, (2022)
Austrian Danube	Austria	-	-	Visualization	0.317 p/m ³	-	Lechner and Ramler, (2015)
Rhine river	Netherlands	Enzyme + H ₂ O ₂	Sieves	Stereomicroscope and FTIR	8.92 × 10 ² p/m ³	PS, PP, PE, PVC	Mani et al., (2015)
Dutch river delta and Amsterdam canals	Netherlands	-	0.7 mm glass filters		1 × 10 ⁵ p/m ³	-	Leslie et al., (2017)
Great Paris	France	-	1.6 mm filter	Visualization	30 p/m ³	-	Dris et al., (2015)
Great Paris	France	-	1.6 mm filter	Visualization	0.35 p/m ³	-	Dris et al., (2015)
Three Gorges Dam	China	-	1.6mm stainless sieve		8.47 × 10 ⁶ p/m ³	PE, PP, PS	Zhang et al., (2015)
Three Gorges Dam	China	30% H ₂ O ₂	0.45 mm glass microfiber filter	Visualization through Raman Spectroscopy	4.70 × 10 ³ p/m ³	PP, PE	Di and Wang, (2017)
Yangtze Estuary	China	30% H ₂ O ₂	1.2 mm cellulose nitrate filters	Visualization	4.14 × 10 ³ p/m ³	-	Zhao et al., (2014)
Lakes Wuhan	China	30% H ₂ O ₂	0.45 mm glass microfiber filter		-	PETE, PE	Wang et al., (2017)

Table 2.1 Continued

Freshwater	Location	Purification method	Separation substrate	Identification method	Mean Abundance (particles/ m³; particle/km²)	Composition	Reference
Taihu lake	China	30% H ₂ O ₂	47-mm-diameter filter	+ SEM-EDS	-	PP	Su et al., (2016)
Lake Winnipeg	Canada	30% H ₂ O ₂	250 mm sieve	SEM-EDS	1.93 × 10 ⁵ p/km ²	-	Anderson et al., (2017)
Los Angeles river, San Gabriel river, Coyote Creek	USA	-	Tyler sieves	Visualization	-	PS	Moore et al., (2011)
Milwaukee River Basin to Lake Michigan, USA	USA	-	Water column: neuston net 333-µm mesh	FTIR spectroscopy	0.21 to 19.1 particle/m ³	PP, PETE	Lenaker et al., (2019)
29 Great Lakes Tributaries	Canada	30% H ₂ O ₂ + Fe	125 mm sieve	Visualization	4.2 p/m ³	-	Baldwin et al., (2016)
Laurentian Great Lakes	USA	2M HCl	Tyler sieves	SEM-EDS	4.30 × 10 ⁴ p/km ²	PS, PES, Acrylic, <i>PADC</i> ,	Eriksen et al., (2013)
Raritan River	USA	30% H ₂ O ₂ + Fe	Sieves	Visualization	-	-	Estahbanati and Fahrenfeld, (2016)
Goiana Estuary	USA	-	45 mm mesh	Visualization	3.1 × 10 ⁴ -2.6 × 10 ³ p/m ³	-	Lima et al., (2014)

Table 2.2 Selected studies showing the micro- and nanoplastic pollution in wastewater treatment plant (WWTP), DF = Disc-filter, RSF = Rapid sand filtration, SAF = Sand filter

Location	WWTP Capacity (m ³ /day)	Treatment Process	Source of WWTP	Influent MP Abundance (MP/L)	References
Cartagena, Spain	35,000	Primary, Secondary	Municipal and Industrial	1.08	Bayo et al., 2020
Daegu, Korea	26,545	Primary, Secondary, Tertiary (Coagulation, O ₃)	Municipal and Industrial	4200	Hidayaturrahman & Lee, 2019
Daegu, Korea	469,249	Primary, Secondary, Tertiary (Coagulation, DF)	Municipal and Industrial	31,400	Hidayaturrahman & Lee, 2019
Daegu, Korea	20,840	Primary, Secondary, Tertiary (Coagulation, RSF)	Municipal and Industrial	5840	Hidayaturrahman & Lee, 2019
Turku, Finland	-	Tertiary Rapid Sand Filtration	Municipal	0.7	Talvitie et al., 2017
Vancouver, Canada	493,271	Primary, Secondary	Municipal	21.5	Gies et al., 2018
Northern, Italy	400,000	Primary, Secondary, Tertiary (SAF)	Combined sewers	2.5	Magni et al., 2019

2.7 Micro- and nanoplastics in wastewater

Microplastics have been found in wastewater effluent (Mani et al., 2015) suggesting the contribution of municipal wastewater treatment plants (MWWTPs) to MNP pollution (Sun et al., 2019). MWWTPs are not generally designed to remove these particles (Leslie et al., 2017), and sources of MNPs in wastewater treatment plants are mainly from primary MNPs such as personal care products which contain microbeads (Chang, 2015), and a study by Napper et al (2015) showed that a single-use exfoliant wash can release 4500–94,500 microbeads. The concentration of MNPs in wastewater may change for several factors, including production rate, sales and usage of products, per capita water consumption/day, and climatic conditions (Goswami et al., 2018). Another research result states that toothpaste releases around 4000 microbeads per usage (Carr et al., 2016). Although MNPs are highly removed during wastewater treatment, a significant volume of microplastics are found in effluents and discharged after the treatment (Murphy et al., 2016, Talvitie et al., 2017). **Table 2.2** outlines a review of MNP pollution in WWTPs across the globe.

Removals vary depending on the treatment and also the conditions of each unit process. Combined coagulation, flocculation and sedimentation had shown poor removal efficiency of microplastics (Zhang et al., 2020). With the coagulation process, highest 81.6% of MP removal efficiency has been obtained from the study of Hidayaturrahman and Lee, 2019. Primary and secondary treatment for wastewater can remove MPs from 78 to 98% depending on concentration (Carr et al., 2016; Talvitie et al., 2017). Membrane bioreactor (MBR) was found to remove MPs by >98% efficacy (Lv et al., 2019, Lares et al., 2018) and was further improved when secondary sedimentation was applied (~99.5%) (Lv et al., 2019) suggesting that WWTPs can be optimized to improve MNP removals. Microplastic particle removal efficacy by MBR was 98.83%, and overall microplastic removal efficacy was 79.01% (Bayo et al., 2020).

A survey of a WWTP in Finland suggested that the rapid sand filtration (RSF) process removed 97.1% MPs (0.7–0.02 MP/L) and capably eradicated the smaller sized MPs (0.02–0.1 mm) (Talvitie et al., 2017). A similar study is observed that the removal percentage of MPs in the RSF process stage was 73.8% in higher concentrations of 433 MP/L in influent (Hidayaturrehman and Lee, 2019), which indicates the efficiency will decrease with an increase of high-concentration plastics. Besides, the RSF process for MPs removal WWTP is more significant compared to dissolved air flotation, granular activated carbon and membrane filtration (Ahmed et al., 2021). When RSF was used with coagulation, the overall removal efficiency improved from 73.8 to 98.95% (Hidayaturrehman and Lee, 2019). Moreover, the coagulation process improved the reduction efficiency of MPs, if it is operated before the disc filter (Ahmed et al., 2021).

Diverse physical, chemical treatment and biological treatment technologies have been applied to remove MPs from water including sedimentation, rapid sand filtration, adsorption, coagulation/flocculation and activated sludge. According to Xu et al. (2018), the removal of microplastic fibres emerges in the early stage of sedimentation. The sedimentation with scum and grease removal process decreases the fibre MPs by 92.8% (Gies et al., 2018 and Magni et al., 2019). With sufficient retention time, larger MPs removed a higher percentage than smaller-sized MPs by sedimentation (Hamidian et al., 2021). Arenas et al., 2022 showed that 88.1% of nanoplastics are removed by filtration. Due to the economic feasibility, rapid sand filtration (RSF) is the most applied water treatment (Ahmed et al., 2021), which lowered MPs from wastewater also (Simon et al., 2018). Granular activated carbon (GAC) and biochar (BC) are broadly operated as adsorbents to treat MP-contaminated stormwater (Ahmed et al., 2016). Specifically, steam-activated BC has experimented as an appropriate adsorbent for MPs removal from water (Siipola et al., (2020) but the process is quite expensive. When MPs wash through an adsorption column packed with AC, it works as good filter unit (Zhang et al., 2020).

2.8 Micro- and nanoplastics in drinking water

MNPs have been found in tap water (Tong et al., 2020) and bottled drinking water (Gambino et al., 2022). Polymers associated with MNPs have been found in drinking water in Barcelona (Vega-Herrera et al., 2022), highlighting the widespread occurrence of MPs in our environment and drinking water and raising concerns about potential impacts on human health. Recent studies demonstrate the significant presence of MPs in our environment, and drinking may cause the potential impact on human health (Katyal et al., 2020). This emphasizes the need for effective treatment methods to remove these particles from drinking water source and its additional implementation to ensure safe consumption. Some water treatment processes are very effective to remove micro/nanoplastics. For example, granular filtration is very effective at filtering out micro- and nanoplastics, from 86.9% to nearly complete removal (99.9% for particles larger than 100 μm) (Zhang et al., 2020). Another study also revealed that coagulation/flocculation combined with sedimentation (CFS) had limited efficiency, while granular filtration exhibited higher effectiveness, particularly for particles above 100 μm (Murray and Örmeci, 2020). While certain treatments have successfully removed particles, it is important to understand that even a small number of particles escaping treatment can result in higher nanoplastics concentrations in the water body.

2.9 Sorption behavior of micro- and nanoplastics (MNPs)

Micro- and nanoplastics (MNPs) exhibit a large capacity for adsorbing both heavy metals and organic compounds, with smaller-sized MNPs displaying a heightened propensity for capturing these pollutants compared to their larger counterparts. This phenomenon stems from the increased surface area inherent to smaller MNPs, offering a large number of adsorption sites, thereby enhancing their pollutant uptake capability (Zhang et al., 2019).

MNPs, in general, showcase a greater affinity for adsorbing hydrophobic pollutants, suggesting a potential interplay between hydrophobic and hydrophilic compounds (Fu et al.,

2021; X. Liu et al., 2019). The intricate dynamics of adsorption are also influenced by environmental factors such as pH and salinity, especially notable in marine contexts, where the interplay of ionic charges between microplastics and contaminants becomes pivotal (Yu et al., 2019). Zhao et al. (2022) further underscore the role of temperature, functional groups present on plastics, and the aging process of plastics as influential parameters affecting adsorption behavior.

Specific organic compounds, including phenanthrene, nitrobenzene, and naphthalene, have shown variable adsorption behaviors on microplastics, which are linked to the size and crystallinity of the microplastics themselves (Wang et al., 2019). Intriguingly, the ingestion of smaller-sized plastics has been associated with observed developmental changes in aquatic organisms (Bringer et al., 2020). While the bioavailability of trace chemicals adsorbed onto exposed aquatic organisms remains an area of ongoing research, there is a consensus about their potential for harm (Cormier et al., 2021; Yu et al., 2022; Zhu et al., 2022). The concentration and adsorption concentration have been identified as significant factors influencing the adsorption process (Liu et al., 2018; Bao et al., 2021). These multifaceted dynamics collectively emphasize the intricate interplay between MNPs, pollutants, and the aquatic environment, urging further investigation for a comprehensive understanding of their potential impacts.

2.10 Environmental and human health impacts of micro- and nanoplastics

Due to their size, MNPs is characterized to have a long-range transport and can therefore travel into and out of environmental compartments easily. Their presence in the environment can have potential impacts on ecosystem structure and function. As microplastics are ubiquitously found in water bodies, it is very natural to detect them in aquatic organisms like fish, turtles and other aquatic organisms at the higher food web levels.

The existence of MPs in our environment and drinking water have garnered significant attention worldwide because of the potential effects on human health (Lehner et al., 2019, Katyal et al., 2020). It is estimated that humans may be consuming 39,000 to 52,000 microplastic particles a year (Cox et al., 2019) and more recently, Schwabl et al. (2019) detected various microplastics in human stool. A recent finding showed the presence of plastic particles found in human blood with an ~ mean concentration of 1600 $\mu\text{g/L}$ (Leslie et al., 2022). Prata et al. (2020) suggest that exposure to microplastics could lead to particle toxicity, oxidative stress, inflammation, and increased uptake or movement within organisms. Also, the immune system function can be influenced by chronic inflammation and increase the risk of neoplasia (abnormal growth of cells) in all biological systems (Prata et al., 2020). As nanoplastic pollution is an emerging research area, still, a lot of studies are needed to confirm the core health impacts on humans.

MNPs also represent a potential threat to soil biota due to changes in soil habitat (Machado et al., 2018). Around 32 % of all plastic manufactured is environmentally available in continental systems (Jambeck et al., 2015) and soils might store more MNP litter than oceanic basins (Nizzetto et al., 2016, Machado et al., 2018). It includes agricultural/farmland, greenhouse, home garden, coastal, industrial and floodplain soils, with a wide array of concentrations.

While aquatic microplastic pollution has been well documented, information about MNP pollution in the air is still limited (Chen et al., 2020). MNPs are probably transferred to air and are quickly carried by the wind, because of their small size and low density (Chen et al., 2019, Allen et al., 2019). Compared to MNPs in other ecosystems, MNPs in the air are able to be directly inhaled into the human body, posing additional health risk (Gasperi et al., 2018; Prata, 2018).

Beside MNPs, the aquatic environment also accumulates many classes of organic contaminants ranging from conventional priority pollutants (such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides like dichlorodiphenyltrichloroethane (DDT)) (Bakir et al., 2014) as well as emerging substances of concern (e.g., pharmaceuticals, personal care products). It has been hypothesized that organic contaminants can attach and adsorb onto MNPs, and due to their long-range transport, they can carry with them these harmful contaminants that exacerbate the impact of individual pollutants (Li et al., 2015, Koelmans et al., 2016, Toussaint et al., 2019). This is known as the “Trojan Horse Effect” or simply called the co-contaminant transport. It is therefore possible that their co-presence can enhance toxicity as the combined effect of the plastic particle and the chemical contaminant may be more toxic than either one alone.

2.11 Co-contamination of nanoplastics with organic compounds

Co-contamination of nanoplastics with organic molecules refers to the simultaneous existence of both substances in a medium (it could be soil, water, air or others). These can happen for a variety of ways, for example, the co-release of chemicals from the same sources into the environment or the adsorption of organic molecules onto the surface of nanoplastics. Moreover, it may have an impact on the chemical and physical characteristics like bioavailability, toxicity, and aggregation behavior (Lu et al., 2018). **Table 2.3** shows recent studies on the co-contamination of chemical compounds with nanoplastics and their influences on aquatic organisms. It has been observed that MNPs can increase pesticide adsorption level and co-exposure can create additional ecotoxicological effects (Junaid et al., 2023). Not only the aquatic organisms, but exposure to a combination of MNPs, heavy metals, and pharmaceuticals can also trigger a hormetic adaptive response in edible plants (Naziri et al., 2023). Also, combined exposure of polystyrene microplastics and antibiotics can be adsorbed by plant roots, shoots and leaves and also can impact their metabolism (Khan et al., 2023).

However, one study showed that polystyrene nanoplastics could reduce cadmium-induced toxicity in wheat partially, and was found to be helpful abatement to metal contamination. Therefore, it is essential to explore which factors are behind the increasing or decreasing toxicities so the co-contamination of NPs with organic chemicals can be effectively understood. This is especially important when assessing the risk related to their environmental fate, transit, and possible dangers to ecosystems and human health.

Table 2.3 Micro/nanoplastics (MNPs) co-contamination with other chemicals in water and their additional impact on toxicities

Chemical Compound	Micro/nanoplastic	Organism	Toxicity	References
Glyphosate	Polyethylene (PE) and polyethylene terephthalate/polyamide	<i>Daphnia magna</i>	modified the toxicity and mortality increased	Zocchi and Sommaruga, 2019
Glyphosate	Polystyrene	<i>Daphnia magna</i>	increased immobility, production of reactive oxygen species (ROS), and decreased swimming activity and reproduction	Nogueira et al., 2022
Cadmium	Polystyrene	Zebrafish (<i>Danio rerio</i>)	increased apoptotic cells in both vertebral body and esophagus	Chen et al., 2022
Lead	Polystyrene	Zebrafish	influenced enterocytes, macrophages, B cells, T cells, and goblet cells	(Yu et al., 2022)
PAH	Polystyrene	Zebrafish (embryo)	increased the uptake of PAH, changed in gene expression related to oxidative stress, inflammation, and immune response in the embryos	Zhang and Goss, (2020)
Benzo[a]pyrene (BaP)	Polystyrene (mPS), Polyethylene terephthalate (mPET)	Algae <i>Chaetoceros muelleri</i>	inhibited the growth, photosynthesis, and antioxidant capacity	Su et al., 2022
Cadmium	Not mentioned (anonymous nanoparticles)	Largemouth bass (<i>Micropterus salmoides</i>)	triggered oxidative stress, intestinal microbiota dysbiosis	Chen et al., 2023
Methylmercury	Polystyrene	Zebrafish larvae	aggravate neurotoxicity even in low dose	Zhu et al., 2022
Chlorpyrifos	Polystyrene	Zebrafish	negative impacts of growth and behavior	Huang et al., 2023

Chapter 3 – Materials and Methods

3.1 Materials

The 500 nm and 20 nm fluorescent polystyrene nanoplastic solutions (2% solids) in 2 mM sodium azide were purchased from Thermo Fisher Scientific. Both particles have a density of 1.055 g/cm³ and a manufacturer-reported surface area of 1.1×10^{11} and 2.1×10^{11} cm²/g, respectively (Supplier Certificate of Analysis). The concentrations of 500 nm and 20 nm particle stock solutions are 2.9×10^{11} and 1.9×10^{15} particles/mL, respectively. The equivalent mass concentration of the nanoplastic solution is 20 g/L. The nanoplastics were kept in the dark at 4°C and were sonicated (Branson 5800, ultrasonic cleaner) for 15 min prior to any experiments to ensure a homogenized nanoplastic solution. The ¹⁴C-labeled compounds (glyphosate, methyl parathion, fluoxetine, perfluorooctanoic acid [PFOA] and phenanthrene) were purchased from the American Radiolabeled Chemicals and were stored in a locked refrigerator for radioactive materials until use. Additional properties of the radiolabeled chemicals included in this study is shown in Table 3.1. Ultrapure water was obtained from a MilliQ IQ 7000 purification system with a resistivity of 18.2 MΩ-cm (25°C) and total organic carbon (TOC) ≤ 5 ppb.

The experiments were conducted using OECD (Organisation for Economic Co-operation and Development) water as a base water matrix. OECD water contains 0.29 g/L CaCl₂ (calcium chloride), 0.12 g/L MgSO₄·7H₂O (hydrated magnesium sulphate or epsomite), 0.06 g/L NaHCO₃ (sodium bicarbonate) and 0.006 g/L KCl (potassium chloride). These compounds were purchased from Fisher Scientific (ACS grade). Centrifugal filtration was done through Amicon Ultra-2 Centrifugal filter units (10 kilodaltons). The liquid scintillation cocktail (LSC) was purchased from PerkinElmer (Ultima-Gold, Catalog #6013309). The amount of radioactive materials in each trial was measured using a beta counter (Hitachi AccuFLEX LSC-8000). The Suwanee River Natural organic matter (NOM) and alginic acid

were purchased from the International Humic Substances Society. The chemicals (CaCl₂.2H₂O, MgCl₂ 6H₂O, NaNO₃ CaSO₄.2H₂O) used to prepare synthetic water were purchased from Fisher Scientific (ACS grade).

Table 3.1 Properties of 14C-labeled chemical compounds are included in this thesis. PFOA = perfluorooctanoic acid; “+” = Positive; “-” = Negative; “~” = Neutral; “≠” = Non-ionizable. LogKow = octanol-water partitioning coefficient, LogDow = pH corrected LogKow. Information for LogKow, LogDow, and charge (both at pH 8) collected from <http://chemicalize.com>.

Properties	Glyphosate	Methyl Parathion	Fluoxetine	PFOA	Phenanthrene
Class	herbicide	insecticide	antidepressant	industrial chemical	PAH
Concentration (mCi mL ⁻¹)	0.1	0.1	0.1	0.1	0.1
Molecular Weight (g/mol)	169.1	291.3	345.79	436.05	178.2
Specific Activity (mCi mmol ⁻¹)	50	75	55	55	55
Solvent	Sterile water	Toluene in sealed ampoule	Ethanol	Ethanol	Ethanol
LogDow (pH 8)	-7.75	2.60	2.76	1.58	3.95
LogKow	-3.10	2.60	4.17	5.11	3.95
Charge (pH 8)	-1.97	~	+0.96	-1.00	≠

3.2 Study design

This thesis completed a set of experiments as shown in Figure 3.1 which begins with material characterization, method development for sorption experiments via radiolabeled techniques, adsorption kinetics, and finally, assessing the impacts of pH, NOM, and wastewater matrices on sorption of chemicals on 500 and 20 nm PSNPs. The specific experimental conditions are described subsequently below.

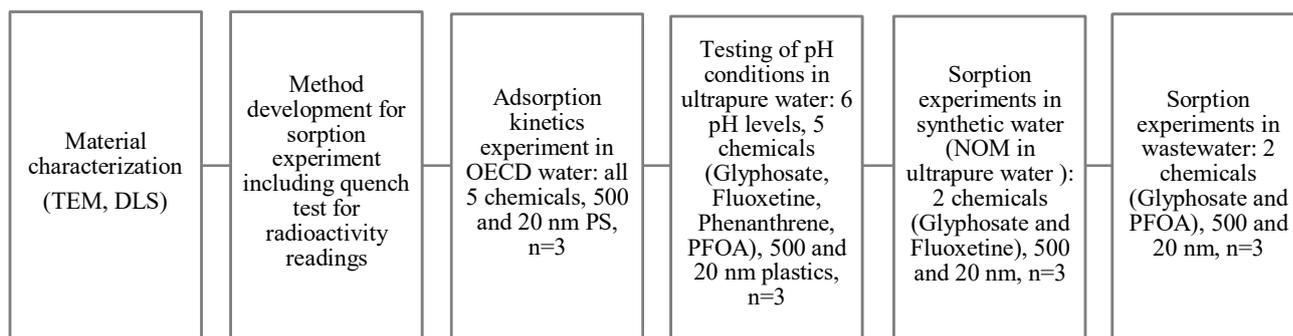


Figure 3.1 Layout of the experiments completed in this thesis.

3.3 Characterization of nanoplastics

The nanoplastic samples were visually characterized in transmission electron microscopy (TEM) using JEOL JEM-ARM200CF S/TEM located in the nanoFAB, Fabrication & Characterization Centre, University of Alberta. TEM settings used include 0.23 nm point resolution and 0.10 nm lattice image at 200 kV, whereas the S/TEM resolution is 0.10 nm (Darkfield, DF lattice image at 200 kV). TEM analysis was used to visualize the structure of the sample at high resolution and STEM was utilized for elemental mapping of a particular area of interest. Continuous ultrathin carbon film grids (copper grid) were purchased from the nanoFAB and used for TEM imaging. A copper grid was placed on a filter paper in a petri dish, where a 5 μ L sample was added for priming and analysis before leaving the grid to dry in a cabinet overnight.

Dynamic Light Scattering or DLS analysis (Zetasizer Nano S Dynamic Light Scattering) was performed to measure the zeta potential and Polydispersity Index (PDI) of the

polystyrene nanoplastics (500 nm) samples at different pH levels. Approximately 700 μL of the sample (triplicate for each pH) was poured into the cuvette and inserted into the machine. The analysis was completed by Zetasizer software (refractive index and adsorption coefficient at ~ 600 nm, temperature 21°C).

3.4 Experiment preparation and development

The OECD water was first prepared, sterilized (via liquid cycle autoclaving), and stored at room temperature for no more than 4 weeks. Nanoplastics solutions in OECD water were made fresh from the sonicated stock solution, and the amount of nanoplastics vary depending on the experiment as discussed in specific experiments below. Generally, 100 mL water (OECD water for kinetic study, DI water for others) (**Figure 3.2**) was aliquoted in a 3×100 mL glass solvent bottle, spiked with a known amount of plastics, mixed to ensure homogeneity, and then spiked with a known volume of radiolabeled compounds (amount varies depending on the experiments). The solvent bottles were covered in aluminum foil to prevent the influence of photodegradation and the solutions were mixed in a 9-position magnetic stir plate (Stirrer Mltipos MP9I 12Q821236) throughout the duration of the experiment. A 2 mL sample was taken at different time points and then transferred into a pre-weighed centrifugal filter. The nanoplastics were then separated via centrifugation (3220 rpm, 20 min) and 1 mL filtrate (the liquid that passed through the centrifugal filters) was transferred in a glass scintillation vial where 5 mL of LSC was added. The vials were allowed to sit for a minimum of 2 h and then measured for radioactivity. From the radioactivity measurements, the amount sorbed onto the plastics was calculated as discussed below.

Radioactivity was recorded as counts per minute (CPM) and must be converted to nanomolar (nM). First, the beta counter counting efficiency via a quench test was determined using equation 3.1a below.

$$Efficiency(\%) = \frac{CPM \times 100}{DPM} \quad \text{eqn 3.1a}$$

where DPM is the disintegration per minute. The equation was further manipulated using the

chemical's radioactive concentration $\left(\frac{mCi}{mL}\right)$ and volume of stock (mL) used for testing

given that $1 \text{ mCi} = 2.22 \times 10^9 \text{ DPM}$. Therefore, the efficiency is now calculated as

$$Efficiency(\%) = \frac{CPM \times 100}{Concentration \left(\frac{mCi}{ml}\right) \times Volume \text{ of Stock } (ml) \times \frac{2.22 \times 10^9 (DPM)}{mCi}} \quad \text{eqn 3.1b}$$

Given the specific activity of the radiolabeled chemicals is expressed in $mCi/mmol$, this unit

was converted to $\left(\frac{CPM}{fmol}\right)$ using equation 3.2

$$\text{Specific Activity (SA)} \left(\frac{mCi}{mmol}\right) = \left(\frac{Ci}{mol}\right), \text{ given } 1Ci = 2.22 \times 10^{12} \text{ DPM}$$

$$\text{Specific Activity (SA)} = \frac{2.22 \times 10^{12} \text{ DPM}}{mmol}, \text{ substituting eqn 3.1 b} \quad \text{eqn 3.2}$$

$$\text{Specific Activity (SA)} = \frac{2.22 \times 10^{12} \times CPM}{10^{12} fmol \times efficiency}, \text{ where } 1 \text{ mmol} = 10^{12} \text{ fmol}$$

The specific activity of the radiolabeled compound is known (from the supplier). Hence, the $nmol/L$ (nM) concentration can be determined by rearranging equation 3.2, converting $fmol$ to $nmol$ and dividing by the solution volume. Finally, using values in nM , the percent of the chemical adsorbed in the plastics is then calculated as:

$$Adsorption\% = \frac{C_o - C_e}{C_o} \times 100 \quad \text{eqn 3.3}$$

where C_o is the initial concentration (nM) in the solution and C_e is the equilibrium concentration (nM). The sorption coefficient, K_d (L/Kg) was then calculated as the ratio of the

amount sorbed (q_e) in the plastics (ng/ μ g) and C_e (ng/L). q_e was determined via the mass balance.

$$q_e = \frac{C_0 - C_e}{\text{weight of plastic}(\mu\text{g})} \times MW(\text{ng/nmol}) \times Vol_{\text{workingsolution}}(\text{L}) \quad \text{eqn 3.5}$$

$$K_d = \frac{\left(\frac{q_e}{C_e}\right)}{10^{-9}} \quad \text{eqn. 3.6}$$

Finally, to determine the centrifugal filtration method for measuring radioactivity remaining in the solution (i.e., the amount that is not sorbed), a separate “wash” test was completed where the radioactivity from the filters after 3-step washing (see section 3.9, Quality Assurance).

3.5 Kinetic sorption experiments

For the kinetic sorption experiments, 100 mg/L of 500 nm and 20 nm PS were prepared by pipetting 500.90 μ L of nanoplastic stock solution into 100 mL OECD water. Then, 10 μ L of the chemical compound (glyphosate, methyl parathion, fluoxetine, PFOA and phenanthrene) was spiked into the nanoplastic solution. During the kinetic sorption experiments, various time intervals were examined, ranging from 10 min to 72 h (with $n = 2$ to 3). These time points were selected based on the hypothesis that some of the chemicals will reach equilibrium quickly while others will take some time due to variations in their physico-chemical properties. Sample preparation and analysis were completed similarly to how it was described in section 3.4 (centrifugal filtration, addition of LSC, equilibration for a minimum of 2h, and then radioactivity measurements via the beta counter).

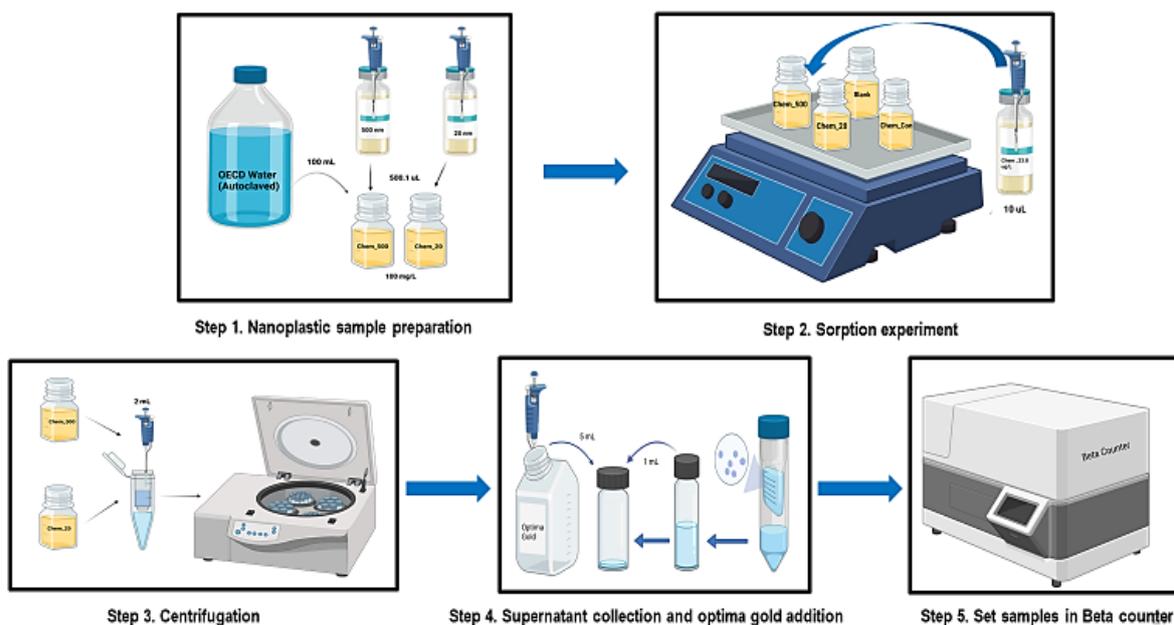


Figure 3.2 General graphical procedure of sorption experiments. Variations in the procedure were completed depending on the experiment (e.g., additional pH adjustments). Figure created from BioRender.

3.6 pH experiments

Similar procedures were completed as in Figure 3.2, except that pH of the solution was adjusted with 0.01 N NaOH and HCl to a pH 2, 4, 6, 8.4, 9.8, and 12. Also, 0.5 mg/L concentrated 500 nm PS in ultrapure water was prepared and experiments were conducted using all the chemicals except methyl parathion. For the adsorption experiments, 500 nm PS was employed for all, except for glyphosate, where both 500 and 20 nm PS were explored. Consistency was ensured as the same as in the kinetic sorption experiment throughout.

3.7 Natural organic matter experiments (NOM)

Synthetic water was prepared as shown in Appendix. The solution contains 2.26 mg/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 8.36 mg/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.41 mg/L NaNO_3 salts, 2.95 mg/L $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ solution, humic (Suwannee river NOM) acid and alginic acid in ultrapure water (100 mL). As with pH experiments, 0.5 mg/L concentrated 500 and 20 nm PS solution was prepared in

synthetic water. The nominal concentrations for “low NOM” and “high NOM” experiments are 0.25 mg/L and 0.51 mg/L, respectively. In the sorption experiment, only glyphosate and fluoxetine were used and the volume was less (5 μ L) than previously used.

3.8 Wastewater effluent experiments

Pre-UV-treated and post-UV-treated wastewater (4L in amber bottles) was collected from a local wastewater treatment plant (WWTP) on December 2, 2022 (10:30 am). To characterize the quality of the wastewater, additional samples were submitted to a certified laboratory in Edmonton for analysis of heavy metals, organic carbon, anions and nutrients. As in the case of NOM experiments, 0.5 mg/L nanoplastic solution was prepared for both sized plastics by adding 5% and 50% of the pre and post-UV-treated wastewater. The sorption experiment was investigated on glyphosate and PFOA.

3.9 Quality assurance

To verify the accuracy of the methodology, a series of centrifugal filter “wash” cycles were carried out. After the plastic and aqueous solution separation, the centrifugal filters were stored by wrapping them in aluminum foil and keeping them refrigerated. For wash experiments, 1 mL of methanol was added into the centrifugal filter unit, vortexed, and centrifuged. The filtrate (in methanol) was then transferred to the resulting sample in a scintillation vial. This process was done three times to ensure that the total radioactivity was collected. The filtrate was then measured for radioactivity. Our methodology proved to be reliable and accurate, as evidenced by the results of our rinsed experiments (Appendix). To prevent additional contamination, the radioactive samples were individually placed in amber bottles and stored under refrigeration. To maintain the integrity of the wastewater, the samples were stored at 4°C and the testing of sorption on wastewater samples was conducted within a period of three weeks.

3.10 Data Analysis

A combination of software SigmaPlot (Version 14.5) and Microsoft Excel 2019 was utilized for data visualization, data analysis, and statistical analysis. The resulting data is presented in the format of mean \pm standard error of the mean, ensuring accuracy and precision in our findings (One-way, ANOVA, $\alpha = 0.5$).

Chapter 4 – Result and Discussion

4.1 Polystyrene nanoplastic characterization

4.2 Dynamic light scattering (DLS) analysis

The DLS technique was used to determine the zeta potential or charge of polystyrene particles (500 nm) at varying pH ranges (Figure 4.1). As expected, PS particles are negatively charged at all pH conditions given that their surface has been pre-modified with carboxylate (RCOO^-), a surface functional group with a negative charge. The zeta potential at pH 2 (-5.06 mV) significantly differed among other pH conditions (ANOVA, $p < 0.001$, $\alpha = 0.05$), but the zeta potential appeared to be more negative and stable at increasing pH. The zeta potential at pH = 8.4 is -16mV; this is the pH of the OECD water, the baseline matrix employed in this study. A similar result was found in a previous study by Zhang et al. in 2020 which showed that the zeta potential of nano-PS-COOH (mean diameter of 487.2 ± 80 nm) became more negative as the pH increased. Zajac et al., 2023 also found similar conditions for commercially available 100 nm PS (experiments in 0.3 mM NaCl), although it is unclear if the particles have been pre-modified with surface functional groups such as carboxylate or amines. Nonetheless, it appears that deprotonation occurs (i.e., RCOOH into RCOO^-) in the surface of 500 nm PS employed in this study at higher pH conditions, further rendering the particles as more negative. Many plastics are also manufactured with negative charge to improve their stability in suspensions, thereby promoting strong electrostatic repulsion (Zhang et al., 2020) with other particles (i.e., less aggregation).

While all the pH conditions showed negative zeta potential values, the value at pH 12 was found to + 16.43 mV (Figure 4.1 a), with an average polydispersity index (PDI) of 0.169. According to International Standards Organizations (ISOs), for monodisperse samples, PDI generally is < 0.05 and for polydisperse samples is > 0.7 (ISO 22,412:2017) suggesting that the

particles start to aggregate. This aggregation was not only evident visually but was also reflected in the size distribution where the mean size of 3000 nm was observed for 500 nm plastic particle solution (Figure 4.1). The OECD water was prepared with salts (CaCl₂, MgSO₄·7H₂O, NaHCO₃ and KCl) which can initiate aggregation (Lu et al., 2018). The examination of particle aggregation is outside the scope of this study, but sufficient care was done throughout the duration of all experiments to ensure that the particles do not aggregate and therefore confound the results observed.

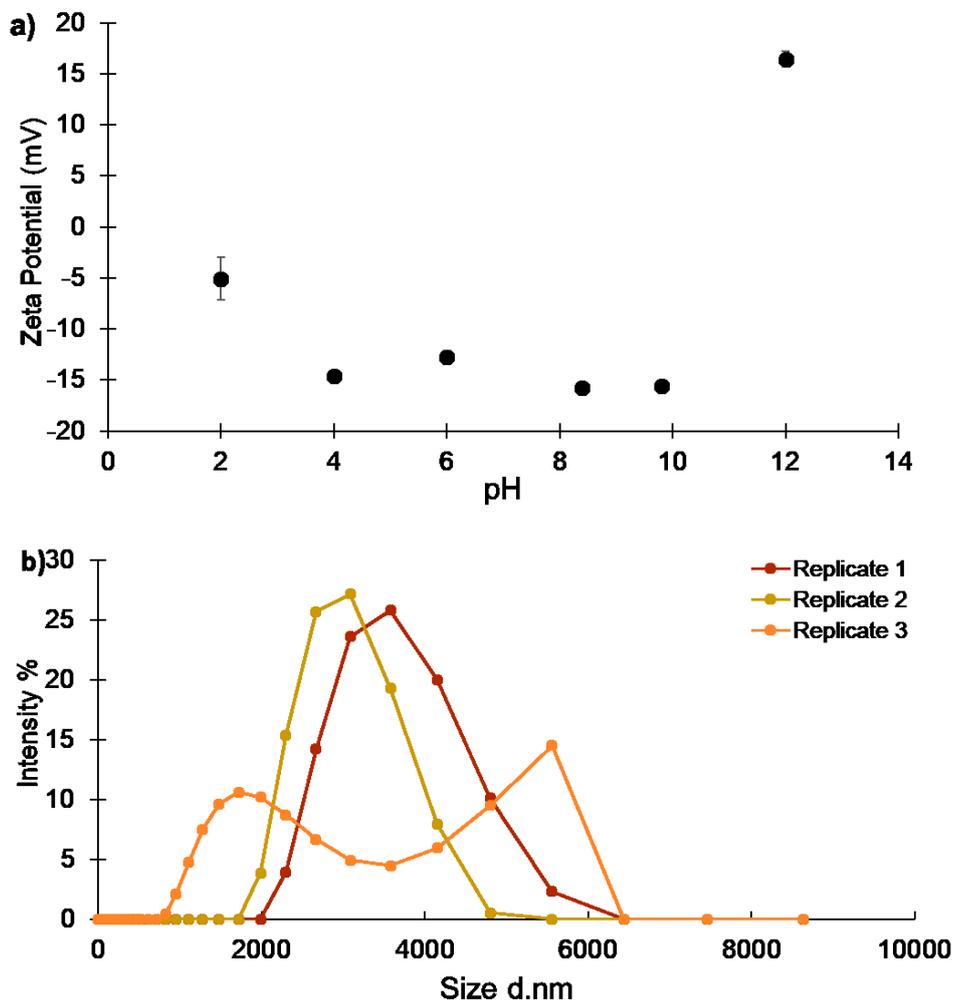


Figure 4.1 Dynamic light scattering (DLS) analysis of polystyrene (500 nm). (a) in OECD water at different pH at pH 2, 4, 6, 8.4, 9.8 and 12, (0.01 M NaOH, 0.01 M HCl); (b) polystyrene nanoparticles size distribution by intensity at pH 12. Aggregation of nanoplastics

as evident by the large mean particle diameter (~3000–3500 nm) for replicates 1 and 2 and a multi-modal distribution in replicate 3.

Nevertheless, the surface charge conditions are important when assessing the sorption mechanisms of target organic pollutants with nanoplastics as many studies have shown that this process is affected by the surface chemistries of NPs, which is further impacted by different solution chemistries in aquatic environments. For instance, functionalized nanoparticles either by carboxyl- or amino-functional group improve the sorption of anionic and cationic substances, respectively (Song et al., 2019). This hypothesis drove this study to explore the sorption of the target compounds with 500 and 20 nm PS NPs at different pH conditions. This information is explained in more detail in **Section 4.5**.

4.3 TEM and Elemental Analysis

The TEM images for 500 and 20 nm PS prepared in different water matrices clearly showed the spherical shape of the particles. A notable difference in TEM images is the impurities observed on the surface of plastics prepared in synthetic and wastewater solutions (e.g., Figure 4.3(a) vs (c)), suggesting that substances sorb onto the plastic surface and can therefore impact the sorption conditions of the target organic contaminants. Note that “bubbles” were observed in Figure 4.2(e) at the outer side of polystyrene (whiter part) which could be a possible limitation of TEM sample preparation. The changes that the water matrices impose on the sorption behaviour are described in detail in **Section 4.5-4.6**.

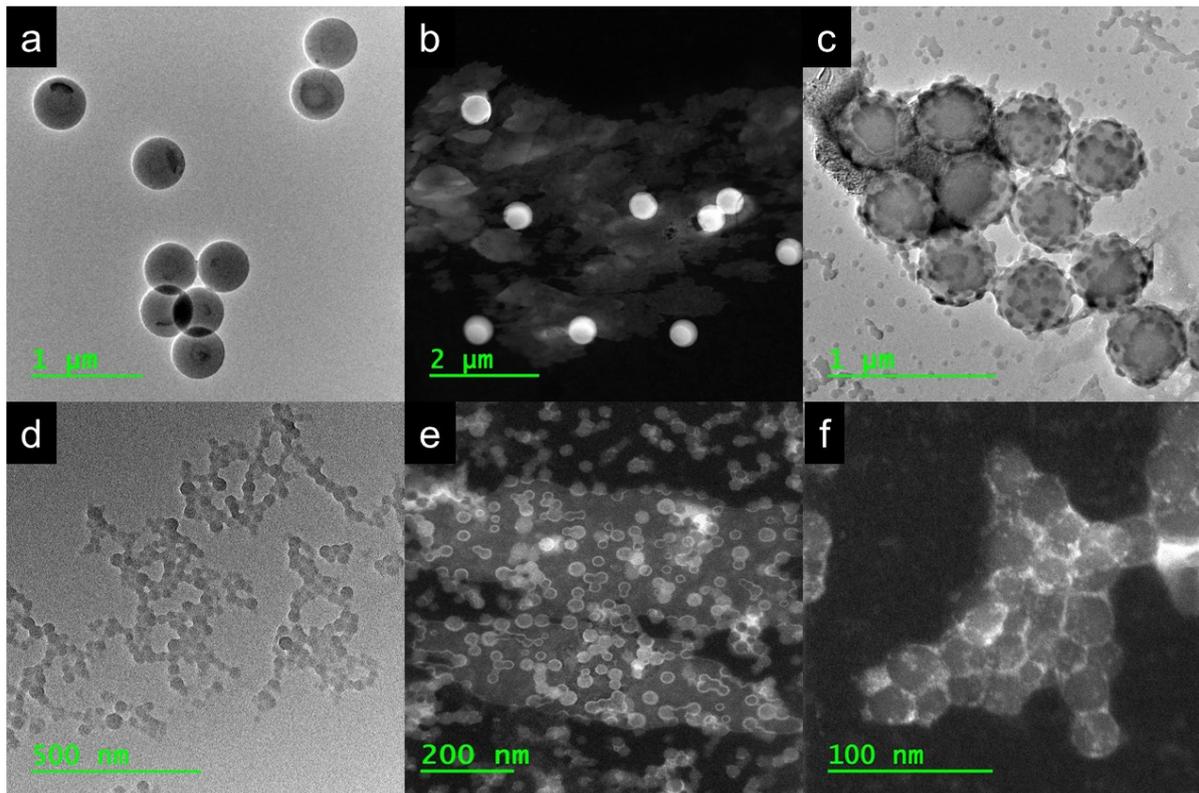


Figure 4.2 TEM images of 500 nm polystyrene in a) OECD water, b) in synthetic water and c) in pre-UV treated effluent and 20 nm polystyrene in d) OECD water, e) in synthetic water and f) in pre-UV treated effluent. The images b, e and f are dark field (DF) images of S/TEM (0.10 nm at 200 kV)

The elemental analysis on the TEM images of NPs in synthetic and wastewater solutions was completed and strongly correlated with the presence of the ions and organic matter in these solutions (data shown in Appendix). **Figure 4.3a**, in particular, shows the presence of substances in pre-UV treated wastewater mainly calcium, chlorine, magnesium, sodium, oxygen, sulfur, and potassium (**Figure 4.3b**). For PS solution in synthetic water (with NOM), the same cations and anions were seen as those in PS in wastewater samples but with an addition of silicon. It is currently difficult to determine whether the carbon observed at high intensity near the particle surface is from the organic matter in the synthetic and wastewater solutions, or an artifact from the STEM sample preparation. STEM utilizes a carbon-coated grid to introduce carbon, which could impact elemental mapping. Of the cations, sodium and

calcium were found at higher intensities on the particle surface suggesting in pre-UV treated wastewater (**Figure 4.3**) which was expected as for both of the matrices (wastewater and NOM) have higher concentration of sodium and calcium.

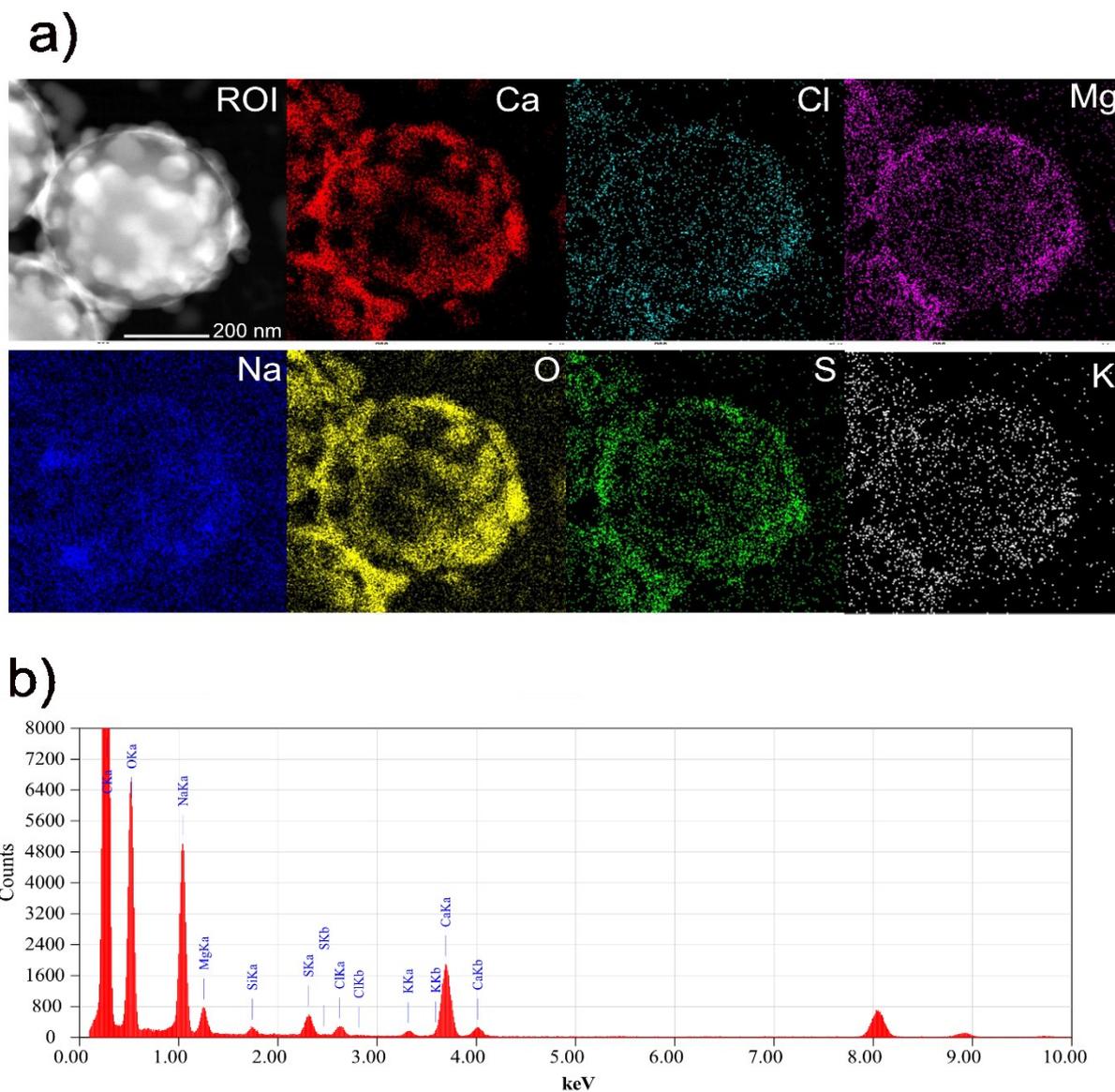


Figure 4.3 a) TEM EDX mapping of 500 nm PS in pre-UV treated wastewater and **b)** spectrum of relative intensities of the ions attached on the surface of 500 nm PS (K-edge mapping). Note that it is difficult to assess whether the attachment of the substances on the surface happens during the experiments or were subsequently observed after the sample preparation for TEM imaging. ROI = region of interest.

4.4 Kinetic experiments with OECD water

The five substances evaluated in this study showed varying sorption affinity with both 500 and 20 nm PS. Among these substances, fluoxetine and phenanthrene showed the best sorption with sorption coefficients (K_d) of 4.46×10^5 and 3.86×10^5 L/kg (20 nm PS), respectively. In addition, >97% of fluoxetine and phenanthrene in aqueous solution sorbed in both sized PSNPs (**Figure 4.2. a**) compared to glyphosate, methyl parathion and PFOA that showed K_d in 20 nm PS of 1.75×10^3 , 1.49×10^5 and 8.91×10^3 L/kg respectively after 72 h. Fluoxetine and phenanthrene are considered hydrophobic compounds ($\log K_{ow} \geq 4$) with $\log K_{ow}$ values of 4.17 and 3.95 respectively (**Table 3.1**) and this property could explain the sorption behaviour of these compounds with the 500 and 20 nm PSNPs. Although PFOA has the higher $\log K_{ow}$ (5.11) than fluoxetine and phenanthrene, it sorbed the least. Sorption coefficients (K_d) for polyfluoroalkyl substances (PFAS) with polystyrene carboxylate (PS-COOH) (2 mg/L) had been reported to range from 0.0093– 2.071 L/kg (Llorca et al., 2018) which are indeed at lower values compared to other substances. Furthermore, PFOA and glyphosate did not show significant differences in the adsorption between 500 and 20 nm sized plastics (ANOVA, $p > 0.052$, $\alpha = 0.05$). As discussed later in this chapter (Section 4.5), PFOA's behaviour may be attributed to electrostatic repulsion given that both NPs and PFOA are negatively charged at pH 8.4.

Glyphosate and methyl parathion are hydrophilic compounds and their $\log K_{ow}$ values are -3.10 and 2.86, respectively. However, when compared to PFOA, methyl parathion showed excellent adsorption with polystyrene nanoplastics (84.56% and 92.72% with 500 nm and 20 nm PS respectively) despite its hydrophilicity. Methyl parathion contains phosphorothioate which has partial negative charges on the oxygen atoms and partial positive charges on the sulfur atom. Additionally, it has phenyl and nitrophenyl with charges that potentially cancel each other. Although methyl parathion is neutral, the positive charge on sulfur can create

attractive electrostatic forces with the negatively charged PSNPs, which could be a possible reason for the high adsorption observed in this study.

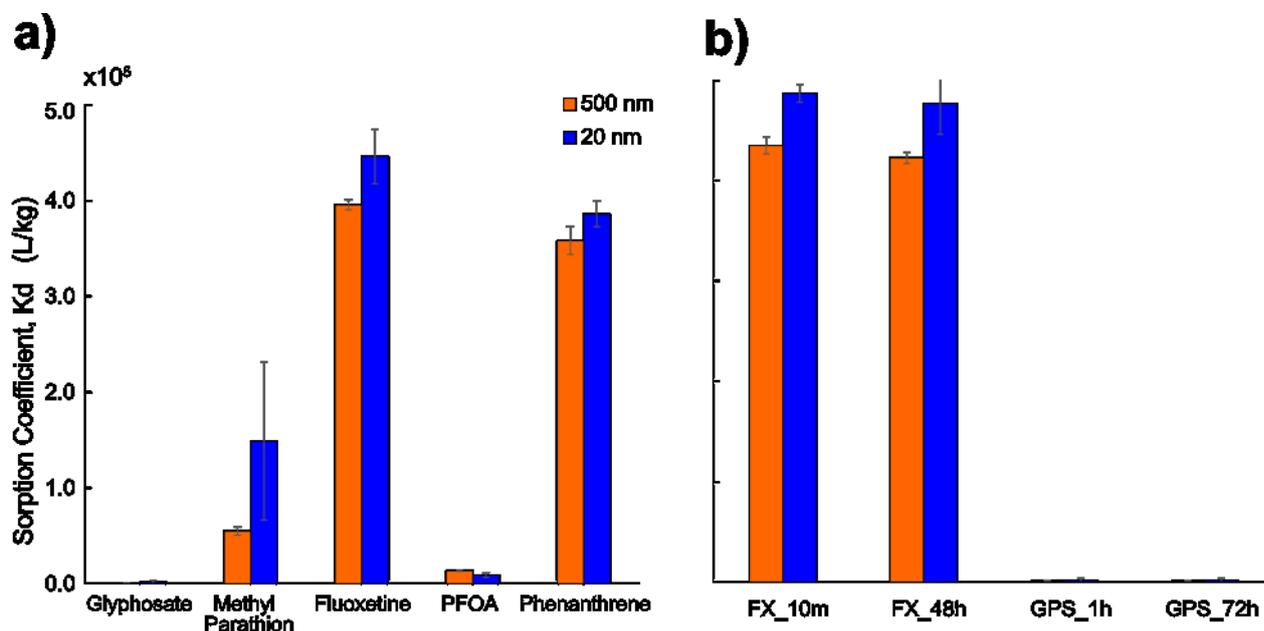


Figure 4.4 a) Sorption coefficient (Kd, L/kg) of all chemicals on 500 and 20 nm PS, **b)** long-term vs short-term sorption comparison between fluoxetine and glyphosate. FX=Fluoxetine; GPS = glyphosate.

The charged functional groups present in hydrophilic compounds can further establish attractive or repulsive electrostatic forces with the surface of PSNPs (Zhang et al., 2020). Glyphosate possesses various functional groups, including a net negative charge attributed to the negative charges from the phosphonate ($-\text{PO}(\text{OH})_2$) and carboxyl groups ($-\text{COOH}$), alongside a positive amino group ($-\text{NH}_2$). Hence, the present study shows an electrostatic repulsion between glyphosate and PSNPs which is likely the reason for poor sorption onto the PSNPs. However, in a previous study that modified the surface characteristics of PSNPs to include amine group ($\text{R}-\text{NH}_2$) (positively charged, 200 nm) showed an excellent adsorption capacity for glyphosate (Zhang et al., 2018), further suggesting the electrostatic interactions play a role in NP-compound interaction.

It is evident that, except for PFOA, all chemicals demonstrated significantly higher sorption coefficients with 20 nm PS compared to 500 nm PS (One-Way ANOVA, $p < 0.001$ and $\alpha = 0.05$), owing to the larger surface area-to-volume ratio of the former. In freshwater, phenanthrene has been shown to have a higher partitioning on nanoplastics (log K_d : 5.82 ± 5.23) compared to microplastics (log K_d : 4.23 ± 3.04) (Ma et al., 2016). This phenomenon aligns with previous findings where K_d values for phenanthrene increased with decreasing particle size (from 170 μm to 50 nm) of PS micro and nanoplastics (Wang et al., 2019). Furthermore, in aqueous conditions, hydrophobic organic contaminants, including polybrominated diethers (PBDs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), phthalates, surfactants, personal care products (PCPs), and pharmaceuticals (such as tetracycline, ciprofloxacin, sertraline, propranolol, and sulfamethoxazole), exhibit a high affinity towards microplastics again due to their high surface area-to-volume ratio (Agboola and Benson, 2021). Therefore, the observation of higher sorption in much smaller particle sizes, such as in the case of 20 nm PS is not surprising. Smaller PVC microplastics ($<1 \mu\text{m}$) have been found to possess greater sorption coefficient (K_d) values (1350 L/kg) for neutral charged triclosan (an antibacterial and antifungal agent) compared to larger microplastics ($\sim 74 \mu\text{m}$) (Ma et al., 2019). Similarly, the adsorption of various plastics (polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP), and high-density polyethylene (HDPE)) with neutral charged pharmaceuticals has shown an increase in adsorption capacity by decreasing particle sizes from 1 mm to 20 μm (Munoz et al., 2021). Polypropylene MP showed four-fold increased sorption capacities by decreasing the sizes from 0.6 to 0.2 mm with difenoconazole (fungicide) adsorption (Goedecke et al., 2017). In other instances, cationic pharmaceuticals (including fluoxetine) have been observed to sorb onto microplastics (90 μm , polyamide) within 24 h (Wagstaff et al., 2022), but they desorb relatively quickly in simulated gastric fluid (Wagstaff and Petrie, 2022). Notably, not only does

reactivity and toxicity increase with decreasing particle sizes (Zhang and Goss, 2020; Zhang and Goss, 2021), but smaller particles also possess a larger capacity to carry potentially harmful trace organic chemicals, as demonstrated in the context of this study.

The kinetic data (Appendix) further shows rapid and slow sorption for fluoxetine and glyphosate, respectively. Hence, a series of short-term and long-term experiments (**Figure 4.4b**) were conducted to assess whether these equilibrium conditions change (i.e., given more time, would glyphosate sorption change). Here, fluoxetine and glyphosate sorption coefficients did not statistically differ between short-term (10 min and 1 h of sorption) compared to longer-term sorption (2-3-day experiment) (ANOVA, $p > 0.01$, $\alpha = 0.05$) suggesting stability of both plastics and compound in the solution after an equilibrium is reached. Overall, the preliminary results of the kinetic experiments provided a foundation for pursuing additional experiments related to surface charge interactions. In the next subsequent sections, changes related to pH and water matrices were evaluated to determine the impact of surface charge changes and other impurities in the aqueous matrix on the overall sorption of chemicals onto PS NPs.

4.5 Impact of pH variation on sorption

The experiment examined six different pH levels to determine the sorption of glyphosate, fluoxetine, PFOA, and phenanthrene on 500 nm polystyrene. The findings showed that the adsorption of fluoxetine and glyphosate increased as the pH levels increased, while the adsorption of PFOA decreased (**Figure 4.5a**). However, the adsorption of phenanthrene did not change. These differences of adsorption could be attributed to the charge conditions of the compounds in response to pH changes. For instance, the percent adsorption of 500 nm PS with fluoxetine significantly increased with the increase of pH (One-Way ANOVA, $p < 0.001$, $\alpha = 0.05$) but no significant differences were observed between pH 6 and 12 (One-Way ANOVA, $p > 0.081$). Fluoxetine is positively charged from pH 2-6 (**Figure 4.6**) but the PSNP charge is

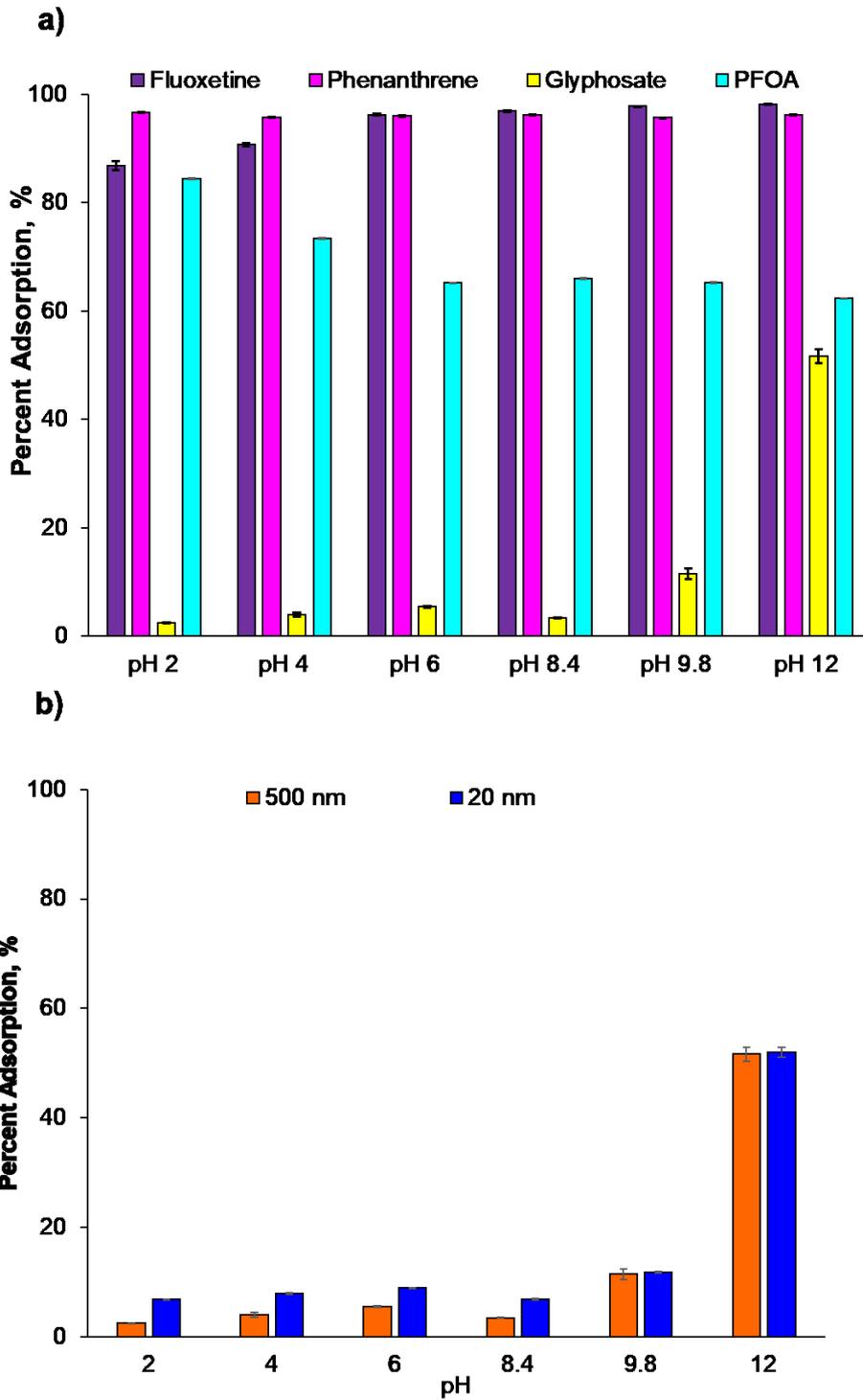


Figure 4.5 a) Adsorption % of fluoxetine, phenanthrene, glyphosate and PFOA on 500 nm PS at different pH conditions, **b)** Adsorption % differences of glyphosate on 500 and 20 nm PS at different pH conditions (pH 2-12)

becoming more negative (**Figure 4.1**), thus improving the electrostatic interactions between the PS NP and fluoxetine. As the pH increases, fluoxetine becomes less positive (to neutral) whereas the PS NP charge stabilizes. Hence, no changes in sorption can be observed under these conditions. A comparable investigation conducted by Wagstaff et al. (2022) suggested that during the adsorption of fluoxetine, negatively charged polyamide microplastics (with a median size of 90 μm) demonstrated an increase in their sorption coefficient as the pH levels increased from 3 to 11. Recent studies in the literature point out that positively charged substances (i.e., cationic such as fluoxetine) are favoured during microplastic sorption in wastewater (Wagstaff et al., 2022; McDougall et al., 2022), similar to what has been observed here.

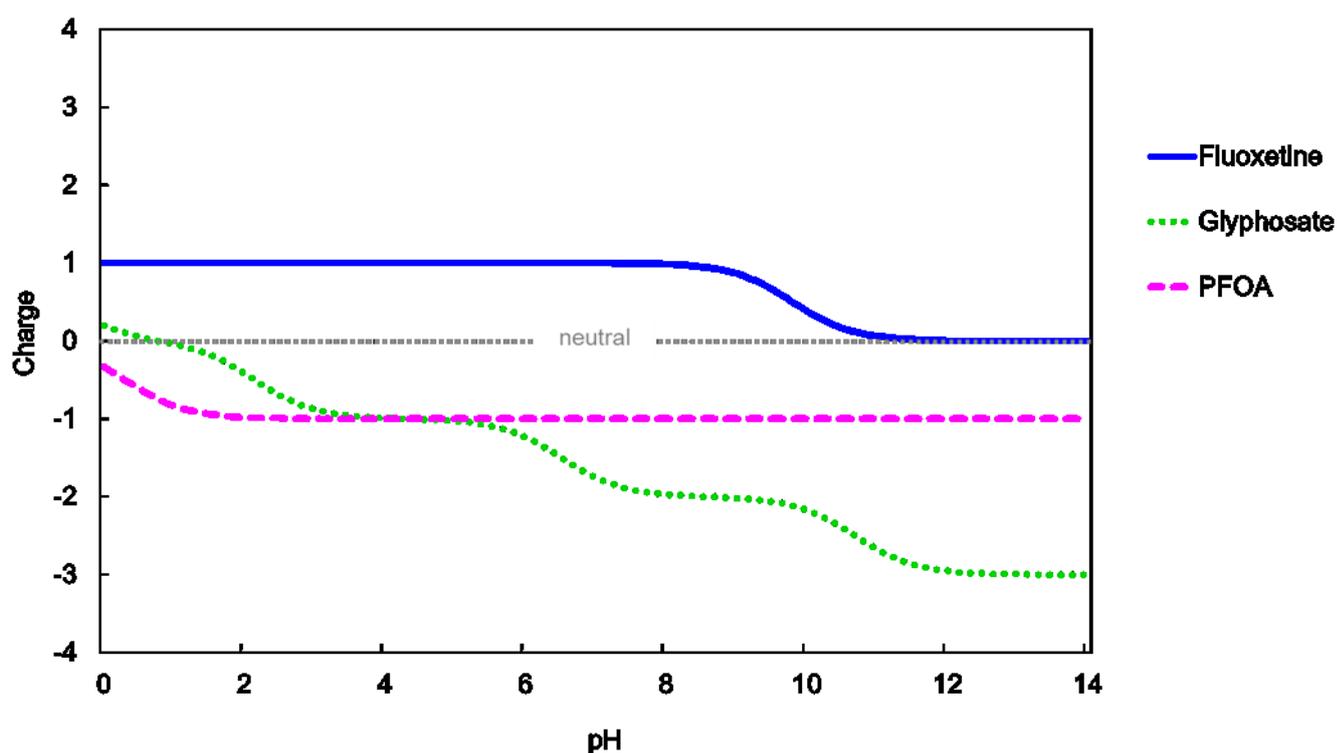


Figure 4.6 pH vs charge of fluoxetine, glyphosate and PFOA (data obtained from ChemAxon. Phenanthrene not shown here as it is not ionizable. pH experiment was not completed for methyl parathion.

Furthermore, the percent adsorption of phenanthrene on 500 nm PS remained constant (96%) throughout. Phenanthrene is non-ionizable and cannot dissociate into specific ions that would carry a charge (positive or negative). Hence, its interaction with the NPs is likely hydrophobic in nature ($\log K_{ow} = 3.95$) as its sorption is not impacted by the change in charge in the NPs (becoming more negative from pH 2-6). For PFOA adsorption with 500 nm PS, a decrease in percent adsorption (84.46 % to 62.33 %) was observed with increasing pH. PFOA becomes more negative as the pH increases and therefore, the electrostatic repulsion between a negatively charged PS NP is greater. However, once the PFOA and NP charge stabilized at pH = 2 and pH = 6, the percent adsorption also remained unchanged.

The percent of glyphosate adsorption with PSNPs is the most dynamic of all the compounds examined due to the presence of several ionizable function groups in glyphosate including amine ($R-NH_2$), carboxyl ($-COOH$), and phosphonate ($-PO(OH)_2$) groups. More specifically, the adsorption coefficients at all pH conditions are significantly different (One-Way, ANOVA, $P < 0.001$, $\alpha = 0.05$). Although it was hypothesized that sorption would decrease with increasing pH due to glyphosate becoming more negatively charged, it might be possible that some level of aggregation happened during the experiment which caused glyphosate to bind to the plastic (**Figure 4.5a**). Given this behaviour, another experiment was performed to assess the sorption of glyphosate with smaller-sized PSNPs (20 nm). The percent adsorption trend remained the same (**Figure 4.4b**) but with 20 nm PS showing greater adsorption (6.84 - 51.97%) with glyphosate from pH 2-8.4. Positively charged PSNP- NH_2 displayed substantial adsorption percentages (55-97%) for glyphosate, mainly around pH 7, attributed to the interaction between the amino group of PS and the carboxyl group of glyphosates (Zhang et al., 2018; Yang et al., 2009). A previous study also emphasized the pH influence on glyphosate adsorption onto a cationic polymer layer in aqueous solutions (Pérez-Chávez et al., 2021)

which aligns with our study, where an anionic polymer led to lower adsorption percentages under acidic conditions.

Currently, it's unclear if there are additional adsorption mechanisms of these compounds attach to nanoparticles apart from the hydrophobicity and electric interactions. Exploring the major differences between these interactions is outside this scope of this thesis, although compound physicochemical properties such as hydrophobicity and charge affect their interaction with the NPs (McDougall et al., 2022). These properties might become important when nanoparticles carrying organic substances interact with aquatic organism such as fish and invertebrates. Therefore, delving deeper into how these conditions impact more broadly in how particles and chemicals interact with each other in aquatic ecosystems requires further research.

4.6 Natural Organic Matter (NOM) and wastewater addition

In natural environments, adsorption is influenced by various factors and is not as controlled as in lab-based experiments. When nanoplastics mix with aquatic systems, they may combine with multiple compounds simultaneously. Based on this concept, two different water matrices, natural organic matter (NOM) and wastewater effluent, were used to detect nanoplastic sorption conditions by considering sorption kinetic experiments and pH differences.

4.6.1 Natural organic matter (NOM)

Experiments where NOM was spiked into the chemical and PSNP solutions were completed for fluoxetine and glyphosate, the most and the least adsorbed organic chemicals according to the kinetic study. In this experiment, two different concentrations of synthetic water solution were used: 0.25 mg/L and 0.50 mg/L which are considered low NOM and high NOM, respectively. Both fluoxetine and glyphosate showed greater adsorption in low NOM condition with K_d values of 8.53×10^7 and 3.95×10^2 L/kg for 20 nm PSNPs. On the contrary,

by adding a more concentrated NOM solution, the PSNPs adsorption capacity for both compounds was hindered with K_d of 3.32×10^7 and 2.75×10^2 L/kg for fluoxetine and glyphosate respectively (**Figure 4.5a**). There were no statistically significant differences between 500 nm and 20 nm PS (ANOVA, $p=0.53$) for high NOM concentration in fluoxetine experiments. However, for low NOM concentration, differences were obtained (ANOVA, $p=0.05$).

NOM is considered a matrix of organic compounds and can therefore have hydrophobic (i.e., aromatic content in humic substances) and hydrophilic (i.e., aliphatic carbon content such as proteins and amino acids) properties (Ali et al., 2022). These can be attractive for both PSNPs and the organic substances themselves as they both can sorb onto NOM. However, given that higher concentrations of fluoxetine and glyphosate were observed in the aqueous phase when NOM levels were low suggested that NOM might be competing with the chemicals for adsorption sites on the PSNP surface (Ali et al., 2022). This potential for competitive adsorption has been observed in a previous study that showed a reduction in norfloxacin (antibiotic) sorption on several types of microplastics under the presence of NOM (Zhang et al., 2021).

A similar study reveals that higher levels of fulvic acid (a humic substance) can reduce the binding of the tetracycline (antibiotic) to polyethylene, polypropylene and polystyrene MPs, but tetracycline is more attracted to fulvic acid than to microplastics (Xu et al., 2018). It has been shown that organic chemicals such as benzo[a]pyrene may be trapped and encapsulated by organic matter itself (NOM) (Feng et al., 2022), preventing its sorption onto the NPs. Since this thesis did not measure the organic content before and after the adsorption, it is difficult to assess whether fluoxetine and glyphosate were bound to NOM that are suspended in the aqueous solution (i.e., portion of NOM that are not bound to the PSNPs). Nonetheless, this experiment shows that impurities in the water matrix impact sorption of particles and can have an effect on their overall fate and transport.

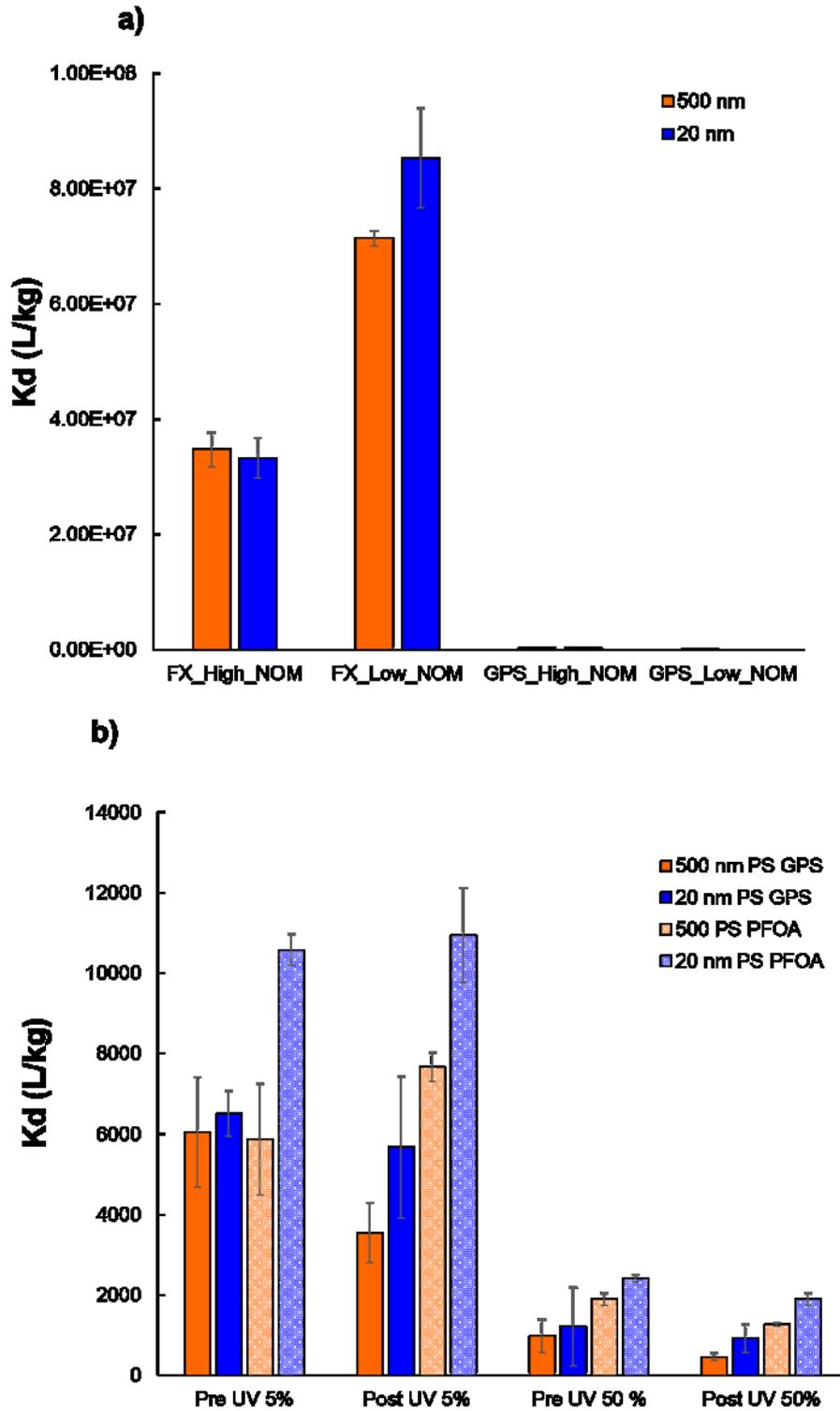


Figure 4.7 a) Sorption coefficient (K_d , L/kg) values of fluoxetine (FX) and glyphosate (GPS) on 500 and 20 nm polystyrene in high and low-concentrated natural organic matter solution and **b)** Sorption coefficient (K_d , L/kg) values of PFOA and glyphosate (GPS) on 500 and 20 nm polystyrene in pre-UV and post-UV treated effluent (5% and 50%).

Several studies have contributed to the understanding of natural organic matter (NOM) effects on microplastic (MP) sorption behavior. NOM, including dissolved organic matter (DOM), can interact with polystyrene, resulting in PS-DOM complexes (Yan et al., 2020). Similar to what had been observed in this study, Munoz et al. (2021) also found that NOM presence led to a reduction in MP sorption capacity for other dissolved constituent by blocking sorption sites. The pH of the solution can also impact adsorption of NOM on PS microplastics (MPs), and although not explored here, Abdurahman et al. (2020) investigated DOM's high adsorption on PSMPs under low pH conditions (pH 2). Similar trends were identified in another study, where the adsorption of humic acid (HA), FA, and tannic acid (TA) onto PSMPs was enhanced under acidic conditions (Li et al., 2022). This study also noticed the role of divalent cation (Ca^{2+}) in improving HA, FA, and TA adsorption compared to monovalent ions (K^+ and Na^+) which are present in the synthetic water solution. Therefore, the composition of the surrounding water and the types of ions present can significantly influence the adsorption behavior in NPs and their subsequent interactions with organic substances. Importantly, these effects could vary based on the specific plastic type, highlighting the complex and diverse nature of interactions between microplastics and pollutants within distinct environmental contexts.

4.6.2 Impact of wastewater on sorption

The impact of pre-UV and post-UV treated effluents on the sorption of chemicals were assessed. Here, two different concentrations of pre-UV and post-UV treated wastewater (5% and 50%) were tested to observe the variation in glyphosate and PFOA adsorption. The results showed that both glyphosate and PFOA had greater adsorption in 5% effluent compared to 50% (**Figure 4.7b**). Additionally, there were significant differences in glyphosate adsorption for two different sized nanoplastics in both 5% and 50% pre-UV treated water (p -value= 0.005, 0.039 respectively). For PFOA, there was a significant difference in sorption between 500 nm

and 20 nm PS in both 50% pre-UV and post-UV treated effluent (p -value = 0.04, 0.005 respectively) but none was observed for glyphosate. Similar to NOM experiments above, higher composition of more complex water matrix (i.e., wastewater effluents) influence adsorption, but this time the PSNPs size matters especially for PFOA (i.e., 20 nm K_d is approximately twice the 500 nm K_d). Glyphosate continues to exhibit a lower sorption than PFOA, and as mentioned previously, it is likely due to the electrostatic repulsion (negative charge). NOM presence and other impurities in WWTP effluents diminishes sorption capacity of chemicals to various microplastics (Munoz et al., 2021), a process that is described as extremely complex since sorption mechanisms cannot only be controlled by electrostatic interactions but also by complexation and π - π , hydrophobic, and hydrogen bonding (Syranidou and Kalogerakis, 2022).

McDougall et al. (2022) showed the strong adsorption of pharmaceuticals (fluoxetine, propranolol, atorvastatin, ketamine, and carbamazepine) to polyethylene MPs (150 μ m) within wastewater systems (fluoxetine K_d = 3350 L/kg). Their K_d values are similar to what have been observed here (**Figure 4.7b**), except for PFOA sorption to 20 nm PSNPs where K_d is an order of magnitude higher. Given that PFOA can sorb onto smaller PSNPs (20 nm) quite effectively in 5% wastewater, a matrix to represent aquatic environments that receive municipal effluent discharges. This result suggests that contaminants (PFOA and glyphosate) can be associated with PSNPs and with a potential to be carried to different ecosystems at larger distances. PFOA and other PFAS compounds are also considered “mobile” due to their surfactant properties (FitzGerald et al., 2022) and can therefore sorb-desorb onto the surfaces of the PSNPs, further extending their reach to other ecosystems.

To qualitatively assess the impacts of impurities in wastewater effluents, the TEM elemental analysis was further utilized. It was found that sodium, calcium and chlorine were attached to the PSNPs mostly (**Figure 4.3**) and these substances were detected in pre- and post-

UV treated water (**Figure 4.8**). Caution must be exercised to avoid the overinterpretation of the results, given that TEM elemental analysis may be a result of a sample preparation artifact. Nonetheless, there is a general consensus that NPs can be coated with several substances such as dissolved molecules, macromolecules and ions, NOM, and natural colloidal particles. The extent of glyphosate and PFOA adsorption onto nanoplastics revolves on how well their chemical structures align for interaction and whether other compounds in the wastewater hinder or facilitate these interactions. All these interactions can lead to changes in charge (e.g., NOM can impart negative charge) or aggregation via bridging by other ions (Halle and Ghiglione, 2021). Aggregation and its impact on sorption is not considered in this thesis but appears to be an important process that occurs spontaneously and highly dynamic.

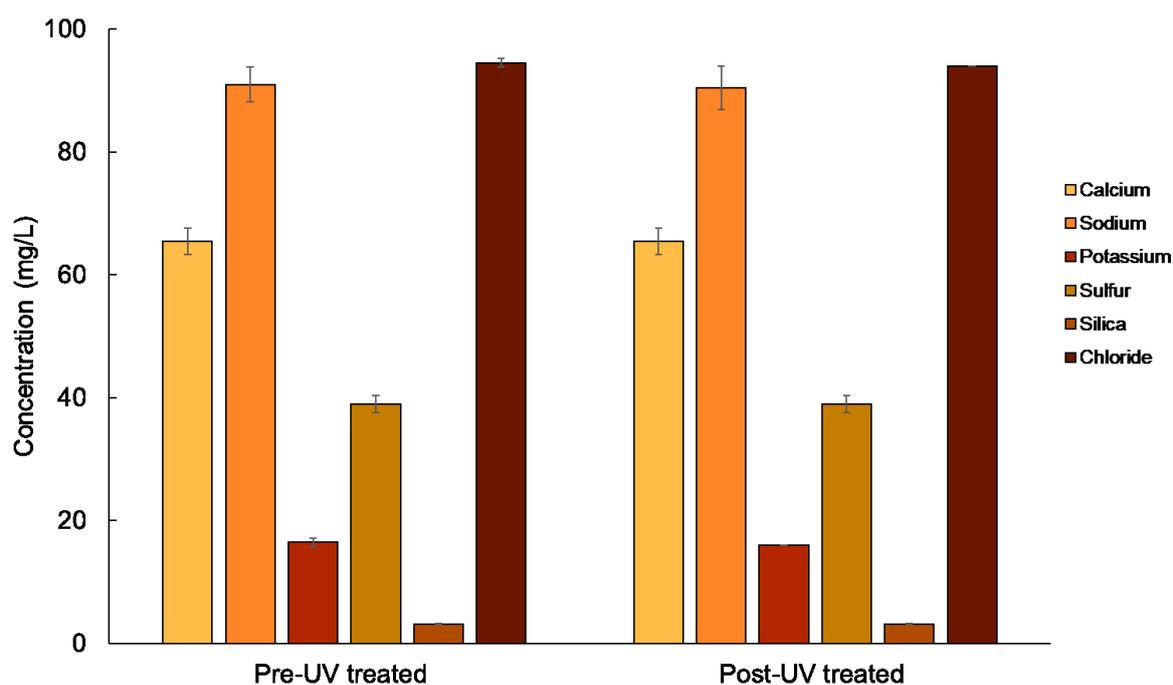


Figure 4.8 Elements found in the certificate of chemical analysis in both pre-UV and post-UV treated effluent.

Chapter 5 – Conclusion and Recommendations

The findings from this thesis offer valuable insights into the sorption behaviour of diverse chemicals on differently-sized PSNPs. Notably, cationic (fluoxetine) and hydrophobic (phenanthrene, methyl parathion) compounds demonstrated a higher tendency to sorb onto both 20 and 500 nm PSNPs. More sorption (i.e., higher K_d values) were observed for 20 nm than 500 nm PSNPs which is attributable to their larger surface area-to-volume ratio. The study also highlighted the pivotal role of pH conditions in sorption, pointing to interactions that depend on electrical charges. Additionally, the presence of natural organic matter (NOM) influenced the sorption dynamics by lowering the overall adsorption of the chemicals assessed. Furthermore, the investigation shed light on the influence of varying wastewater effluent concentrations on sorption efficiency, and the importance of the complex interactions of real-world environmental elements on the sorption processes.

Overall, this thesis advanced the overall understanding of the intricate interplay between organic contaminants and nanoplastics. There are, however, a few more insights derived from this work that could provide valuable avenues for future investigations. Research directions that merit exploration include:

- Extend the “electrostatic interactions” hypothesis to a wider array of chemicals with varying hydrophobic and ionizable traits to solidify the outputs of this study;
- Investigate the sorption of chemicals on other types of nanoplastics such as polyethylene, polypropylene, and polyamide to assess differences across plastic types;
- Evaluate the ecotoxicological consequences of nanoplastic-contaminant interactions including the desorption mechanisms and how these dynamics impact uptake and accumulation;

- Develop experiments under realistic environmental conditions such as the use of weathered nanoplastics, mixed-contaminant systems (metals + organics) and variable aquatic scenarios (seawater);
- Integrate factors like pH, nanoplastic size, and NOM for predictive models that offer insights into varying contaminant interactions with nanoplastics, further supporting risk assessment; and
- Validate laboratory findings through field studies in aquatic environments to better understand nanoplastic-contaminant interactions in natural settings.

Chapter 6 – References

- Abbasi, S., Keshavarzi, B., Moore, F., Turner, A., Kelly, F. J., Dominguez, A. O., & Jaafarzadeh, N. (2019). Distribution and potential health impacts of microplastics and microrubbers in air and street dusts from Asaluyeh County, Iran. *Environmental pollution*, 244, 153-164.
- Abdurahman, A., Cui, K., Wu, J., Li, S., Gao, R., Dai, J., Liang, W., & Zeng, F. (2020). Adsorption of dissolved organic matter (DOM) on polystyrene microplastics in aquatic environments: Kinetic, isotherm and site energy distribution analysis. *Ecotoxicology and Environmental Safety*, 198, 110658. <https://doi.org/10.1016/j.ecoenv.2020.110658>
- Agarwal, S., & Gupta, R. K. (2018). The use of thermosets in the building and construction industry. In *Thermosets* (pp. 279-302). Elsevier.
- Agboola, O. D., & Benson, N. U. (2021). Physisorption and Chemisorption Mechanisms Influencing Micro (Nano) Plastics-Organic Chemical Contaminants Interactions: A Review. *Frontiers in Environmental Science*, 9, 678574. <https://doi.org/10.3389/fenvs.2021.678574>
- Ahmed, M. B., Rahman, M. S., Alom, J., Hasan, M. S., Johir, M., Mondal, M. I. H., Lee, D., Park, J., Zhou, J. L., & Yoon, M. (2021). Microplastic particles in the aquatic environment: A systematic review. *Science of The Total Environment*, 775, 145793. <https://doi.org/10.1016/j.scitotenv.2021.145793>
- Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., & Chen, M. (2016). Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresource Technology*, 214, 836-851. <https://doi.org/10.1016/j.biortech.2016.05.057>

- Ajith, N., Arumugam, S., Parthasarathy, S. *et al.* Global distribution of microplastics and its impact on marine environment—a review. *Environ Sci Pollut Res* **27**, 25970–25986 (2020). <https://doi.org/10.1007/s11356-020-09015-5>
- Ali, I., Tan, X., Li, J., Peng, C., Naz, I., Duan, Z., & Ruan, Y. (2022). Interaction of microplastics and nanoplastics with natural organic matter (NOM) and the impact of NOM on the sorption behavior of anthropogenic contaminants – A critical review. *Journal of Cleaner Production*, **376**, 134314. <https://doi.org/10.1016/j.jclepro.2022.134314>
- Ali, M. U., Lin, S., Yousaf, B., Abbas, Q., Munir, M. A. M., Ali, M. U., Rasihd, A., Zheng, C., Kuang, X., & Wong, M. H. (2021). Environmental emission, fate and transformation of microplastics in biotic and abiotic compartments: Global status, recent advances and future perspectives. *Science of The Total Environment*, **791**, 148422. <https://doi.org/10.1016/j.scitotenv.2021.148422>
- Alice, Pradel., Séléna, Ferreres., Cloé, Veclin., Hind, El, Hadri., Maud, Gautier., Bruno, Grassl., Julien, Gigault., Julien, Gigault. (2021). Stabilization of Fragmental Polystyrene Nanoplastic by Natural Organic Matter: Insight into Mechanisms. doi: 10.1021/ACSESTWATER.0C00283
- Alimi, O. S., Farner, J. M., Roweczyk, L., Petosa, A. R., Claveau-Mallet, D., Hernandez, L. M., ... & Tufenkji, N. (2022). Mechanistic understanding of the aggregation kinetics of nanoplastics in marine environments: Comparing synthetic and natural water matrices. *Journal of Hazardous Materials Advances*, **7**, 100115.

- Allen, S., Allen, D., Phoenix, V. R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S., & Galop, D. (2019). Atmospheric transport and deposition of microplastics in a remote mountain catchment. *Nature Geoscience*, *12*(5), 339-344. <https://doi.org/10.1038/s41561-019-0335-5>
- Anderson, P. J., Warrack, S., Langen, V., Challis, J. K., Hanson, M. L., & Rennie, M. D. (2017). Microplastic contamination in Lake Winnipeg, Canada. *Environmental Pollution*, *225*, 223-231. <https://doi.org/10.1016/j.envpol.2017.02.072>
- Andrady, A. L., & Neal, M. A. (2009). Applications and societal benefits of plastics. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *364*(1526), 1977-1984.
- Andrady, A. L. (2011). Microplastics in the marine environment. *Marine Pollution Bulletin*, *62*(8), 1596-1605. <https://doi.org/10.1016/j.marpolbul.2011.05.030>
- Asim, M., Jawaid, M., Saba, N., Nasir, M., & Sultan, M. T. H. (2017). Processing of hybrid polymer composites—a review. In *Hybrid Polymer Composite Materials* (pp. 1-22). Woodhead Publishing.
- Baekeland, L. H. (1909). The synthesis, constitution, and uses of Bakelite. *Industrial & Engineering Chemistry*, *1*(3), 149-161.
- Bakir, A., Rowland, S. J., & Thompson, R. C. (2014). Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environmental Pollution*, *185*, 16-23. <https://doi.org/10.1016/j.envpol.2013.10.007>
- Baldwin, A. K., Corsi, S. R., & Mason, S. A. (2016). Plastic debris in 29 Great Lakes tributaries: relations to watershed attributes and hydrology. *Environmental science & technology*, *50*(19), 10377-10385. <https://doi.org/10.1021/acs.est.6b02917>

- Bao, Z., Chen, Z., Lu, S., Wang, G., Qi, Z., & Cai, Z. (2021). Effects of hydroxyl group content on adsorption and desorption of anthracene and anthrol by polyvinyl chloride microplastics. *Science of The Total Environment*, 790, 148077. <https://doi.org/10.1016/j.scitotenv.2021.148077>
- Barletta, M., Lima, A. R., & Costa, M. F. (2019). Distribution, sources and consequences of nutrients, persistent organic pollutants, metals and microplastics in South American estuaries. *Science of The Total Environment*, 651, 1199-1218. <https://doi.org/10.1016/j.scitotenv.2018.09.276>
- Barnes, D. K., Galgani, F., Thompson, R. C., & Barlaz, M. (2009). Accumulation and fragmentation of plastic debris in global environments. *Philosophical transactions of the royal society B: biological sciences*, 364(1526), 1985-1998.
- Bayo, J., López-Castellanos, J., & Olmos, S. (2020). Membrane bioreactor and rapid sand filtration for the removal of microplastics in an urban wastewater treatment plant. *Marine Pollution Bulletin*, 156, 111211. <https://doi.org/10.1016/j.marpolbul.2020.111211>
- Betts, K. (2008). Why small plastic particles may pose a big problem in the oceans.
- Bianco, A., & Passananti, M. (2020). Atmospheric Micro and Nanoplastics: An Enormous Microscopic Problem. *Sustainability*, 12(18), 7327. <https://doi.org/10.3390/su12187327>
- Biron, M. (2018). Thermoplastics and thermoplastic composites. William Andrew.
- Boucher, J., & Friot, D. (2017). *Primary microplastics in the oceans: a global evaluation of sources* (Vol. 10). Gland, Switzerland: IUCN

- Bringer, A., Thomas, H., Prunier, G., Dubillot, E., Bossut, N., Churlaud, C., Clérandeau, C., Le Bihanic, F., & Cachot, J. (2020). High density polyethylene (HDPE) microplastics impair development and swimming activity of Pacific oyster D-larvae, *Crassostrea gigas*, depending on particle size. *Environmental Pollution*, 260, 113978. <https://doi.org/10.1016/j.envpol.2020.113978>
- British Plastics Federation. "Plastic in Transport Applications." *British Plastics Federation*, https://www.bpf.co.uk/Sustainability/Plastics_in_Transport.aspx.
- Browne, M. A., Galloway, T. S., & Thompson, R. C. (2010). Spatial patterns of plastic debris along estuarine shorelines. *Environmental science & technology*, 44(9), 3404-3409.
- Browne, M. A., Galloway, T., & Thompson, R. (2007). Microplastic--an emerging contaminant of potential concern?. *Integrated environmental assessment and Management*, 3(4), 559-561.
- Carr, S. A., Liu, J., & Tesoro, A. G. (2016). Transport and fate of microplastic particles in wastewater treatment plants. *Water Research*, 91, 174-182. <https://doi.org/10.1016/j.watres.2016.01.002>
- Chang, M. (2015). Reducing microplastics from facial exfoliating cleansers in wastewater through treatment versus consumer product decisions. *Marine Pollution Bulletin*, 101(1), 330-333. <https://doi.org/10.1016/j.marpolbul.2015.10.074>
- Chen, G., Feng, Q., & Wang, J. (2020). Mini-review of microplastics in the atmosphere and their risks to humans. *Science of The Total Environment*, 703, 135504. <https://doi.org/10.1016/j.scitotenv.2019.135504>

- Chen, X., Peng, L.-B., Wang, D., Zhu, Q.-L., & Zheng, J.-L. (2022). Combined effects of polystyrene microplastics and cadmium on oxidative stress, apoptosis, and GH/IGF axis in zebrafish early life stages. *Science of The Total Environment*, 813, 152514. <https://doi.org/https://doi.org/10.1016/j.scitotenv.2021.152514>
- Chen, M., Bao, X., Yue, Y., Yang, K., Liu, H., Yang, Y., Yu, H., Yu, Y., & Duan, N. (2023). Combined effects of cadmium and nanoplastics on oxidative stress, histopathology, and intestinal microbiota in largemouth bass (*Micropterus salmoides*). *Aquaculture*, 569, 739363. <https://doi.org/10.1016/j.aquaculture.2023.739363>
- Cheng, S. Z., & Jin, S. (2002). Crystallization and melting of metastable crystalline polymers. *Handbook of thermal analysis and calorimetry*, 3, 167-195.
- Claessens, M., De Meester, S., Van Landuyt, L., De Clerck, K., & Janssen, C. R. (2011). Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Marine pollution bulletin*, 62(10), 2199-2204.
- Cole, M., Lindeque, P., Halsband, C., & Galloway, T. S. (2011). Microplastics as contaminants in the marine environment: a review. *Marine pollution bulletin*, 62(12), 2588-2597.
- Cormier, B., Gambardella, C., Tato, T., Perdriat, Q., Costa, E., Veclin, C., Le Bihanic, F., Grassl, B., Dubocq, F., Kärrman, A., Van Arkel, K., Lemoine, S., Lagarde, F., Morin, B., Garaventa, F., Faimali, M., Cousin, X., Bégout, M., Beiras, R., . . . Cachot, J. (2021). Chemicals sorbed to environmental microplastics are toxic to early life stages of aquatic organisms. *Ecotoxicology and Environmental Safety*, 208, 111665. <https://doi.org/10.1016/j.ecoenv.2020.111665>
- Cousins, K. (2002). *Polymers in building and construction*. iSmithers Rapra Publishing
- Crawford, R. J., & Martin, P. J. (2020). *Plastics engineering*. Butterworth-Heinemann.

- Cox, K. D., Covernton, G. A., Davies, H. L., Dower, J. F., Juanes, F., & Dudas, S. E. (2019). Human consumption of microplastics. *Environmental science & technology*, 53(12), 7068-7074. <https://doi.org/10.1021/acs.est.9b01517>
- “Crops.” *FAOSTAT*, Food and Agriculture Organization of the United Nations (FAO), Accessed on 15 June 2020, www.fao.org/faostat/en/#data/QC/visualize.
- de Souza Machado, A. A., Lau, C. W., Till, J., Kloas, W., Lehmann, A., Becker, R., & Rillig, M. C. (2018). Impacts of microplastics on the soil biophysical environment. *Environmental science & technology*, 52(17), 9656-9665. <https://doi.org/10.1021/acs.est.8b02212>
- Demaid, A., Spedding, V., & Zucker, J. (1996). Classification of plastics materials. *Artificial intelligence in engineering*, 10(1), 9-20.
- Derraik, J. G. (2002). The pollution of the marine environment by plastic debris: a review. *Marine pollution bulletin*, 44(9), 842-852.
- Di, M., & Wang, J. (2018). Microplastics in surface waters and sediments of the Three Gorges Reservoir, China. *Science of The Total Environment*, 616-617, 1620-1627. <https://doi.org/10.1016/j.scitotenv.2017.10.150>
- Dong, C., Chen, C., Chen, Y., Chen, H., Lee, J., & Lin, C. (2020). Polystyrene microplastic particles: In vitro pulmonary toxicity assessment. *Journal of Hazardous Materials*, 385, 121575. <https://doi.org/10.1016/j.jhazmat.2019.121575>
- Dris, R., Gasperi, J., Rocher, V., Saad, M., Renault, N., & Tassin, B. (2015). Microplastic contamination in an urban area: a case study in Greater Paris. *Environmental Chemistry*, 12(5), 592-599. <https://doi.org/10.1071/EN14167>

Ebbing, D., & Gammon, S. D. (2016). General chemistry. Cengage Learning.

Eerkes-Medrano, D., Thompson, R. C., & Aldridge, D. C. (2015). Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Research*, 75, 63-82.
<https://doi.org/10.1016/j.watres.2015.02.012>

Environment and Climate Change Canada, *Consultation Document Pollution Prevention Planning Notice for Primary Food Plastic Packaging: Targets for Reduction, Reuse, Redesign, and Recycled Content - Canada.Ca*, / Gouvernement du Canada, 15 Aug. 2023, www.canada.ca/en/environment-climate-change/corporate/transparency/consultations/consultation-pollution-prevention-planning-notice-primary-food-plastic-packaging.html.

Environment and Climate Change Canada, Managing and Reducing Plastic Waste. Retrieved from <https://www.canada.ca/en/environment-climate-change/services/managing-reducing-waste/reduce-plastic-waste.html>

Eriksen, M., Mason, S., Wilson, S., Box, C., Zellers, A., Edwards, W., Farley, H., & Amato, S. (2013). Microplastic pollution in the surface waters of the Laurentian Great Lakes. *Marine Pollution Bulletin*, 77(1-2), 177-182.
<https://doi.org/10.1016/j.marpolbul.2013.10.007>

Estahbanati, S., & Fahrenfeld, N. (2016). Influence of wastewater treatment plant discharges on microplastic concentrations in surface water. *Chemosphere*, 162, 277-284.
<https://doi.org/10.1016/j.chemosphere.2016.07.083>

- Fan, J., & Njuguna, J. (2016). An introduction to lightweight composite materials and their use in transport structures. *Lightweight Composite Structures in Transport*, 3-34.
<https://doi.org/10.1016/B978-1-78242-325-6.00001-3>
- Feng, H., Liu, Y., Xu, Y., Li, S., Liu, X., Dai, Y., Zhao, J., & Yue, T. (2022). Benzo[a]pyrene and heavy metal ion adsorption on nanoplastics regulated by humic acid: Cooperation/competition mechanisms revealed by molecular dynamics simulations. *Journal of Hazardous Materials*, 424, 127431.
<https://doi.org/10.1016/j.jhazmat.2021.127431>
- FitzGerald, L. I., Olorunyomi, J. F., Singh, R., & Doherty, C. M. (2022). Towards Solving the PFAS Problem: The Potential Role of Metal-Organic Frameworks. *ChemSusChem*, 15(19), e202201136.
<https://doi.org/10.1002/cssc.202201136>
- Flory, P. J. (1946). Fundamental principles of condensation polymerization. *Chemical Reviews*, 39(1), 137-197.
- Fu, L., Li, J., Wang, G., Luan, Y., & Dai, W. (2021). Adsorption behavior of organic pollutants on microplastics. *Ecotoxicology and Environmental Safety*, 217, 112207.
<https://doi.org/10.1016/j.ecoenv.2021.112207>
- Gambino, I., Bagordo, F., Grassi, T., Panico, A., & De Donno, A. (2021). Occurrence of Microplastics in Tap and Bottled Water: Current Knowledge. *International Journal of Environmental Research and Public Health*, 19(9), 5283.
<https://doi.org/10.3390/ijerph19095283>
- Gasperi, J., Wright, S. L., Dris, R., Collard, F., Mandin, C., Guerrouache, M., Langlois, V., Kelly, F. J., & Tassin, B. (2018). Microplastics in air: Are we breathing it in? *Current*

Opinion in Environmental Science & Health, 1, 1-5.

<https://doi.org/10.1016/j.coesh.2017.10.002>

Genevieve D'Avignon, Irene Gregory-Eaves, and Anthony Ricciardi. 2021. Microplastics in lakes and rivers: an issue of emerging significance to limnology. *Environmental Reviews*. **30**(2): 228-244. <https://doi.org/10.1139/er-2021-0048>

Geueke, B., Groh, K., & Muncke, J. (2018). Food packaging in the circular economy: Overview of chemical safety aspects for commonly used materials. *Journal of cleaner production*, *193*, 491-505.

Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science advances*, *3*(7), e1700782.

Gies, E. A., LeNoble, J. L., Noël, M., Etemadifar, A., Bishay, F., Hall, E. R., & Ross, P. S. (2018). Retention of microplastics in a major secondary wastewater treatment plant in Vancouver, Canada. *Marine Pollution Bulletin*, *133*, 553-561. <https://doi.org/10.1016/j.marpolbul.2018.06.006>

Gigault, J., Halle, A. T., Baudrimont, M., Pascal, P., Gauffre, F., Phi, T., El Hadri, H., Grassl, B., & Reynaud, S. (2018). Current opinion: What is a nanoplastic? *Environmental Pollution*, *235*, 1030-1034. <https://doi.org/10.1016/j.envpol.2018.01.024>

Goedecke, C., Mülow-Stollin, U., Hering, S., Richter, J., Piechotta, C., Paul, A., & Braun, U. (2017). A first pilot study on the sorption of environmental pollutants on various microplastic materials. *Journal of Environmental Analytical Chemistry*, *4*(1), Article-1000191.

Goswami, L., Vinoth Kumar, R., Borah, S. N., Arul Manikandan, N., Pakshirajan, K., & Pugazhenth, G. (2018). Membrane bioreactor and integrated membrane bioreactor

- systems for micropollutant removal from wastewater: A review. *Journal of Water Process Engineering*, 26, 314-328. <https://doi.org/10.1016/j.jwpe.2018.10.024>
- Gradin, P., Howgate, P. G., Seldén, R., & Brown, R. (1989). Dynamic--Mechanical Properties. *Pergamon Press plc, Comprehensive Polymer Science: the Synthesis, Characterization, Reactions & Applications of Polymers.*, 2, 533-569.
- Graham, E. R., & Thompson, J. T. (2009). Deposit-and suspension-feeding sea cucumbers (Echinodermata) ingest plastic fragments. *Journal of experimental marine biology and ecology*, 368(1), 22-29.
- Grassie, N., & Scott, G. (1988). *Polymer degradation and stabilisation*. CUP Archive.
- Gregory, M. R. (1996). Plastic ‘scrubbers’ in hand cleansers: A further (and minor) source for marine pollution identified. *Marine Pollution Bulletin*, 32(12), 867-871. [https://doi.org/10.1016/S0025-326X\(96\)00047-1](https://doi.org/10.1016/S0025-326X(96)00047-1)
- Hamidian, A. H., Ozumchelouei, E. J., Feizi, F., Wu, C., Zhang, Y., & Yang, M. (2021). A review on the characteristics of microplastics in wastewater treatment plants: A source for toxic chemicals. *Journal of Cleaner Production*, 295, 126480. <https://doi.org/10.1016/j.jclepro.2021.126480>
- Hasirci, V., Yilgor, P., Endogan, T., Eke, G., & Hasirci, N. (2011). *1.121-polymer fundamentals: polymer synthesis* (pp. 349-371). Oxford, Elsevier.
- Hedenqvist, M. S. (2005). Barrier packaging materials. In *Handbook of environmental degradation of materials* (pp. 547-563). William Andrew Publishing.
- Hernandez, L. M., Xu, E. G., Larsson, H. C., Tahara, R., Maisuria, V. B., & Tufenkji, N. (2019). Plastic teabags release billions of microparticles and nanoparticles into

tea. *Environmental science & technology*, 53(21), 12300-12310.
<https://doi.org/10.1021/acs.est.9b02540>

Hidayaturrahman, H., & Lee, T. (2019). A study on characteristics of microplastic in wastewater of South Korea: Identification, quantification, and fate of microplastics during treatment process. *Marine Pollution Bulletin*, 146, 696-702.
<https://doi.org/10.1016/j.marpolbul.2019.06.071>

Hochheiser, S. (1983). A 19th-Century Material: Pioneer Plastic. The Making and Selling of Celluloid. Robert Friedel. University of Wisconsin Press, Madison, 1983. xxii, 154

Huang, Z., Xiao, X., Wang, D., Zhong, Y., Ding, Q., & You, J. (2023). Joint effects of micro-sized polystyrene and chlorpyrifos on zebrafish based on multiple endpoints and gut microbial effects. *Journal of Environmental Sciences*, 126, 184-197.
<https://doi.org/10.1016/j.jes.2022.06.001>

International Organization for Standardization. (2017). ISO 22412:2017. *Particle size analysis — Dynamic light scattering (DLS)*.
<https://www.iso.org/obp/ui/en/#iso:std:iso:22412:ed-2:v1:en>

Issac, M.N., Kandasubramanian, B. Effect of microplastics in water and aquatic systems. *Environ Sci Pollut Res* **28**, 19544–19562 (2021).
<https://doi.org/10.1007/s11356-021-13184-2>

Ivanov, D. A., Amalou, Z., & Magonov, S. N. (2001). Real-time evolution of the lamellar organization of poly (ethylene terephthalate) during crystallization from the melt: high-temperature atomic force microscopy study. *Macromolecules*, 34(26), 8944-8952.

- Ivar do Sul, J. A., Costa, M. F., Barletta, M., & Cysneiros, F. J. A. (2013). Pelagic microplastics around an archipelago of the Equatorial Atlantic. *Marine Pollution Bulletin*, 75(1-2), 305-309. <https://doi.org/10.1016/j.marpolbul.2013.07.040>
- Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., Narayan, R., & Law, K. L. (2015). Plastic waste inputs from land into the ocean. *Science*. <https://doi.org/1260352>
- Jansen, J. A. (2016). Plastics—It's All About Molecular Structure. *Plast Eng Plastics Engineering*, 72(8), 44-49.
- Jiang, B., Kauffman, A., Li, L. *et al.* Health impacts of environmental contamination of micro- and nanoplastics: a review. *Environ Health Prev Med* **25**, 29 (2020). <https://doi.org/10.1186/s12199-020-00870-9>
- Joksimovic, N., Selakovic, D., Jovicic, N., Jankovic, N., Pradeepkumar, P., Eftekhari, A., & Rosic, G. (2022). Nanoplastics as an Invisible Threat to Humans and the Environment. *Journal of Nanomaterials*, 2022, 1-15. <https://doi.org/10.1155/2022/6707819>
- Junaid, M., Abbas, Z., Siddiqui, J. A., Liu, S., Tabraiz, S., Yue, Q., & Wang, J. (2023). Ecotoxicological impacts associated with the interplay between micro(nano)plastics and pesticides in aquatic and terrestrial environments. *TrAC Trends in Analytical Chemistry*, 165, 117133. <https://doi.org/10.1016/j.trac.2023.117133>
- Jung, Y. S., Sampath, V., Prunicki, M., Aguilera, J., Allen, H., LaBeaud, D., Veidis, E., Barry, M., Erny, B., Patel, L., Akdis, C., Akdis, M., & Nadeau, K. (2022). Characterization and regulation of microplastic pollution for protecting planetary and human health. *Environmental Pollution*, 315, 120442. <https://doi.org/10.1016/j.envpol.2022.120442>

- Katyal, D., Kong, E., & Villanueva, J. (2020). Microplastics in the environment: impact on human health and future mitigation strategies. *Environmental Health Review*, 63(1), 27-31. <https://doi.org/10.5864/d2020-005>
- Khan, K. Y., Li, G., Du, D., Ali, B., Zhang, S., Zhong, M., Stoffella, P. J., Iqbal, B., Cui, X., Fu, L., & Guo, Y. (2022). Impact of polystyrene microplastics with combined contamination of norfloxacin and sulfadiazine on *Chrysanthemum coronarium* L. *Environmental Pollution*, 316, 120522. <https://doi.org/10.1016/j.envpol.2022.120522>
- Koelmans, A. A., Bakir, A., Burton, G. A., & Janssen, C. R. (2016). Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. *Environmental science & technology*, 50(7), 3315-3326. <https://doi.org/10.1021/acs.est.5b06069>
- Landeros, Lupita, Williams, Ian, Shaw, Peter, Hudson, Malcolm and Dominguez Cortinas, Gabriela (2022) A review of the origins of microplastics arriving at wastewater treatment plants. *Detritus*, 20, 41-55. (doi:10.31025/2611-4135/2022.15224).
- Lares, M., Ncibi, M. C., Sillanpää, M., & Sillanpää, M. (2018). Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. *Water research*, 133, 236-246. <https://doi.org/10.1016/j.watres.2018.01.049>
- Leal Filho, W., Saari, U., Fedoruk, M., Iital, A., Moora, H., Klöga, M., & Voronova, V. (2019). An overview of the problems posed by plastic products and the role of extended producer responsibility in Europe. *Journal of Cleaner Production*, 214, 550-558. <https://doi.org/10.1016/j.jclepro.2018.12.256>

- Lechner, A., & Ramler, D. (2015). The discharge of certain amounts of industrial microplastic from a production plant into the River Danube is permitted by the Austrian legislation. *Environmental Pollution*, 200, 159-160. <https://doi.org/10.1016/j.envpol.2015.02.019>
- Lehner, Roman, Christoph Weder, Alke Petri-Fink, and Barbara Rothen-Rutishauser. "Emergence of nanoplastic in the environment and possible impact on human health." *Environmental science & technology* 53, no. 4 (2019): 1748-1765. <https://doi.org/10.1021/acs.est.8b05512>
- Lenaker, P. L., Baldwin, A. K., Corsi, S. R., Mason, S. A., Reneau, P. C., & Scott, J. W. (2019). Vertical distribution of microplastics in the water column and surficial sediment from the Milwaukee River Basin to Lake Michigan. *Environmental science & technology*, 53(21), 12227-12237. <https://doi.org/10.1021/acs.est.9b03850>
- Leslie, H. A., Van Velzen, M. J., Brandsma, S. H., Vethaak, A. D., Garcia-Vallejo, J. J., & Lamoree, M. H. (2022). Discovery and quantification of plastic particle pollution in human blood. *Environment International*, 163, 107199. <https://doi.org/10.1016/j.envint.2022.107199>
- Leslie, H., Brandsma, S., Van Velzen, M., & Vethaak, A. (2017). Microplastics en route: Field measurements in the Dutch river delta and Amsterdam canals, wastewater treatment plants, North Sea sediments and biota. *Environment International*, 101, 133-142. <https://doi.org/10.1016/j.envint.2017.01.018>
- Li, Q., Zhai, J., Zhang, W., Wang, M., Zhou, J.: Kinetic studies of adsorption of Pb (II), Cr (III) and Cu (II) from aqueous solution by sawdust and modified peanut husk. *Journal of hazardous materials*. 141(1), 163-167 (2007). <https://doi.org/10.1016/j.jhazmat.2006.06.109>

- Li, J., Ma, S., Li, X., & Wei, W. (2021). Adsorption of Tannic Acid and Macromolecular Humic/Fulvic Acid onto Polystyrene Microplastics: A Comparison Study. *Water*, 14(14), 2201. <https://doi.org/10.3390/w14142201>
- Li, J., Yang, D., Li, L., Jabeen, K., & Shi, H. (2015). Microplastics in commercial bivalves from China. *Environmental Pollution*, 207, 190-195. <https://doi.org/10.1016/j.envpol.2015.09.018>
- Lima, A., Costa, M., & Barletta, M. (2014). Distribution patterns of microplastics within the plankton of a tropical estuary. *Environmental Research*, 132, 146-155. <https://doi.org/10.1016/j.envres.2014.03.031>
- Liu, X., Sun, P., Qu, G., Jing, J., Zhang, T., Shi, H., & Zhao, Y. (2021). Insight into the characteristics and sorption behaviors of aged polystyrene microplastics through three type of accelerated oxidation processes. *Journal of Hazardous Materials*, 407, 124836. <https://doi.org/10.1016/j.jhazmat.2020.124836>
- Liu, X., Zheng, M., Wang, L., Ke, R., Lou, Y., Zhang, X., Dong, X., & Zhang, Y. (2018). Sorption behaviors of tris-(2,3-dibromopropyl) isocyanurate and hexabromocyclododecanes on polypropylene microplastics. *Marine Pollution Bulletin*, 135, 581-586. <https://doi.org/10.1016/j.marpolbul.2018.07.061>
- Liu, X., Shi, H., Xie, B., Dionysiou, D. D., & Zhao, Y. (2019). Microplastics as both a sink and a source of bisphenol A in the marine environment. *Environmental Science & Technology*, 53(17), 10188-10196. <https://doi.org/10.1021/acs.est.9b02834>
- Llorca, M., Schirinzi, G., Martínez, M., Barceló, D., & Farré, M. (2018). Adsorption of perfluoroalkyl substances on microplastics under environmental conditions. *Environmental Pollution*, 235, 680-691. <https://doi.org/10.1016/j.envpol.2017.12.075>

- Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R.: Relative distribution of Pb²⁺ sorption mechanisms by sludge-derived biochar. *Water research*. 46(3), 854-862 (2018). <https://doi.org/10.1016/j.watres.2011.11.058>
- Lv, X., Dong, Q., Zuo, Z., Liu, Y., Huang, X., & Wu, W. M. (2019). Microplastics in a municipal wastewater treatment plant: Fate, dynamic distribution, removal efficiencies, and control strategies. *Journal of Cleaner Production*, 225, 579-586. <https://doi.org/10.1016/j.jclepro.2019.03.321>
- Ma, J., Zhao, J., Zhu, Z., Li, L., & Yu, F. (2019). Effect of microplastic size on the adsorption behavior and mechanism of triclosan on polyvinyl chloride. *Environmental Pollution*, 254, 113104. <https://doi.org/10.1016/j.envpol.2019.113104>
- Ma, Y., Huang, A., Cao, S., Sun, F., Wang, L., Guo, H., & Ji, R. (2016). Effects of nanoplastics and microplastics on toxicity, bioaccumulation, and environmental fate of phenanthrene in fresh water. *Environmental Pollution*, 219, 166-173. <https://doi.org/10.1016/j.envpol.2016.10.061>
- Magni, S., Binelli, A., Pittura, L., Avio, C. G., Della Torre, C., Parenti, C. C., Gorbi, S., & Regoli, F. (2019). The fate of microplastics in an Italian Wastewater Treatment Plant. *Science of The Total Environment*, 652, 602-610. <https://doi.org/10.1016/j.scitotenv.2018.10.269>
- Mandal, S., Bolan, N. S., Sarkar, B., Wijesekara, H., Bradney, L., & Kirkham, M. B. (2020). Environmentally Toxic Components of Particulate Plastics. In *Particulate Plastics in Terrestrial and Aquatic Environments* (pp. 165-179). CRC Press.
- Mani, T., Hauk, A., & Walter, U. (2015). Microplastics profile along the Rhine River. *Scientific Reports*, 5(1), 1-7. <https://doi.org/10.1038/srep17988>

- McDougall, L., Thomson, L., Brand, S., Wagstaff, A., Lawton, L. A., & Petrie, B. (2022). Adsorption of a diverse range of pharmaceuticals to polyethylene microplastics in wastewater and their desorption in environmental matrices. *Science of The Total Environment*, 808, 152071. <https://doi.org/10.1016/j.scitotenv.2021.152071>
- Meijer et al. (2021). More than 1000 rivers account for 80% of global riverine plastic emissions into the ocean. *Science Advances*.
- Moore, Charles James, Gwendolyn L. Lattin, and A. F. Zellers. "Quantity and type of plastic debris flowing from two urban rivers to coastal waters and beaches of Southern California." *Revista de Gestão Costeira Integrada-Journal of Integrated Coastal Zone Management* 11.1 (2011): 65-73.
- More, C. V., Alsayed, Z., Badawi, M. S., Thabet, A. A., & Pawar, P. P. (2021). Polymeric composite materials for radiation shielding: A review. *Environmental chemistry letters*, 19, 2057-2090.
- Mulder, K., & Knot, M. (2001). PVC plastic: a history of systems development and entrenchment. *Technology in Society*, 23(2), 265-286.
- Munoz, M., Ortiz, D., Nieto-Sandoval, J., de Pedro, Z. M., & Casas, J. A. (2021). Adsorption of micropollutants onto realistic microplastics: Role of microplastic nature, size, age, and NOM fouling. *Chemosphere*, 283, 131085. <https://doi.org/10.1016/j.chemosphere.2021.131085>
- Murphy, F., Ewins, C., Carbonnier, F., & Quinn, B. (2016). Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. *Environmental science & technology*, 50(11), 5800-5808. <https://doi.org/10.1021/acs.est.5b05416>

- Murray, A., & Örmeci, B. (2020). Removal Effectiveness of Nanoplastics (<400 nm) with Separation Processes Used for Water and Wastewater Treatment. *Water*, 12(3), 635. <https://doi.org/10.3390/w12030635>
- Napper, I. E., Bakir, A., Rowland, S. J., & Thompson, R. C. (2015). Characterisation, quantity and sorptive properties of microplastics extracted from cosmetics. *Marine Pollution Bulletin*, 99(1-2), 178-185. <https://doi.org/10.1016/j.marpolbul.2015.07.029>
- Naziri, A., Mina, T., Manoli, K., Beretsou, V. G., Christou, A., Michael, C., Agathokleous, E., & Fatta-Kassinos, D. (2023). Looking into the effects of co-contamination by micro(nano)plastics in the presence of other pollutants on irrigated edible plants. *Science of The Total Environment*, 892, 164618. <https://doi.org/10.1016/j.scitotenv.2023.164618>
- Nizzetto, L., Bussi, G., Futter, M. N., Butterfield, D., & Whitehead, P. G. (2016). A theoretical assessment of microplastic transport in river catchments and their retention by soils and river sediments. *Environmental Science: Processes & Impacts*, 18(8), 1050-1059. <https://doi.org/10.1039/C6EM00206D>
- Nkwachukwu, O. I., Chima, C. H., Ikenna, A. O., & Albert, L. (2013). Focus on potential environmental issues on plastic world towards a sustainable plastic recycling in developing countries. *International Journal of Industrial Chemistry*, 4, 1-13.
- Nogueira, D. J., Silva, A. C. D. O. D., da Silva, M. L. N., Vicentini, D. S., & Matias, W. G. (2022). Individual and combined multigenerational effects induced by polystyrene nanoplastic and glyphosate in *Daphnia magna* (Strauss, 1820). *Science of The Total Environment*, 811, 151360. <https://doi.org/10.1016/j.scitotenv.2021.151360>

- Parkes, A. (1866). On the properties of parkesine and its application to the arts and manufactures. *Journal of the Franklin Institute*, 81(6), 384-388.
- Patel, M.M., Goyal, B.R., Bhadada, S.V. *et al.* Getting into the Brain. *CNS Drugs* 23, 35–58 (2009). <https://doi.org/10.2165/0023210-200923010-00003>
- Patra, I., Huy, D.T.N., Alsaikhan, F. *et al.* Toxic effects on enzymatic activity, gene expression and histopathological biomarkers in organisms exposed to microplastics and nanoplastics: a review. *Environ Sci Eur* 34, 80 (2022). <https://doi.org/10.1186/s12302-022-00652-w>
- Prata, J. C., Da Costa, J. P., Lopes, I., Duarte, A. C., & Rocha-Santos, T. (2020). Environmental exposure to microplastics: An overview on possible human health effects. *Science of The Total Environment*, 702, 134455. <https://doi.org/10.1016/j.scitotenv.2019.134455>
- Prata, J. C. (2018). Airborne microplastics: Consequences to human health? *Environmental Pollution*, 234, 115-126. <https://doi.org/10.1016/j.envpol.2017.11.043>
- Pérez-Chávez, N.A., Albesa, A.G. & Longo, G.S. Molecular theory of glyphosate adsorption to pH-responsive polymer layers. *Adsorption* 25, 1307–1316 (2019). <https://doi.org/10.1007/s10450-019-00091-9>
- Piperagkas, O., Papageorgiou, N., & Karakassis, I. (2019). Qualitative and quantitative assessment of microplastics in three sandy Mediterranean beaches, including different methodological approaches. *Estuarine, Coastal and Shelf Science*, 219, 169-175. <https://doi.org/10.1016/j.ecss.2019.02.016>
- Ramirez Arenas, L., Ramseier Gentile, S., Zimmermann, S., & Stoll, S. (2022). Fate and removal efficiency of polystyrene nanoplastics in a pilot drinking water treatment plant.

Science of The Total Environment, 813, 152623.
<https://doi.org/10.1016/j.scitotenv.2021.152623>

Rayner, L. W. A. (1960). Non-metallic materials used in shipbuilding. *International Shipbuilding Progress*, 7(75), 456-468.

Ritchie, H., & Roser, M. (2018). Plastic pollution. *Our World in Data*.

Rosato, D. V. (2003). *Plastics engineered product design*. Elsevier.

Ryan, P. G., Moore, C. J., Van Franeker, J. A., & Moloney, C. L. (2009). Monitoring the abundance of plastic debris in the marine environment. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526), 1999-2012.

Scanes, E., Wood, H., & Ross, P. (2019). Microplastics detected in haemolymph of the Sydney rock oyster *Saccostrea glomerata*. *Marine Pollution Bulletin*, 149, 110537.

Schwabl, P., Köppel, S., Königshofer, P., Bucsics, T., Trauner, M., Reiberger, T., & Liebmann, B. (2019). Detection of various microplastics in human stool: a prospective case series. *Annals of internal medicine*, 171(7), 453-457. <https://doi.org/10.7326/M19-0618>

“Science of Plastics.” *Science History Institute*, 31 Jan. 2023,
www.sciencehistory.org/science-of-plastics.

Shah, A. A., Hasan, F., Hameed, A., & Ahmed, S. (2008). Biological degradation of plastics: A comprehensive review. *Biotechnology Advances*, 26(3), 246-265.
<https://doi.org/10.1016/j.biotechadv.2007.12.005>

- Shekoohiyan, S., & Akbarzadeh, A. (2022). The abundance of microplastic pollution along the Jajroud river of Tehran: Estimating the water quality index and the ecological risk. *Ecological Indicators*, *145*, 109629. <https://doi.org/10.1016/j.ecolind.2022.109629>
- Siipola, V., Pflugmacher, S., Romar, H., Wendling, L., & Koukkari, P. (2019). Low-Cost Biochar Adsorbents for Water Purification Including Microplastics Removal. *Applied Sciences*, *10*(3), 788. <https://doi.org/10.3390/app10030788>
- Simon, M., Van Alst, N., & Vollertsen, J. (2018). Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. *Water Research*, *142*, 1-9. <https://doi.org/10.1016/j.watres.2018.05.019>
- Song, J., Jin, X., Wang, X. C., & Jin, P. (2019). Preferential binding properties of carboxyl and hydroxyl groups with aluminium salts for humic acid removal. *Chemosphere*, *234*, 478-487. <https://doi.org/10.1016/j.chemosphere.2019.06.107>
- Su, L., Xue, Y., Li, L., Yang, D., Kolandhasamy, P., Li, D., & Shi, H. (2016). Microplastics in Taihu Lake, China. *Environmental Pollution*, *216*, 711-719. <https://doi.org/10.1016/j.envpol.2016.06.036>
- Su, Y., Qi, H., Hou, Y., Gao, M., Li, J., Cai, M., Zhu, X., Chen, M., Ge, C., Fu, D., Wang, Z., & Peng, L. (2022). Combined Effects of Microplastics and Benzo[a]pyrene on the Marine Diatom *Chaetoceros muelleri*. *Frontiers in Marine Science*, *8*, 779321. <https://doi.org/10.3389/fmars.2021.779321>
- Syranidou, E., & Kalogerakis, N. (2022). Interactions of microplastics, antibiotics and antibiotic resistant genes within WWTPs. *Science of The Total Environment*, *804*, 150141. <https://doi.org/10.1016/j.scitotenv.2021.150141>

- Talvitie, J., Mikola, A., Koistinen, A., & Setälä, O. (2017). Solutions to microplastic pollution – Removal of microplastics from wastewater effluent with advanced wastewater treatment technologies. *Water Research*, *123*, 401-407. <https://doi.org/10.1016/j.watres.2017.07.005>
- Ter Halle, A., & Ghiglione, J. F. (2021). Nanoplastics: a complex, polluting terra incognita. *Environmental Science & Technology*, *55*(21), 14466-14469. <https://doi.org/10.1021/acs.est.1c04142>
- Thirumavalavan, M., Lai, Y.L., Lin, L.C., Lee, J.F.: Cellulose-based native and surface modified fruit peels for the adsorption of heavy metal ions from aqueous solution: Langmuir adsorption isotherms. *Journal of Chemical and Engineering Data*. *55*(3), 1186-1192 (2010). <https://doi.org/10.1021/je900585t>
- Thompson, R. C., Swan, S. H., Moore, C. J., & Frederick, S. (2009). vom Saal. 2009. "Our Plastic Age." *Philosophical Transactions of the Royal Society B: Biological Sciences*, *364*(1526), 1973-1976.
- Tong, H., Jiang, Q., Hu, X., & Zhong, X. (2020). Occurrence and identification of microplastics in tap water from China. *Chemosphere*, *252*, 126493. <https://doi.org/10.1016/j.chemosphere.2020.126493>
- Toussaint, B., Raffael, B., Angers-Loustau, A., Gilliland, D., Kestens, V., Petrillo, M., ... & Van den Eede, G. (2019). Review of micro-and nanoplastic contamination in the food chain. *Food Additives & Contaminants: Part A*, *36*(5), 639-673. <https://doi.org/10.1080/19440049.2019.1583381>
- Vaid, M., Sarma, K., & Gupta, A. (2021). Microplastic pollution in aquatic environments with special emphasis on riverine systems: Current understanding and way forward. *Journal*

of Environmental Management, 293, 112860.
<https://doi.org/10.1016/j.jenvman.2021.112860>

Vega-Herrera, A., Llorca, M., Borrell-Diaz, X., Redondo-Hasselerharm, P. E., Abad, E., Villanueva, C. M., & Farré, M. (2022). Polymers of micro(nano) plastic in household tap water of the Barcelona Metropolitan Area. *Water Research*, 220, 118645.
<https://doi.org/10.1016/j.watres.2022.118645>

Vivaldo-Lima, E., & Saldívar-Guerra, E. (2013). *Handbook of polymer synthesis, characterization, and processing*. John Wiley & Sons, Incorporated.

Wagstaff, A., Lawton, L. A., & Petrie, B. (2022). Polyamide microplastics in wastewater as vectors of cationic pharmaceutical drugs. *Chemosphere*, 288, 132578.
<https://doi.org/10.1016/j.chemosphere.2021.132578>

Wang, W., Ndungu, A. W., Li, Z., & Wang, J. (2017). Microplastics pollution in inland freshwaters of China: A case study in urban surface waters of Wuhan, China. *Science of The Total Environment*, 575, 1369-1374.
<https://doi.org/10.1016/j.scitotenv.2016.09.213>

Wang, X., Bolan, N., Tsang, D. C., Sarkar, B., Bradney, L., & Li, Y. (2021). A review of microplastics aggregation in aquatic environment: Influence factors, analytical methods, and environmental implications. *Journal of Hazardous Materials*, 402, 123496. <https://doi.org/10.1016/j.jhazmat.2020.123496>

Wang, J., Liu, X., Liu, G., Zhang, Z., Wu, H., Cui, B., Bai, J., & Zhang, W. (2019). Size effect of polystyrene microplastics on sorption of phenanthrene and nitrobenzene. *Ecotoxicology and Environmental Safety*, 173, 331-338.
<https://doi.org/10.1016/j.ecoenv.2019.02.037>

- World Health Organization. Guidelines for drinking-water quality. Fourth Edition (2017).
Incorporating the First Addendum. World Health Organization.
- Xu, B., Liu, F., Brookes, P. C., & Xu, J. (2018). Microplastics play a minor role in tetracycline sorption in the presence of dissolved organic matter. *Environmental Pollution*, 240, 87-94. <https://doi.org/10.1016/j.envpol.2018.04.113>
- Yan, Y., Li, Q., Bolan, S. S., Bolan, N. S., Ok, Y. S., Kirkham, M. B., & Kwon, E. E. (2020). Interaction of dissolved organic matter with particulate plastics. In *Particulate Plastics in Terrestrial and Aquatic Environments* (pp. 95-105). CRC Press.
- Yang, H., Liu, Z., Li, L., Zhao, X., Xu, Y., 2009. Study on adsorption of glyphosate on modified activated carbon. *Environ. Pollut. Control*. 31, 10-23
- Yousif, E., & Hasan, A. (2015). Photostabilization of poly (vinyl chloride)–Still on the run. *Journal of Taibah University for Science*, 9(4), 421-448.
- Yu, F., Yang, C., Zhu, Z., Bai, X., & Ma, J. (2019). Adsorption behavior of organic pollutants and metals on micro/nanoplastics in the aquatic environment. *Science of The Total Environment*, 694, 133643. <https://doi.org/10.1016/j.scitotenv.2019.133643>
- Yu, J., Chen, L., Gu, W., Liu, S., & Wu, B. (2022). Heterogeneity effects of nanoplastics and lead on zebrafish intestinal cells identified by single-cell sequencing. *Chemosphere*, 289, 133133. <https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.133133>
- Zajac, M., Kotyńska, J., Zambrowski, G., Breczko, J., Deptuła, P., Cieśluk, M., Zambrzycka, M., Świącicka, I., Bucki, R., & Naumowicz, M. (2023). Exposure to polystyrene nanoparticles leads to changes in the zeta potential of bacterial cells. *Scientific Reports*, 13(1), 1-16. <https://doi.org/10.1038/s41598-023-36603-5>

- Zhang, Q., Qu, Q., Lu, T., Ke, M., Zhu, Y., Zhang, M., Zhang, Z., Du, B., Pan, X., Sun, L., & Qian, H. (2018). The combined toxicity effect of nanoplastics and glyphosate on *Microcystis aeruginosa* growth. *Environmental Pollution*, 243, 1106-1112. <https://doi.org/10.1016/j.envpol.2018.09.073>
- Zhang, K., Gong, W., Lv, J., Xiong, X., & Wu, C. (2015). Accumulation of floating microplastics behind the Three Gorges Dam. *Environmental Pollution*, 204, 117-123. <https://doi.org/10.1016/j.envpol.2015.04.023>
- Zhang, Y., & Goss, G. G. (2021). The “Trojan Horse” effect of nanoplastics: Potentiation of polycyclic aromatic hydrocarbon uptake in rainbow trout and the mitigating effects of natural organic matter. *Environmental Science: Nano*, 8(12), 3685-3698.
- Zhang, Y., Diehl, A., Lewandowski, A., Gopalakrishnan, K., & Baker, T. (2020). Removal efficiency of micro- and nanoplastics (180 nm–125 µm) during drinking water treatment. *Science of The Total Environment*, 720, 137383. <https://doi.org/10.1016/j.scitotenv.2020.137383>
- Zhang, Y., Ni, F., He, J., Shen, F., Deng, S., Tian, D., Zhang, Y., Liu, Y., Chen, C., & Zou, J. (2021). Mechanistic insight into different adsorption of norfloxacin on microplastics in simulated natural water and real surface water. *Environmental Pollution*, 284, 117537. <https://doi.org/10.1016/j.envpol.2021.117537>
- Zhang, Y., & Goss, G. G. (2020). Potentiation of polycyclic aromatic hydrocarbon uptake in zebrafish embryos by nanoplastics. *Environmental Science: Nano*, 7(6), 1730-1741. <https://doi.org/10.1039/D0EN00163E>

- Zhang, Y., Gao, T., Kang, S., & Sillanpää, M. (2019). Importance of atmospheric transport for microplastics deposited in remote areas. *Environmental Pollution*, 254, 112953. <https://doi.org/10.1016/j.envpol.2019.07.121>
- Zhao, H., Cao, Z., Liu, X., Zhan, Y., Zhang, J., Xiao, X., Yang, Y., Zhou, J., & Xu, J. (2017). Seasonal variation, flux estimation, and source analysis of dissolved emerging organic contaminants in the Yangtze Estuary, China. *Marine Pollution Bulletin*, 125(1-2), 208-215. <https://doi.org/10.1016/j.marpolbul.2017.08.034>
- Zhao, M., Huang, L., Arulmani, S. R., Yan, J., Wu, L., Wu, T., Zhang, H., & Xiao, T. (2021). Adsorption of Different Pollutants by Using Microplastic with Different Influencing Factors and Mechanisms in Wastewater: A Review. *Nanomaterials*, 12(13), 2256. <https://doi.org/10.3390/nano12132256>
- Zhao, Y., Yang, Y., Yang, S., Wang, Q., Feng, C., Zhang, Z.: Adsorption of high ammonium nitrogen from wastewater using a novel ceramic adsorbent and the evaluation of the ammonium-adsorbed-ceramic as fertilizer. *Journal of colloid and interface science*. 393, 264-270 (2013). <https://doi.org/10.1016/j.jcis.2012.10.028>
- Zhu, J., Zhang, Y., Xu, Y., Wang, L., Wu, Q., Zhang, Z., & Li, L. (2022). Effects of microplastics on the accumulation and neurotoxicity of methylmercury in zebrafish larvae. *Marine Environmental Research*, 176, 105615. <https://doi.org/10.1016/j.marenvres.2022.105615>
- Zitko, V., & Hanlon, M. J. M. P. B. (1991). Another source of pollution by plastics: skin cleaners with plastic scrubbers. *Marine pollution bulletin*, 22(1), 41-42. [https://ui.adsabs.harvard.edu/link_gateway/1991MarPB..22...41Z/doi:10.1016/0025-326X\(91\)90444-W](https://ui.adsabs.harvard.edu/link_gateway/1991MarPB..22...41Z/doi:10.1016/0025-326X(91)90444-W)

Zocchi, M., & Sommaruga, R. (2019). Microplastics modify the toxicity of glyphosate on *Daphnia magna*. *Science of The Total Environment*, 697, 134194.
<https://doi.org/10.1016/j.scitotenv.2019.134194>

Appendix

Synthetic water preparation

This describes the preparation of synthetic “natural” water with the following composition:

	Ca ²⁺	Mg ²⁺	Na ⁺	(CO ₃) _{TOT}	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NOM	Alginic Acid
mg/L	29.1	9.99	36.2	90	3.00 (0.679 as N)	40.0	55.0	2.56	5.32

Three stock solutions are required, called A, B, and C. Preparation of these solutions is described first, followed by the synthetic water preparation. All volumes and masses can be doubled, tripled, etc, as you see fit for preparing the required volume of solution. Tolerance for final concentrations is $\pm 10\%$.

Stock A - 10x Salt Mixture (CaCl₂, MgCl₂, NaNO₃)

In a 1 L volumetric flask, place: 0.2264 g CaCl₂*2H₂O

0.8356 g MgCl₂*6H₂O

0.0412 g NaNO₃

Dissolve with D.I. H₂O, then dilute to the mark and mix well. Store at room temperature.

Stock B - 3x CaSO₄ Solution

In a 1 L volumetric flask, place: 0.2954 g CaSO₄*2H₂O

Dissolve with ~ 900 mL D.I. H₂O (this takes a little while to all dissolve), then dilute to the mark and mix well. Store at room temperature.

Table S1. 500 nm polystyrene and fluoxetine adsorption washed result

Sample_label	C-CPM
Chem_Control	23447.7
0.1 ug/L_iso	541.6
0.1 ug/L_washed (1,2,3)	22529.7
Expected washed result	22906.1
0.5 ug/L_iso	558.7
0.5 ug/L_washed (1,2,3)	19538
Expected washed result	22889
1 ug/L_iso	596.9
1 ug/L_washed (1,2,3)	20044.35
Expected washed result	22850.8
5 ug/L_iso	618.4
5 ug/L_washed (1,2,3)	20,119.4
Expected washed result	22829.3
10 ug/L_iso	625.2
10 ug/L_washed (1,2,3)	19811.25
Expected washed result	22822.5
Sample_label	C-CPM
50_iso	930.6
50 ug/L_washed (1,2,3)	20899
Expected washed result	22517.1
500_iso	975.5
500 ug/L_washed (1,2,3)	18904.1
Expected washed result	22472.2

Kinetic study results

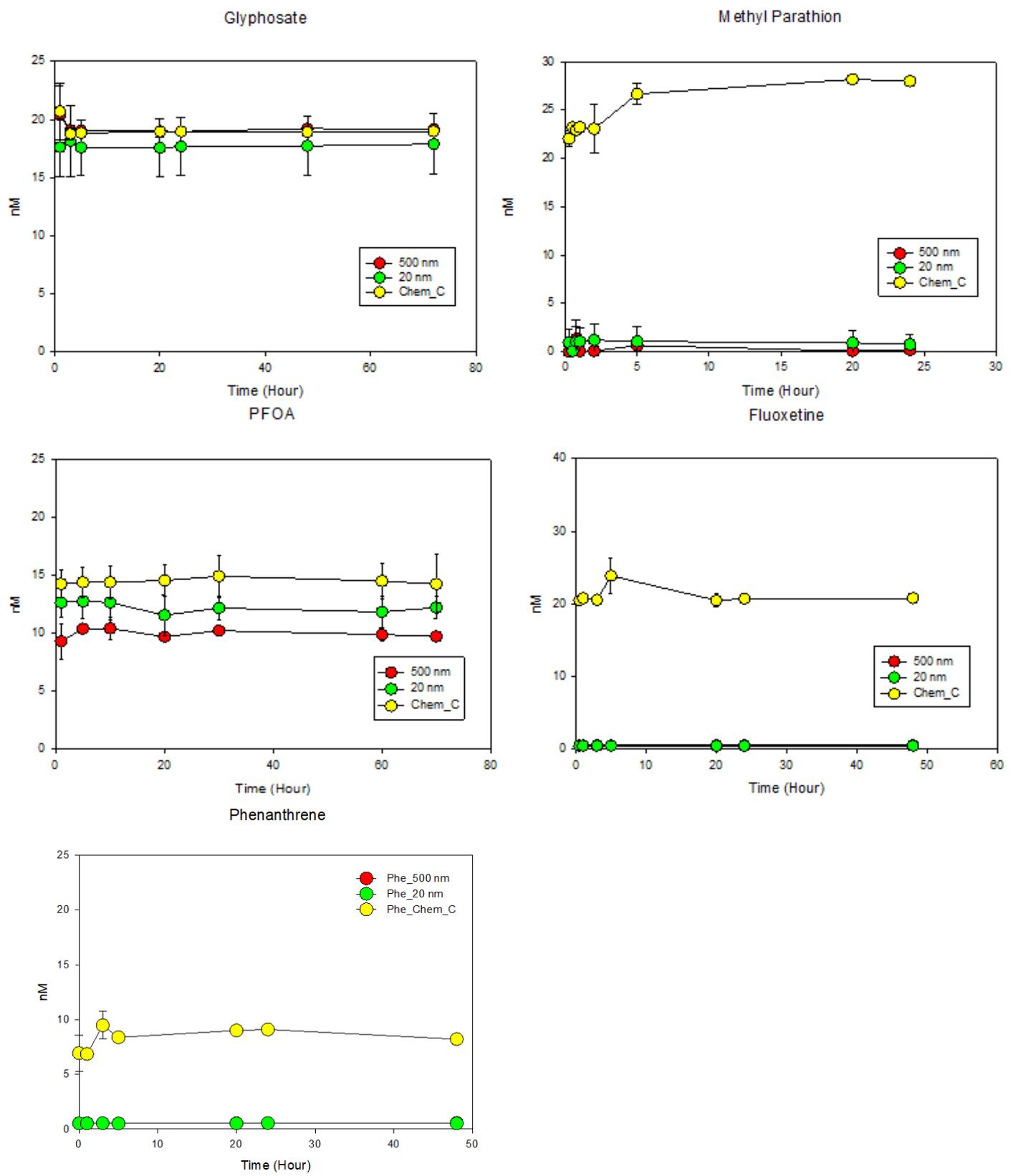


Figure S1. Kinetic study of adsorption of nanoplastics with organic chemicals of interest

Table S2. Sorption Coefficient (Kd) values for Kinetic Studies

Chemicals	500 nm PS (Avg. L/Kg)	20 nm PS (Avg. L/Kg)
Glyphosate	7.96E-07	1.75E-06
Methyl Parathion	5.49E-05	1.49E-04
Fluoxetine	3.95E-04	4.46E-04
PFOA	1.36E-05	8.91E-06
Phenanthrene	3.58E-04	3.86E-04

Table S3. Statistical significance at One-way ANOVA for Kinetic Studies ($\alpha = 0.05$)**(Holm-Sidak method)**

Comparison	P value (< 0.01)
PFOA with 500 nm PS vs 20 nm PS	0.026
Glyphosate with 500 nm PS vs 20 nm PS	0.427
Fluoxetine with 500 nm PS vs 20 nm PS	0.039
Methyl Parathion with 500 nm PS vs 20 nm PS	0.120
Fluoxetine short term vs long term	> 0.01
Glyphosate short term vs long term	> 0.01

Table S4. Statistical significance at One-way ANOVA for pH Studies ($\alpha = 0.05$) (Holm-Sidak method)

Fluoxetine (sorption coefficient)	P value (< 0.01)
pH 12 vs pH 2	< 0.01
pH 9.8 vs pH 2	< 0.01
pH 8.4 vs pH 2	< 0.01
pH 6 vs pH 2	< 0.01
pH 12 vs pH 4	< 0.01
pH 9.8 vs pH 4	< 0.01
pH 8.4 vs pH 4	< 0.01
pH 6 vs pH 4	< 0.01
pH 4 vs pH 2	< 0.01
pH 12 vs pH 6	< 0.01
pH 9.8 vs pH 6	0.01
pH 12 vs pH 8.4	0.005
pH 9.8 vs pH 4	0.034
pH 8.4 vs pH 6	0.081
pH 12 vs pH 9.4	1.232

Table 52. Sorption Coefficient (Kd) values for NOM Studies

Chemicals	500 nm PS (Avg. L/Kg)	20 nm PS (Avg. L/Kg)
FX_High_NOM	3.47E+07	3.32E+07
FX_Low_NOM	7.14E+07	8.53E+07
GPS_High_NOM	2.75E+05	2.75E+05
GPS_Low_NOM	2.41E+02	3.95E+02

Table S6. Sorption Coefficient (Kd) values for wastewater effluent studies

Chemicals	500 nm PS (Avg. L/Kg)	20 nm PS (Avg. L/Kg)
GPS_Pre UV 5%	6041.061	6502.866
PFOA_Pre UV 5%	5871.699	10577.44
GPS_Post UV 5%	3545.538	5670.689
PFOA_Post UV 5%	7666.98	10936.6
GPS_Pre UV 50%	983.7276	1214.699
PFOA_Pre UV 50%	1890.242	2416.613
GPS_Post UV 50%	456.3836	925.8618
PFOA_Post UV 50%	1264.216	1888.652

Table S7. Mean chemical concentration (mg/L) of wastewater effluent

Elements	Calcium	Sodium	Potassium	Sulfur	Silica	Chloride	TOC
Pre-UV treated	65.5	91	16.5	39	3.15	94.5	140
Post-UV treated	65.5	90.5	16	39	3.15	94	290