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Microplastic accumulation and transport in the subsurface under weathering cycles

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Microplastic accumulation and transport in the subsurface under weathering cycles

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Civil Engineering

by

Vera Smirnova Koutnik

2022

ABSTRACT OF THE DISSERTATION

Microplastic accumulation and transport
in the subsurface under weathering cycles

by

Vera Smirnova Koutnik
Doctor of Philosophy in Civil Engineering
University of California, Los Angeles, 2022
Professor Sanjay K. Mohanty, Chair

Microplastics are continuously released into the terrestrial environment from sources near where they are used and produced. These microplastics are conveyed via wind and water to the surrounding areas, where they accumulate in soil, sediment, and freshwater environments. The concentration gradient between terrestrial inland and boundary regions, the factors that influence the concentration, and the fundamental transport processes that could dynamically affect the microplastic transport in subsurface soil are unclear. In urban areas, stormwater control measures can accumulate microplastics, where they can break down into smaller fragments and be transported into the subsurface environment to groundwater. Subsurface soil experiences weathering cycles such as freeze-thaw cycles and dry-wet cycles, which could increase the downward transport potential of the accumulated microplastics. Yet, it is unknown whether or how the fluctuation in the water phase and content during these transient weather conditions could affect

microplastic transport in the subsurface. The overall objective of the dissertation is to improve the understanding of microplastic transport and accumulation pathways in terrestrial environments with an emphasis on urban areas and stormwater.

The dissertation consists of six research chapters. Chapter 2 estimates the global distribution and abundance of microplastics in terrestrial environments and shows that urban areas and glaciers are the hotspots of microplastic pollution. Chapter 3 calculates the mass balance of microplastics in wastewater treatment plants based on the global data and reveals that wastewater sludge could contain 25 times more microplastics than the reported concentration. Chapter 4 analyzes microplastic sources and types inside urban playgrounds in Los Angeles and shows that playgrounds could contain a higher concentration of microplastics than the surrounding due to extensive release of the microplastics from plastic structures inside the playground. Chapter 5 analyzes microplastic contamination across stormwater treatment systems in Los Angeles and shows atmospheric deposition, not just stormwater, could be the major conveyor of microplastics to the stormwater treatment systems, but the accumulated microplastic concentration decreased exponentially with an increase in soil depth. Chapter 6 shows that freeze-thaw cycles increase the vertical penetration of microplastics in the subsurface, but the effect is more prominent if the subsurface media contain more sand. Chapter 7 shows that microplastics of higher density can be preferentially transported deeper into subsurface during the freeze-thaw cycles. Overall, the results help understand the transport and accumulation of microplastics in urban areas and identify research needs to assess microplastic exposure in urban areas.

The dissertation of Vera Smirnova Koutnik is approved.

Shaily Mahendra

Eric Hoek

David Jassby

Sanjay K. Mohanty, Committee Chair

University of California, Los Angeles

2022

Dedication

I dedicate my dissertation to my role model and the most influential person in my life, my incredible grandfather Vladimir Sergeevich Smirnov. He sadly left us in the middle of my Ph.D. but the lessons he taught me of hard work, perseverance, and dedicating your work to a meaningful purpose helped me complete my Ph.D. and will stay with me the whole life.

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VITA

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CONFERENCE PRESENTATIONS

Koutnik, V. S., Borthakur, A., Leonard, J., Alkidim, S., Koydemir, H., Tseng, D., Ozcan, A., and Mohanty, S. K. Enhanced downward transport of microplastics in stormwater biofilters during freeze-thaw cycles. American Chemical Society Spring 2022 National Meeting. San Diego, CA, USA. March 20-24, 2022.

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1. CHAPTER 1 – MICROPLASTIC ACCUMULATION AND TRNASPORT IN THE TERRESTRIAL ENVIRONMENTS

1.1. Background

Microplastics— plastic particles smaller than 5 mm—are increasingly ubiquitous in environments due to several decades of production and use of plastics in nearly all sectors (Geyer et al., 2017). Exposure to these microplastics could increase human health risks (Bouwmeester et al., 2015; Karbalaei et al., 2018; Prata, 2018; Sharma et al., 2020) as they could adsorb toxic chemicals (Barnes et al., 2009; Wang et al., 2018) and bioaccumulate in food and tissue (Merga et al., 2020; Ribeiro et al., 2019). Microplastics could also alter soil microbiomes (de Souza Machado et al., 2018; Fei et al., 2020; Hüffer et al., 2019) and affect ecological processes (Barnes et al., 2009; He et al., 2018; Huerta Lwanga et al., 2017). Thus, it is critical to identify microplastic hotspots, estimate their accumulation in sediment and freshwater bodies, and identify dominant transport processes in air and water, so that appropriate mitigation strategy can be strategically implemented to minimize their spread in natural environments.

Microplastics are produced and used in the terrestrial environment, released from consumer products (van Wezel et al., 2016) and wastes (Canopoli et al., 2020; He et al., 2019). Some of these microplastics are conveyed by wind and water via surface runoff, rivers, and canals (Amrutha and Warrier, 2020; Hitchcock, 2020; Piñon-Colin et al., 2020) and deposited in downwind or downstream in regions within the terrestrial boundary or transported across the boundary to the ocean (Figure 1-1). Microplastics are released into the environment due to deterioration of discarded plastic products by physical (S.-Y. Ren et al., 2020), chemical (Cai et al., 2018; Song et al., 2017), and biological (Auta et al., 2018; Matjašič et al., 2020) processes. Microplastics are also released directly from consumer products such as the face or body scrubs (Anderson et al., 2016; Habib et al., 2020), wastewater sludge (Edo et al., 2020; Li et al., 2018) applied onto the

agricultural land (Corradini et al., 2019; Crossman et al., 2020; van den Berg et al., 2020; L. Zhang et al., 2020), fabrics during washing (Belzagui et al., 2019; Henry et al., 2019; Siegfried et al., 2017), and automobile tires and brake systems (Knight et al., 2020; Sieber et al., 2020). While most microplastics in stormwater are conveyed to freshwater bodies, microplastics in wastewater are relocated into the sludge (Edo et al., 2020; Li et al., 2018), which can then be released into the environment due to their application as biosolids on agricultural land (Corradini et al., 2019; Crossman et al., 2020; van den Berg et al., 2020; L. Zhang et al., 2020). Thus, the relative abundance of microplastics in the terrestrial environment could be correlated to the types of plastic produced and the types that end up in the waste stream.

Stormwater runoff conveys microplastics to surface waters and deposits them downstream (Liu et al., 2019; Malaviya and Singh, 2012; Olesen et al., 2019). To treat stormwater, green infrastructures such as biofilters have been used, which are designed to rapidly infiltrate stormwater to lower the runoff volume and filter pollutants (Elliott and Trowsdale, 2007; Malaviya and Singh, 2012). Microplastics are expected to be deposited on the surface of biofilters and later infiltrate during intermittent infiltration of stormwater. Yet, the mechanism by which microplastics can transport in the subsurface is not clear. In particular, stormwater biofilters are naturally subjected to intermittent weather conditions such as wetting events punctuated by drying or freeze-thaw cycles. These conditions could increase the downward migration of microplastics (O'Connor et al., 2019) by disrupting the soil pore structure and releasing soil colloids carrying microplastics (Mohanty et al., 2015a). The same conditions could also increase their weathering and affect the partitioning of sequestered pollutants in biofilters by concentrating the solutes near microplastics surface via solute exclusion during drying or freezing (Figure 1-1). Understanding whether and how microplastics transport in biofilters and how their surface properties evolve with time is

relevant not only to predict the accumulation of pollutants on their surface (or toxicity of microplastics) but also to assess their impact on the biochemical function of biofilters.

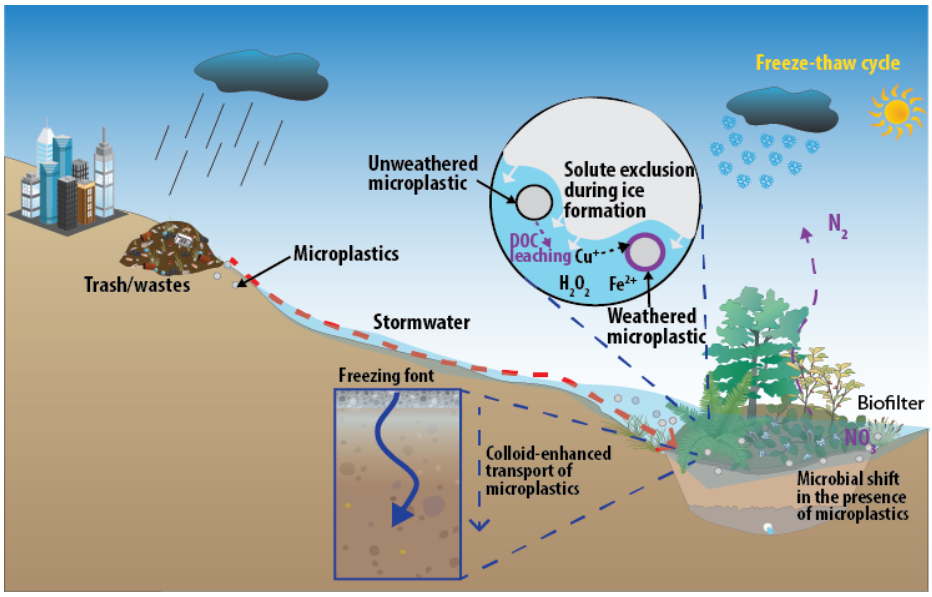

Figure 1-1. Potential transport and weathering processes of microplastics in stormwater biofilters, and their impact on biochemical processes in the subsurface.

1.2. Research gaps

1.2.1. Lack of global data on the distribution and abundance of microplastics in terrestrial environments

Microplastic concentration can also vary by location, based on how far they are from the source and net accumulation rate. Yet, the relative distribution and abundance of microplastics or the concentration gradient between locations or water bodies, the factors that influence the distribution (e.g., microplastic shape and location types), and the fundamental transport processes that could dynamically affect the distribution are unclear. Thus, it is essential to collect and analyze a comprehensive dataset for the microplastic distribution in the world, rather than a specific geographical region (Fu and Wang, 2019; Kutralam-Muniasamy et al., 2020; Sarker et al., 2020), and to provide insights on factors that could affect the concentration in freshwater and soil based on analysis of quantitative data. Further study is needed to fill the knowledge gaps on the

distribution of microplastics on a global scale, and modeling transport processes, which have not been addressed in recent reviews on analysis techniques (Elkhatib and Oyanedel-Craver, 2020; Fok et al., 2020; Li et al., 2019; Yang et al., 2021), sources types (Guo et al., 2020; Wong et al., 2020), and risks assessment (He et al., 2018; Li et al., 2020). The analysis could help identify the hotspots for microplastic sources and evaluate the concentration gradient between water bodies to estimate the number of microplastics removed during their transport in rivers or streams.

1.2.2. Lack of data on mass balance of microplastics in municipal wastewater treatment plants

Several studies (Carr et al., 2016; Gies et al., 2018; Lares et al., 2018; Lee and Kim, 2018; Lv et al., 2019; Magni et al., 2019; Raju et al., 2020; P. Ren et al., 2020; Talvitie et al., 2017) reveal a lack of mass balance: the total number of microplastics removed from wastewater in those studies exceeds the microplastics found in the sludge. In particular, 22-89% of microplastics relocated into sludge may be undetected or unaccounted for, leading to underestimation of annual loading of microplastics via land application of sludge. However, the cause of the discrepancy is unknown. Thus, further analysis is needed to evaluate if the discrepancy is consistent across WWTPs in the world. It is necessary to synthesize data reported from all studies in the world and estimate the annual emission of microplastics from WWTPs via sludge, including the unaccounted fraction and its loading on agricultural land via biosolids application. Furthermore, it is important to conduct a meta-analysis of concentration data in influent and effluent to identify the source of high variability in the concentration estimation so that future studies should optimize the protocols to sample and identify microplastics in wastewater samples. The analysis could provide an annual flow of microplastics from wastewater treatment plants to the environment via land application of sludge. The analysis could also address the knowledge gap on unaccounted microplastics and differs from other reviews that primarily focus on the fate of microplastics (Gatidou et al., 2019;

Okoffo et al., 2019; Sun et al., 2019), their removal processes (Freeman et al., 2020; Masia et al., 2020; Xu et al., 2019; X. Zhang et al., 2020), and their identification methods in WWTPs (Bakaraki Turan et al., 2021; Elkhatib and Oyanedel-Craver, 2020).

1.2.3. Microplastic accumulation pathways in urban green spaces such as children's playgrounds

No study to date has quantified the microplastic concentrations in playgrounds nor determined the source pathways of microplastics accumulated in the playgrounds in urban areas. Microplastics in the playground could be accumulated by different processes. First, microplastics can be transported from surrounding areas by water and wind (Piñon-Colin et al., 2020; Rezaei et al., 2019). Playgrounds are typically located in elevated areas to minimize flooding risks. Thus, the runoff would not flow into the playground. This limits the amount of microplastics accumulated in the areas by surface runoff. In contrast to water, wind can transport microplastics from different parts of the urban areas across any geographical boundary and deposit them on playgrounds or leaves in the tree canopy. The deposition of microplastics in any urban areas thus depends on the wind profile in that region. The urban canopy could intercept wind and inhibit its ability to carry microplastics and other dust, resulting in atmospheric deposition of the microplastics (Allen et al., 2019; Yumei Huang et al., 2021; Klein and Fischer, 2019). However, microplastics deposited by wind inside the playground have not been compared to that deposited outside the playground. As leaves contain high concentrations of microplastics in urban areas (Li et al., 2022), concentrations on leaves in trees within and outside the playground boundary can be used to compare the deposition of microplastics via wind.

A major source of microplastics in the playground could be the built-in plastic structures such as slides, plastic carpet flooring, and houses or roof. Additionally, children bring toys and other plastic products into the sandpits in the play area. Abrasion of sand with these plastic

structures could release microplastics (S.-Y. Ren et al., 2020; Sipe et al., 2022). Furthermore, many playgrounds are directly exposed to sunlight, which can degrade plastic products (P. Liu et al., 2020; Ren et al., 2021). Consequently, high concentrations of microplastics could be released from these structures by physical and biochemical weathering (Duan et al., 2021). Yet, no study to date has examined the extent of microplastics released from these structures and their contribution to the net accumulation of microplastics in children's playgrounds in urban areas. Future study should quantify the concentration of microplastics in children's playgrounds in urban areas and identify the dominant source of microplastics present in the playground.

1.2.4. Source of microplastics and their transport pathways in stormwater treatment systems

Stormwater runoff is typically assumed to be the main source of microplastics in the SCM (Liu et al., 2019; Werbowski et al., 2021), even though atmospheric deposition can be a significant source (Brahney et al., 2020; Dris et al., 2016). Unlike stormwater loading, which is episodic and happens a few times a year in response to precipitation events, atmospheric deposition is continuous throughout the year. Thus, net loading via atmospheric deposition could add up to a significant amount. Other studies have examined atmospheric transport of microplastics (Mbachu et al., 2020; Roblin et al., 2020; Wang et al., 2021), and some of which could deposit in the SCM (Smyth et al., 2021). Several studies have examined microplastic concentration in soil or filter media in SCM (Boni et al., 2021; Gilbreath et al., 2019; Lange et al., 2021; Smyth et al., 2021), but they did not examine the concentration of microplastics accumulated on the vegetation. Vegetation canopy can intercept microplastics (K. Liu et al., 2020; Sun et al., 2021) and contribute to the net inventory of microplastics in SCM. High concentrations of microplastics are frequently found in the dust (Abbasi et al., 2019; J. Zhang et al., 2020), which can be transported by wind (Bullard et al., 2021; Rezaei et al., 2019) and redistributed in urban areas. As microplastics

concentration in the canopy in SCM can serve as an indicator of microplastics deposition from the atmosphere, it is critical to estimate microplastic concentration trapped by vegetation on SCM.

The extent to which the accumulated microplastics can move downward in SCM in field conditions has not been evaluated, despite earlier evidence of subsurface mobility of microplastics during intermittent infiltration of rainwater (Mohanty et al., 2015a). Microplastic removal and transport processes in SCM can be inferred from the knowledge of particulate transport or removal mechanisms in the SCM (Tirpak et al., 2021). Microplastics, similar to particles or sediments, can be removed by settling, adsorption, and filtration from stormwater (Gavrić et al., 2019; Massoudieh et al., 2017). Although most microplastics, owing to their large size, are expected to be filtered out in topsoil (Luo et al., 2020), smaller microplastics could potentially migrate downward with infiltrating stormwater. Previous studies have shown that microspheres of size greater than 2 μm are retarded rapidly with limited transport potential (Gao et al., 2021; Zhou et al., 2020). Furthermore, PM10, or particulate matter with a size less than 10 μm, is relevant for air transport, as any larger particles are less likely to be relevant for long-range transport and disposition on SCM by the wind. The hydraulic conductivity and porosity of the filter layer in SCM are typically high to facilitate a faster infiltration (Tirpak et al., 2021), which can also enhance the downward migration of microplastics. Furthermore, SCMs are exposed to intermittent infiltration of stormwater or dry-wet cycles, which could accelerate the downward migration of microplastics in the subsurface (Mohanty et al., 2015b; O'Connor et al., 2019). However, a lack of depth distribution data from SCM where microplastics have been accumulated for years precludes our understanding of the vertical migration of microplastics in SCM. Future study should evaluate the contribution of atmospheric deposition on the net accumulation of microplastics in SCM and examine the downward mobility potential of the accumulated microplastics.

1.2.5. Effect of freeze-thaw cycles on the mobility of microplastics in subsurface

Understanding the microplastic transport processes in biofilters can help predict their distribution in the root zone (Yuyue Huang et al., 2021) and the potential of groundwater pollution (Selvam et al., 2021). However, only a few studies have examined the transport of the deposited microplastics in stormwater biofilters (Kuoppamäki et al., 2021; Lange et al., 2021), and they did not account for weathering treatments such as drying or freeze-thaw cycle that all biofilters experience naturally. Transport processes relevant for microplastics in stormwater biofilters can be inferred from earlier studies on natural soil colloids or other particulate pollutants (DeNovio et al., 2004). Plastic microspheres have been used as a tracer for pathogens in numerous studies for the last 3 decades (Becker et al., 1999; Burkhardt et al., 2008; Mohanram et al., 2012; Yu et al., 2013). These studies provide insights into the behavior of spherical microplastics in saturated soil under a steady infiltration of water. However, microplastics typically found in stormwater are of irregular shape (Sang et al., 2021; Sutton et al., 2016; Werbowski et al., 2021). Furthermore, the stormwater infiltration events are intermittent, typically followed by drying or freeze-thaw cycles based on seasons. Dry-wet and freeze-thaw cycles have been shown to increase mobilization of natural colloids (Mohanty et al., 2014) and pollutants accumulate in biofilters (Borthakur et al., 2021; Mohanty and Boehm, 2015). Recent studies found that dry-wet cycles could increase the penetration depth of microplastics in soil (Gao et al., 2021; O'Connor et al., 2019). In contrast to dry-wet cycles, freeze-thaw cycles could either increase mobility by disrupting the deposited microplastics during the expansion of ice crystals (Mohanty et al., 2014) or decrease mobility by increasing their aggregation (Alimi et al., 2021). Thus, the net effect of freeze-thaw cycles on microplastic transport is unclear. Future studies should evaluate the effect of freeze−thaw cycles on the mobilization of previously deposited microplastics in biofilter media.

1.2.6. Effect of density on the subsurface transport of microplastics during freeze-thaw cycles

Subsurface soil naturally experiences dry-wet and freeze-thaw cycles, which could increase the transport of the deposited microplastics (Dong et al., 2022; Gao et al., 2021; O'Connor et al., 2019). Compared to numerous studies that have examined the mechanism of particle transport by dry-wet cycles (Borthakur et al., 2021; Gu et al., 2018; Mohanty et al., 2015b; O'Connor et al., 2019; Seiphoori et al., 2020), fewer studies have examined the mechanism of particle transport by freeze-thaw cycles (Alimi et al., 2021; Mohanty et al., 2014). Freeze-thaw cycles could either increase microplastic mobility by disrupting the deposited microplastics during the expansion of ice crystals (Mohanty et al., 2014) or decrease the mobility by increasing their aggregation (Alimi et al., 2021). Both aggregation or transport in pore water or porous media depends on particle properties such as density, size, and surface properties (Bennacer et al., 2013; Bradford et al., 2003, 2002; Zhang et al., 2014). Yet, none of the previous studies on microplastics examined whether and how the properties of microplastics could affect their mobility by oscillating the ice-water interface during freeze-thaw cycles.

Many studies have examined the dynamics of colloids at freezing interfaces (Asthana and Tewari, 1993; Azouni et al., 1997; Hattori et al., 2020; Körber et al., 1985; Lin et al., 2020; Rempel and Worster, 2001, 1999; Saint-Michel et al., 2017; Shangguan et al., 1992; Tyagi et al., 2020), and they can help explain the behavior of microplastics in subsurface subjected to freeze-thaw cycles. During freeze-thaw cycles, colloids in pore water could experience three types of forces: gravitational force owing to particle size and density, buoyancy owing to the density of the water displaced by the submerged particle, and the interfacial force exerted by moving ice-water interfaces when the interface comes close to within few nanometer distances of the colloid (Azouni et al., 1997; Spannuth et al., 2011; Tyagi et al., 2020). The interfacial force can be sensitive to colloid surface properties (Körber et al., 1985; Shangguan et al., 1992; Thompson and Wettlaufer,

1999). The resulting force balance determines the velocity of colloids near ice font. At a close distance (~ few nm) between the particle and ice front, the drag force also changes due to the movement of water molecules from bulk to the interface, where the curvature of the ice surface near the particle could change based on the thermal conductivity of the particle (Rempel and Worster, 2001). Microplastics are insulators with thermal properties different from water. The particle thermally shields the local interface underneath the particle, creating a cooler spot where the ice interface grows faster to create a convex protuberance that prevents the engulfment of microplastics (Asthana and Tewari, 1993). Thus, convex protuberance could push microplastics and accelerate their mobility in the subsurface (Asthana and Tewari, 1993). Consequently, the transport of microplastics by these forces could depend on the density, thermal and surface properties of microplastics. Thus, their mobility by freeze-thaw cycles could vary with density and other properties. Yet, no study to date has examined the effect of microplastic size and density on their mobility in porous media under freeze-thaw cycles. Future study should examine how the density of microplastics could affect their mobility in the subsurface subjected to freeze−thaw cycles.

1.3. Objectives

The overall objective of the dissertation is to improve the understanding of microplastic transport and accumulation pathways in terrestrial environments with an emphasis on urban areas and stormwater. The dissertation consists of six research chapters that examine the distribution and accumulation of microplastics in terrestrial and urban environments and evaluate their transport through subsurface systems under dry-wet and freeze-thaw cycles. Chapters 2 and 3 examine the distribution and accumulation of microplastics in terrestrial environments and wastewater treatment plants, respectively, based on the analysis of global data. Chapters 4 and 5

quantify the source and accumulation pathways of microplastics in the urban playground and stormwater infrastructures, respectively, based on the analysis of field data. Chapters 6 and 7 examine how freeze-thaw cycles could increase the mobility of microplastics based on subsurface soil properties and plastic density, respectively. Specific goals are described below.

Chapter 2 critically reviews and analyzes a comprehensive quantitative dataset for microplastic distribution throughout the world, rather than a specific geographical region, to provide insights on factors that could affect microplastic concentrations in freshwater and soil. The outcome of Chapter 2:

> **Koutnik, V.S**., Leonard, D. J., Alkidim, S., DePrima, F., Ravi, S., Hoek, E., and Mohanty, S. (2021) Distribution of microplastics in soil and freshwater environments: Global analysis and framework for transport modeling. *Environmental Pollution*. 116552. https://doi.org/10.1016/j.envpol.2021.116552

Chapter 3 estimates the amount of unaccounted microplastics in the sludge of wastewater treatment plants by estimating the concentration of microplastics entering and exiting the wastewater treatment plants and analyzing the cause of the concentration variability by meta-analysis. The outcome of Chapter 3:

> **Koutnik, V.S**., Alkidim, S., Leonard, D. J., DePrima, F., Cao, S., Hoek, E., and Mohanty, S.K. (2021) Unaccounted microplastics in wastewater sludge: Where do they go? *ACS ES&T Water*. 1, 5, 1086–1097. https://doi.org/10.1021/acsestwater.0c00267

Chapter 4 examines the concentration and the composition of microplastics in children's playgrounds in urban areas and identifies the dominant source of microplastics present in the playgrounds in Los Angeles. The outcome of Chapter 4:

Koutnik, V.S., El Rassi, L.A., Choy, M. M., Brar, J., Leonard, J., Glasman, J.B., Cowger, W., and Mohanty, S. Elevated microplastic exposure to children in urban playgrounds: Dominant deposition pathways and population density effect. *Science of the Total Environment.* [In Review May 2022]

Chapter 5 evaluates the contribution of atmospheric deposition on the net accumulation of microplastics in stormwater control measures and examines their potential to be removed by straining or move downward. The outcome of Chapter 5:

Koutnik, V.S., Leonard, J., Glasman, J.B., Koydemir, H.C., Novoselov, A., Brar, J., Bertel, R., Tseng, D., Ozcan, A., Ravi, S., Mohanty, S.K. (2022) Microplastics retained in stormwater control measures: Where do they come from and where do they go? *Water Research*. 118008. https://doi.org/10.1016/j.watres.2021.118008

Chapter 6 evaluates the effect of freeze-thaw cycles and filter media composition on the mobilization of previously deposited microplastics. The outcome of Chapter 6:

Koutnik, V.S., Borthakur, A., Leonard, J., Alkidim, S., Koydemir, H.C., Tseng, D., Ozcan, A.,Ravi, S., Mohanty, S.K. (2022) Mobility of polypropylene microplastics in stormwater biofilters under freeze-thaw cycles. *Journal of Hazardous Materials Letters.* 100048. https://doi.org/10.1016/j.hazl.2022.100048

Chapter 7 examines how the density of microplastics could affect their mobility in the subsurface subjected to freeze−thaw cycles. Using a force balance on microplastics near the ice interface, this

chapter estimates how the transport velocity of microplastics could change as a function of plastic size and density. The outcome of Chapter 7:

Koutnik, V.S., Leonard, J., Brar, J., Cao, S., Glasman, J.B., Cowger W., Ravi S., Mohanty, S.K. Microplastic transport in the subsurface by oscillating ice-water interface: Critical role of the plastic density. *Environmental Science and Technology*. [In review March 2022]

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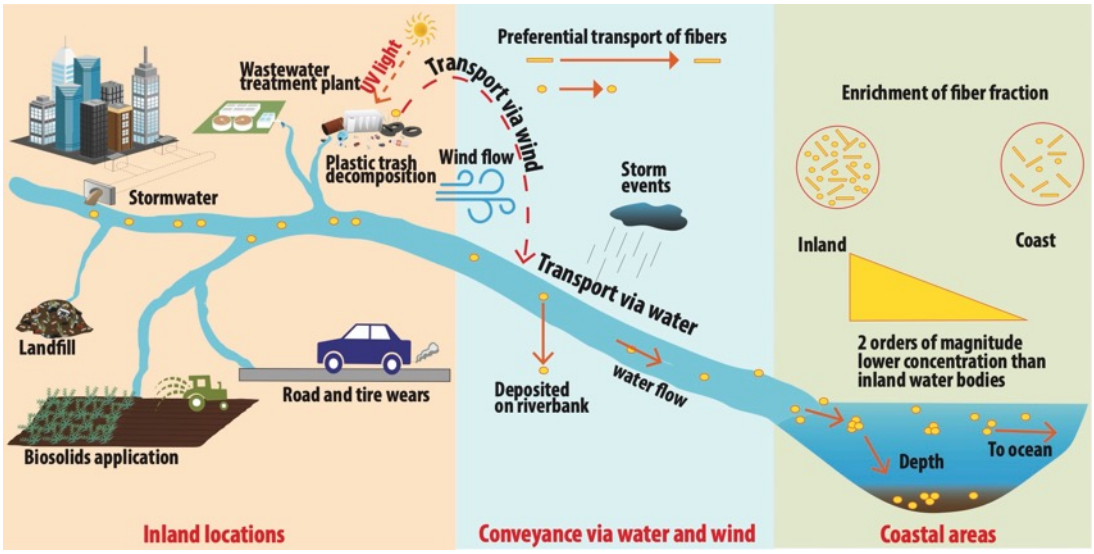
2. CHAPTER 2 – DISTRIBUTION OF MICROPLASTICS IN SOIL AND FRESHWATER ENVIRONMENTS: GLOBAL ANALYSIS AND FRAMEWORD FOR TRANSPORT MODELING



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Koutnik, V.S., Leonard, D. J., Alkidim, S., DePrima, F., Ravi, S., Hoek, E., and Mohanty, S. (2021) Distribution of microplastics in soil and freshwater environments: Global analysis and framework for transport modeling. *Environmental Pollution*. 116552. https://doi.org/10.1016/j.envpol.2021.116552

Abstract

Microplastics are continuously released in the terrestrial environment from sources near where they are used and produced. These microplastics accumulate in the soil, sediment, and freshwater, and some are conveyed via wind and water to the oceans. The concentration gradient between terrestrial inland and boundary regions, the factors that influence the concentration, and the fundamental transport processes that could dynamically affect the distribution are unclear. We analyzed microplastic concentration reported in 196 studies from 49 countries or territories from all continents and found that microplastic concentrations in soil or sediment and water could vary by up to eight orders of magnitude. Mean microplastic concentrations in inland locations such as glacier (191 n L^{-1}) and urban stormwater (55 n L^{-1}) were up to two orders of magnitude greater than the concentrations in rivers (0.63 n L^{-1}) that convey microplastics from inland locations and water bodies in terrestrial boundary such as estuaries (0.15 n L^{-1}). However, only 20% of studies reported microplastics below 20 μm, indicating the concentration in these systems can change with the improvement of detection technology. Analysis of data from laboratory studies reveals that biodegradation can also reduce the concentration and size of deposited microplastics in the terrestrial environment. Fiber percentage was higher in the sediments in the coastal areas than the sediments in inland water bodies, indicating fibers are preferentially transported to the terrestrial boundary. Finally, we provide theoretical frameworks to predict microplastics transport and identify potential hotspots where microplastics may accumulate.

2.1. Introduction

Microplastics — plastic particles smaller than 5 mm —are increasingly ubiquitous in environments due to several decades of production and use of plastics in nearly all sectors (Geyer et al., 2017). Exposure to these microplastics can increase human health risks (Bouwmeester et al., 2015; Karbalaei et al., 2018; Prata, 2018; Sharma et al., 2020) as they can adsorb toxic chemicals (Barnes et al., 2009; Wang et al., 2018) and bioaccumulate in food and tissue (Merga et al., 2020; Ribeiro et al., 2019). Microplastics can also alter soil microbiomes (de Souza Machado et al., 2018; Fei et al., 2020; Hüffer et al., 2019) and affect ecological processes (Barnes et al., 2009; He et al., 2018; Huerta Lwanga et al., 2017b). Thus, it is critical to identify microplastic hotspots, estimate their accumulation in sediment and freshwater bodies, and identify dominant transport processes in air and water, so that appropriate mitigation strategy can be strategically implemented to minimize their spread in natural environments. Microplastics are produced and used in the terrestrial environment, released from consumer products (van Wezel et al., 2016) and wastes (Canopoli et al., 2020; He et al., 2019a). Some of these microplastics are conveyed by wind and water via surface runoff, rivers, and canals (Amrutha and Warrier, 2020; Hitchcock, 2020; Piñon-Colin et al., 2020a) and deposited in downwind or downstream in regions within the terrestrial boundary or transported across the boundary to the ocean (Figure 2-1).

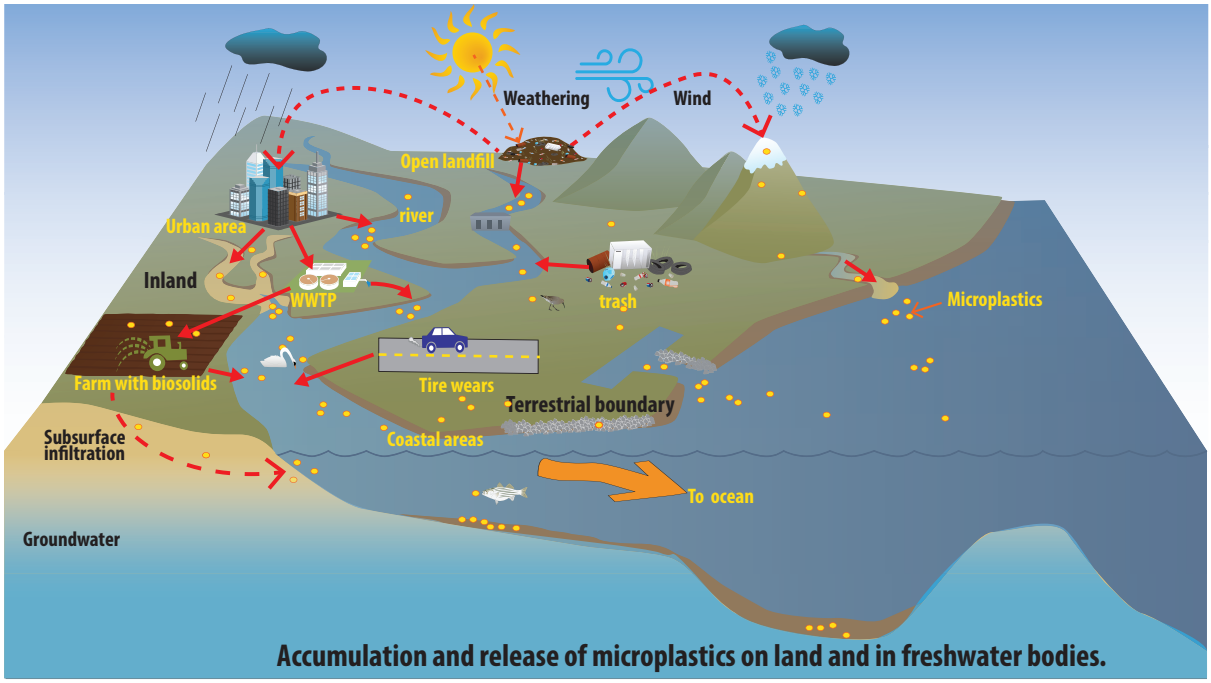

Figure 2-1. Transport of microplastics on the terrestrial environment. Microplastics are released from hotspots, conveyed by surface runoff, river networks, and atmospheric transport, and deposited on soil or sediments or in freshwater bodies. Thus, the concentration at a location could vary based on source type, release and transport processes, environmental conditions, and relative position of the location towards the source.

Microplastics are released into the environment due to deterioration of discarded plastic products by physical (S.-Y. Ren et al., 2020), chemical (Cai et al., 2018; Song et al., 2017a), and biological (Auta et al., 2018; Matjašič et al., 2020) processes. Microplastics are also released directly from consumer products such as the face or body scrubs (A. G. Anderson et al., 2016; Habib et al., 2020), wastewater sludge (Edo et al., 2020; X. Li et al., 2018) applied onto the agricultural land (Corradini et al., 2019; Crossman et al., 2020a; van den Berg et al., 2020; L. Zhang et al., 2020), fabrics during washing (Belzagui et al., 2019; Henry et al., 2019; Siegfried et al., 2017), and automobile tires and brake systems (Knight et al., 2020; Sieber et al., 2020). While most microplastics in stormwater are conveyed to freshwater bodies, microplastics in wastewater are relocated into the sludge (Edo et al., 2020; X. Li et al., 2018), which can then be released into the environment due to their application as biosolids on agricultural land (Corradini et al., 2019;

Crossman et al., 2020a; van den Berg et al., 2020; L. Zhang et al., 2020). The production of plastic varies with polymer types (Figure 2-2). Thus, their relative abundance in the terrestrial environment could be correlated to the types of plastic produced and the types that end up in the waste stream easily. Plastics have been used in nearly all products since 1950, most of which are disposed of into the environment (Geyer et al., 2017), where they can last for several decades due to slower degradation rates compared to other organic materials (Gewert et al., 2015; Raddadi and Fava, 2019; Zhu et al., 2019). In 2015 alone, 407 Mt of primary plastics were produced, with the production amount varied by polymer type (decreasing order): PE > PP > PET > PS > PU > PVC (Figure 2-2). By 2015, approximately 8,300 Mt of plastic waste had been generated, and almost 60% of this waste had accumulated in landfills or the natural environment (Geyer et al., 2017). From these sources, plastics can be released either as primary microplastics, directly from products such as toothpaste or facial and body scrubs, (A. G. Anderson et al., 2016) or as secondary microplastics- due to deterioration of large plastic-containing materials in the environment (Auta et al., 2018; Cai et al., 2020; P. Liu et al., 2019; Sieber et al., 2020).

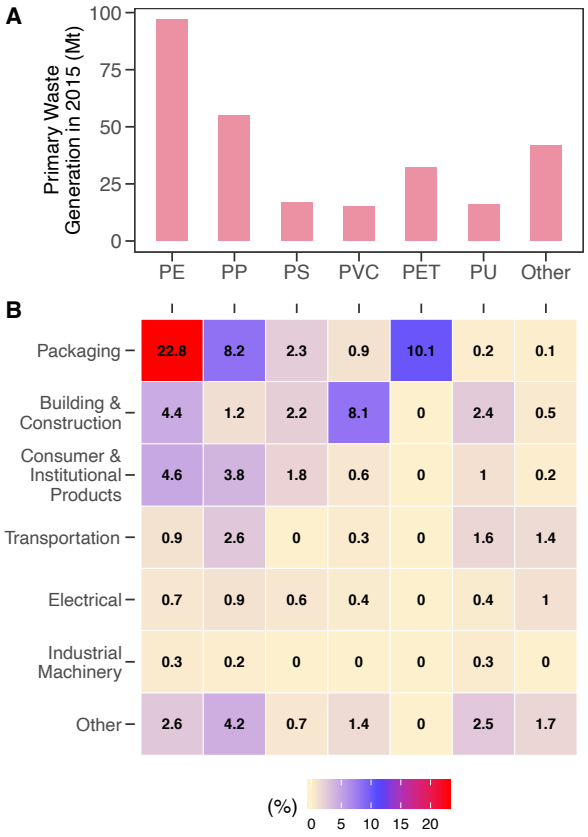

Figure 2-2. (a) Global primary waste generation (in million metric tons) in 2015 according to polymer types: (polyvinyl chloride (PVC), polyurethane (PU), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), polyethylene (PE), and other. Other include polyester, polyamide, and acrylic (PP&A) fibers. (b) Percentage of polymer resin (non-fiber) produced by polymer types and industrial uses based on data for Europe, the United States, China, and India covering the period 2002–2014. Source of data (Geyer et al., 2017).

Microplastic concentration can also vary by location, based on how far they are from the source and net accumulation rate. Yet, the relative distribution and abundance of microplastics or the concentration gradient between locations or water bodies, the factors that influence the distribution (e.g., microplastic shape and location types), and the fundamental transport processes that could dynamically affect the distribution are unclear.

The goals of this critical review are to collect and analyze a comprehensive dataset for the microplastic distribution in the world, rather than a specific geographical region (Fu and Wang, 2019; Kutralam-Muniasamy et al., 2020; Sarker et al., 2020), and to provide insights on factors

that could affect the concentration in freshwater and soil based on analysis of quantitative data. Furthermore, theoretical frameworks based on existing models on particle transport are provided to predict the transport of microplastics in soil, water, and air. The review aims at filling the knowledge gaps on the distribution of microplastics on a global scale, and modeling transport processes, which have not been addressed in recent reviews on analysis techniques (Elkhatib and Oyanedel-Craver, 2020; Fok et al., 2020; Q. Li et al., 2019; L. Yang et al., 2021), sources types (Guo et al., 2020; Wong et al., 2020), and risks assessment (He et al., 2018; J. Li et al., 2020). Analyzing 196 studies from 49 countries or territory spanning over 7 continents, resulting in 2014 concentration data in water and soil (Koutnik, 2020a), we identify the hotspots for microplastic sources and evaluate the concentration gradient between water bodies to estimate the number of microplastics removed during their transport in rivers or streams.

2.2. Distribution and abundance of microplastics

2.2.1. Data collection method

We used the Web of Science database to search studies using a combination of keywords including “microplastic” and one of the following: “soil”, “terrestrial”, “sediment”, “dust”, “stream”, “stormwater”, “pond”, “wetland”, “snow”, “estuary”, “runoff”, “lake”, “river”, “freshwater”, “glacier”, “surface water”. The searched items were further refined to peer-reviewed research articles. These searches resulted in a total of 1407 research articles, which were further evaluated based on title and abstract and narrowed down to studies focus on terrestrial or freshwater environments. Eliminating studies in marine environments, ingestion of microplastics by fishes or other animals, microplastics identification method comparisons, and lab simulated studies, we selected 351 studies for detailed evaluation. Of those 351 studies, 196 studies that reported units of number (n) of microplastics per volume of water (n L^{-1}, n m^{-3}) or per mass of

sediment (n kg^{-1}, n g^{-1}) were selected for our analysis. These studies, spanning over 47 countries in 7 continents (Figure 2-3), provide a global dataset to estimate the distribution of microplastics on land, sediments, and water bodies based on total 2014 concentration values in water and soil or sediment samples. The data was provided in an online open-access repository (Koutnik, 2020a).

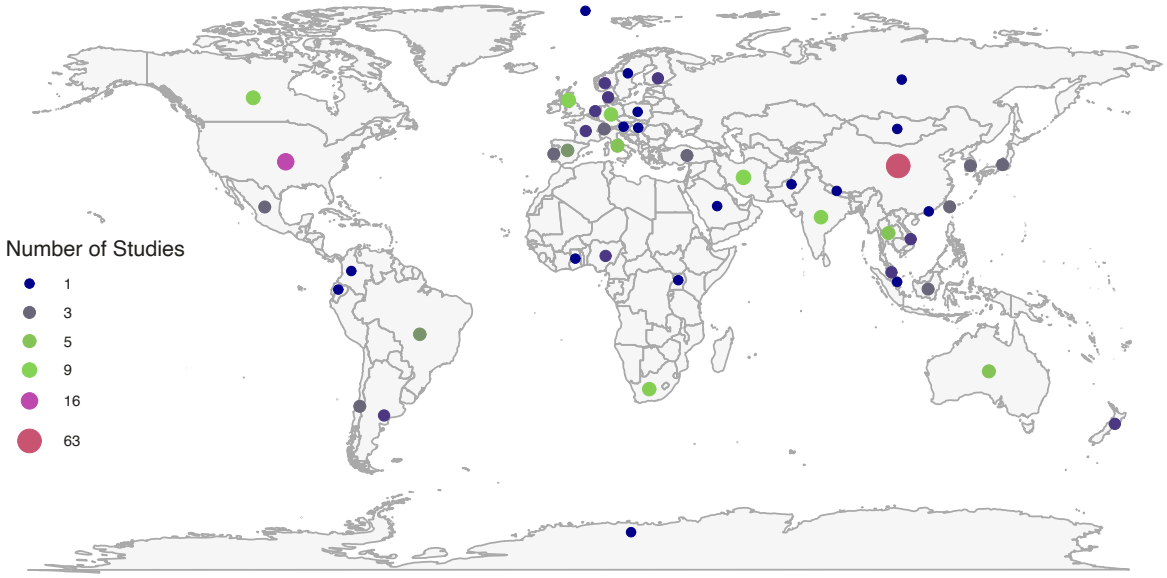

Figure 2-3. Locations of 196 studies that reported the concentration of microplastics in water and soil samples in n L^{-1} or n kg^{-1}, respectively, where n is the number of microplastics.

2.2.2. Distribution in freshwater

Microplastics can enter freshwater bodies from a variety of sources by stormwater runoff, WWTP effluent, and atmospheric deposition. Based on the analysis of 109 studies (Figure 2-4), microplastic concentration in freshwater bodies could vary by 8 orders of magnitude. Among all water bodies, urban streams, and glaciers had the greatest concentrations of microplastics, similar to the observation in other studies (Baldwin et al., 2019; Dikareva and Simon, 2019). As urban areas are the major source of microplastics, it is expected that the concentration of microplastics in urban water bodies would be higher (Järlskog et al., 2020; F. Liu et al., 2019b; Moruzzi et al.,

2020). However, our analysis reveals that the concentration of microplastics on glaciers or snow is surprisingly higher than even urban water bodies, even though microplastics are not directly used or produced at that location. We attributed high concentration in glaciers to a net accumulation of microplastic during snow deposition with limited opportunity to be washed off. In contrast, microplastics in urban locations can be accumulated and washed off by surface runoff. A difference in detection method resolution—minimum size detected—could also affect the concentration reported. The estimated concentration of microplastics in glaciers is based on four studies (Ambrosini et al., 2019; Bergmann et al., 2019; Kelly et al., 2020; Scopetani et al., 2019), which identify microplastics smaller than 10 μm. Thus, a lack of consistent cutoff size between studies could introduce errors in comparing the reported concentration. Nevertheless, a higher concentration of microplastics in glaciers indicates that transport via wind is a significant pathway to distribute microplastics in the environment. Our analysis confirms the recent evidence of the microplastic presence in remote locations such as mountains, glaciers, and lakes (Allen et al., 2019; Brahney et al., 2020b; Evangeliou et al., 2020). Thus, future studies should examine the mechanism of wind-driven transport of microplastics in remote locations and their impact on the glacier ecology.

Our analysis reveals that the concentration of microplastics in the river, among all water bodies, varies the most: 8 orders of magnitude. There could be several reasons for the wider variability. First, rivers transport microplastics from their sources to the terrestrial boundary and across the boundary to the ocean. Thus, the proximity of the river to the hotspots such as wastewater treatment plants, urban stormwater discharge points, and runoff from open landfills could affect the concentration (Grbic et al., 2020; Kay et al., 2018; Kazour et al., 2019). Second, the concentration of microplastics in the river could vary with the flow rate due to dilution (H.

Chen et al., 2020). Third, sampling time following a rainfall or antecedent weather conditions could affect microplastics concentration as runoff from a rainfall after a longer duration tends to convey a high amount of accumulated microplastics from land (Balthazar-Silva et al., 2020; Cheung et al., 2019; Stanton et al., 2020; Xia et al., 2020). Even the time of day, seasonal variation, and weather conditions could affect the concentration of microplastics for studies done in the same location (Barrows et al., 2018; Eo et al., 2019). As microplastics are typically carried by stormwater or runoff, sampling time in relation to storm events can influence the concentration (Hitchcock, 2020). Fourth, the depth of the sampling point relative to the water surface also has an impact on microplastic abundance (Eo et al., 2019; Gerolin et al., 2020) due to the settling of microplastics. Thus, sampling protocols should be carefully evaluated to account for all these factors on microplastic concentration in rivers (Stanton et al., 2020).

The shape of microplastics could affect their transport in the environment (He et al., 2020; Khatmullina and Isachenko, 2017; Y. Li et al., 2019). However, previous studies have rarely compared the concentration of fibers with plastic fragments or non-fibrous microplastics on a global scale. Our analysis shows that the fiber percentage in the total microplastic samples also varied between locations (Figure 2-4c). The urban water bodies had more fibers than the coastal region, indicating fiber fraction in water decreases downstream (Figure 2-4c). Urban water bodies are expected to contain more fibers because of their release from textile products. Due to their long aspect ratio, fibers can be preferentially removed by aggregation (Wu et al., 2017) during their transport in the environment. Surprisingly high concentration fibers in glaciers indicate that fibers may be preferentially suspended in air and transported by wind. A recent wind tunnel experiment found a high proportion of fibers in dust confirming this theory (Bullard et al., 2021). The median fiber percentage in the samples was positively correlated with median microplastic concentration.

An order of magnitude increases in the median concentration of total microplastics in water results in an increase in the fiber by only 7.73% (Figure 2-4c), which indicates that fibers are disproportionally harder to remove from water by settling. If both fibers and fragments are removed equally, then there should not be any change in fiber percentage with increases in total microplastics concentration. The fact that fiber fraction increases in water indicate that fibers are more likely to float in water than non-fibrous microplastics. Thus, it appears that the shape of the microplastics affects their fate in surface waters.

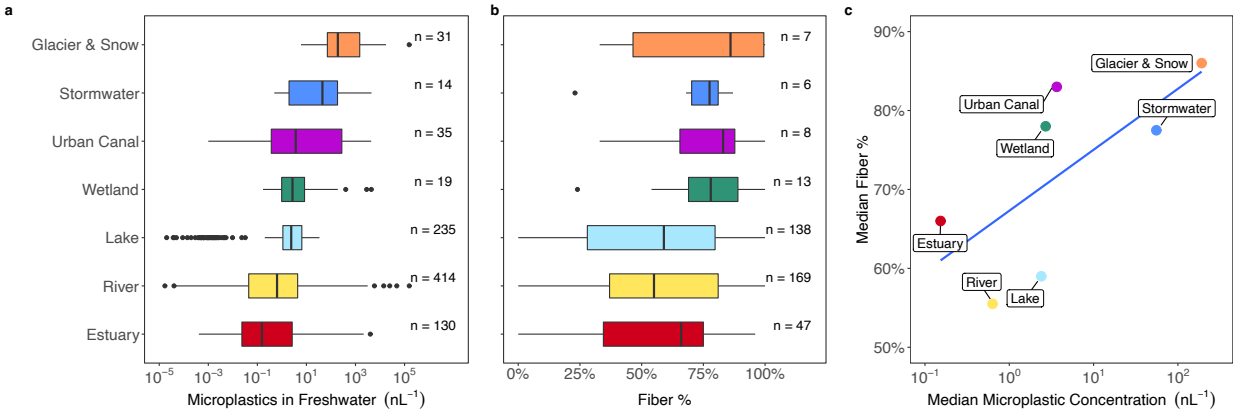

Figure 2-4. (a) Microplastic concentrations in water based on 109 studies (n = 878); (b) Percentage of fiber microplastics in the contaminated water samples based on 83 studies (n = 388); (c) Increase in fiber percent with an order of magnitude increase in microplastics concentration in water samples.

2.2.3. Distribution in soils and sediments

Microplastics in soil or sediments are deposited (Waldschlaeger and Schuettrumpf, 2019) via water and wind from different sources including sewage sludge (Corradini et al., 2019; X. Li et al., 2018), plastic mulch (Steinmetz et al., 2016), street runoff (Piñon-Colin et al., 2020a), litters (Asensio-Montesinos et al., 2020; Huerta Lwanga et al., 2017a), landfill leachate (Yadav et al., 2020) and atmospheric dust (Abbasi et al., 2019; Cai et al., 2017). Although numerous studies have measured microplastics concentration in soil or sediments, a comparison of concentration in soil or sediments between locations is lacking. Analyzing data from 117 studies, we show that the

concentration (n kg^{-1}) of microplastics in soil or sediment can vary by up to 8 orders of magnitude (Figure 2-5, Table 2-1), which is consistent with the microplastics concentration variation in surface waters. Thus, a decrease in the concentration of microplastics in water decreases the accumulation of microplastics in soil proportionally.

Our analysis showed that urban hotspots could have concentrations at least an order of magnitude higher than the concentration of microplastics in coastal soil and estuary. A two-order magnitude decrease in median concentration indicates that nearly 99% of microplastics are deposited during their transport to coastal regions. Concentration gradients within terrestrial environments provide clues on where microplastics are more likely to accumulate (Barnes et al., 2009). The abundance of microplastics in river sediment was found to decrease from upstream to downstream due to natural deposition over time (Scherer et al., 2020). Similarly, the concentration of microplastics in river and stream sediments was in between the extremes, which confirms the hypothesis that the concentration of microplastics decreases with an increase in the distance traveled from the source. As more microplastics are removed with distance from their source, the concentration available for deposition decreases, resulting in a significant concentration gradient from source to terrestrial boundaries.

Our analysis reveals the terrestrial hotspots for microplastics. Among all locations analyzed, dust, soil, and sediments from urban areas contain the highest number of microplastics, potentially due to their proximity to the locations where most plastics are used, discarded, or released. An increase in urbanization and population density drives plastic use and the release of microplastics (Koop and van Leeuwen, 2017). Thus, soil and sediment samples from the areas closer to industrial emission sites contained a high concentration of microplastics (Dikareva and Simon, 2019; Klein et al., 2015), underscoring the fact that proximity to source is closely tied to

microplastic accumulation rate. Among all locations, agricultural soils had the greatest range of variation in the concentration of microplastics. A wide variation at a site is attributed to the collection methodology including the depth of the collection, the amount of soil processed, processing methodology, and the cutoff size (Elert et al., 2017). Agricultural soils typically receive microplastics from 3 sources: plastic mulch used for weed control (Steinmetz et al., 2016), wastewater biosolids (Ng et al., 2018), and dust (Klein and Fischer, 2019). Thus, depending on the source, microplastic concentrations can vary. The concentration can also vary based on biosolid application rates (Corradini et al., 2019; Crossman et al., 2020a; Nizzetto et al., 2016b; L. Zhang et al., 2020) and site conditions such as the potential for surface runoff (Fahrenfeld et al., 2019; Gray et al., 2017a). Furthermore, irrigation runoff can transport microplastics away from farms to other terrestrial compartments (Fahrenfeld et al., 2019). Similarly, wind can also transport microplastics from agricultural land (Abbasi et al., 2019; Crossman et al., 2020a; Rezaei et al., 2019). Thus, microplastics distribution in soil could change based on the soil depth at which samples were collected in agricultural soil (S. Zhang et al., 2020). Thus, future studies should focus on mechanisms by which microplastics can leave the agricultural lands and the risk they pose to people or animals in nearby areas.

An unexpected insight from the analysis of 117 studies is the inverse relationship between fiber percentage in soil and the total concentration of microplastics (Figure 2-5c). While it is expected that an increase in the concentration of microplastics should increase the percentage of fibers in the sample, the opposite trend was observed. With an order of magnitude increase in the median concentration of microplastics in soil, the fiber percentage in soil decreased by 31.3%. This result indicates that the majority of settled plastics in urban soils are large fragments, and the fiber fractions in sediment increased downstream. A high fiber percentage in the sediment near

terrestrial boundaries where the overall concentration of microplastics is relatively low indicates that large fragments are removed inland, and more fibers might be transported to coastal areas. Overall, the result reveals that the long aspect ratio of microplastic may enhance their transport in water or decrease their deposition on sediment.

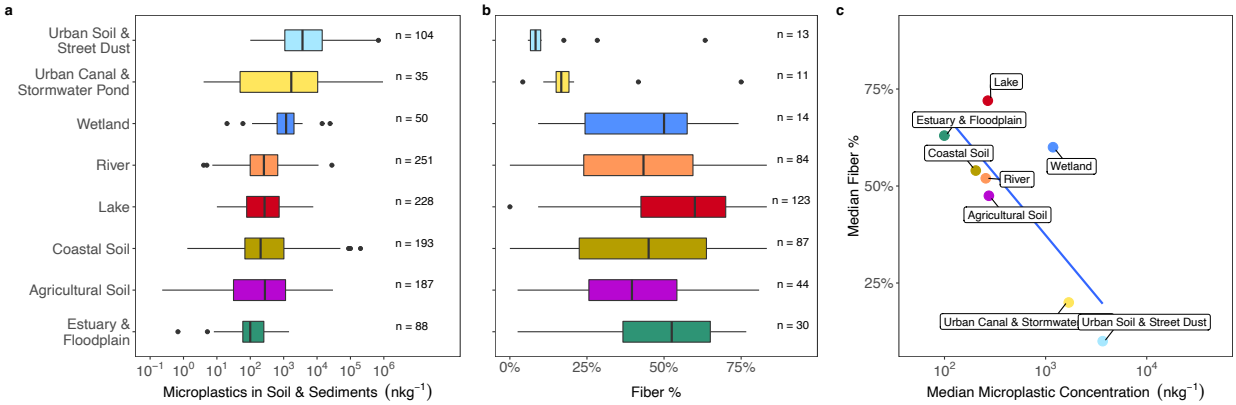

Figure 2-5. (a) Microplastic concentrations in soil or sediments from terrestrial environments based on 117 studies (n = 1136); (b) ratio of fibrous to total microplastic in the contaminated soil samples based on 115 studies (n = 406); (c) the media fiber percentage in the soil samples decreased with increases in the concentration of microplastics

Table 2-1. Showing median concentration of microplastics in number of microplastics per L or per kg and % of fibers in each water and soil type.

Location	Sample Type	Median Concentration	Unit of Concentration	Median Fiber %
Estuary & Floodplain	Soil	99.7	nkg-1	63.0%
Agricultural Soil	Soil	274.5	nkg-1	47.5%
Coastal Soil	Soil	204.0	nkg-1	54.0%
Lake	Sediment	268.1	nkg-1	72.0%
River	Sediment	256.0	nkg-1	52.0%
Wetland	Sediment	1183.0	nkg-1	60.0%
Urban Canal & Stormwater Pond	Sediment	1691.0	nkg-1	20.0%
Urban Soil & Street Dust	Soil and Dust	3666.7	nkg-1	10.0%
Estuary	Water	0.153	nL-1	66.0%
River	Water	0.635	nL-1	55.5%
Lake	Water	2.400	nL-1	59.0%
Wetland	Water	2.700	nL-1	78.0%
Urban Stream	Water	3.660	nL-1	83.0%
Stormwater	Water	55.45	nL-1	77.5%
Glacier & Snow	Water and Snow	191.0	nL-1	86.0%

2.2.4. The abundance of microplastics by location

The change in the abundance of different types of microplastics by locations has not been evaluated before. Our analysis reveals that abundance varies by location and microplastic types. PP, PE, PET, and PS were identified in the majority of the studies; in particular, PP tends to be most prevalent in the water column while PE is more prevalent in sediment samples (Figure 2-6). The most commonly reported plastic type was PET for glaciers and lakes, PE for rivers, and PP for other environments such as estuaries, urban streams, and retention ponds. Surprisingly, PE was not found to be the most common polymer in all water samples, even though it is the most produced and used in packaging materials (Figure 2-2). As expected, PVC was not detected as often in water because it is heavier than water and is rarely used in the single-use packaging industry. PET has a similar density to PVC, but it is detected more often possibly because nearly 10% of the packaging industry uses PET. Glaciers had the most diverse distribution of commonly reported plastics potentially due to the atmospheric deposition of plastics from a variety of sources. Compared to water samples, soil samples have narrow distributions of microplastic types, where PE, PP, and PET were reported in nearly 80% of the studies. This is expected as these three polymers are among the most commonly used plastic types (Figure 2-2). While Figure 2-6 provides a good overview of most commonly identified plastic types found at each location, Urban Canal Water, Wetland Water and Stormwater only had a limited number of studies (Table 2-2) reporting plastic type found and therefore their plastic distribution cannot be relied as much as other location with higher number of studies.

Overall, these results indicate that the abundance of microplastics in the soil is similar to the production and use of plastic material, whereas water samples contain diverse types of microplastics due to transport and exchange between terrestrial compartments.

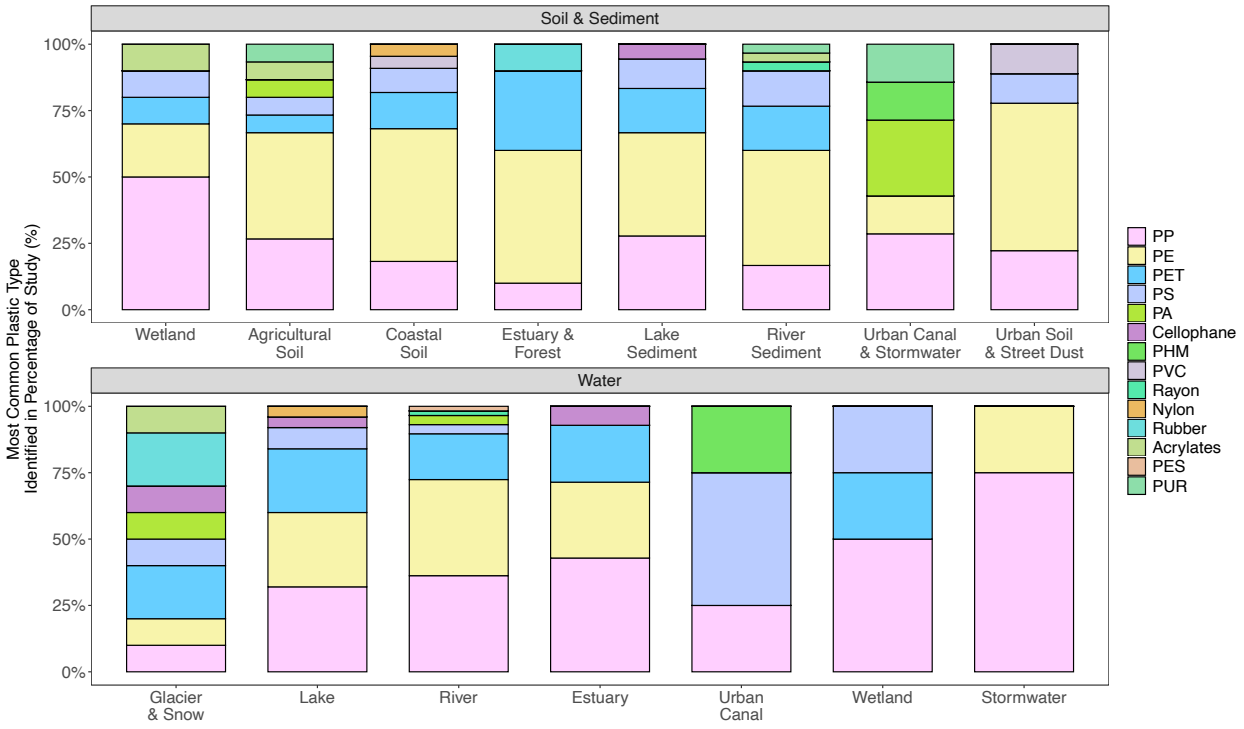

Figure 2-6. (a) The most common plastic polymer types in fresh water and (b) in soil or sediment, based on the analysis of 136 articles (n = 240).

Table 2-2. Table of number of respective plastic types reported for Figure 2-6.

Location	Number of reported common plastic types	Sample
Estuary	14	Water
Glacier & Snow	10	Water
Lake	25	Water
River	58	Water
Stormwater	4	Water
Urban Canal	4	Water
Wetland	4	Water
Agricultural Soil	15	Soil
Coastal Soil	22	Soil
Estuary & Forest Soil	10	Soil
Lake	18	Soil
River	30	Soil
Urban Canal & Stormwater Pond	7	Soil
Urban Soil & Street Dust	9	Soil
Wetland	10	Soil

2.2.5. Potential limitations of data analysis

Detection methodology. The analysis does not account for the potential effect of detection methodology on reported concentration. To create our global dataset, we collected data from studies published between 2013-2020, and they all used different methodologies to collect samples and detect microplastics, with different minimum cutoff size. We found that only around 20% of reported studies reported microplastics below 20 μm (Figure 2-7, Table 2-3), indicating most studies may have missed smaller microplastics. This is particularly problematic because the microplastic concentration in the environment is dependent on particle size and expected to follow power-law; that is, the concentration of smaller microplastics increases by a power function. Thus, most of the reported studies could have underestimated the concentration of microplastics. A lack of information on sampling and analysis details precludes the normalization of reported data between studies. Thus, improvement in detection technologies could change the estimated mean concentration of microplastics in water bodies reported in this study. The methodologies for isolation and counting microplastics are still evolving as noted in the reviews (Elert et al., 2017; Fok et al., 2020; Joon Shim et al., 2017; L. Yang et al., 2021). Future studies should report smaller microplastics for accurate estimation of concentration in the environment.

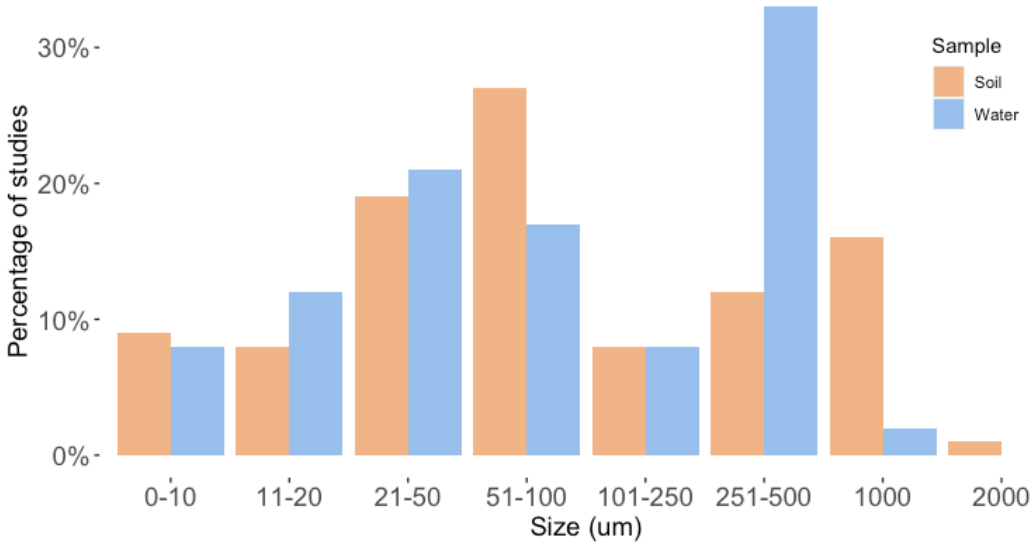

Figure 2-7. Detection limits used by soil and water studies.

Table 2-3. Analysis of the methodology used: lowest size of filtration and lowest size reported by each study used in this review.

doi	Author	Lowest size of filtration (µm)	Lowest size reported (µm)	Sample Type
https://doi.org/10.1007/s12665-017-7137-0	Abbasi et al. 2017	2	< 100	Soil
https://doi.org/10.1016/j.envpol.2018.10.039	Abbasi et al. 2019	2	< 100	Soil
https://doi.org/10.1007/s10708-020-10273-6	Adu-Boahen et al. 2020	20	N/A	Water
https://doi.org/10.1016/j.envpol.2016.10.038	Akhbarizadeh et al., 2017	2	< 100	Soil
https://doi.org/10.1016/j.chemosphere.2019.02.188	Alam et al. 2019	1.2	50	Soil
https://doi.org/10.1016/j.chemosphere.2019.02.188	Alam et al. 2019	1.2	50	Water
https://doi.org/10.1016/j.scitotenv.2020.139385	Alfonso et al. 2020	8	< 200	Water
https://doi.org/10.1016/j.marpolbul.2019.05.064	Alvarez-Hernandez et al., 2019	1000	1000	Soil
https://doi.org/10.1016/j.marpolbul.2019.06.042	Alves and Figueiredo 2019	15	< 200	Soil
https://doi.org/10.1016/j.envpol.2019.07.005	Ambrosini et al. 2019	0.45	< 100	Water
https://doi.org/10.1016/ j.scitotenv.2020.140377	Amrutha and Warrier 2020	300	300	Soil
https://doi.org/10.1016/j.scitotenv.2020.140377	Amrutha and Warrier 2020	300	300	Water
https://doi.org/10.1080/15275922.2019.1693442	Ashwini and Varghese 2020	1000	1000	Soil
https://pubmed.ncbi.nlm.nih.gov/32512330/	Bagheri et al. 2020	100	100	Soil
https://doi.org/10.1021/acs.est.6b02917	Baldwin et al. 2016	333	355	Water
https://doi.org/10.1371/journal.pone.0228896	Baldwin et al. 2020	355	355	Water
https://doi.org/10.1016/j.marpolbul.2016.06.037	Ballent et al 2016	63	< 2000	Soil
https://doi.org/10.1016/j.marpolbul.2019.01.028	Bancin et al. 2019	1000	1000	Soil
https://doi.org/10.1016/j.watres.2018.10.013	Barrows et al. 2018	0.45	100	Water
https://doi.org/10.1007/s11356-019-04632-1	Battulga et al. 2019	0.7	< 500	Soil
https://doi.org/10.1016/j.scitotenv.2020.139013	Benson and Fred-Ahmadu 2020	1000	1000	Soil
https://doi.org/10.1126/sciadv.aax1157	Bergmann et al. 2019	11	11	Water
https://doi.org/10.1016/j.marpolbul.2020.111257	Bikker et al. 2020	330	100	Water
doi.org/10.1016/j.marpolbul.2020.111345	Bissen and Chawchai 2020	1.2	< 500	Soil
https://doi.org/10.1007/s11356-019-04678-1	Blair et al. 2019	63	< 63	Soil
https://doi.org/10.1016/j.chemosphere.2018.10.110	Bordós et al. 2019	100	100	Water
https://doi.org/10.1021/es903784e	Browne et al. 2010	N/A	< 1000	Soil
https://doi.org/10.1016/j.envpol.2019.113284	Campanale et al. 2020	333	< 500	Water
https://doi.org/10.1016/j.envpol.2019.113449	Chen et al. 2020	0.45	20	Soil
https://doi.org/10.1016/j.scitotenv.2018.01.338	Cheung et al. 2018	333	355	Water
https://doi.org/10.1007/s40710-018-0345-0	Cheung et al. 2018	270	355	Water
https://doi.org/10.1007/s11368-020-02759-0	Choi et al 2020	0.45	< 1000	Soil
https://doi.org/10.1007/s11270-020-04653-4	Çomakli et al. 2020	45	8	Water
https://doi.org/10.1016/j.scitotenv.2020.136984	Constant et al. 2020	63	63	Soil
10.1016/j.scitotenv.2020.136984	Constant et al. 2020	333	N/A	Water
https://doi.org/10.1016/j.envpol.2015.04.009	Corcoran et al. 2015	< 500	500	Soil
https://doi.org/10.1021/acs.est.9b04896	Corcoran et al. 2020.	63	63	Soil
https://doi.org/10.1016/j.scitotenv.2020.141917	Corradini et al 2021	2.5	80	Soil
https://doi.org/10.1016/j.scitotenv.2019.03.368	Corradini et al.2019	2.5	8	Soil
https://doi.org/10.1007/s10661-009-1113-4	Costa et al. 2009	< 1000	< 1000	Soil
10.1016/j.scitotenv.2020.138018	Cozzolino et al. 2018	1.2	45	Soil
https://doi.org/10.1016/j.envpol.2020.113994	Crew et al. 2020	1	< 10	soil
https://doi.org/10.1016/j.envpol.2020.113994	Crew et al. 2020	100	N/A	Water
https://doi.org/10.1016/j.scitotenv.2020.138334	Crossman et al. 2020	1.6	50	Soil
https://doi.org/10.1016/j.rsma.2020.101119	Cutroneo et al. 2020	0.45	< 63	Soil
https://doi.org/10.1016/j.marpolbul.2020.111555	D. Hu et al. 2020	333	333	Water
https://doi.org/10.1016/j.marpolbul.2020.111555	D. Hu et al. 2020	0.45	< 100	Soil
https://doi.org/10.1016/j.scitotenv.2020.138893	Dahms et al. 2020	53	< 200	Soil
https://doi.org/10.1016/j.scitotenv.2020.138893	Dahms et al. 2020	53	< 200	Water
10.1016/j.envpol.2018.07.131	Dai et al 2018	50	< 100	Soil
10.1016/j.scitotenv.2019.135411	de Jesus Pinon-Colin et al. 2020	25	N/A	Water

https://doi.org/10.1016/j.marpolbul.2018.07.058	de Villiers et al 2017	40	< 1000	Soil
10.1016/j.jglr.2018.07.014	Dean et al. 2018	25		Soil
https://doi.org/10.1007/s11356-017-9674-1	Dehghani et al. 2017	2	< 100	Soil
https://doi.org/10.1016/j.envpol.2019.113658	Deng et al. 2020	20	17	Water
https://doi.org/10.1016/j.envpol.2019.113658	Deng et al. 2020	20	64	Soil
https://doi.org/10.1016/j.scitotenv.2017.10.150	Di et al 2018	48	< 500	Soil
https://doi.org/10.1016/j.scitotenv.2017.10.150	Di et al 2018	48	< 500	Water
https://doi.org/10.1016/j.marchem.2020.103780	Díez-Minguito et al. 2020	300	300	Water
https://doi.org/10.1016/j.envpol.2019.03.105	Dikareva & Simon, 2019	63	63	Soil
https://doi.org/10.1016/j.envpol.2019.03.105	Dikareva & Simon, 2019	63	63	Water
https://doi.org/10.1016/j.scitotenv.2019.02.332	Ding et al. 2019	75	< 500	Water
https://doi.org/10.1016/j.scitotenv.2020.137525	Ding et al. 2020	0.45	<49	Soil
https://doi.org/10.1038/s41598-020-57933-8	Dong et al. 2020	5	100	Soil
https://doi.org/10.1016/j.heliyon.2020.e04302	Donoso et al. 2020	250	N/A	Water
https://doi.org/10.1007/978-3-319-61615-5_4	Dris et al. 2015	80	N/A	Water
https://doi.org/10.3390/ijerph17030845	Du et al. 2020	N/A	< 10	Soil
https://doi.org/10.1016/j.envpol.2019.113232	Duan et al. 2020	N/A	13	Soil
https://doi.org/10.1016/j.scitotenv.2020.138824	Edo et al. 2020	25	< 50	Soil
https://doi.org/10.1016/j.scitotenv.2020.140201	Egessa et al. 2020	300	300	Water
https://doi.org/10.1016/j.watres.2019.05.053	Eo et al. 2019	20	20	Water
https://doi.org/10.1016/j.dib.2019.104887	Esiukova et al. 2020	174	200	Soil
https://doi.org/10.1016/j.chemosphere.2016.07.083	Estahbanti and Fahrenfeld 2016	153	63	Water
https://doi.org/10.1016/j.scitotenv.2020.140087	Feng et al. 2020	0.45	20	Soil
https://doi.org/10.1016/j.scitotenv.2020.140087	Feng et al. 2020	15	20	Water
https://doi.org/10.1016/j.marpolbul.2019.110790	Firdaus et al. 2020	300	< 1000	Soil
https://doi.org/10.1016/j.envpol.2016.03.012	Fischer et al 2016	13	< 300	Soil
https://doi.org/10.1016/j.envpol.2016.03.012	Fischer et al. 2016	300	300	Water
https://doi.org/10.1016/j.ecoenv.2020.110536	Fraser et al. 2020	8	50	Soil
https://doi.org/10.1021/acs.est.6b00816	Fuller & Gautam et al. 2016	< 1000	< 1000	Soil
https://doi.org/10.1016/j.scitotenv.2020.141604	Gerolin et al. 2020	63	63	Soil
https://doi.org/10.1016/j.cscee.2020.100020	Gimilani et al. 2020	250	250	Soil
10.1007/s11356-020-09622-2	Gopinath et al. 2020	120	300	Water
DOI:10.1016/j.marpolbul.2018.01.030	Gray et al 2018	63	63	Water
https://doi.org/10.1016/j.watres.2020.115623	Grbic et al. 2020	10	125	Water
https://doi.org/10.1016/j.marpolbul.2019.02.015	Haave et al 2019	30	11	Soil
https://doi.org/10.1016/j.scitotenv.2019.135601	Han et al. 2020	50	50	Water
https://doi.org/10.1016/j.scitotenv.2019.134467	He et al. 2019	0.45	< 1000	Soil
https://doi.org/10.1016/j.envpol.2019.113402	Helcoski et al. 2020	75	N/A	Soil
https://doi.org/10.1016/j.marenvres.2013.02.015	Hidalgo-Ruz et al.	1000	1000	Soil
https://doi.org/10.1016/j.scitotenv.2020.139436	Hitchcock, 2020	10	50	Water
DOI: 10.1086/693012	Hoellein et al. 2017	333	333	Water
https://doi.org/10.1016/j.watres.2019.05.053	Hong et al. 2019	20	50	Water
https://doi.org/10.1016/j.marpolbul.2016.09.004	Horton et al. 2017	1000	1000	Soil
https://doi.org/10.1038/s41598-017-14588-2	Huerta Lwanga et al. 2017	< 5000	10	Soil
https://doi.org/10.1007/s11356-020-07833-1	Irfan et al. 2020	0.7	< 1000	Water
https://civiclaboratory.files.wordpress.com/2017/07/wang-et-al.pdf	J. Wang et al 2017	1	< 1000	Soil
https://doi.org/10.1016/j.scitotenv.2020.138950	Järlskog et al 2020	20	20	Water
https://doi.org/10.1016/j.scitotenv.2020.138950	Järlskog et al 2020	100	100	Soil
https://doi.org/10.1016/j.marpolbul.2013.10.024	Jayasiri et al. 2013	1000	1000	Soil
10.3390/ijerph15102164	Jiang et al. 2018	45	< 500	Water
https://doi.org/10.1016/j.envpol.2019.03.022	Jiang et al. 2019	45	<500	Water
https://doi.org/10.1016/j.envpol.2019.03.022	Jiang et al. 2019	0.22	<500	Soil
https://doi.org/10.1016/j.marpolbul.2020.111482	Jun Deng et al 2020	38	38	Soil
10.1016/j.chemosphere.2020.126915	Karaoglu & Gul, 2020	1.2	N/A	Water
10.1016/j.chemosphere.2020.126915	Karaoglu & Gul, 2020	1.2	N/A	Soil
https://doi.org/10.1016/j.envpol.2018.10.111	Kataoka et al. 2019	335	< 400	Water
https://doi.org/10.1016/j.marpolbul.2020.111130	Kelly et al 2020	0.2	11	Water

https://doi.org/10.1021/acs.est.5b00492	Klein et al. 2015	63	63	Soil
10.1016/j.marpolbul.2020.111383	Lam et al., 2020	333	355	Water
https://doi.org/10.1016/j.envpol.2014.02.006	Lechner et al. 2014	500	N/A	Water
https://doi.org/10.1021/acs.est.9b03850	Lenaker et al. 2019	125	125	Soil
https://doi.org/10.1021/acs.est.9b03850	Lenaker et al. 2019	333	355	Water
https://doi.org/10.1016/j.envint.2017.01.018	Leslie et al. 2017	0.7	10	Soil
https://doi.org/10.1016/j.envint.2017.01.018	Leslie et al. 2017	0.7	10	Water
https://doi.org/10.1016/j.scitotenv.2020.138560	Lestari et al. 2020	333	N/A	Water
https://doi.org/10.1186/s12302-020-0297-7	Li et al. 2020	300	300	Water
https://doi.org/10.1016/j.scitotenv.2018.06.327	Lin et al. 2018	20	20	Water
10.1016/j.scitotenv.2018.06.327	Lin et al., 2018	5	20	Soil
https://doi.org/10.1016/j.envpol.2018.07.051	Liu et al. 2018	20	30	Soil
https://doi.org/10.1016/j.envpol.2019.113335	Liu et al. 2019	10	10	Soil
https://doi.org/10.1016/j.scitotenv.2019.03.416	Liu et al. 2019	10	16	Water
https://doi.org/10.1016/j.scitotenv.2019.07.144	Liu et al. 2020	20	32.7	Soil
10.1016/j.envpol.2020.114261	Liu et al. 2020	1.2	< 50	Water
https://doi.org/10.1016/j.envpol.2018.11.081	Luo et al. 2019	20	20	Water
https://doi.org/10.1016/j.scitotenv.2018.10.321	Lv et al. 2019	20	< 1000	Soil
https://doi.org/10.1016/j.scitotenv.2020.140679	Ma et al 2020	0.22	< 100	Water
https://doi.org/10.1021/acs.est.9b04838	Mai et al. 2019	330	300	Water
https://doi.org/10.3390/w12041219	Manana et al. 2020	1.2	50	Water
https://doi.org/10.1016/j.scitotenv.2019.135579	Mani & Burkhardt-Holm, 2019	300	300	Water
DOI: 10.1021/acs.est.9b01363	Mani et al. 2019b	10	11	Soil
https://doi.org/10.1016/j.scitotenv.2020.137820	Mao et al. 2020	75	< 500	Water
https://doi.org/10.1016/j.envpol.2020.115033	Mao et al. 2020 (b)	64	64	Water
https://doi.org/10.3390/w12041210	Martinez Silva & Nanny 2020	20	5	Water
https://doi.org/10.3390/w12041210	Martinez Silva & Nanny 2020	0.45	< 5	Soil
https://doi.org/10.1016/j.jglr.2019.12.012	Mason et al. 2020	333	350	Water
https://doi.org/10.1007/s00244-017-0414-9	Matsuguma et al. 2017	315	315	Soil
https://doi.org/10.1021/es503610r	McCormick et al. 2014	333	N/A	Water
10.1002/ecs2.1556	McCormick et al. 2016	333	N/A	Water
https://doi.org/10.1016/j.scitotenv.2020.140824	Minor et al. 2020	0.45	<100	Soil
https://doi.org/10.1016/j.watres.2020.115723	Mintenig et al. 2020	20	< 25	Water
https://doi.org/10.1016/j.marpolbul.2013.11.025	Mohamed Nor et al. 2014	1.6	< 20	Soil
https://doi.org/10.1080/00288330.2019.1703015	Mora-Teddy & Matthaei, 2019	250	250	Water
https://doi.org/10.1016/j.marpolbul.2015.09.044	Naidoo et al. 2015	300	250	Water
https://doi.org/10.1016/j.marpolbul.2016.11.032	Naji et al. 2017a	25	20	Soil
https://doi.org/10.1007/s11356-017-9587-z	Naji et al. 2017b	25	60	Soil
https://doi.org/10.1016/j.envpol.2019.113865	Nan et al. 2020	20	36	Water
https://doi.org/10.1007/s11356-020-08831-z	Narciso-Ortiz et al. 2020	0.001	0.716	Water
https://doi.org/10.1016/j.marpolbul.2015.09.043	Nel et al 2015	65	65	Soil
10.1016/j.ecoenv.2020.111137	Nematollahi et al. 2020	2	100	Soil
https://doi.org/10.3390/w11071466	Olesen et al. 2019.	10	4	Soil
https://doi.org/10.3390/w11071466	Olesen et al. 2019.	10	6	Water
https://doi.org/10.1016/j.ecoenv.2020.110656	Oni et al. 2020	0.4	20	Water
https://doi.org/10.1016/j.marpolbul.2020.111516	Pan et al. 2020	1.6	300	Water
10.1016/j.chemosphere.2020.127876	Pan et al. 2020	0.7	300	Water
https://doi.org/10.1016/j.envpol.2018.08.064	Pazos et al. 2018	0.2	100	Water
10.1039/c9em00193j	Peller et al. 2019	0.45	100	Water
https://doi.org/10.1016/j.envpol.2016.12.064	Peng et al. 2017b	1	46.8	Soil
https://doi.org/10.1016/j.envpol.2017.11.034	Peng et al. 2018	1	< 100	Soil
https://doi.org/10.1016/j.scitotenv.2019.135021	Picó et al. 2020	333	250	Water
https://doi.org/10.1038/s41598-018-36172-y	Piehl et al.	1000	1000	Soil
https://doi.org/10.1007/s00128-019-02771-2	Rao et al 2020	30	< 200	Soil
10.1016/j.marpolbul.2020.111541	Rasta et al. 2020	5	< 500	Soil
10.1016/j.marpolbul.2020.111541	Rasta et al. 2020	350	< 500	Water
https://doi.org/10.1016/j.scitotenv.2018.03.233	Rodrigues et al 2018	55	N/A	Water
https://doi.org/10.1016/j.scitotenv.2018.03.233	Rodrigues et al 2018.	55	N/A	Soil

10.1016/j.scitotenv.2020.140018	Rowley et al. 2020	250	32	Water
https://doi.org/10.1016/j.scitotenv.2019.135091	S. Zhang et al. 2020	3	< 50	Soil
https://doi.org/10.1016/j.scitotenv.2019.133712	Sarkar et al. 2019	63	63	Soil
https://doi.org/10.1016/j.scitotenv.2020.139866	Scherer et al. 2020	150	150	Water
https://doi.org/10.1021/acs.est.7b06003	Scheurer & Bigalke et al 2017	0.45	125	Soil
https://doi.org/10.1002/etc.4698	Scircle et al. 2020	30	30	Water
https://doi.org/10.1007/s10661-019-7843-z	Scopetani et al. 2019	1.2	5.5	Water
https://doi.org/10.1016/j.envpol.2018.02.008	Sighicelli et al. 2018	300	1000	Water
https://doi.org/10.1016/j.scitotenv.2019.06.168	Simon-Sanchez et al 2019	0.7	< 50	Soil
https://doi.org/10.1016/j.scitotenv.2019.06.168	Simon-Sanchez et al 2019	5	< 50	Water
10.1016/j.envpol.2020.114481	Stanton et al. 2020	0.45	< 100	Water
https://doi.org/10.1038/s41598-020-70306-5	Stead et al. 2020	N/A	N/A	Water
https://doi.org/10.1016/j.envpol.2016.06.036	Su et al. 2016	0.45	5	Water
https://doi.org/10.1016/j.envpol.2016.06.036	Su et al. 2016.	0.45	5	Soil
https://doi.org/10.1016/j.envpol.2017.11.075	Su et al. 2018	0.45	22	Soil
https://doi.org/10.1016/j.envpol.2017.11.075	Su et al. 2018	0.45	22	water
10.1016/j.chemosphere.2020.127234	Ta and Babel, 2020	50	50	Soil
10.1016/j.chemosphere.2020.127234	Ta and Babel, 2020	300	50	Water
10.5614/j.eng.technol.sci.2020.52.4.6	Ta et al. 2020	50	53	Soil
10.5614/j.eng.technol.sci.2020.52.4.6	Ta et al. 2020	300	53	Water
https://doi.org/10.1016/j.scitotenv.2018.03.336	Tang et al. 2018	20	N/A	Soil
https://doi.org/10.1007/s11356-020-10424-9	Tavsanoglu et al. 2020	100	N/A	Water
10.17576/jsm-2020-4907-01	Tee et al., 2020	60	< 100	Water
https://doi.org/10.1016/j.envpol.2020.114962	Tien et al. 2020	50	50	Soil
https://doi.org/10.1016/j.envpol.2020.114962	Tien et al. 2020	50	50	Water
https://doi.org/10.1007/s10933-019-00071-7	Turner et al. 2019	0.45	<500	Soil
https://doi.org/10.1016/j.marpolbul.2020.111170	Urban-Malinga et al. 2020	2.7	12	Soil
10.1002/wer.1229	Uurasjarvi et al. 2019	20	<100	Water
https://doi.org/10.1016/j.envpol.2017.05.057	Vaughan et al. 2017	500	N/A	Soil
10.1139/facets-2016-0070	Vermaire et al. 2017	100	100	Water
10.1016/j.scitotenv.2016.09.213	Wang et al. 2017	0.45	50	Water
https://doi.org/10.1016/j.scitotenv.2018.03.211	Wang et al. 2018	50	50	Water
https://doi.org/10.1016/j.marpolbul.2019.110664	Weideman et al. 2019	N/A	N/A	Water
https://doi.org/10.1016/j.marpolbul.2018.09.043	Wen et al. 2018	N/A	< 500	Soil
https://doi.org/10.1016/j.envpol.2020.113935	Wong et al. 2020	300	300	Water
https://doi.org/10.1039/C9EM00148D	Wu et al. 2019	48	< 300	Water
https://doi.org/10.1016/j.scitotenv.2019.135187	Wu et al. 2020	0.45	10	Water
https://doi.org/10.1016/j.scitotenv.2019.134431	Wu et al. 2020	1	100	Soil
https://doi.org/10.1016/j.scitotenv.2020.139065	Xia et al. 2020	0.45	< 500	Water
https://doi.org/10.1016/j.envpol.2017.12.081	Xiong et al., 2018	112	112	Water
https://doi.org/10.1016/j.envpol.2017.12.081	Xiong et al., 2018	2000	112	Soil
https://doi.org/10.1016/j.scitotenv.2020.139218	Xu et al. 2020	50	20	Water
https://doi.org/10.1016/j.scitotenv.2020.139025	Xu et al. 2020	5	N/A	Soil
https://doi.org/10.3390/ijerph16091650	Yin et al. 2019	45	50	Water
https://doi.org/10.1016/j.chemosphere.2019.125486	Yin et al. 2020	1000	50	Soil
https://doi.org/10.1016/j.envpol.2016.04.080	Yu et al. 2016	1	N/A	Soil
https://doi.org/10.1016/j.ecoenv.2018.11.126	Yuan et al. 2019	0.45	50	Water
https://doi.org/10.1016/j.ecoenv.2018.11.126	Yuan et al. 2019	0.45	50	Soil
https://doi.org/10.1016/j.envpol.2019.113447	Yukioka et al. 2020	75	100	Soil
https://doi.org/10.1016/j.scitotenv.2018.06.004	Zhang & Liu et al 2018	50	50	Soil
https://doi.org/10.1016/j.envpol.2016.05.048	Zhang et al. 2016	1.2	< 500	Soil
https://doi.org/10.1016/j.scitotenv.2018.02.300	Zhang et al. 2018	1	50	Water
https://doi.org/10.1016/j.marpolbul.2019.110569	Zhang et al. 2019	5	20	Water
https://doi.org/10.1007/s12403-018-00296-3	Zhang et al. 2019	0.45	300	Water
https://doi.org/10.1016/j.scitotenv.2019.135176	Zhang et al. 2020	25	300	Soil
https://doi.org/10.1021/acs.est.9b07905	Zhang et al. 2020	0.45	< 200	Soil
https://doi.org/10.1016/j.scitotenv.2019.135176	Zhang et al. 2020	25	< 75	Water

https://doi.org/10.1016/j.scitotenv.2017.10.213	Zhang et al., 2018	3	< 50	Soil
https://doi.org/10.1016/j.envpol.2015.08.027	Zhao et al. 2015	1.2	< 500	Water
https://doi.org/10.1016/j.marpolbul.2020.111152	Zhao et al. 2020	20	45	Water
https://doi.org/10.1016/j.scitotenv.2019.133798	Zhou et al. 2019.	0.45	10	Soil
https://doi.org/10.1016/j.jhazmat.2019.121814	Zhou et al. 2020	5	50	Soil
https://doi.org/10.1016/j.envres.2020.109893	Zhou et al. 2020	0.45	< 500	Water
https://doi.org/10.1016/j.geoderma.2018.02.015	Zhou et al.2018	300	100	Soil
https://doi.org/10.1016/j.scitotenv.2019.136356	Ziajahromi et al. 2019	25	25	Water
https://doi.org/10.1016/j.scitotenv.2019.136356	Ziajahromi et al. 2019	25	< 100	Soil
https://doi.org/10.1016/j.scitotenv.2020.138344	Zuo et al. 2020	1.2	<50	Soil

Unit bias. Our analysis includes more research papers measuring microplastic concentration in soil and sediment than that about microplastics in water because many of the earlier water studies have not reported concentration in n L^{-1}. We chose to only evaluate the number per volume of research papers due to the availability of more data points. Additionally, microplastic concentration can be influenced by the depth of the collection. Since calculating the microplastic concentration using number per area papers do not account for depth, we chose to not use these data points for our analysis.

Fragmentation and formation of microplastics by physical abrasion – Ex: tires and textiles. Automobile tire wear releases most secondary rubber polymers (Knight et al., 2020; Sieber et al., 2020). While mechanical abrasion creates relatively large particles, friction heat evaporates polymers, and causes the formation of relatively small or sub-micrometer particles (Kole et al., 2017a). The release of microplastics from tires can be exacerbated by many factors including road roughness, composition and temperature of the road surface, local climate, tire age, composition and structure, tire pressure, vehicle weight, and driving speed (Eisentraut et al., 2018; Halle et al., 2020; Unice et al., 2019). The relative contribution of tire wear is estimated to be 5–10% of the total number of microplastics in oceans and 3–7% of the total airborne particulate matter (PM 2.5) (Kole et al., 2017a). Around 74% of microplastics emitted from tire wear were found to remain within 5 meters from the source; however, around 22% reached surface waters by stormwater

runoff and wind deposition (Sieber et al., 2020). Stormwater runoff can also carry them to retention ponds (F. Liu et al., 2019b) and wetlands (Ziajahromi et al., 2020), where around 90% of the tire wear particulates can settle by gravity (Kloeckner et al., 2019; Unice et al., 2019). As microplastics from tire wear often contain high concentrations of heavy metals such as zinc (Councell et al., 2004), it is important to develop best management practices to decrease their release or capture them near the road by appropriate stormwater infrastructures (Kabir et al., 2014; Malaviya and Singh, 2012).

Textile industries, which include clothing and household furnishing, are also a source of microplastics or microfibers- making up nearly a third of modeled marine microplastics (Belzagui et al., 2019; Henry et al., 2019; Siegfried et al., 2017). The textile exportation value for polyester yarn alone is over 16 billion USD, and fiber production worldwide was over 105 Mt in 2018 (Stone et al., 2020). Microfiber detachment rates are estimated to be 30,000-465,0000 fibers per square meter of the garment, which account for an annual release of 17,830 tons of microfibers (Belzagui et al., 2019; Yang et al., 2019). The in-use textile microfiber release rate during machine washing depends on many factors (Figure 2-8), such as machine type and laundry parameters such as water temperature, chemical additives, and textile characteristics like fabric structure and garment type (Cesa et al., 2017). The release typically decreases with laundry cycles (Belzagui et al., 2019; Cai et al., 2020) and increases with mechanical mixing and heat (Belzagui et al., 2019), use of detergents (Henry et al., 2019; Hernandez et al., 2017), longer washing times (Dalla Fontana et al., 2020). The release of microfibers tends to be higher for processed textiles such as including fleece, acetate fabric, and polyethylene terephthalate (PET) textiles (Cai et al., 2020; Stone et al., 2020; Yang et al., 2019). The release also increased with increases in edge-to-acreage ratio and the use of scissor-cut fabrics compared to laser-cut ones (Cai et al., 2020). The fibers released from

textiles end up in the atmosphere (Dris et al., 2016b) or surface waters (Cesa et al., 2017). Thus, the best management strategies to minimize their release should be developed. Since most of the laundry water then passes through wastewater treatment plants, where it loses up to 98% of microplastics to sewage sludge (Corradini et al., 2019; X. Li et al., 2018; Lv et al., 2019), a regulatory measure should be taken to prevent deposition of highly polluted microplastics sewage sludge onto agricultural land, into oceans, or other environments.

Fragmentation and degradation of microplastics by UV radiation. Exposure to UV radiation from sunlight leads to deterioration and release of microplastics. UV radiation induces autocatalytic oxidation through the creation of free radicals (Feldman, 2002), which helps cleave internal polymer bonds and shortens the polymer chain (Andrady et al., 2019; Cole et al., 2011; Gewert et al., 2015). This process can decrease the material surface toughness, elasticity, rigidity, and uniformity (Iniguez et al., 2018; Moezzi and Ghane, 2013; ter Halle et al., 2017; Weinstein et al., 2016) and make them more susceptible for release by abrasion. The surface deterioration increases (Figure 2-8b) with decreasing wavelengths (Stephenson et al., 1961), increasing exposure time (Cai et al., 2018), and increasing inflow of water compared to stagnant water (Hebner and Maurer-Jones, 2020). In general, PP is the most susceptible polymer for deterioration under UV light (Chen et al., 2019; Gewert et al., 2015; Iniguez et al., 2018; Song et al., 2017a; Weinstein et al., 2016). These complexities should be included in the models predicting the release of microplastics by UV radiation.

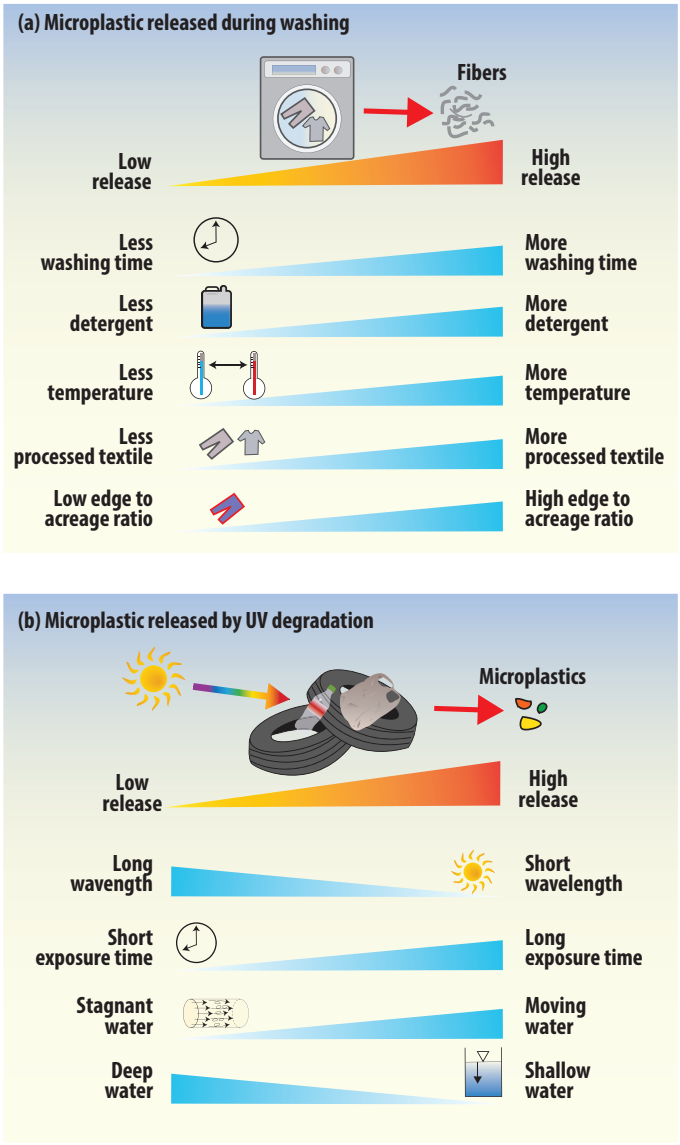

Figure 2-8. Factors that affect the release of fibers during (a) washing of clothes, and (b) degradation of bulk plastics under sunlight exposure.

Change in microplastic numbers due to fragmentation and weathering are not considered. The number concentration of microplastics at a location could change based on fragmentation. Microplastics can become fragmented by physical abrasion, and photodegradation and biodegradation can accelerate the fragmentation by weakening the surface (Barnes et al., 2009; Song et al., 2017a; Zhu et al., 2020). We have provided a summary of conditions that affect these processes in the Supplementary Materials (Figure 2-8). In contrast to UV degradation,

biodegradation of microplastics receives less attention despite several pieces of evidence (Auta et al., 2018; Paço et al., 2017; Yoshida et al., 2016). Microplastics are degraded when exposed to microbial exudates (Zettler et al., 2013) and enzymes (Shen et al., 2019). Biodegradation appears to depend on polymer types (Austin et al., 2018), fungal (Paço et al., 2017), and bacterial (Sivan, 2011) communities. Analyzing 13 studies published to date, we found that biodegradation rates vary with experimental duration, plastics type, and type of microorganism used (Figure 2-9). However, these studies measured biodegradation in controlled laboratory conditions lasting less than 50 days. The degradation rate in the natural environment could be a lot slower due to the presence of other easily biodegradable materials. The degradation rate typically slows down after the initial period (Chamas et al., 2020). Nevertheless, these studies show that biodegradation can be significant in the long-term, and the rate can vary with the type of microbe (Shah et al., 2008) and the weather conditions (Debroas et al., 2017; Gewert et al., 2015). Weathering by photo- or biodegradation can increase fragmentation of microplastics and potentially increase the number concentration, despite a net mass loss.

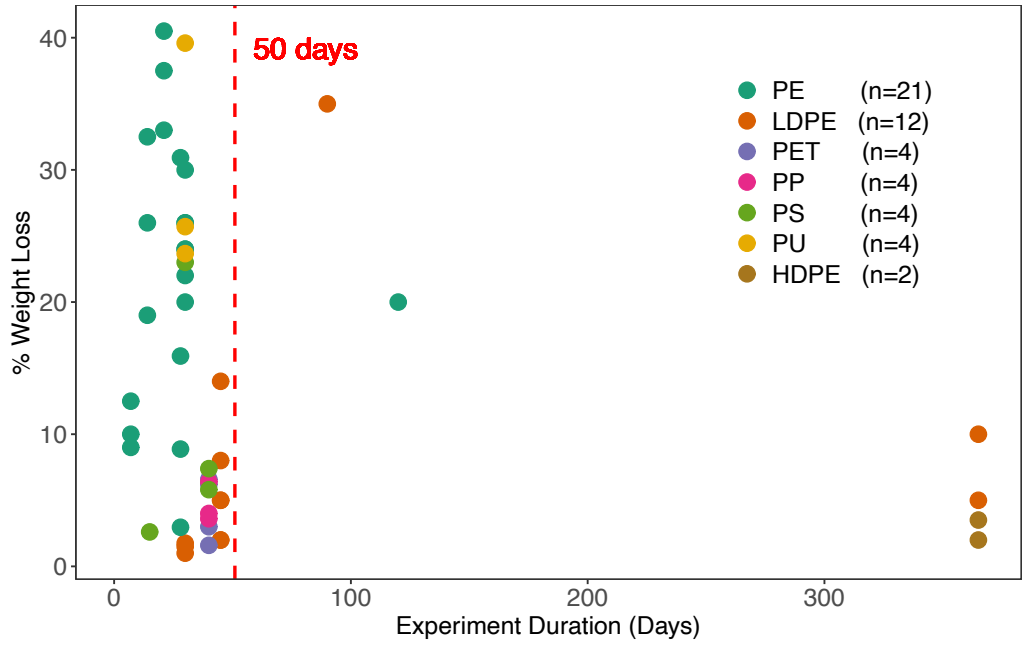

Figure 2-9. Biodegradation of 7 types of plastics: high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyurethane (PU). Biodegradation efficiency was proxied by the percent loss of weight.

2.3. Microplastic transport modeling frameworks in air, water, and atmosphere

The distribution of microplastics in terrestrial environments and water bodies are affected by processes including advection, dispersion, diffusion, degradation, settling, adsorption, and aggregation. Thus, it is critical to developing models to predict the concentration at a location based on local conditions. Although numerous studies have reported the concentration and abundance of microplastics in environments, far few studies attempted to model the transport of microplastics in the environment. Microplastic transport is expected to follow similar processes as any other natural particles. In this section, we use previous modeling studies on particle transport to develop theoretical frameworks that can be used in future modeling efforts for the prediction of microplastics in the environment based on microplastics properties and local conditions.

Transport of microplastics can vary with microplastics types because of a difference in their fundamental properties such as density, contact angle, and dielectric constant (Figure 2-10). While density can affect their diffusion and settling (Khatmullina and Isachenko, 2017; Waldschlaeger and Schuettrumpf, 2019), the contact angle can affect the interparticle forces between microplastics and other natural particles (Hossain et al., 2019; Van Melkebeke et al., 2020). The particle density of polypropylene and polyethylene is lower than that of water, indicating they are more likely to stay in the water. Microplastics made out of PVC and PET have a higher density than other plastics, indicating they are going to settle quickly on sediments. Compared with sand, all types of microplastics have a higher contact angle, indicating strong hydrophobic interaction between plastics particles. This will affect their aggregation behavior and attachment to other environmental media.

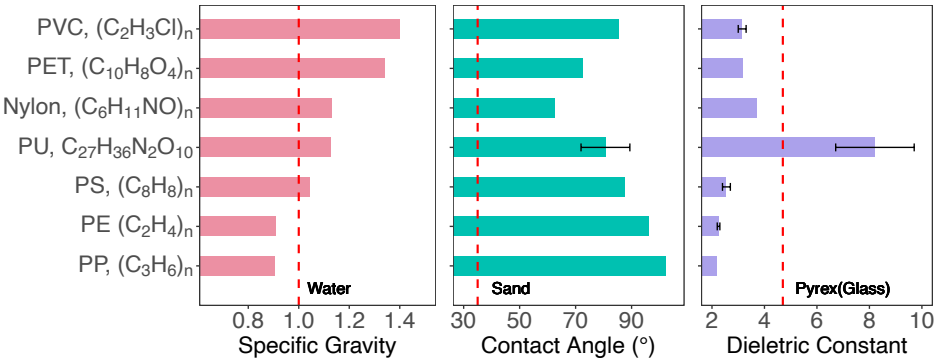

Figure 2-10. Comparison of polymer properties (specific gravity, contact angle, and dielectric constant) across various plastic polymer types (polyvinyl chloride (PVC), polyurethane (PU), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), polyethylene (PE), and nylon (Chiou and Hsieh, 2015; Driedger et al., 2015; Lusher et al., 2017).

2.3.1. Transport by wind

Many studies have provided evidence of microplastic transport via wind (Dehghani et al., 2017; Dris et al., 2016b; Harrison et al., 2012; Y. Li et al., 2020; Wright et al., 2020) by analyzing dust deposits on the surface (Mbachu et al., 2020) and tree canopies (K. Liu et al., 2020). However, the model describing microplastic emission by wind has not been developed. Herein, we provide

a theoretical framework that could help develop the emission model. This framework is based on a modeling framework used to describe the transport of biochar particles (Ravi et al., 2020), which have a similar density as plastic. Similar to biochar or soil particles (Kok et al., 2012; Ravi et al., 2011), microplastics can be entrained by wind due to several processes including direct emission from soil surfaces, emission from bombardment during saltation (movement of sand particles close to the surface), and emission from the disintegration of large particles of aggregates (Figure 2-11). Microplastics can be trapped within rough surfaces or in between soil particles, which prevents their suspension. The contribution of each of these processes and their relative importance on microplastic emission is unknown. Incorporating all these processes (Hagen, 1991, Ravi et al. 2020), microplastic concentration in the air within a control volume can be modeled as time-dependent conservation of mass of sources and sinks (Eq 2-1):

$$\frac{\partial C(h)}{\partial t} = -\frac{\partial q_x}{\partial x} - \frac{\partial q_y}{\partial y} + E_{ds} + E_a - E_t - E_{ss} \quad \text{(Eq. 2-1)}$$

where $C(h)$ is the average concentration of microplastics in a control volume of height h during time t; q_x and q_y are the component of saltation discharge q, in the x and y direction; E_{ds} is the net vertical microplastics fluxes from the direct emission of loose microplastics from soil; E_a is the emission by physical abrasion or saltation bombardment; E_t is the decrease in emission by trapping of saltation; E_{ss} is the emission loss of fine microplastics due to transport out of the control volume. Saltation only starts once the wind velocity exceeds the threshold shear velocity (u^*), which can be affected by several factors including wind characteristics, soil surface conditions, size and shape of the soil particles, and soil water content. At the instant of the threshold, there exists a balance between the stabilizing or retarding forces such as gravity force (F_g) and the interparticle force (F_i) with aerodynamic forces such as aerodynamic drag (F_d) and the aerodynamic lift (F_l) (Shao et al., 1993).

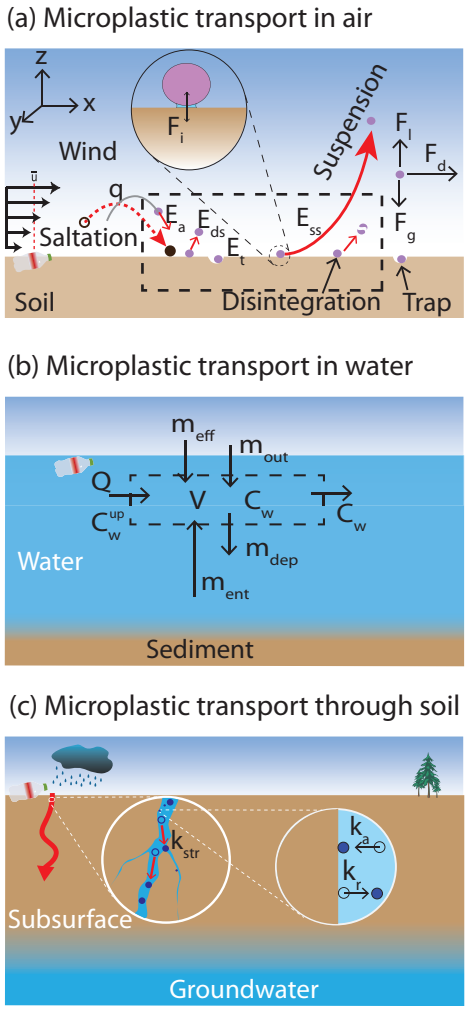

Figure 2-11. Modeling framework for the emission potential of microplastics in the atmosphere, surface water, and through the soil.

A semi-empirical formula (Eq. 2-2) can be used to estimate the threshold shear velocity (Shao and Lu, 2000):

$$u_{*t} = A_N \sqrt{\frac{\rho_p - \rho_a}{\rho_a} g D_p + \frac{\gamma}{\rho_a D_p}} \quad \text{(Eq. 2-2)}$$

where the $\rho_a$is the air density, ρ_p is the microplastics density, D_p is the microplastic diameter, g is the acceleration due to gravity, A_N is a dimensionless parameter, and γ is a parameter that scales the strength of the interparticle forces. The interparticle forces between soil particles become increasingly important as the particle size becomes smaller and smaller (Kok et al., 2012;

Ravi et al., 2011). The nature of interparticle forces between microplastics and between soil and microplastics is not well understood. However, it is reasonable to assume that cohesive forces due to moisture—which are often the dominant interparticle force—can be lower for microplastic particles, as these particles are generally hydrophobic or water repellent. Water repellency has been shown to increase the contact angles and decrease interparticle bonding forces (Ravi et al., 2006). As the microplastic surface is typically hydrophobic, it would reduce the impact of moisture film on the cohesion of microplastics on the soil. Thus, future studies should evaluate the effect of all these factors on microplastics emissions by the wind.

2.3.2. Transport in water

Transport of microplastics in water (Figure 2-11) is governed by similar fundamental processes including advection, dispersion, aggregation, sedimentation, degradation or disintegration, resuspension, and burial (Besseling et al., 2017). Several studies attempted to develop models to describe the change in microplastic concentration in water and sediments in water bodies (Besseling et al., 2017; Daily and Hoffman, 2020; Díez-Minguito et al., 2020; Nizzetto et al., 2016a). Recently, a sediment transport module (Lazar et al., 2010) was used to derive the mass balance of microplastics for a particular size class (Eq. 2.3 and 2.4) in the river/bed sediment system (Nizzetto et al., 2016a):

$$\boldsymbol{V\frac{dC_w}{dt} = QC_w^{up} - QC_w + m_{eff} + \sum_u A\, m_{out} + LW\left(m_{ent} - m_{dep}\right)} \quad \text{(Eq. 2-3)}$$

$$\boldsymbol{\frac{dM_{sed}}{dt} = m_{dep} - m_{ent}} \quad \text{(Eq. 2-4)}$$

where, $C_w(kgm^{-3})$ is the concentration of microplastics suspended in water in the control volume of length L and width W; C_w is assumed to be the same as the concentration downstream, and C_w^{up} $(kg\ m^{-3})$ is the concentration of suspended microplastics from the upstream; Q is river discharge; m_{eff} is the microplastics discharge from point source effluents such as wastewater

treatment plants; A is the surface of each land use unit (u) contributing to delivering microplastics to the stream or river; m_{out} $(kg\ m^{-2}\ s^{-1})$ is the mass of microplastics delivered to the stream by overland runoff during rainfall. Sediment burial occurs when long-term deposition exceeds resuspension. $m_{ent}(kg\ m^{-2}\ s^{-1})$ is the mass of microplastics entrained from the sediment bank, which is a function of flow conditions and size of microplastics: $m_{ent} = a_8 M_{sed} \omega\ f\ r$; where $M_{sed}(kg\ m^{-2})$ is the mass of microplastics of specific size class present in sediment at the time; $\omega(J\ s^{-1}m^{-2})$ is the stream power per unit of bed surface; f is the dimensionless friction factor based on channel characteristics; $a_8(s^2kg^{-1})$ is a tunable scaling factor, and r is the entrainable fraction of microplastics of a given size class, which is the ratio of the difference between maximum size of entrainable microplastics (D_{max}) and minimum size of microplastics (D_{low}) to the difference between the minimum (D_{low}) and maximum size (D_{up}) of microplastics present in the sediment. $m_{dep}(kg\ m^{-2}\ s^{-1})$ is the mass of microplastics deposited from the water column on the sediment, which can be determined by Stokes' law: $C_w w_s$, where w_s is the settling velocity of the microplastics of a specific size class.

The settling velocity (w_s) can change based on an aggregation of microplastics (Lagarde et al., 2016). Other articles or reviews describe in detail the aggregation behavior of nano- and microplastics in aquatic environments in the presence of other particles (Alimi et al., 2018; Wu et al., 2019). A common model to predict the rate of hetero-aggregation is Smoluchowski's population equation:

$$\frac{dN}{dt} \approx \frac{1}{2}\boldsymbol{\alpha\beta n_1 n_2} \qquad \text{(Eq. 2-5)}$$

where α is the attachment efficiency, and β is the collision frequency between two number populations, n_1, n_2 (Y. Li et al., 2019). The rate of aggregation, also referred to as aggregation frequency, can be defined as how often the particles collide and is: $k \propto \frac{1}{N_0}(\frac{dD_h(t)}{dt})_{t\to 0}$, where N_0

is the initial concentration of plastics in the suspension; D_h is the hydrodynamic size of the plastics (Mao et al., 2020). The hydrodynamic size, the transport, and the concentration can be predicted using extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory (Eq. 6). Extended DLVO theory takes into different interacting forces including the Van Der Waals attraction (V_{VDW}), Electric Double layer repulsion (V_{EDL}), and Lewis Acid-Base interactions (V_{AB}) (Hoek and Agarwal, 2006; S. Li et al., 2018). The total interaction energy V_{tot} determines the particle stability as two surfaces approach each other (Hoek and Agarwal, 2006; Mao et al., 2020; Petosa et al., 2010; van Oss, 2008):

$$V_{tot} = V_{VDW} + V_{EDL} + V_{AB} \quad \text{(Eq. 2-6)}$$

where each term can be calculated as follows:

$$V_{VDW} = \frac{aA}{12h\left(1+14\frac{h}{\lambda}\right)}; \quad \text{(Eq. 2-7)}$$

$$\boldsymbol{V_{EDL} = \frac{32\pi\varepsilon\varepsilon_0 K^2 T^2 a}{Z^2 e^2}\left(\tan\left(h\frac{Ze\phi}{4KT}\right)\right)^2 \exp\left(-C^{-1}h\right);\ C^{-1} = \sqrt{\frac{2IN_a e^2}{\varepsilon\varepsilon_0 KT}};} \quad \text{(Eq. 2-8)}$$

$$\boldsymbol{V_{AB} = 2\pi a\lambda\Delta G_{h_0}^{AB} \exp\left(\frac{h_o - D}{\lambda}\right).} \quad \text{(Eq. 2-9)}$$

a is the radius of nano-PS (m), ϕ is the zeta potential of the nanoplastics (mV); ε_0 is the permittivity of vacuum (8.854x 10-12 CV-1m-1); ε is the relative permittivity of the solvent (78.5 for water); h is the distance between two nanoplastics (m); h_0 (0.158nm) is the minimum separation distance due to Born repulsion; C is the inverse of the Debye length (m-1); A is the Hamaker constant; N_a is the Avogadro number; T is the temperature (298.15 K), and e is the elementary electric charge; I is the ionic strength; K is the Boltzmann constant; Z is the valence of metal ion; λ is the decay length for acid-base interactions in water (0.6nm) and $\Delta G_{h_0}^{AB}$ is the acid-base free energy per unit area between the nanoparticle and membrane surfaces at contact. $\Delta G_{h_0}^{AB}$ is typically determined experimentally using contact angle for each polymer type in different

liquids (van Oss, 2008). Most modeling efforts in water are limited to aggregation and settling of microplastics in water (Alimi et al., 2018; Leiser et al., 2020; Y. Li et al., 2019), however, these models rarely account for the heterogeneous shape of microplastics.

2.3.3. Transport through soil

Plastic microspheres have been used in numerous studies as a tracer to examine colloid and pathogen transport in soil (Becker et al., 1999; Burkhardt et al., 2008; Close et al., 2006; Harvey et al., 1993; Knappett et al., 2008; McCarthy et al., 2002; Mohanram et al., 2012, 2010; Mondal and Sleep, 2013, 2012; Yu et al., 2013; Zhuang et al., 2005). These studies provided the basis of microplastic transport models reported in a recent study (Johnson, 2020). Based on the model (Figure 2-11), the concentration of microplastics in pore water (C_w) and soil with moisture content (θ) can be predicted based on the change in concentration as a result of advection, dispersion, attachment and release of microplastics on the soil surface, and straining when the particle size of microplastics is relatively large compared with the pore size (Eq. 2-10).

$$\frac{\partial C_w}{\partial t}\theta = -v\frac{\partial C_w}{\partial x} + D\frac{\partial^2 C_w}{\partial^2 x}\theta - k_a C_w\theta + k_r C_s \rho_b - k_{str} C_w \psi_{str}\theta \quad \text{(Eq. 2-10)}$$

The concentration of microplastics in the soil can be predicted based on the rate of attachment (k_a) and detachment (k_r) of microplastics on the soil surface (Eq. 2-11). k_r can be negligible when conditions favor microplastics-surface attachment (Johnson, 2020). The rate coefficient for attachment (k_a) considers medium as a series of collectors with efficiency (η): $k_a = -(\frac{N_c}{L}v)ln\,(1-\eta)$. $\frac{N_c}{L}$ is the number of collectors or soil grains per unit length, which can be determined assuming Happel sphere-in-cell collector (Gasperi et al., 2018): $N_c/L = 3\frac{(1-\theta)^{1/3}}{2d_c}$, where d_c is the soil grain or collector's diameter. Thus, the transport and retention of microplastic depend highly on the characteristics of the soil (Wu et al., 2020).

$$\frac{\partial C_s}{\partial t}\theta = k_a C_w \theta - k_r C_s \rho_b \quad \text{(Eq. 2-11)}$$

Where ρ_b is bulk density of the water-saturated soil, v is the mean pore-water velocity, and D is the dispersion coefficient. The rate coefficient for attachment (k_a) considers medium as a series of collectors with efficiency (η) and is described below (Johnson 2020): $k_f = -(\frac{N_c}{L}v)ln\,(1-\eta)$. Nc/L is the number of collectors or soil grain per unit length, which can be determined by using the equation (Johnson, 2020; Nelson and Ginn, 2011): $\frac{N_c}{L} = 3\frac{(1-\theta)^{\frac{1}{3}}}{2d_c}$, where d_c is the soil grain or collector's diameter. Thus, transport and retention of microplastic depend highly on the characteristics of the contaminated medium (Wu et al., 2020). k_{str} is the rate of straining and ψ_{str} is a dimensionless colloid straining function (Bradford et al., 2003). Straining is a function of transport distance in soil. ψ_{str} can be estimated using a power function: $\psi_{str} = \left(\frac{d_{50}+z}{d_{50}}\right)^{-\beta}$, where β is a fitting parameter that controls the shape of the microplastics spatial distributions, z is the downgradient distance from the inlet, and d_{50} can be estimated from soil grain size distribution. These models are typically validated using microspheres. Thus, future studies should examine the transport of microplastics of different shapes, as the shape of particles plays a critical role in their transport in soil (Aramrak et al., 2013; Seymour et al., 2013; Weiss et al., 1995).

2.4. Conclusion

Our analysis of microplastic concentration reported in 196 studies from 49 countries yields the following conclusions. The concentration of microplastics can vary up to 8 orders of magnitude depending on the location. The concentration decreases by up to two order magnitude from urban areas inland to estuaries in coastal areas or terrestrial boundary. This result indicates that despite

additional input of microplastics during conveyance of water by rivers and stormwater from surrounding areas and fragmentation of microplastics during transport, the concentration of microplastics in water in the coastal areas did not exceed the concentration in inland locations. As expected, the concentration of microplastics is the highest in urban soil/water mediums where usage and disposal of plastics are high. Thus, developing best management practices such as stormwater treatment in these hotspots could minimize microplastics dissemination into the environment. Remote glaciers contain higher concentrations of microplastics than urban hotspots, indicating that wind-driven transport is significant. Our analysis reveals that the shape of microplastics affects their transport and distribution in the environment. The fiber fraction is enriched in the sediment in coastal areas or estuaries and on the glacier, indicating fibers are preferentially transported from the source. The abundance of microplastics varies with plastic polymer type. PP, PE, PET, and PS were most commonly identified. Most studies model microplastic transport using spherical particles. Future studies should update the models for microplastics with different shapes, particularly fibers as our data reveals that their transport and accumulations differ from that of spherical particles.

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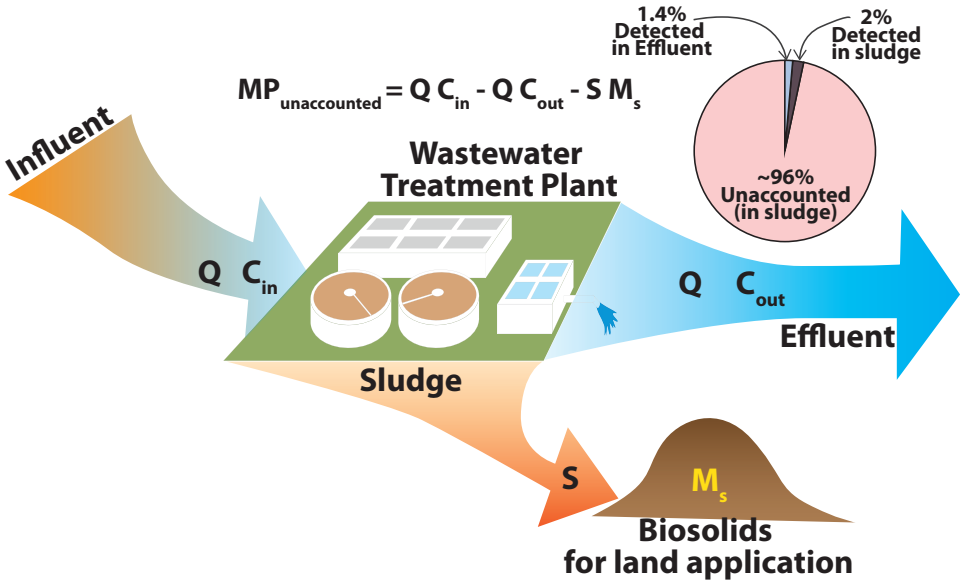
3. CHAPTER 3 – UNACCOUNTED MICROPLASTICS IN WASTEWATER SLUDGE: WHERE DO THEY GO?



Koutnik, V.S., Alkidim, S., Leonard, D. J., DePrima, F., Cao, S., Hoek, E., and Mohanty, S.K. (2021) Unaccounted microplastics in wastewater sludge: Where do they go? ACS ES&T Water. 1, 5, 1086–1097. https://doi.org/10.1021/acsestwater.0c00267

Abstract

Wastewater treatment plants (WWTPs) could reintroduce microplastics into environments via biosolid application on land. Yet, the annual emission of microplastics via wastewater biosolids is unclear. Analyzing results from 76 studies, we estimate median concentrations of microplastics in influent, effluent, and sludge in various regions in the world and found that only 4% of microplastics removed in WWTPs are detected in the biosolids, and the remaining 96% could be unaccounted for. Unaccounted microplastics are attributed to limitations of current methodologies to isolate and identify small (< 10 μm) microplastics in organic-rich sludge, although there is high variability in estimating the concentration in influent and effluent. A meta-analysis of microplastics data reveals that variability is high if wastewater sample has low volume (<1 L, particularly for effluent), organic debris is not digested or digested without Fenton reagent, microplastics are isolated without density separation or using NaCl solution, and microplastics are counted using microscope without spectroscopic identification. Based on the median concentration of microplastics in influent, effluent, and biosolids, land application of biosolids in the U.S. alone could annually release 785-1080 trillion microplastics, of which only 29-46 trillion are accounted for or detected. Thus, the true concentration of microplastics in biosolids could be significantly underestimated.

3.1. Introduction

Plastic polymers in consumer products are ubiquitous, with estimated global production reaching 380 billion kilograms of plastics by 2015 (Geyer et al., 2017). From these products, microplastics, plastic polymers with a size smaller than 5 mm, are released directly (Praveena et al., 2018; van Wezel et al., 2016) or indirectly by degradation and fragmentation, (González-Pleiter et al., 2019; Julienne et al., 2019; Song et al., 2017a) and conveyed to wastewater treatment plants (WWTPs) via combined stormwater and wastewater sewer systems (He et al., 2019b). As these microplastics could adsorb high concentrations of pollutants on their surfaces (Godoy et al., 2019; Hüffer et al., 2018; X. Li et al., 2019; Puckowski et al., 2021; Wang et al., 2018; Zhao et al., 2020), their presence could threaten aquatic (J. C. Anderson et al., 2016; Hui Ma et al., 2020; Pannetier et al., 2020; Wang et al., 2019; Ziccardi et al., 2016) and terrestrial ecosystems (Abbasi et al., 2020; Dong et al., 2020; Yuyue Huang et al., 2021; Ju et al., 2019; J. Ma et al., 2020; Song et al., 2019) and their exposure via ingestion and inhalation (De-la-Torre, 2020; Shruti et al., 2020; Van Cauwenberghe and Janssen, 2014; J. Zhang et al., 2020; Q. Zhang et al., 2020) can potentially increase cancer risk (Sharma et al., 2020) and oxidative stress in lungs (Prata, 2018). To assess exposure – a key component of risk, it is critical to estimate the annual loading of microplastics to the environment from various sources including WWTPs. Data related to the total volume of wastewater treated and the amount of sludge produced in other countries are not available. In the U.S., WWTPs treat approximately 34 billion gallons of wastewater daily (U.S. E.P.A., 2013), relocating the majority of microplastics from influent wastewater into sludges (Bretas Alvim et al., 2020a; Edo et al., 2020; Gao et al., 2020) by different processes including filtration, coagulation, and sedimentation (Long et al., 2019; Lv et al., 2019; Ngo et al., 2019; Sun et al., 2019; X. Zhang et al., 2020; Zhang and Chen, 2020). Wastewater sludges are a significant source of microplastics

(Corradini et al., 2019; Rolsky et al., 2020). More than half of the sludge produced is applied as fertilizer or biosolids on agricultural soil (Corradini et al., 2019; Crossman et al., 2020b; Jiang et al., 2020) from where microplastics carrying contaminants (Chen et al., 2021; X. Li et al., 2019; Liu et al., 2018; Magadini et al., 2020) can be transported by agricultural runoff (Crossman et al., 2020b; Gray et al., 2017b) or wind, if aerosolized (Rezaei et al., 2019). However, the annual load of microplastics to agricultural land via biosolids is unclear.

Microplastic concentration in sludge can be estimated by two methods: first, indirectly by calculating total microplastics removed from wastewater based on the difference in the concentration in influent and effluent, and second, directly by measuring their concentration in sludge and multiplying that with the total amount of sludge produced. Both methods have high uncertainty due to the inherent variation in concentrations of wastewater influent and effluent and sludge. For instance, direct estimation of microplastics in sludge can produce a large error (Bretas Alvim et al., 2020a; Campo et al., 2019; Q. Li et al., 2019) due to a difference in parameters used for the isolation and detection of microplastics: smallest size detected, the liquid used for density separation, the effectiveness of the organic digestion step (Hurley et al., 2018; Lares et al., 2019; X. Li et al., 2020), and interference of organics during detection (Elkhatib and Oyanedel-Craver, 2020; Kaeppler et al., 2016). The removal can also vary based on the size, density, morphology (Ngo et al., 2019), and shape of the microplastic influent (Wei et al., 2020), as well as differences in treatment steps (Akarsu et al., 2020), thereby adding uncertainty to the effluent concentration. Thus, a large number of studies are needed to increase the confidence in the estimation of microplastic concentrations in sludge, influent, and effluent.

Several studies (Carr et al., 2016; Gies et al., 2018; Lares et al., 2018; Lee and Kim, 2018; Lv et al., 2019; Magni et al., 2019; Raju et al., 2020; P. Ren et al., 2020; Talvitie et al., 2017a)

reveal a lack of mass balance (Error! Reference source not found.); specifically, the total number of microplastics removed from wastewater in those studies exceeds the microplastics found in the sludge. In particular, 22-89% of microplastics relocated into sludge may be undetected or unaccounted for, leading to underestimation of annual loading of microplastics via land application of sludge. However, the cause of the discrepancy is unknown. Thus, further analysis is needed to evaluate if the discrepancy is consistent across WWTPs in the world. We synthesize data reported in 76 studies from 24 countries in the world and estimate the annual emission of microplastics from WWTPs via sludge, including the unaccounted fraction and its loading on agricultural land via biosolids application. Furthermore, we conduct a meta-analysis of concentration data in influent and effluent to identify the source of high variability in the concentration estimation so that future studies should optimize the protocols to sample and identify microplastics in wastewater samples. The analysis provides an annual flow of microplastics from wastewater treatment plants to the environment via land application of sludge. The review addresses the knowledge gap on unaccounted microplastics and differs from other reviews that primarily focus on the fate of microplastics (Gatidou et al., 2019; Okoffo et al., 2019; Sun et al., 2019), their removal processes (Freeman et al., 2020; Masia et al., 2020; Xu et al., 2019; X. Zhang et al., 2020), and their identification methods in WWTPs (Bakaraki Turan et al., 2021; Elkhatib and Oyanedel-Craver, 2020).

Table 3-1. Amount of microplastics removed in selected wastewater treatment plants reported in 9 studies. Only studies that had reported microplastics concentrations in influent, effluent, and sludge are included (Carr et al., 2016; Gies et al., 2018; Lares et al., 2018; Lee and Kim, 2018; Lv et al., 2019; Magni et al., 2019; Raju et al., 2020; Talvitie et al., 2017b).

Author	*Influent (p/L)*	*Effluent (p/L)*	*Removal %*	*Sludge concentration*	*Sludge units*	*Microplastics in by influent (p/day)*	*Microplastics out via effluent (p/day)*	*Microplastics out via sludge (p/day)*	*Difference*	*% Unaccounted*
Carr et al. 2016	1.00	0.001	99.91%	1,000	p/kg	1,510,000,000	930,000	1,090,000,000	419,070,000	28%
Gies et al. 2018	31.10	0.500	98.39%	14,900	p/kg	14,040,000,000	230,000,000	3,506,849,315	10,303,150,685	73%
Lares et al. 2018	30.53	0.344	98.87%	124,054	p/kg	626,428,761	3,328,421	460,000,000	163,100,340	26%
Lares et al. 2018	28.76	0.751	97.39%	235,135	p/kg	645,483,628	3,328,421	460,000,000	182,155,207	28%
Lares et al. 2018	59.96	0.316	99.47%	122,432	p/kg	328,696,460	3,631,005	460,000,000	-134,934,545	-41%
Lares et al. 2018	62.83	0.450	99.28%	181,622	p/kg	676,447,788	4,740,478	460,000,000	211,707,309	31%
Lares et al. 2018	58.19	0.316	99.46%	79,459	p/kg	309,641,593	7,917,608	460,000,000	-158,276,015	-51%
Lares et al. 2018	38.72	1.598	95.87%	152,432	p/kg	416,825,221	16,843,828	460,000,000	-60,018,607	-14%
Lares et al. 2018	124.78	3.000	97.60%	301,622	p/kg	1,343,368,142	31,620,000	460,000,000	851,748,142	63%
Lee and Kim 2018	2.95	0.050	98.31%	2,315	p/kg	234,821,918	3,945,205	140,712,329	90,164,384	38%
Lee and Kim 2018	3.70	0.180	95.14%	2,585	p/kg	399,315,069	18,904,110	143,315,069	237,095,890	59%
Lee and Kim 2018	6.10	0.105	98.28%	1,620	p/kg	123,780,822	2,000,000	32,301,370	89,479,452	72%
Lee and Kim 2018	10.17	0.100	99.02%	10,615	p/kg	1,097,260,274	10,493,151	589,315,069	497,452,055	45%
Lee and Kim 2018	13.50	0.090	99.33%	7,340	p/kg	1,074,575,342	7,095,890	444,602,740	622,876,712	58%
Lee and Kim 2018	23.75	0.330	98.61%	13,275	p/kg	481,945,206	6,328,767	266,547,945	209,068,493	43%
Lv et al. 2019	0.28	0.050	82.14%	1.60	p/L	33,600,000	3,500,000	290,000	29,810,000	89%
Lv et al. 2019	0.28	0.130	53.57%	0.70	p/L	33,600,000	6,500,000	1,650,000	25,450,000	76%
Magni et al. 2019	2.50	0.400	84.00%	113,000	p/kg	1,000,000,000	160,000,000	3,400,000,000	-2,560,000,000	-256%
Raju et al. 2020	11.80	2.760	76.61%	7.91	p/L	566,400,000	111,724,800	12,165,580	442,509,620	78%
Ren et al. 2020	16.00	2.900	81.88%	2,920	p/kg	4,800,000,000	870,000,000	315,000,000	3,615,000,000	75%
Talvitie et al. 2017	686.70	0.700	99.90%	186,700	p/kg	193,649,400,000	197,000,000	151,000,000,000	42,452,400,000	22%

3.2. Methods

3.2.1. Data Collection

We used the "Web of Science" database to search articles with the following keywords: "microplastics wastewater" or "microplastics sludge" or "microplastics biosolids". All studies cataloged in the database before January 21, 2021, were included in the analysis. Out of 336 articles found, 162 articles were selected based on abstracts for further evaluation. Finally, 76 articles or studies from 24 countries (Figure 3-1) were selected for analysis based on the following criteria: concentration data in the study must be reported as number per liter of wastewater or number per kg of biosolids. The data from 76 studies (not all are cited in this study) are shared in an online open access repository (Koutnik, 2020b). Because of the difficulty in measuring the mass of very small particles, most studies predominantly report number concentration, instead of mass concentration, even though the number of microplastics is not conservative due to potential fragmentation of plastics during wastewater treatment (Enfrin et al., 2020; Julienne et al., 2019; Song et al., 2017a). To estimate the amount of sludge produced and the downstream use of biosolids, we used the 2019 Water Biosolids annual reports from the U.S. E.P.A., which only includes 2,311 of the largest publicly owned WWTPs. Hence, the actual amount of biosolids produced and the number of microplastics exiting WWTPs in the U.S. could be higher than the estimated values.

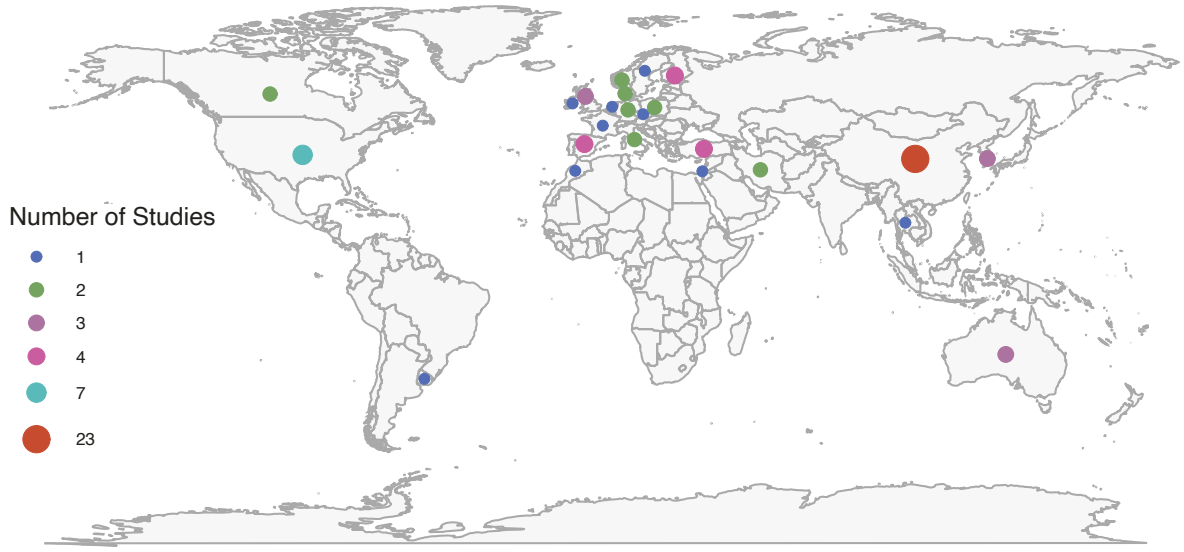


Figure 3-1. The number of studies on the fate of microplastics in WWTP reported based on countries. Total 76 studies are from 24 countries with China and the U.S. contributing ~40% of the reported studies.

3.2.2. Statistical Analysis

To find confidence intervals for the influent, effluent, and sludge data, we identify outliers that are not within 1.5 IQR (interquartile range) of the median value. The number of available samples and studies were determined by selecting all samples that fit the requirement for the category. The confidence intervals were constructed using at-statistics with 95% confidence. The meta-analysis of concentration data in wastewater samples was completed by using the R package meta. Only studies with 2 or more samples that contain both influent and effluent concentrations were selected because the standard deviation of samples from the same study is required to calculate an effect size. Hedge's g method was used to calculate effect size as some studies have a relatively small number of samples. The metagen function from the meta package was used to conduct the meta-analysis, which is then plotted by the function forest.

3.2.3. Mass balance calculation

The mass balance equation for microplastics in WWTPs under steady state can be determined from,

$$\boldsymbol{M_s S = Q\,(C_{in} - C_{out})}\,, \qquad \text{(Eq. 3-1)}$$

where Q is the annual wastewater flow, C_{in} is the median concentration of microplastics in the influent, C_{out} is the median concentration of microplastics in the effluent, M_s is the dry mass of sludge produced annually, and S is the median concentration of microplastics in the sludge (Figure 3-2). Thus, unaccounted microplastics in sludge, $MP_{unaccounted}$, is calculated from

$$\boldsymbol{MP_{unaccounted} = Q\,(C_{in} - C_{out}) - M_s S}\,. \qquad \text{(Eq. 3-2)}$$

We used median concentration because of the high variability in available data, which does not follow a normal distribution but is rather negatively skewed.

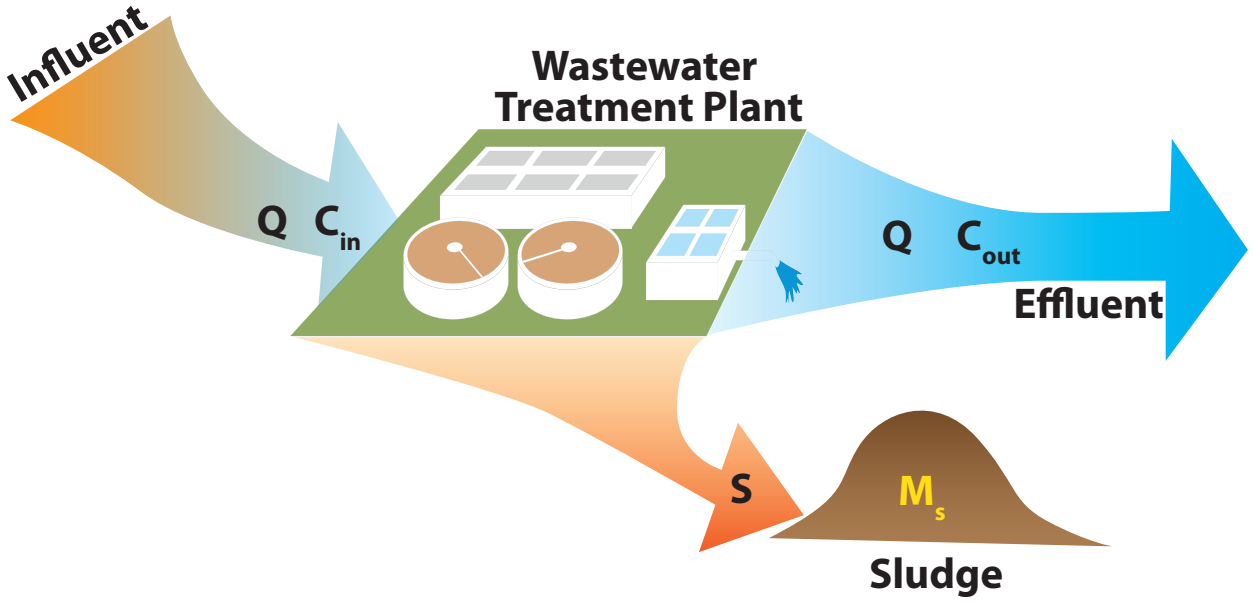


Figure 3-2. Mass balance for microplastics in a wastewater treatment plant.

3.3. Results and Discussion

3.3.1. Microplastics removal varies by orders of magnitude

Our analysis suggests that the concentration of microplastics in wastewater influent and effluent varies (95% confidence interval) by 5 orders of magnitude, and by 3 orders of magnitude in sludge. The microplastic distribution in water is negatively skewed towards higher concentrations. When studies measure smaller microplastics of 1-10 um, the concentration increases substantially. To alleviate the variability, we provided two confidence intervals: one for studies that identified microplastics below 10 μm and another for the rest of the studies (Table 3-2). The abundance of microplastics in water is much higher in samples measuring below 10 μm, while abundance in sludge is consistent with previously reported values (Mahon et al., 2017).

Table 3-2. Concentration of microplastics varies based on whether microplastics lower than 10 μm are accounted.

Sample Type	Water Samples with the smallest size reported (p L^{-1})				Sludge (p kg^{-1})
	<10 μm		>10 μm		
	Influent	Effluent	Influent	Effluent	
95% Confidence Interval - Lower	1638	406	33	0.63	11947
95% Confidence Interval - Upper	2346	495	45	0.99	18802
Available Studies/ Data points	6/40	8/57	44/229	52/286	29/89
After Removing Outliers	5/37	3/41	38/198	42/223	23/77

Several factors can contribute to a variation in microplastics concentration. First, the WWTP influent and effluent sampling time (Blair et al., 2019; Cao et al., 2020), location (Carr et al., 2016; Lares et al., 2018; Wolff et al., 2019), and depth (Tagg et al., 2020) can affect the concentrations. Similarly, concentrations in sludge can vary based on how they were processed: activated sludge (Bretas Alvim et al., 2020a), digested sludge (Mahon et al., 2017), or even dewatered sludge (EL Hayany et al., 2020). Furthermore, microplastic distribution in sludge is not

uniform (Bretas Alvim et al., 2020a), leading to potential error if representative homogenized or composite samples were not collected. Second, pretreatment methods of samples before analysis can influence microplastic concentration. For instance, most sludge samples are subjected to density separation without or with a digestion step to separate organics (Lares et al., 2019) using hydrogen peroxide (Bretas Alvim et al., 2020b), or strong bases (Hurley et al., 2018). Because sludge contains high organic matter, microplastic concentrations can be overestimated without digestion due to interference with organic debris (Hurley et al., 2018). Third, wastewater samples may be passed through a screen to filter microplastics before density separation and organic digestion (Gundogdu et al., 2018; Mahon et al., 2017). For a similar reason, microplastics in the ocean are underestimated (Enders et al., 2015; Lindeque et al., 2020). Therefore, the pore size of the screen used can exert a primary constraint on the smallest size of microplastics isolated from wastewater.

Our analysis reveals the abundance of microplastics in sludge based on the size of microplastics (Figure 3-3). Based on the available data, microplastics between 50 to 250 μm are frequently reported, and nearly 70% of microplastics detected in sludge are smaller than 500 μm. Notably, studies rarely detected microplastics smaller than 10 μm, possibly because they are harder to detect by traditional methods or visual counting in sludge (Erni-Cassola et al., 2017). A decrease in abundance of microplastics with a decrease in size below 250 μm is inconsistent as the microplastic concentration in the environment follows a power law with respect to particle size (Kang et al., 2018; Kooi and Koelmans, 2019); that is, a decrease in size rapidly increases the abundance of microplastics particles (Pivokonsky et al., 2018). Two studies (Talvitie et al., 2017b; Ziajahromi et al., 2017) reported the power-law distribution of microplastics in wastewater, which shows that the slope of the power-law distribution, $\log(\Delta N/\Delta dp)\ vs\ dp$, is around 1.08 to 2.68,

where N is the number concentration of microplastic (particle L^{-1}) and dp is the median size in μm for the number concentration of microplastics. However, further analysis of reported studies (Table 3-3) that examined microplastics concentration in sludge reveals that minimum cut-off size microplastics detected in sludge is about 7 times larger than the cutoff size of the filter used to isolate microplastics from sludge. This result indicates that even though most studies capture small microplastics, the detection method is not suitable to identify smaller microplastics (< 50 μm) in sludge. Future studies should follow a uniform robust protocol that can detect smaller microplastics in sludge.

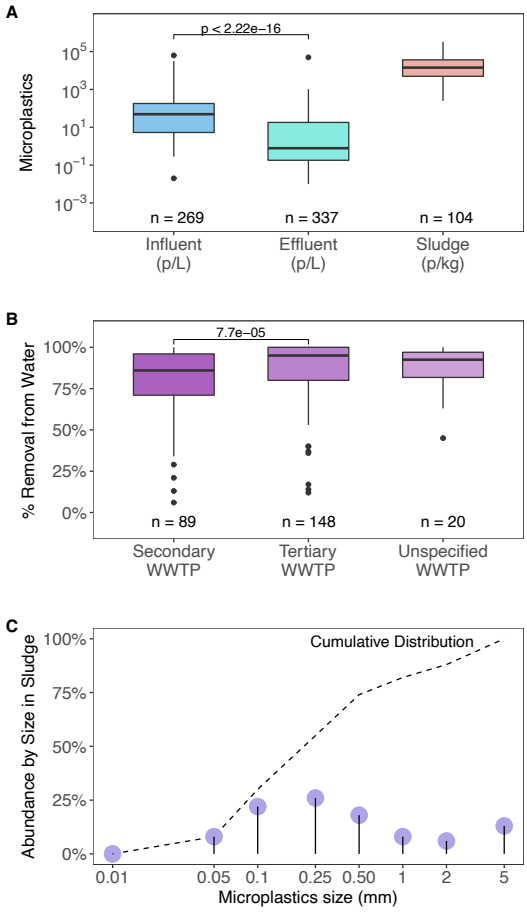


Figure 3-3. (A) Concentration of microplastics in the influent (median, 49 p L^{-1}; mean, 866 p L^{-1}) and effluent water (median, 0.75 p L^{-1}; mean, 220 p L^{-1}) and sludge (median, 14200 p kg^{-1}; mean, 39020 p kg^{-1}) from wastewater treatment plants. A p-value of less than 0.05 shows statistically significant results between influent and effluent. (B) Percentage removal of microplastics from wastewater in secondary WWTP (median, 86%; mean, 79%), tertiary WWTP (median, 95%; mean, 87%) and unspecified treatment level WWTP (median, 92.5%; mean, 86%). The p-value shown above the graph is less than 0.05 meaning a statistically significant difference between tertiary and secondary plant. The unit "p" represents the number of microplastic particles per liter (L) of water or kilogram (kg) of sludge. "n" represents the number of data points for each category of statistics. Data were collected from a total of 76 peer-reviewed studies or government reports.(Koutnik, 2020b) (C) Abundance and cumulative distribution of microplastics of each size range in sludge based on 18 studies.

Table 3-3. Measurement size cutoff and reported distribution for the studies measuring microplastics in the sludge (Bretas Alvim et al., 2020a; Edo et al., 2020; EL Hayany et al., 2020; Jiang et al., 2020; Lares et al., 2018; Leslie et al., 2017; Q. Li et al., 2019; X. Liu et al., 2019; Lv et al., 2019; Magni et al., 2019; Mahon et al., 2017; Mintenig et al., 2017; Raju et al., 2020; P. Ren et al., 2020; Talvitie et al., 2017b; Wijesekara et al., 2018; L. Zhang et al., 2020).

Author	*Cutoff size used (μm)*	*Reported Size Distribution*							
		<10 μm	50 μm	100 μm	250 μm	500 μm	1000 μm	2000 μm	5000 μm
Bretas Alvim et al. 2020	150					48.00%	39.00%	6.00%	6.00%
Edo et al. 2020	25			50.00%		44.00%			
Edo et al. 2020	25			47.00%		35.00%			
El Hayany et al. 2020	0.45					71.80%	21.10%	4.20%	2.80%
Jiang et al. 2020	20			4.00%		5.60%	11.60%	13.10%	65.70%
Jiang et al. 2020	20			19.30%		35.90%	7.00%	29.20%	8.60%
Jiang et al. 2020	20			74.30%		10.00%	6.60%	4.90%	3.20%
Jiang et al. 2020	20			63.70%		19.70%	8.40%	5.40%	2.80%
Lares et al. 2018	250				11.00%	33.40%	22.30%		33.30%
Lares et al. 2018	250				7.00%	30.60%	31.60%		29.00%
Lares et al. 2018	250				14.80%	45.10%	25.30%		14.80%
Leslie et al. 2017	N/A				62.00%				38.00%
Leslie et al. 2017	N/A				50.00%				50.00%
Li, Q. et al. 2019	20				86.20%	8.10%	3.50%		2.30%
Li, Q. et al. 2019	20				71.30%	13.50%	8.90%		6.30%
Li, Q. et al. 2019	20				73.40%	15.00%	6.70%		4.90%
Liu et al. 2019	20				84.10%		12.20%	3.70%	
Lv et al. 2019	25		8.00%	29.00%	12.00%	11.00%			40.00%
Magni et al. 2019	10			24.00%		54.00%	12.00%		10.00%
Mahon et al. 2017	45		24.00%		76.00%				
Mahon et al. 2017	45		0.80%		99.20%				
Mahon et al. 2017	45		2.30%		97.70%				
Mintenig et al. 2017	20						0.00%	0.00%	0.00%
Raju et al. 2020	1.5		9.70%	21.10%	39.80%		12.70%		9.00%
Ren et al. 2020	80					65.10%		23.20%	11.70%
Talvitie et al. 2017	20			78.60%	12.20%				9.40%
Wijesekara et al. 2018	N/A		35.30%	14.70%	34.30%		17.50%		
Zhang et al. 2020	25				13.70%	20.50%			65.80%
Zhang et al. 2020	25				7.50%	32.30%			60.20%
Zhang et al. 2020	25				17.30%	47.90%			34.80%

3.3.2. Microplastics removal depends on WWTP treatment units.

Our analysis shows that the removal distribution is skewed towards higher removal, and the median removal of microplastics from WWTPs with secondary and tertiary treatment units are 86% and 95%, respectively (Figure 3-3). The result is consistent with previous studies that evaluated the effect of stages of treatment on microplastic removal (P. Ren et al., 2020), including the presence of advanced treatment technologies (Bayo et al., 2020a; Lares et al., 2018; Talvitie et al., 2017b). Our analysis shows that on average, WWTPs with tertiary stages remove around 10% more microplastics from wastewater than the ones with a secondary treatment unit. Treatment techniques such as membrane bioreactor treatment (MBR), rapid sand filtration, and dissolved air flotation have long been identified as being highly efficient at removing microplastics (Talvitie et al., 2017a). Thus, the pore size of the MBR systems (Lares et al., 2018), the retention time (Z. Chen et al., 2020; Rummel et al., 2017), and size of microplastics are a few factors that could affect the efficiency of the removal. Larger microplastics were shown to be more easily removed by anaerobic processes, while smaller microplastics can be efficiently removed by both anoxic and oxic processes (Wei et al., 2020). As a result, future studies should more closely examine the mechanism of microplastics removal in different treatment units. While the removal increases with an increase in treatment steps (Bayo et al., 2020b; Blair et al., 2019), the cause of wide variation in removal percentages in each stage is unknown. As discussed previously, we attributed the high variation in removal to high uncertainty in reporting of the concentration of microplastics in influent and effluent.

3.3.3. The microplastic concentration varies widely based on the methodology used

Influent and effluent microplastic concentrations were based on sample preparation and microplastic identification methods: sample collection method (individual vs composite),

sampling volume used, filter cutoff size used, methods for organic digestion, the solution used for density separation, methods for counting or identification, and smallest size of microplastic reported (Figure 3-4). Both variance and median microplastics concentration in composite samples was lower than individual grab samples. However, the majority of the samples collected were individual samples with higher variance. Thus, future studies should use the composite sampling method. The forest plot for the sample collection method (Figure 3-5) shows that both individual and composite methods produce large variation but the difference in mean between influent and effluent is statistically significant for the individual group. Most studies collected less than 1 L samples, which introduces significantly larger uncertainty than larger volume samples, particularly for the effluent sample. The result indicates that a sample volume less than 1 L might not be sufficient to identify an accurate concentration of microplastics in the effluent. The forest plot confirms the analysis (Figure 3-6).

The filter is typically used to isolate microplastics and other debris from wastewater for further analysis. Thus, the cutoff size used for isolation of microplastic could determine the lowest size microplastics detected. Although many studies used filters with as low as 0.5 μm pores, the lowest size detected is often dictated by the resolution of the microscope used. The use of small filter cutoff sizes of 0-10 μm resulted in higher concentrations of microplastics, but it also introduced a large variance (Figure 3-4C). The result is also supported by a meta-analysis forest plot showing a very high *I* squared value of 88% (Figure 3-7). This variance is attributed to the fact that only a few studies recorded microplastics down to that size. In general, a decrease in the smallest size microplastics identified resulted in a higher concentration of microplastics. The forest plot for the smallest size reported shows extremely large variation for the 1-10 μm category compared to large size range groups (Figure 3-11). However, this variation is due to only having

two studies with both effluent and influent data available. Many studies did not specify the size range of microplastics found. Future studies should provide concentrations of microplastics at different size ranges.

Wastewater can contain suspended particles with similar or higher density than microplastics. Thus, filtered debris is usually subjected to density separation or digested to remove organic non-plastic debris. Our analysis reveals that the choice of both methods affects the variability in the concentration. Although peroxide was most commonly used, variability was significantly lower in studies using Fenton's Reagent (Figure 3-4D). The forest plot for digestion shows that the variation in concentration determined after peroxide digestion is larger than the Fenton reagent or "no digestion" group (Figure 3-8). Fenton reagent is more aggressive than peroxide, which is probably more effective in eliminating organic debris. Thus, Fenton agent should be used compared to peroxide digestion to lower sample variability. While most studies used digestion, less than half reported a density separation step, indicating heavier particles are not separated from samples before analysis. Among the studies that used density separation, ones using NaI and $ZnCl_2$ produced less variability in microplastic concentration than NaCl. The forest plot for density separation confirms that using NaCl leads to the largest variation, indicating other salts should be used to isolate microplastics from heavier particles (Figure 3-9).

Finally, we analyzed the microplastics concentration by different microscopic techniques used for counting and confirming microplastics. We found that studies that used FTIR and Raman in conjunction produced both significantly higher concentrations and significantly less variability (Figure 3-4F). However, the preferred counting method by most studies is FTIR. The result indicates that using a microscope alone can increase the chance of identifying false positives, and thus introduce large variability based on how clean the samples are. The forest plot in meta-

analysis also indicates that using a microscope alone can produce the largest between-sample variation (Figure 3-10). Thus, future studies should use either FTIR or Raman to identify microplastics after isolating them from wastewater influent and effluent.

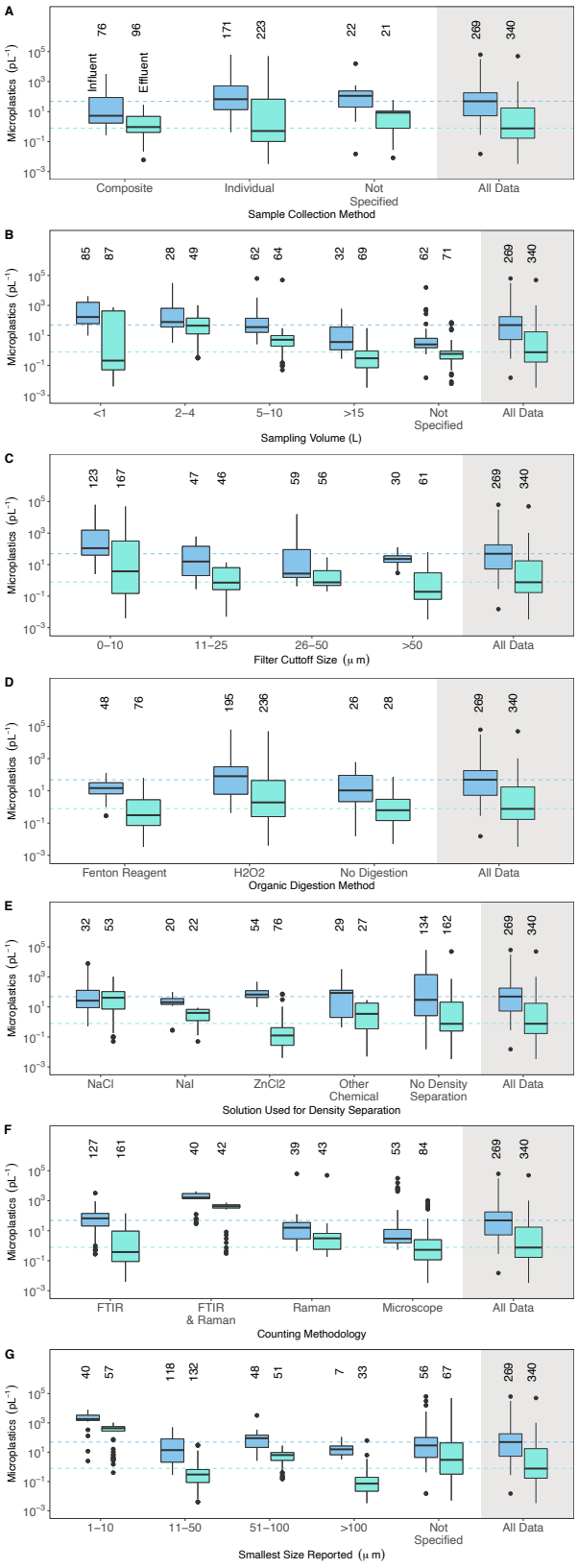

A
Microplastics (pL⁻¹)
Influent
Effluent
76
96
171
223
22
21
269
340
Composite
Individual
Not Specified
All Data
Sample Collection Method
B
85
87
28
49
62
64
32
69
62
71
269
340
<1
2–4
5–10
>15
Not Specified
All Data
Sampling Volume (L)
C
123
167
47
46
59
56
30
61
269
340
0–10
11–25
26–50
>50
All Data
Filter Cuttoff Size (μm)
D
48
76
195
236
26
28
269
340
Fenton Reagent
H2O2
No Digestion
All Data
Organic Digestion Method
E
32
53
20
22
54
76
29
27
134
162
269
340
NaCl
NaI
ZnCl2
Other Chemical
No Density Separation
All Data
Solution Used for Density Separation
F
127
161
40
42
39
43
53
84
269
340
FTIR
FTIR & Raman
Raman
Microscope
All Data
Counting Methodology
G
40
57
118
132
48
51
7
33
56
67
269
340
1–10
11–50
51–100
>100
Not Specified
All Data
Smallest Size Reported (μm)

Figure 3-4. Variability in microplastic concentration in wastewater influent and effluent depends on: (A) sample collection method, (B) sample volume, (C) filter cutoff size used to isolate plastic particles from water, (D) organic digestion method, (E) solution used for separating plastics by density, (F) counting methodology, (G) smallest size detected. The number written above each box plot corresponds to the number of data points (n).

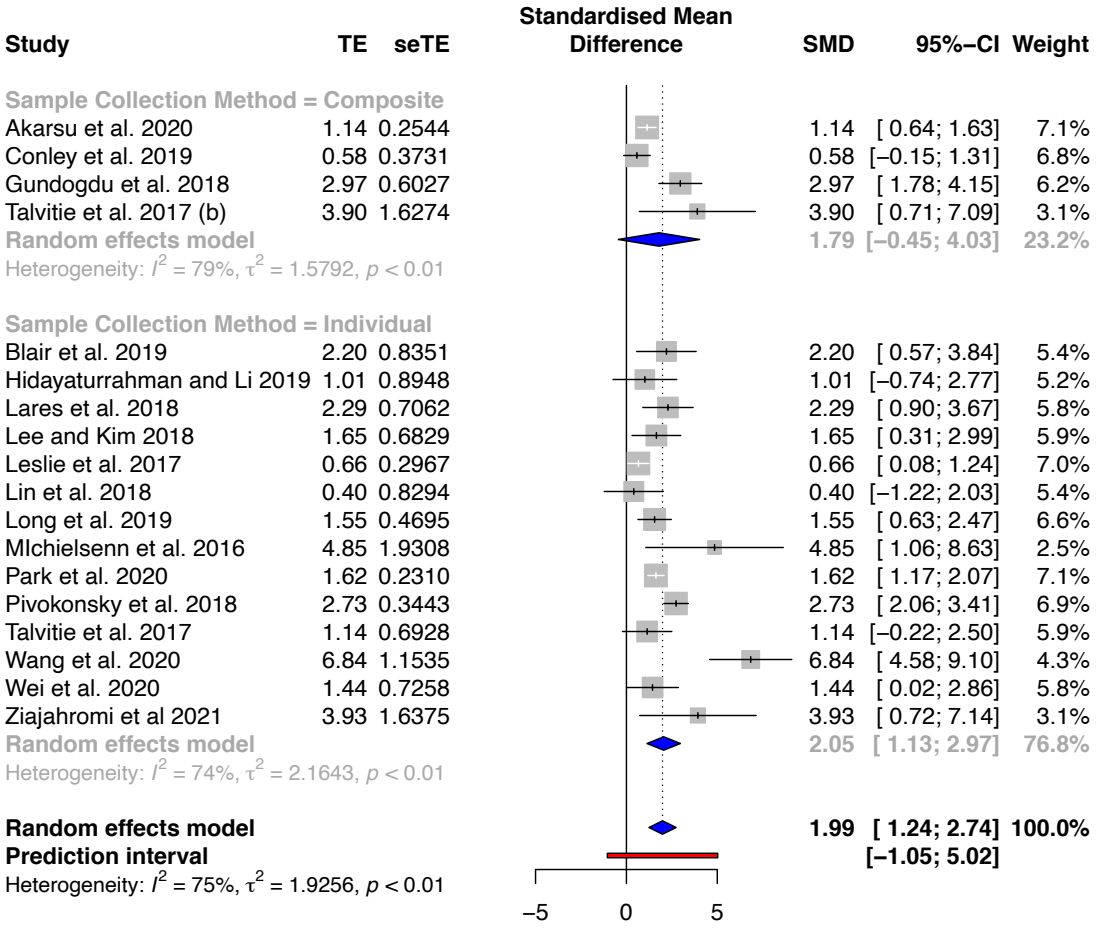


Figure 3-5. Forest plot of meta-analysis done on sample collection method.

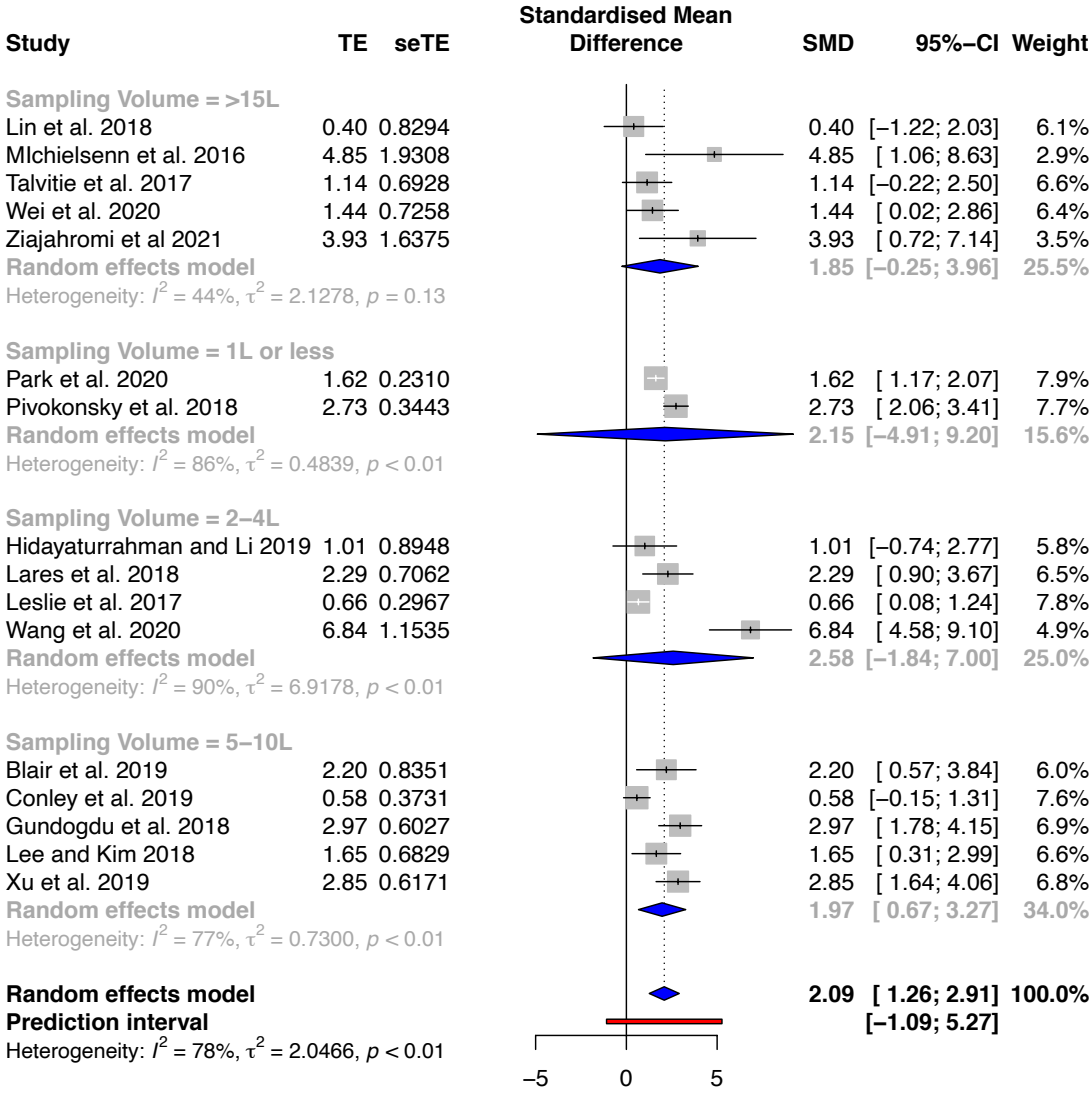


Figure 3-6. Forest plot of meta-analysis done on sample volume collected

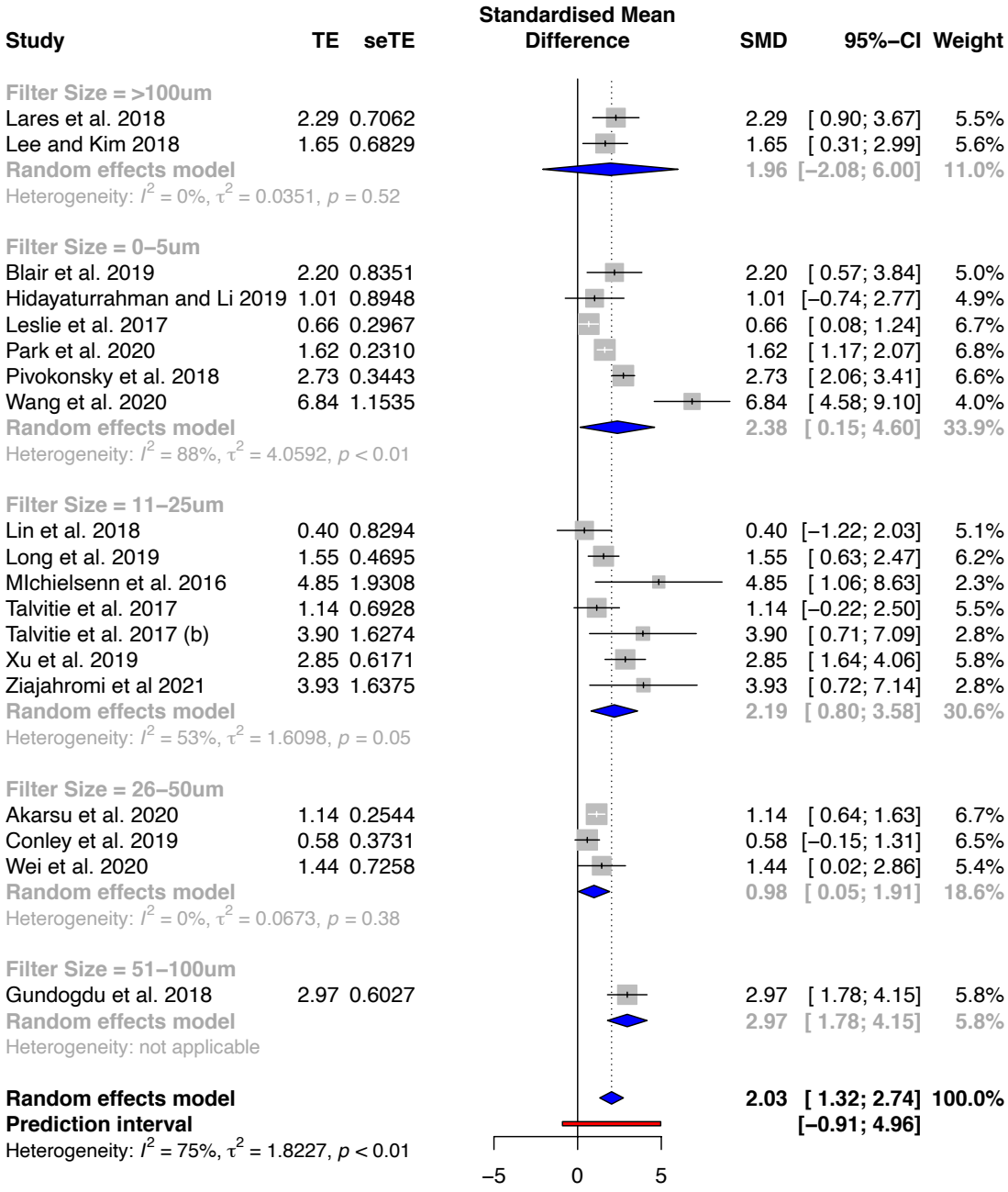


Figure 3-7. Forest plot of meta-analysis done on filter cutoff size used

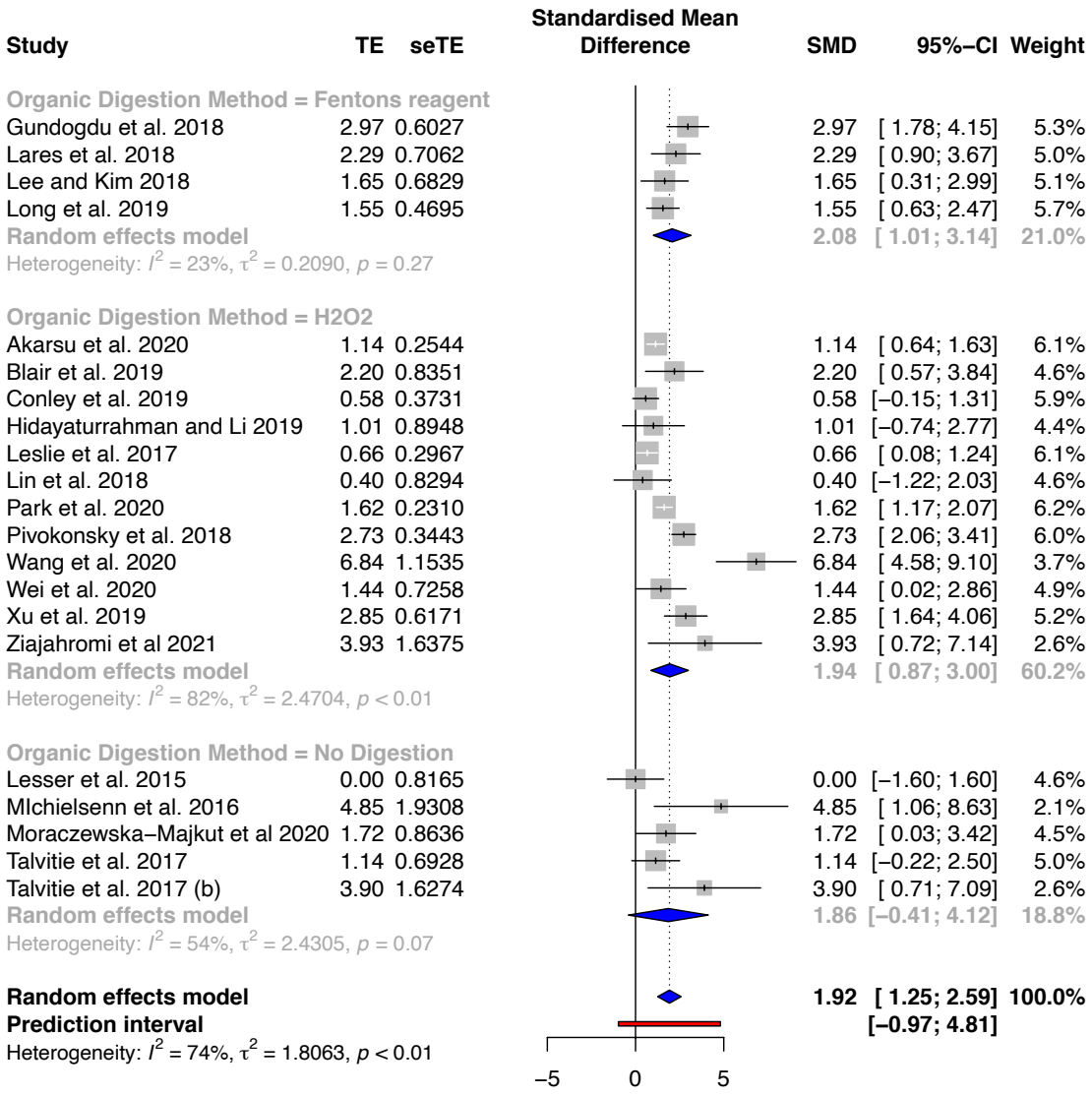


Figure 3-8. Forest plot of meta-analysis done on organic digestion method

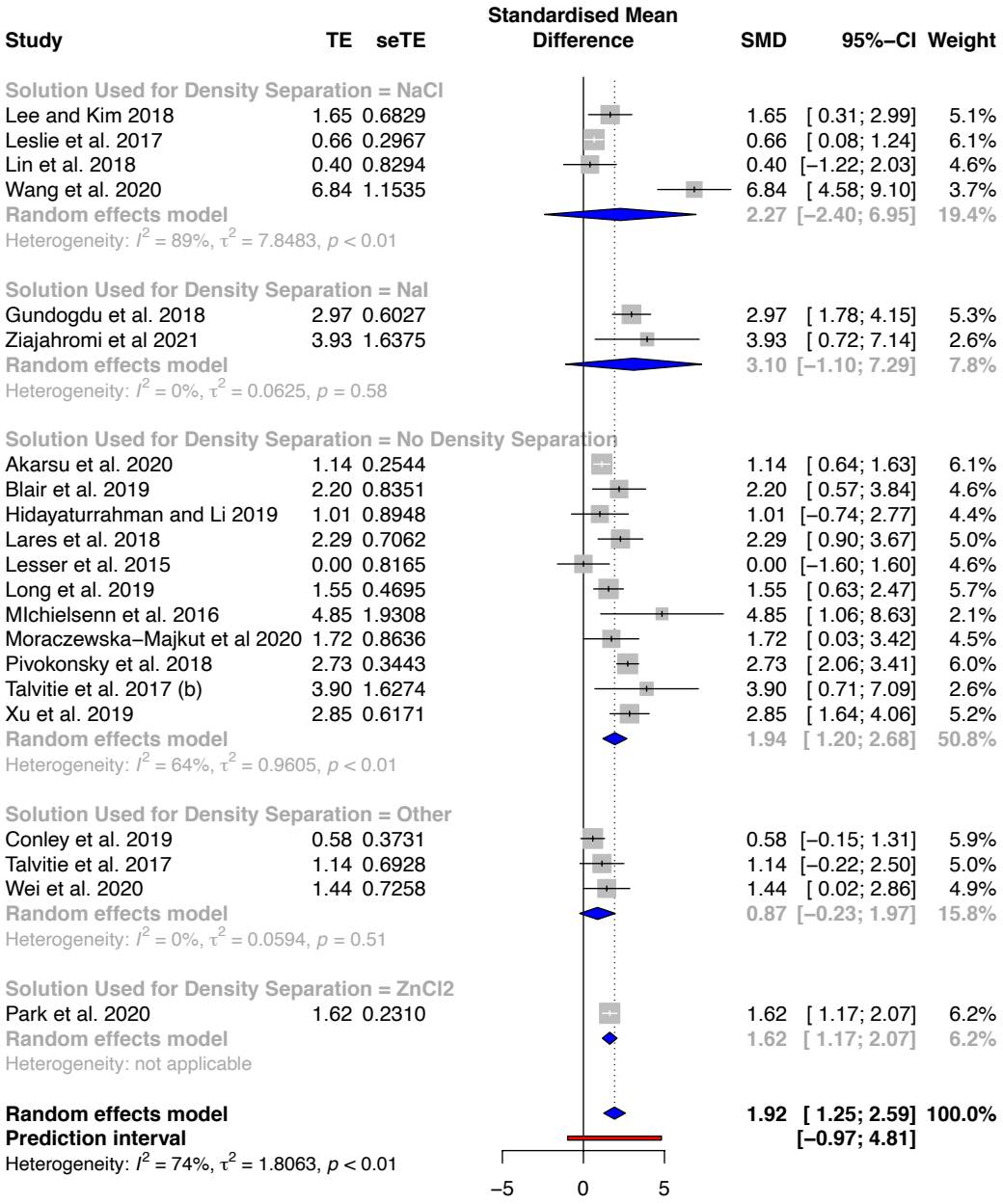


Figure 3-9. Forest plot of meta-analysis done on solution used for density separation.

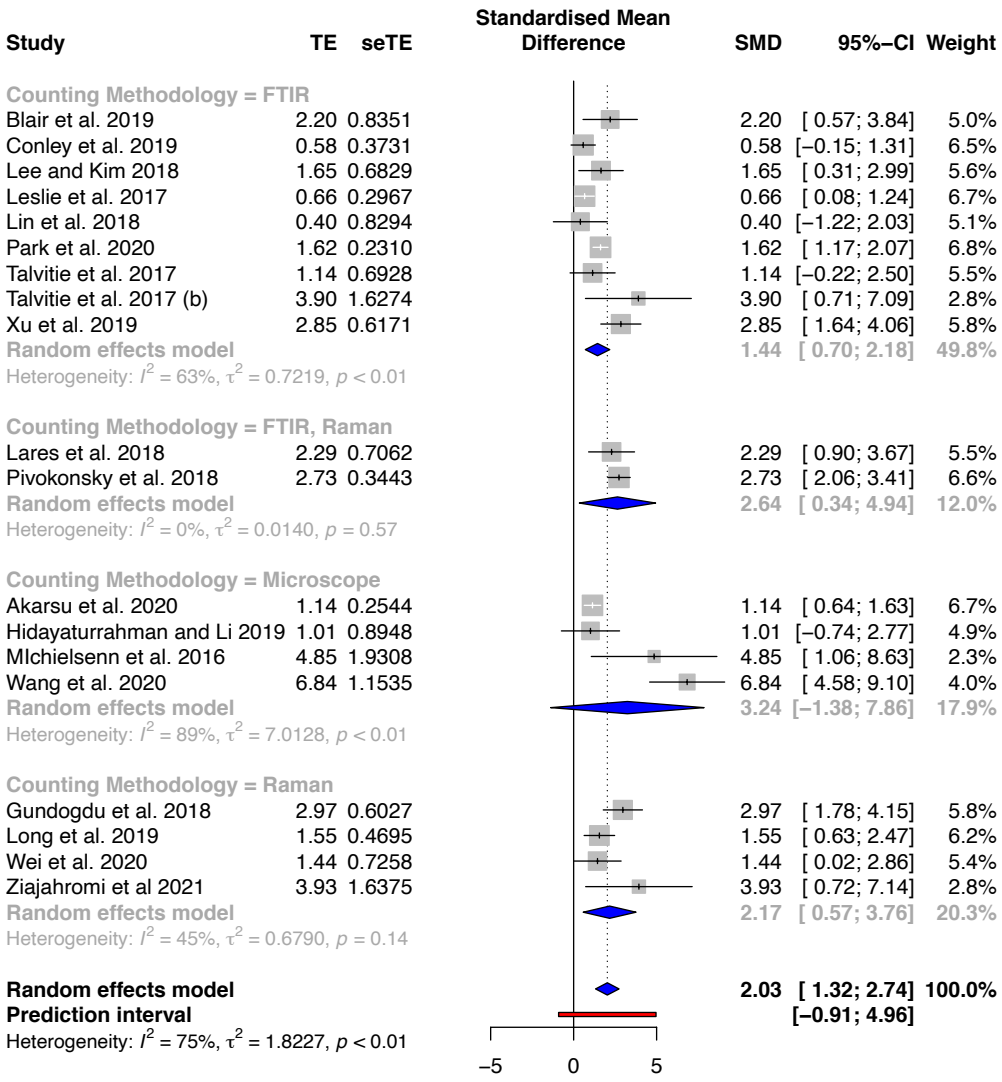


Figure 3-10. Forest plot of meta-analysis done on counting methodology.

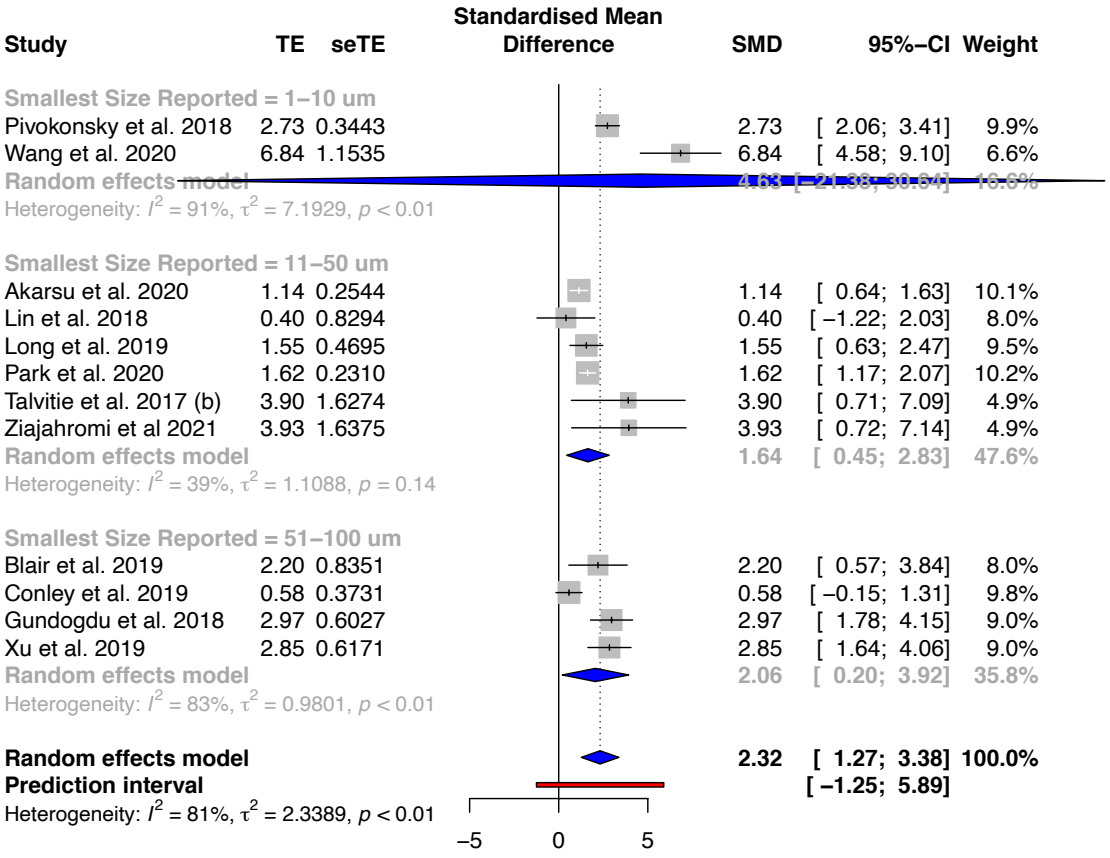


Figure 3-11. Forest plot of meta-analysis done on smallest size reported.

3.3.4. Most of the microplastics removed are unaccounted for in sludge

To calculate the number of microplastics annually deposited in sludge in the U.S., we use the U.S. E.P.A. estimates for the annual biosolids generation (4,750 kilotonnes) and annually treated wastewater (46,972 billion liters). To complete the mass balance, we made several assumptions: (1) uncertainty in the estimation of microplastic concentration in wastewater effluent and influent is lower than the estimation of MPs in sludge due to the difficulty in detecting smaller size (< 50 μm) microplastics in biosolids compared to wastewater (Hurley et al., 2018; Q. Li et al., 2019), as discussed earlier, and (2) loss of microplastics by biodegradation or any other method is insignificant. The typical solid residence time of sludge in WWTPs is less than one month, which is not sufficient to degrade most microplastics (Z. Chen et al., 2020; Matjašič et al., 2020). Furthermore, studies on biodegradation (Auta et al., 2018; Matjašič et al., 2020; Yoshida et al., 2016) rarely included other organic residues that could adsorb plastic-degrading enzymes and thus lower the degradation rates and efficiencies. Based on our analysis, between 1,570 and 2,160 trillion microplastics enter the WWTP in the U.S., between 30 and 47 trillion are discharged via the treated effluent, and the remaining 1,540 to 2,110 trillion should be transferred to sludge. However, based on the concentration of microplastics in sludge and total sludge generated annually, only about 57 and 89 trillion microplastics are accounted for in the sludge (Table 3-4). Thus, the whereabouts of the remaining 1,480-2,020 trillion microplastics, or 94% of microplastics entering WWTPs, are unknown. Our analysis of particle size distribution of microplastics in reported studies indicates that most microplastics are removed but could remain undetected in sludge.

Several additional sources of uncertainty in our calculations could affect our estimates. First, the estimated value for the production of biosolids from the E.P.A. accounts only for a

portion of WWTPs in the U.S. Other studies estimate that the annual generation of sludges in the U.S. could be up to 13,840 kilotonnes (Seiple et al., 2017). However, correcting the generation of sludge still results in 86% of unaccounted microplastics. Second, we used median concentration based on global data, but we have used sludge mass and volume of wastewater treated estimated by the U.S. E.P.A. for WWTP in the U.S. only. Thus, we assume the sludge yield, the mass of sludge produced per volume of wastewater treated, is similar between WWTPs in and outside the U.S. The data related to the total volume of wastewater treated and the mass of sludge produced in other regions in the world is not available. However, we have reported the distribution of microplastics in influent, effluent, and sludge by different world regions so that they can be used to estimate total loading via biosolids application (Figure 3-12).

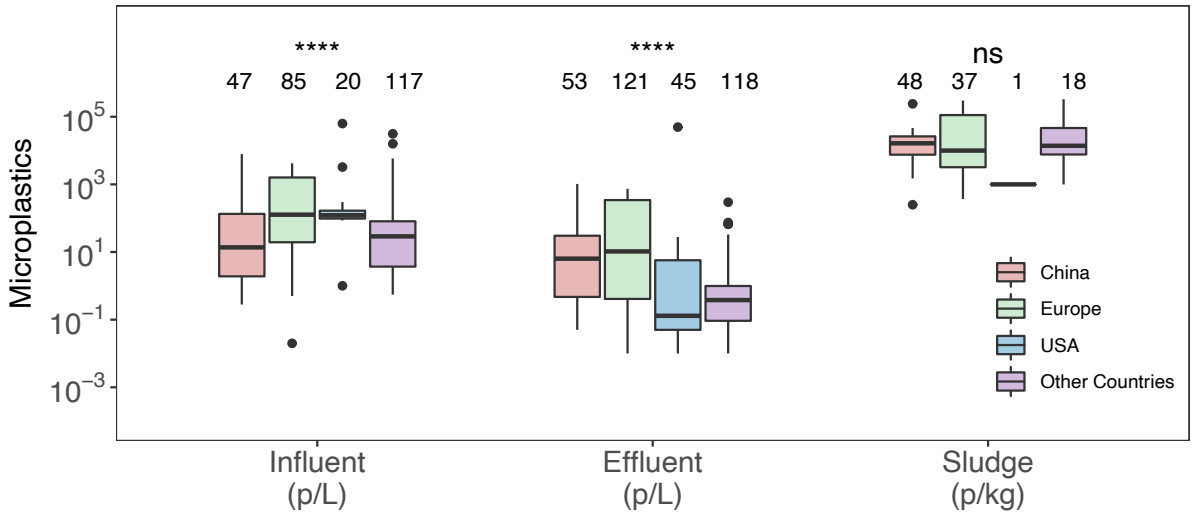


Figure 3-12. Highlighting the distribution of microplastics in influent, effluent and sludge by different world regions. Concentration of microplastics between regions are statistically different for influent and effluent.

Table 3-4. Estimate of microplastics concentration and annual emissions in wastewater treatment plants in the USA in trillion microplastic pieces and kilotonnes. Annual loading is estimated using microplastics concentration for particles >10 µm resulting in 94% unaccounted microplastics.

WWTP	Minimum concentration (pL^{-1} or pkg^{-1})	Maximum concentration (pL^{-1} or pkg^{-1})	Min Annual loading[b] (trillions p)	Max Annual loading[b] (trillions p)	Min Estimated annual loading[a] (kilotonnes)	Min Estimated annual loading[a] (kilotonnes)
Influent	33.4	45.9	1,570	2,160	107	147
Effluent	0.63	0.99	30	47	2.0	3.2
[c]Sludge (total)	324,056	444,106	1,540	2,110	105	143
Sludge (accounted)	11,947	18,802	57	89	3.9	6.1
Sludge (unaccounted)	312,110	425,304	1,480	2,020	101	137
Biosolids land applied (total)	324,056	444,106	785	1,080	53	73
Biosolids land applied (accounted)	11,947	18,802	29	46	2.0	3.1
Biosolids land applied (unaccounted)	312,110	425,304	756	1,030	51	70
Sludge landfilled (total)	324,056	444,106	339	464	23	32
Biosolids landfilled (accounted)	11,947	18,802	13	20	0.8	1.3
Biosolids landfilled (unaccounted)	312,110	425,304	326	444	22	30
Sludge incinerated (total)	324,056	444,106	246	338	17	23
Biosolids incinerated (accounted)	11,947	18,802	9	14	0.6	1.0
Biosolids incinerated (unaccounted)	312,110	425,304	237	323	16	22
Sludge - other (total)	324,056	444,106	169	232	12	16
Biosolids - other (accounted)	11,947	18,802	6	10	0.4	0.7
Biosolids - other (unaccounted)	312,110	425,304	163	222	11	15

Assumptions: (a) mass of each particle = 68 µg. (b) Wastewater treated in the U.S. is 34 billion gallons per day (U.S. E.P.A., 2013), (c) Sludge produced in the U.S. = 4.75 million tonnes annually (US EPA, 2019). (d) 51% of Sludge is land applied (US EPA, 2019).

3.3.5. Annual emission of microplastics from sludge

Of all the microplastics entering WWTP, ~2% leave the plant via the effluent and only ~4% are detected in the sludge. The other ~94% of microplastics entering WWTP may be in the sludge but remain undetected by current analytical methods. Since 51% of sludge in the U.S. is applied to agricultural land as fertilizer (US EPA, 2019), a minimum of 29 trillion of accounted microplastics, and potentially up to 1,030 trillion of unaccounted microplastics are being applied to agricultural land annually (Table 3-4).

Our results revealed that a significant fraction of microplastics removed in WWTP is reintroduced back into the environment via sludge. Thus, it is critical to determine the whole life-cycle emission from sludge based on their end uses or disposal methods. Based on the data provided by the U.S. E.P.A., 22% of sludges are disposed of in landfills, 16% sludge is incinerated, and 11% is disposed or stored via deep well injections or other methods (US EPA, 2019). In other words, up to 464 trillion microplastics are disposed of in the landfill, 338 trillion microplastics are incinerated, and 232 trillion are disposed of by other methods. Although incineration and deep well injection may lower the risks of the reintroduction of microplastics into the environment (Z. Yang et al., 2021), all other methods of handling sludge can lead to the reintroduction of a significant amount of microplastics in sludge into terrestrial environments. For instance, some of the microplastics in landfills can leach into the environment by either wind (in case of open landfill) and water (He et al., 2019b; Su et al., 2019a). Nevertheless, land application of biosolids represents the dominant pathway for reinstruction of sludge-derived microplastics into environments.

To estimate the mass loading of microplastics into the environment, other studies have used average microplastic weight from 10 μg to 1,800 μg (Eo et al., 2019; Schmidt et al., 2017; Sui et

al., 2020; Zhao et al., 2019). Based on our analysis, the common size of microplastic detected in biosolids is 250 μm (Figure 3-3). Assuming spherical shape and the density of microplastics to be 1.04 g cm^{-3} (Eo et al., 2019), each microplastic particle would weigh 68 μg. Thus, the annual emission of microplastics via sludge would be between 105 and 143 kilotonnes, of which only between 3.9 and 6 kilotonnes are detected. Given that 51% of the sludge is applied on land in the U.S. as biosolids, we estimate that between 53 and 73 kilotonnes of microplastics reenter the environment, which is consistent with a recent study that estimated annual application of microplastics in North American agroecosystems to be approximately 44-300 kilotonnes (Nizzetto et al., 2016b). In addition, a recent study estimated that just polyethylene terephthalate (PET) and polycarbonate (PC) account for 3.7 and 0.31 kilotonnes of microplastics annual emission via sludge land application respectively (Zhang et al., 2019). The abundance of other types of the emitted plastics is difficult to estimate, as many studies did not report the composition of microplastics in the sludge (Kang et al., 2018). We also estimated that up to 32 kilotonnes of microplastics are buried in landfills annually, from which some microplastics may be released via leachate (He et al., 2019b; Praagh et al., 2019; Su et al., 2019a). Approximately up to 23 kilotonnes of microplastics are incinerated, although a small fraction of them survives the heat and release to the environment via ash (Z. Yang et al., 2021). Remaining 16 kilotonnes are stored in deep injection well, which are less likely to be released back to the environment.

3.4. Potential Reasons for Unaccounted Microplastics in Sludges

Fragmentation of microplastic during wastewater treatment. Since the estimation of microplastics typically involves a measurement cutoff size during separation or detection, fragments of microplastics below the cutoff are not counted. Microplastics can become fragmented due to heat (Kalogerakis et al., 2017) and physical stress (Enfrin et al., 2020) in different stages of

treatments. Fragmentation can start from the application of shear force to begin the cracking of the surface of the polymer (Enfrin et al., 2020) and can be continued by a variety of oxidative or digestive processes that can break microplastics below the detectable size (Julienne et al., 2019; Mateos-Cárdenas et al., 2020). Fragmentation is preferentially controlled by microplastic surface properties but is also dependent on polymer metrics such as temporal resiliency, hydrophobicity, UV absorption rates, elasticity, shape/thickness, and porosity. For instance, the presence of additives such as UV stabilizers, antioxidants, and surface coatings can make microplastics harder to break down by UV radiation (Julienne et al., 2019; Song et al., 2017a; Zepp et al., 2020). The dry weathering of sludge can also contribute to a steady release of smaller particles (EL Hayany et al., 2020; Zepp et al., 2020). As the result of fragmentation, smaller microplastic particles can be missed during sampling and processing, which leads to an underestimation of the number of microplastics in the sludge or effluent. To mitigate this, sludge should be sampled before pretreatment to determine microplastics concentration. Furthermore, improved methods must be developed to detect smaller microplastics in wastewater sludge, untreated wastewater influent, and treated effluent (Elkhatib and Oyanedel-Craver, 2020; Fok et al., 2020; Ruggero et al., 2020).

Biodegradation of microplastics in WWTPs. Biodegradation can increase the fragmentation of microplastics. Although several plastic-degrading bacteria and fungi are isolated in the environment (Auta et al., 2018; Kim et al., 2020; Masia et al., 2020; Paço et al., 2017; Raddadi and Fava, 2019; Zumstein et al., 2018), they are rarely sampled from WWTPs (Z. Chen et al., 2020; Matjašič et al., 2020; Rom et al., 2017). Furthermore, heat-treatment of sludge can inactivate most enzymes, thereby lowering their potential to degrade microplastics during sludge processing (Zurier and Goddard, 2021). In this condition, hyperthermophilic bacteria can degrade polystyrene in sludge with an estimated half-life of 54 days (Z. Chen et al., 2020), although

biodegradation was found to be infeasible for polylactide fibers under similar conditions (Rom et al., 2017). However, in these controlled lab studies, the degradation rate is expected to be much higher than that in the sludge because non-selective plastic-degrading enzymes can be consumed by reaction with organic matters in sludge. Furthermore, microorganisms in wastewater sludge have less incentive to utilize microplastics as the source of carbon in presence of other easily biodegradable organic carbon. Thus, future studies should examine the biodegradation of microplastics in conditions relevant to wastewater treatment plants and quantify fragmentation rate as a result of biodegradation. Furthermore, the growth of microorganisms on plastics can affect the particle density and accelerate the sinkage of microplastics in the sludge. This highlights the importance of sampling methodology to account for the uneven distribution of microplastics in the sludge (Nguyen et al., 2020). Furthermore, microplastic biodegradation is sensitive to conditions, plastic types, and microorganisms (Mammo et al., 2020; Montazer et al., 2020). Thus, future studies should examine the microbial communities formed on microplastics in sludge and in wastewater to understand their biodegradation potential.

Sampling artifacts and detection limits. A lack of uniform protocols in sampling and analysis of microplastics could contribute to large errors and make the comparison between different studies difficult. For instance, the reported concentrations of microplastics in both sludge and wastewater samples are highly dependent on the lower cut-off size when filtration is used to separate microplastics and on (in)ability to identify smaller microplastics (< 50μm) in sludge. Recent studies have investigated methodologies that can improve the detectability of smaller microplastics (Lê et al., 2021; Z. Xu et al., 2020). Increasing the frequency of sampling or analyzing the composite sample from different locations and times could minimize the role of sampling time and location on concentration fluctuation. Microplastics concentration is reported

in different units such as µg/L water (Bitter and Lackner, 2020), p/L water (Lv et al., 2019), p/kg of wet sludge (Leslie et al., 2017; Magnusson and Norén, 2014), µg/g of sludge (Zhang et al., 2019), or p/kg of dry sludge (Kazour et al., 2019; Mahon et al., 2017; Q. Xu et al., 2020). Most papers use a number of particles estimate for microplastics, even though the number of microplastics is not conservative due to fragmentation or aggregation of microplastics. Our calculation assumed that microplastics have a uniform size and density or one weight value per piece, although the size and density of microplastics can vary widely (Long et al., 2019). Future studies should report size distribution and types of microplastics wherever possible.

3.5. Implications and Needs for Future Research

Human Health Implications. Our study shows that biosolids could contain a much higher amount of microplastics than previously estimated, and these microplastics could be released back to the environment based on sludge disposal methods. Microplastics released from sludge could pose significant health risks by inhalation or ingestion by humans and wildlife. Land application of biosolids can increase the inhalation risk of microplastics due to aerosolization and wind-driven transport of micro- and nano-plastics, specifically in rural populations near agricultural lands (Amato-Lourenço et al., 2020; G. Chen et al., 2020; Rezaei et al., 2019). The aerosolized microplastics can cause breathing irritation, inflammatory responses in airways and bronchi, and oxidative stress in vitro lung tissues (Prata, 2018). Once in the body via water or air, nanoplastics can translocate into internal organs such as lungs, liver, and fetus, causing oxidative stress and genotoxic damage (Rubio et al., 2020). On land, nanoplastics can be taken up by plant roots and soil microbiota and pose ecological risks such as reduced shoot length in plants and decreases in microbial diversity and enzyme activities in soil (Ng et al., 2018; Rillig et al., 2019; van Weert et al., 2019a). Microplastics could also alter nitrification and denitrification rates by altering

microbial community in soil (Seeley et al., 2020), similar to how it is observed in activated sludge processes (L. Li et al., 2020; Song et al., 2020). Contaminants adsorbed on microplastics could make wastewater-derived microplastics more toxic (Fan et al., 2021; X. Li et al., 2019), and thus, can negatively affect the behavior, reproduction, and development of marine organisms such as oysters, shrimps, and copepods (Bringer et al., 2020; Z. Li et al., 2020; Solleiro-Villavicencio et al., n.d.; Suman et al., 2020). For instance, microplastics adsorb heavy metals, including cadmium, copper, and zinc (Brennecke et al., 2016; Ta and Babel, 2020; F. Wang et al., 2020; Wang et al., 2017; Z. Wang et al., 2020; Zhou et al., 2019). Nanoplastics containing antibiotic resistance gene can translocate into the cell and increase risk by horizontal gene transfer (Shi et al., 2020). As microplastics from WWTPs may contain a high concentration of known carcinogens such as polyaromatic hydrocarbons (Sharma et al., 2020), polybrominated diphenyl ethers, and polychlorinated biphenyls (Mohamed Nor and Koelmans, 2019; Yeo et al., 2020), they may serve as a vector for increased cancer risk.

Opportunities. Our results reveal that more than 94% of microplastics entering wastewater treatment plants are not accounted for, and we attribute the discrepancy to several factors, which should be explored in future studies. First, a lack of uniform protocols in the sampling and analysis of microplastics makes it difficult to compare results between different studies. The concentration should be reported in similar units. Second, comparison of removal of microplastics in WWTP between studies is difficult because studies rarely reported concentration of microplastics in all three inlets and outlets: influent, effluent and sludge. Furthermore, most studies have not reported the size, shape, and types of microplastics found in sludge or wastewater. Microplastics smaller than 50 μm are harder to detect in sludge, which we attributed as the main reason for unaccounted microplastics in sludge. Future studies should focus on improving methods of detection of smaller

microplastics and nanoplastics in wastewater sludge, untreated wastewater influent and treated effluent. Loss of microplastics by biodegradation could also explain some of the unaccounted microplastics. Thus, future studies should examine the biodegradation of microplastics in conditions relevant to wastewater treatment plants and quantify fragmentation rate as a result of biodegradation.

We used meta-analysis to identify the best methodology to identify microplastics so that uncertainty in the measurement can be minimized. Future studies are encouraged to use composite sampling and larger sample volume to lower variance in reported microplastic concentrations. If using density separation, NaI or $ZnCl_2$ should be preferred over NaCl. Using a filter with a low pore size can isolate the highest number of microplastics, but microscopic identification should also include FTIR and Raman analysis. These results inform the development of a standard protocol to identify microplastics in wastewater samples.

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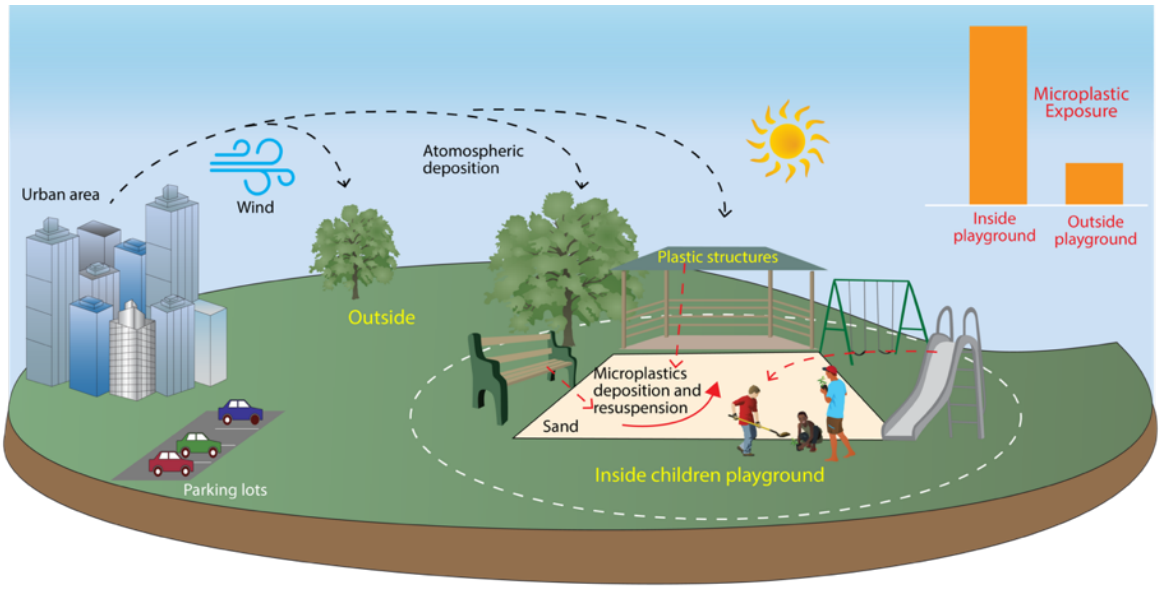
4. CHAPTER 4 – ELEVATED MICROPLASTIC EXPOSURE TO CHILDREN IN URBAN PLAYGROUNDS: DOMINANT DEPOSITION PATHWAYS AND POPULATION DENSITY EFFECT



Koutnik, V.S., El Rassi, L.A., Choy, M. M., Brar, J., Leonard, J., Glasman, J.B., Cowger, W., and Mohanty, S. Elevated microplastic exposure to children in urban playgrounds: Dominant deposition pathways and population density effect. *Science of the Total Environment.* [In Review, May 2022]

Abstract

Children's playgrounds are often assumed to pose a low risk for microplastic exposure to children as they are often located within the green space filled with trees that could filter microplastics released from the surrounding urban hotspots. Many playgrounds also contain plastic structures that could potentially release microplastics into and outside the designated play areas. Yet, no study to date has quantified the microplastic concentration in playgrounds and examined the relative importance of atmospheric deposition of microplastics from urban areas with a wide range of population densities and the release of microplastics from plastic structures within the playground on the accumulation of microplastics in children's playgrounds. We evaluated the extent of microplastic contamination in the sand, soil, and leaf samples from 19 playgrounds and their surrounding areas in Los Angeles, CA, USA. Microplastic concentrations inside the playgrounds were on average more than 5 times greater than concentrations outside the playgrounds, indicating that children playing within the playground boundaries are at an increased risk of exposure to microplastics. By analyzing the microplastic composition found inside and outside the playgrounds and comparing it to the plastic composition of the playground structures, we prove that these plastic structures are the dominant source of microplastics that accumulate in the playgrounds, rather than atmospheric deposition from surrounding urban areas. Population density increased the deposited concentration outside playgrounds but it had no correlation with microplastics inside the playground. Therefore, the sand inside the playgrounds in urban areas could become a hotspot for microplastics and increase the children's inhalation risk.

4.1. Introduction

Microplastics are ubiquitous throughout the natural and built environments, and urban areas often serve as hotspots for microplastics due to the increasing use of plastic products and the release of secondary microplastics from the plastic wastes (Golwala et al., 2021; Song et al., 2017b). Within urban areas, soil (Koutnik et al., 2021b; M. Zhang et al., 2022), water (F. Liu et al., 2019b; Yu et al., 2022), roads (O'Brien et al., 2021; Yukioka et al., 2020) and waste processing sites (He et al., 2019a; Yadav et al., 2020) are often found to contain high concentrations of microplastics due to their proximity to the source of microplastics. Normally, it is expected that green spaces such as playgrounds and parks in urban areas would contain less microplastics than their surroundings due to their distance from sources and filtration of airborne microplastics by tree canopy (Allen et al., 2021; Van Stan II et al., 2021). However, many of the playgrounds, particularly designated areas for children, contain large plastic structures such as slides, playhouses, rides, and rubber flooring. These plastic structures could release microplastics into the sand or soil inside the playground and make them a hotspot for microplastic contamination. Increases in microplastic concentrations in playgrounds could increase the exposure risk to children, who often spend most of their outdoor time in these areas (Mulryan-Kyne, 2014). Recently, microplastics were found in human blood and lungs, indicating the health risks to children could be high (Campanale et al., 2020; Street and Bernasconi, 2021). Yet, no study to date has quantified the microplastic concentrations in playgrounds nor determined the source pathways of microplastics accumulated in the playgrounds in urban areas.

Microplastics in the playground could be accumulated by different processes. First, microplastics can be transported from surrounding areas by water and wind (Piñon-Colin et al., 2020a; Rezaei et al., 2019). Playgrounds are typically located in elevated areas to minimize

flooding risks. Thus, the runoff would not flow into the playground. This limits the amount of microplastics accumulated in the areas by surface runoff. In contrast to water, wind can transport microplastics from different parts of the urban areas across any geographical boundary and deposit them on playgrounds or leaves in the tree canopy. The deposition of microplastics in any urban areas thus depends on the wind profile in that region. The urban canopy could intercept wind and inhibit its ability to carry microplastics and other dust, resulting in atmospheric deposition of the microplastics (Allen et al., 2019; Yumei Huang et al., 2021; Klein and Fischer, 2019). However, microplastics deposited by wind inside the playground have not been compared to that deposited outside the playground. As leaves contain high concentrations of microplastics in urban areas (Koutnik et al., 2022b; Li et al., 2022), concentrations on leaves in trees within and outside the playground boundary can be used to compare the deposition of microplastics via wind.

The major source of microplastics in the playground could be the built-in plastic structures such as slides, plastic carpet flooring, and houses or roof. Additionally, children bring toys and other plastic products into the sandpits in the play area. Abrasion of sand with these plastic structures could release microplastics (S.-Y. Ren et al., 2020; Sipe et al., 2022). Furthermore, many playgrounds are directly exposed to sunlight, which can degrade plastic products (P. Liu et al., 2020; Ren et al., 2021). Consequently, high concentrations of microplastics could be released from these structures by physical and biochemical weathering (Duan et al., 2021). Yet, no study to date has examined the extent of microplastics released from these structures and their contribution to the net accumulation of microplastics in children's playgrounds in urban areas.

The objective of this paper is to quantify the concentration of microplastics in children’s playgrounds in urban areas and identify the dominant source of microplastics present in the playground. We hypothesize that the release of microplastics from built-in plastic structures inside

the playgrounds, not the atmospheric deposition, is the dominant pathway of microplastic accumulation in the playground, and children playing inside the playground would have higher exposure to microplastics than children playing outside. To test the hypotheses, we collected subsurface and leaf samples within and outside the playground boundary from 19 playgrounds in Los Angeles, USA, and compared the concentration of microplastics and their abundance. The results will help determine the microplastic exposure risks to children in the playgrounds.

4.2. Method

4.2.1. Playground Locations

To investigate potential microplastic exposure in urban playgrounds, we collected sand or soil, and leaf samples from 19 playgrounds in the neighborhood to locations with different population densities across Los Angeles County, USA, between January 25th and February 15th, 2022 (Figure 4-1). According to the 2020 census, the population densities near the playgrounds ranged between 0.9 to 20378 people km^{-2} and were categorized into two groups: over 4,000 (9 playgrounds) and under 4,000 people per km^{-2} (10 playgrounds) (Table 4-1).

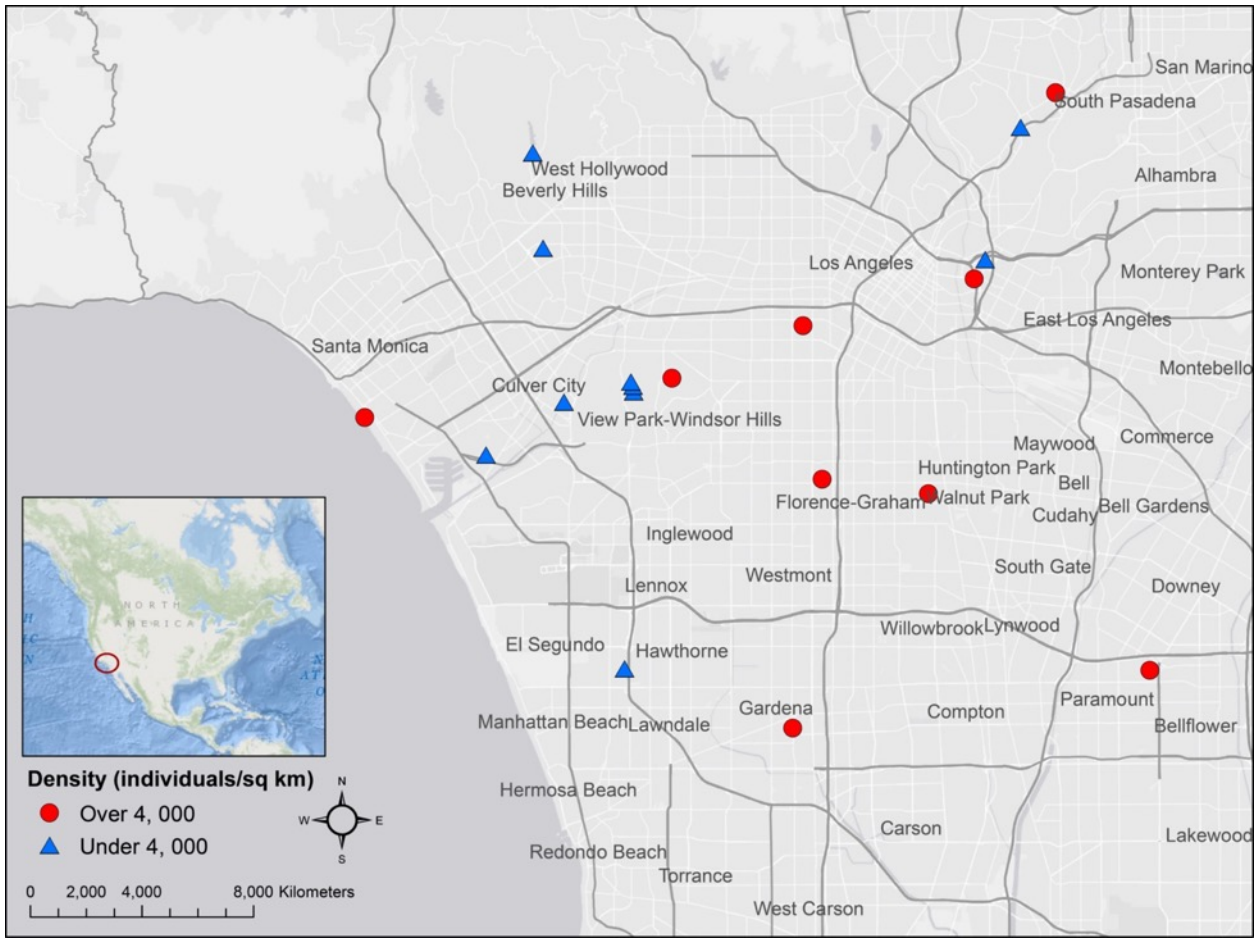


Figure 4-1. Map of Los Angeles with sampled playground locations. Playgrounds in areas with a population density higher than 4,000 individuals km^{-2} are shown in red, and playgrounds with a population density below 4,000 individuals km^{-2} are shown in blue.

Table 4-1. Sampled playground locations and population density classifications

Playground Location	#	Zip code	Sampling Date	Latitude	Longitude	Population Density
Coldwater Canyon Park	A	90210 - Beverly Hills	1/25/22	34.091806	-118.41164	Under 4000
Roxbury Park	B	90212 - Beverly Hills	1/25/22	34.057889	-118.40725	Under 4000
Richardson Family Park	C	90007 - Southeast LA, University Park	1/25/22	34.030361	-118.29564	Over 4000
Jim Gilliam Park	D	90008 - Los Angeles	1/25/22	34.011694	-118.35186	Over 4000
Kenneth Hahn Park	E	90008 - Baldwin Hills	1/25/22	34.006861	-118.36839	Under 4000
Kenneth Hahn Park	F	90008 - Baldwin Hills	1/25/22	34.008778	-118.36861	Under 4000
Kenneth Hahn Park	G	90008 - Baldwin Hills	1/25/22	34.010361	-118.36956	Under 4000
Glen Alla Park	H	90292 - Marina del Rey	1/25/22	33.984306	-118.43172	Under 4000
South Beach Park	I	90405 - Ocean Park, Sunpark	1/25/22	33.997722	-118.48375	Over 4000
Lindberg Park	J	90230 - Culver City	2/15/22	34.003083	-118.39822	Under 4000
Hollyglen Park	K	90250 - Hawthorne (Holly Park)	2/15/22	33.908306	-118.37233	Under 4000
Mas Fukai Park	L	90247 - Gardena	2/15/22	33.887167	-118.30000	Over 4000
Mt. Carmel Recreation Center	M	90044 - Athens	2/15/22	33.975778	-118.28736	Over 4000
Franklin D. Roosevelt Park	N	90001 - Florence Graham	2/15/22	33.970611	-118.24178	Over 4000
Golden Park	O	90242 - Downey	2/15/22	33.907694	-118.14667	Over 4000
Pecan Recreation Center	P	90033 - Boyle Heights	2/15/22	34.047056	-118.22206	Over 4000
Prospect Park	Q	90033 - Boyle Heights	2/15/22	34.053889	-118.21744	Under 4000
Highland Park	R	90042 - Highland Park	2/16/22	34.113222	-118.18717	Over 4000
Sycamore Grove Park	S	90042 - Highland Park	2/16/22	34.100861	-118.20214	Under 4000

4.2.2. Sample Collection

Soil and sand samples were collected inside and outside of the playgrounds using a stainless-steel spatula. Composite samples consisting of more than 10 spoons of media (2-3 g per spoon) were collected at random spots inside, at the boundary, and outside the playground resulting in three composite samples per playground. The inside sample was collected either from the playground's sandbox or the playground itself. The boundary sample was collected from the perimeters of the playground, and the outside sample was collected 50 to 100 m away from the boundary of the designated playground area. The composite samples were mixed inside an aluminum foil packet and labeled. The spatula was thoroughly cleaned using deionized (DI) water and wiped between sampling to prevent cross-contamination.

To analyze the atmospheric deposition of microplastics around the playground, 5-10 leaves were collected at an elevation of 2 m from varying plant species both inside or directly around the

playground, and 50-100 m away outside the playground. Leaves were classified as either inside or outside samples and were wrapped individually in aluminum foil to prevent cross-contamination.

To compare the chemical composition of source plastics released from playground structures with the microplastics found on the ground, small pieces of plastic were scraped off the various plastic structures inside the playgrounds including slides, small houses, and rubber floors in the playgrounds, and collected into an aluminum foil for identification.

4.2.3. Extraction and quantification of microplastics from soil and sand samples

Microplastics were isolated from sand and soil samples following the method described earlier (Koutnik et al., 2022b). Briefly, to separate debris from microplastics, 1 g of each composite sample was mixed with 40 mL of 1.6 g mL^{-1} KI solution and centrifuged at 5000 rpm for 30 min to settle heavier soil particles and isolate lighter (density < 1.6 g cm^{-3}) particles including microplastics. The supernatant was vacuum filtrated to trap floating debris on a 24 mm glass fiber filter paper with a 1.2 µm pore size. The filter was then left to dry for at least two hours. A method blank was processed every day by using DI water in all the steps to estimate any microplastics introduced from the materials used during the extraction steps.

The concentration of microplastics on the filter paper was quantified by dyeing the filter with Nile Red and counting the fluorescent particles as described elsewhere (Leonard et al., 2022). This method has been previously used to assess microplastic concentration in urban stormwater infrastructures (Koutnik et al., 2022b). Briefly, filters in a glass petri dish were dyed with 0.17 mL of 0.5 µg mL^{-1} Nile Red in chloroform solution and air-dried with a glass cover for 24 h in the fume hood. Dried filter membranes were transferred onto glass slides, covered with a glass coverslip to eliminate dust deposition, and imaged using a smartphone-based fluorescence microscope. The method could detect microplastics as small as 10 µm due to a large field of view

of 490 mm^2, and have limitations associated with the selectivity of Nile Red to bind plastic polymers.

4.2.4. Concentrations of microplastics on leaves

To quantify the number of microplastics per unit surface area of leaves, collected leaves were cut using metal scissors into a rectangular shape so that their area can be estimated. Debris from the leaves was washed with 100 mL of DI water into a glass beaker, and the microplastics suspension was vacuum filtrated onto a 24 mm G4 glass fiber membrane. The filter membranes were then dyed with Nile Red and analyzed for microplastic concentration. Blank or pre-washed leaves were also dyed to ensure there are no fluorescent particles on the leaves without microplastics.

4.2.5. Microplastics Characterization

To examine the size distribution of microplastics and their abundance by polymer types, microplastics isolated from leaves and sand samples using KI solution were vacuum filtered on a nitrate cellulose filter and scraped onto a gold-coated slide for Fourier Transform Infrared spectroscopy (FTIR) analysis. Specifically, 3 grams of inside playground samples were analyzed and 3 inside leaves and 3 outside leaves were analyzed using FTIR. The large pieces of scraped microplastics from playground structures were also analyzed for their composition. Microplastics on the gold slides were characterized for their size distribution, shape, and polymer types using FTIR analysis (Thermo Scientific Nicolet iN10). The FTIR microscope was used in the reflectance mode using the particle analysis wizard included in the PICTA software following a similar method as described by Brahney et al., 2020. First, the microscope was calibrated using an in-

house reference standard of high-density polyethylene to ensure that the device was functioning in a reproducible way. Then, sample particles were placed onto a clean gold-coated slide and dispersed with ethanol. A particle map of ~1 cm^2 area was analyzed using the particle analysis wizard included in the PICTA™ software. A portion of the particle map with even particle spacing and a low amount of overlapping particles was selected for FTIR analysis to yield individual spectra for each particle. Image separation settings were tuned to best extract the particles from the gold slide manually. Spectra were measured using a normal resolution setting and 8 scans in 1 second, over a spectral range of 4000 - 675cm^{-1}. The background was collected immediately after the samples at a reference point made of reflective gold. Spectra were automatically converted to absorbance intensities from reflectance in the software. To identify particle composition and frequency of various polymers, the collected spectra were compared across all available commercial libraries. FTIR libraries used to match spectra were Polymer Laminate Films, Cross Sections Wizard, Hummel Polymer Sample, Polystyrene Quality Control, NIR Polystyrene QC, Synthetic Fibers by Microscope, HR Hummel Polymer and Additives, HR Aldrich Hydrocarbons, HR Nicolet Sampler Library, HR Polymer Additives and Plasticizers, HR Specta Polymers and Plasticizers by ATR, HR Specta Polymers and Plasticizers. The OMNIC correlation routine was used to compare each particle to the reference database. The criteria for reporting a match in the spectra libraries was set to a 15% match score. Matches were confirmed if above 60%.

The FTIR microscope can identify the size distribution of microplastics larger than 20 μm based on the image analysis of particles spread on a 1 cm^2 area of the slide. When comparing

sample spectra to spectra databases, 60% match criteria were required to identify the particle. Individual sample spectra were then visually examined against their database match to confirm the identification. If particles were matched to a generic, broad category of plastic— such as polyolefin, which can refer to as either polyethylene or polypropylene — their spectra were uploaded and visually analyzed for a second time using OpenSpecy, an open-source software developed to allow researchers to upload spectra and match their spectra to the existing library (Cowger et al., 2021).

4.2.6. Quality Control

For sampling, storage, and processing, pre-washed glass, and aluminum containers were used. All clean glassware and containers were rinsed with DI water three times. The DI water was analyzed for possible microplastic contamination. No field blanks were collected as the samples were taken from the surface using clean tools. We have performed laboratory blanks to account for any cross-contamination. A method blank was run during each day of analysis, following the same lab procedure as sample analysis. The mean laboratory blank for sediment samples was 3 pieces and the mean for leaf samples was 1 piece. The mean of laboratory blanks for each method was subtracted from the measured concentration of samples to account for any microplastics introduced from any material used. The methodology has an average recovery rate of 93.7% ± 13.7%, a human processing variation of 6.8% of the mean, and a sample processing variation of 9.1% (Koutnik et al., 2022a). Therefore, the total maximum error for each of the microplastic measurements was estimated to be 22.2%.

4.3. Results

4.3.1. Microplastics concentration was the highest inside the playground

Analysis of microplastic concentrations in sand and soil samples collected inside, on the boundary, and outside the playgrounds reveals that microplastic concentration inside the playground is more than 5 times the concentration of microplastics outside the boundary of the playground (Figure 4-2). The average microplastic concentration in sand samples collected inside the playground was 72 p g^{-1}. The concentration decreased to 42 p g^{-1} near the boundary and to 13 p g^{-1} outside the boundary. The difference between concentrations inside and at the boundary is not statistically significant (p = 0.59).

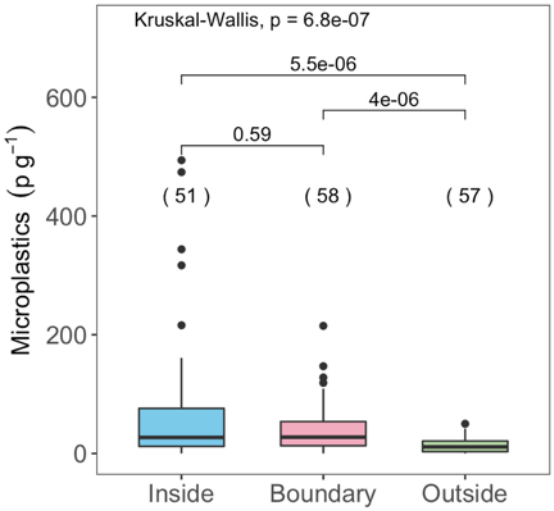


Figure 4-2. Showing microplastic concentration from soil and sand samples inside, on the boundary, and outside (>100 m away) the playground. (n) is the number of samples analyzed for a certain category.

4.3.2. Size and abundance of microplastics within the playground

A comparison of the size and abundance of microplastics within and outside the playground reveals that the size, shape, and type of microplastics found inside the playgrounds were slightly different from those found outside the playground (Figure 4-3). Inside the playground, both sand and leaf samples had PE and PP as the most commonly found microplastics types, meanwhile

leaves from outside the playground had 83% PP and no PE microplastics. Based on FTIR analysis of plastic scraps from the built-in plastic structures in the playgrounds, they are mainly made up of PE and PP (Table 4-2). A similarity of dominant plastic types used in structures and microplastic polymers found in sand and on leaves inside the playground suggests that the plastic structures were the possible source of microplastics inside the playground. This would mean that up to 60% of microplastics in the sand and 73% of positively identified microplastics on the inside leaves are PE and PP, and they could be released from plastic structures within the playground. 25% of microplastics in sand samples were fibers (length-to-width ratio > 3). The fiber fraction on leaves samples inside and outside playgrounds were 9% and 17%, respectively. The results indicate that the dominant shape of microplastics within playgrounds is fragment, which is typically produced by physical abrasions or chemical weathering.

More than 50% of microplastics found in all locations have sizes larger than 100 μm. The majority of pieces both on leaves and in the sand were 100-300 μm indicating large microplastics can be resuspended or be transported by wind. However, leaves contained a greater percentage of the smallest identifiable microplastics (< 50 μm) indicating smaller microplastics are preferentially transported or accumulated on the leaves. It should be noted that the FTIR microscope used in the study could not reliably detect microplastics smaller than 20 μm. Thus, the size distribution reported here could have underestimated the concentration of microplastics smaller than 20 μm.

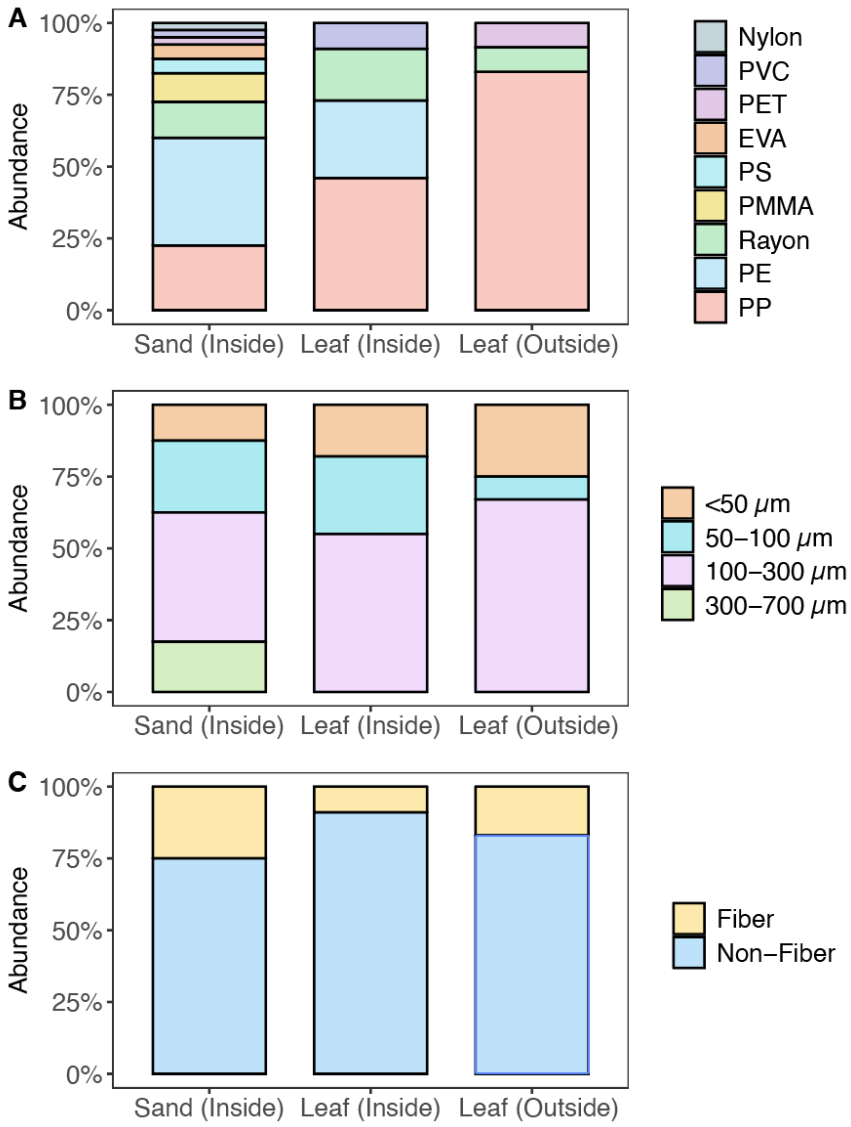


Figure 4-3. Characteristics of microplastics from sand inside three of the playgrounds based on 40 identified microplastic pieces and leaves collected inside and outside the playground based on 21 identifiable pieces from 6 leaves. (A) Shows the distribution of polymer types confirmed using FTIR. (B) the distribution of the longest side of the microplastics, and (C) shows the shape of identified microplastics as fibers with an aspect ratio greater than 3.

Table 4-2. Results of identification of 32/77 plastic pieces scraped off the playground structure and floor identifying majority pieces as PE and PP.

#	Identified Component Name	Match %	Length (¬µm)	Width (¬µm)	Identified Type
1	OLEFIN	90.58	83.9	36.3	PE
2	OLEFIN	90.44	110.1	73.4	PE
3	POLY(ETHYLENE)	85.31	26.2	18.7	PE
4	OLEFIN	85.23	52.4	16.7	PE
5	OLEFIN	84.05	455.3	175	PE
6	Linear low density polyethylene	84.02	2354.4	1032.5	PE
7	Polyethylene; LD	83.76	4012.1	1024.3	PE
8	Linear low density polyethylene	83.57	3119.8	1015.4	PE
9	POLYETHYLENE; LOW-DENSITY WAX	82.43	161.5	38.6	PE
10	Linear low density polyethylene	81.56	52.4	42.7	PE
11	POLYETHYLENE; LOW-DENSITY WAX	80.49	31.5	21.1	PE
12	Linear low density polyethylene	80.26	83.9	23.8	PE
13	Polyethylene Marlex catalyst	78.26	83.9	21.7	PE
14	Linear low density polyethylene	72.34	68.2	23.6	PE
15	ETHYLENE-ACRYLIC ACID COPOLYMER ACRYLIC ACID	68.94	36.7	21.9	PE
16	Linear low density polyethylene	63.42	398.5	131.6	PE
17	Linear low density polyethylene	61.65	52.4	10.7	PE
18	Linear low density polyethylene	60.24	41.9	20	PE
19	POLYESTER	65.94	618.7	180.1	PET
20	Linear low density polyethylene	85.11	194	73.6	PP
21	Linear low density polyethylene	83.38	1464	599.2	PP
22	Linear low density polyethylene	82.97	57.7	18.2	PP
23	POLYOLEFIN ANTI-STATIC CONCENTRATE	81.96	126.8	106	PP
24	OLEFIN	81.49	489.8	216.8	PP

25	POLYOLEFIN ANTI-STATIC CONCENTRATE	80.9	5105	1623.5	PP
26	POLYOLEFIN ANTI-STATIC CONCENTRATE	80.55	125.1	85.4	PP
27	Linear low density polyethylene	80.09	108	72.9	PP
28	POLYOLEFIN ANTI-STATIC CONCENTRATE	79.56	0	0	PP
29	POLYETHYLENE; LOW-DENSITY WAX	77.62	123.7	69.9	PP
30	POLYETHYLENE (TYPE II) #1	68.22	2937.1	1517.4	PP
31	OLEFIN	66.48	135.3	46.6	PP
32	RAYON	32.27	94.4	59.7	Rayon

4.3.3. Microplastic deposition on leaves outside the playground was higher than that inside.

The microplastic concentrations of 91 analyzed leaf samples ranged between 0 to 6.5 p cm^{-2} (Figure 4-4, Figure 4-4). The concentration was significantly higher ($p < 0.05$) on leaves collected from trees outside the playground averaging 2 p cm^{-2}, compared to leaves inside the playground which averaged 1.3 p cm^{-2}.

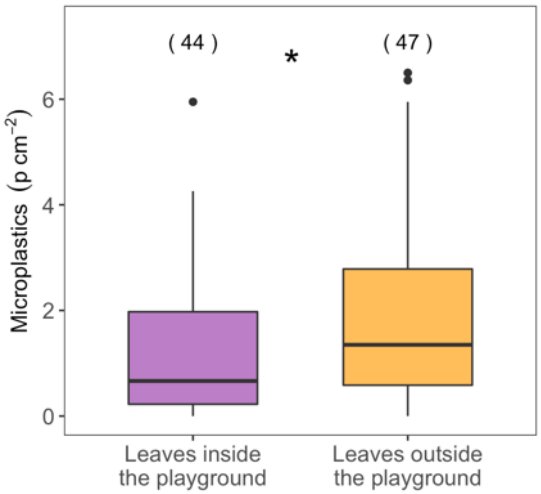


Figure 4-4. Microplastics concentration on leaves collected at 2 m height from trees inside and outside the sampled playgrounds. Wilcoxon rank-sum test was performed (R version 4.0.0), with ∗ indicating a p-value < 0.05. (n) is the number of samples analyzed per category.

4.3.4. Population density did not explain microplastic concentration inside the playground.

An increase in the population density significantly ($p < 0.05$) increased the microplastic concentration in the soil outside the playground (Figure 4-5). Although population density appears to increase the concentration of microplastics outside the playground, the increase in concentration was not significant ($p > 0.05$). Microplastic concentrations in samples collected in areas of high population density varied more widely than the concentrations in samples located with lower population density. The high variability deemed the difference in microplastic concentrations between locations with low and high population density insignificant ($p > 0.05$), both for samples collected inside and boundary samples, even though the average concentrations in samples with higher population density were higher. The concentration of microplastics in the boundary is slightly higher than that outside, indicating playground contaminated adjacent areas.

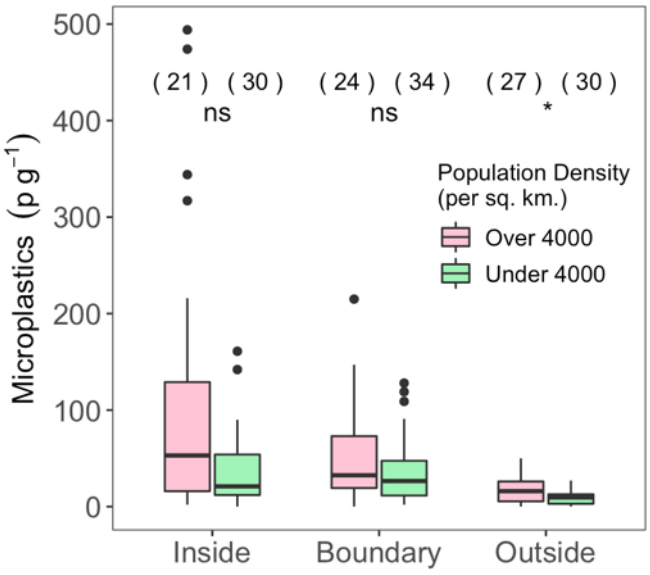


Figure 4-5. Showing microplastic distribution by population density at three locations inside, on the boundary, and outside the playground. (n) indicates the number of samples analyzed in the select category. Wilcoxon rank-sum test was performed (R version 4.0.0), with ∗ indicating a p-value < 0.05 and ns indicating no statistically significant difference.

4.4. Discussion

4.4.1. Cause of elevated microplastic exposure risks in playgrounds

Microplastic concentrations were found to be the highest inside the playground boundary, indicating that children playing inside the designated play area could be exposed to more microplastics than children playing outside the designated area (Figure 4-2). The concentrations decreased from inside to the boundary to outside the playground. We attribute the result to the release of microplastics from built-in plastic structures in the playground, not the atmospheric deposition of microplastics from surrounding areas. The analysis of the playground material revealed the source plastic types were predominantly PE and PP, which matched with microplastics found inside the playground and on the leaves. In addition, children often wear synthetic clothing (Dris et al., 2016b; Y.-Q. Zhang et al., 2022) and bring and play with plastic toys, which can also release microplastics due to mechanical abrasion with sands (S.-Y. Ren et al., 2020; Song et al., 2017b). Even though most of the sampled playgrounds were located inside parks and green spaces, they still lacked shade due to limited vegetation or urban canopy cover. Therefore, the plastic structures were exposed to UV radiation and could be weathered at a high rate especially since LA has perennial sunshine.

Microplastics could be transported by wind over long distances (Brahney et al., 2020b; Bullard et al., 2021). Thus, it is expected that microplastics released in urban areas could also be deposited on the playgrounds. However, our data show that microplastic concentrations on leaves outside the playground were greater than the concentration on the leaves inside the playground, indicating wind contributes a small fraction of microplastics accumulated inside the playground. Thus, sandpits in playgrounds could accumulate microplastics, which can be resuspended into the air when children play with the sand. Activities on the sand inside the playground could increase

microplastic inhalation risks (G. Chen et al., 2020). The long-term effects of microplastic fiber inhalation have been studied in industrial settings and have resulted in increased risks of lung, stomach, and esophageal cancer (Prata, 2018; Y. Wang et al., 2021). Airborne microplastics can also serve as vectors for contaminants (Borthakur et al., 2021a; G. Chen et al., 2020). It should be noted that smaller microplastics were underestimated in this study, as the FTIR microscope could only detect microplastics with sizes larger than 20 μm. However, the inhalation risks increase dramatically as the particle size decreases to micron or submicron levels. Thus, future studies should develop methods to identify smaller microplastics in environmental samples.

4.4.2. Comparison of the characteristics of microplastics on the ground and leaves

Microplastics on the ground inside the playground had different polymer types, and size characteristics compared to the microplastics found on the leaves inside the playground (Figure 4-3), indicating some plastic polymers could be preferentially transported by wind. Specifically, the microplastics identified in samples from inside the playground had a much more diverse range of polymers. However, all microplastic types (PE and PP) identified on leaves inside the playground matched that of plastic types used in the structures inside the playground. Surprisingly, leaves outside playground boundaries contained no PE microplastics, confirming that PE microplastics found inside the playground originated from the plastic structures in the playground. Microplastics on the leaves outside playground boundaries are an indicator of microplastics deposited by the wind, whereas microplastics on the leaves inside playgrounds are an indicator of both microplastic depositions by wind and resuspension of microplastics from sand within the playground. Plants species have been proven to capture atmospheric microplastics (Li et al., 2022; K. Liu et al., 2020), but the source of those atmospheric microplastics has not been confirmed. In this study, we determined that up to 73% of microplastics found on the inside leaves are sourced

from the plastic structures within the playgrounds. When the source plastic pieces were analyzed using FTIR, we were only able to identify 31 out of 77 pieces analyzed as polymers with matches above 60%. Sample FTIR spectra is shown in Figure 4-6. This demonstrates that many of the particles with lower matches could still be polymers, but extensive weathering or the presence of additives prevented their identification using FTIR.

The size of particles influences their transport potential by winds. Generally, soil particles larger than 100 μm are difficult to be suspended by the wind in urban areas. Surprisingly, the majority of microplastics identified on leaves both inside and outside were found to be within a larger size fraction (100-300 μm), indicating large plastic particles could be airborne and transported by wind. Since the majority of microplastics identified on leaves were of low density, even bigger pieces can be preferentially transported. The accumulation of diverse microplastics inside the playground, especially in small size fractions below 100 μm, could increase the inhalation risks. Most particulate air pollutants are sized below 10 μm. However, our study could not identify them by either FTIR or smartphone method due to the resolution limitation. Thus, the microplastic concentration reported in this study provides a conservative estimate of exposure risks in the playground, and the actual risk could be much higher.

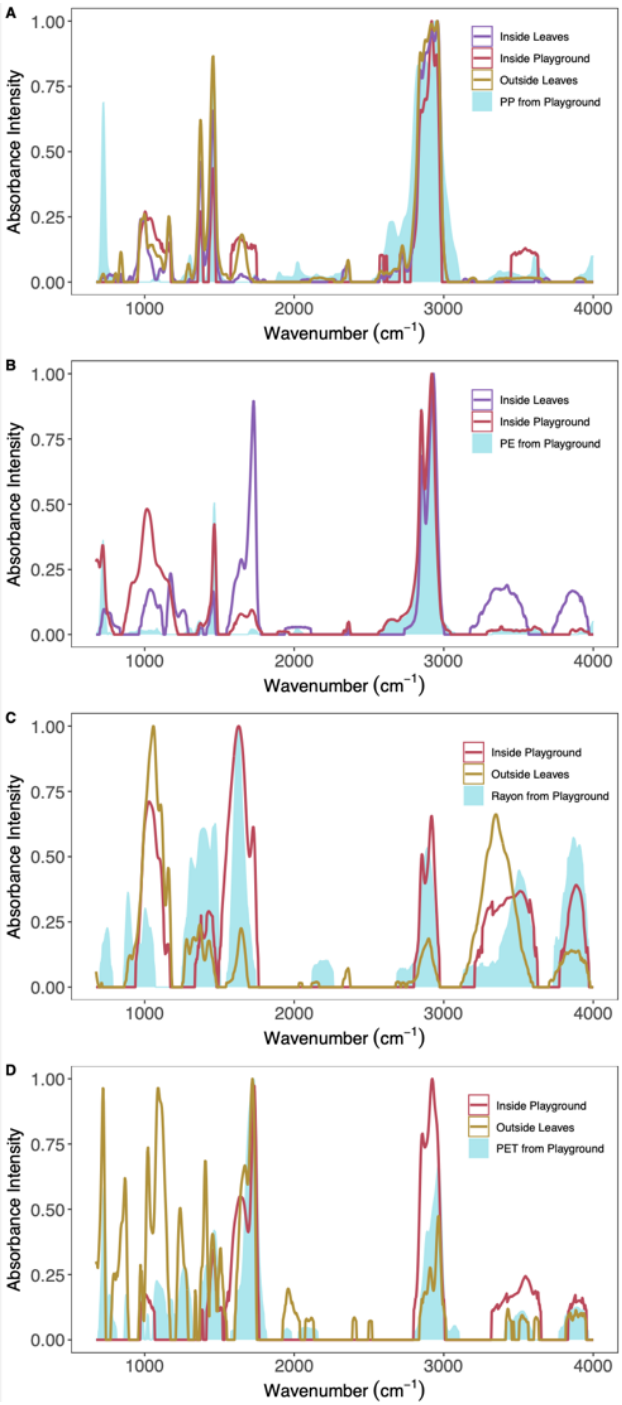


Figure 4-6. FTIR confirmation of microplastics spectra for (A) PP, (B) PE, (C) Rayon, and (D) PET. Spectra from source playground samples scraped off big plastic objects on the playground are shown in shaded blue and are compared to red line representative spectra for each plastic type inside the playground, purple showing spectra for samples collected from leaves inside the playground, and yellow showing spectra for samples collected from leaves outside the playground.

4.4.3. Population density affects microplastic exposure outside the playground, not inside

Population density appears to have no significant effect on microplastic concentrations inside the playground (Figure 4-5), likely because playground usage is not correlated with population density or the microplastic concentration in the playground is more affected by the release of microplastics from built-in plastic structures in the playground than atmospheric deposition from populated areas. However, increases in population density increased microplastics concentration outside the playground area, indicating greater deposition of microplastics by wind (Bullard et al., 2021). Atmospheric deposition of microplastics has been reported all over the world (Abbasi and Turner, 2021; Fang et al., 2022; Liao and Chen, 2021), even in remote areas (Allen et al., 2019; Brahney et al., 2020b; Evangeliou et al., 2020; Y. Zhang et al., 2021). Soil samples outside the playgrounds (at least 100 m away from the sampled playground) were mostly collected from open areas and parks. These outside samples could serve as indicators of the background plastic accumulation and deposition in the area. Population density could affect the outside soil microplastic concentrations due to a proportional increase in the human consumption of plastic products and the generation of plastic wastes that directly release microplastics into urban environments. However, the microplastics created in densely populated areas can still migrate across the geographical boundaries to lower population density areas via wind. Even though we sampled locations with ranging population densities, Los Angeles is still a relatively highly urban and densely populated area. While our study found a preliminary correlation of microplastic concentration with population density, more studies are needed to compare microplastic concentration in areas with more diverse population densities and plastic uses.

4.4.4. Environmental Implications

In highly urbanized regions, playgrounds are often the only outdoor space where children spend a long time. The results of our study demonstrate that the urban playgrounds could be a significant source of microplastics, potentially due to the release of microplastics from plastic structures within the playground. Increased exposure to microplastics could lead to their accumulation in the lungs (Amato-Lourenço et al., 2020; Jenner et al., 2022) and other organs via the blood (Leslie et al., 2022). Increased microplastic exposure could have significant health burdens such as cytotoxicity, hypersensitivity, reduced cell viability, and other harmful immune responses (Hua et al., 2022; Hwang et al., 2019). Children during the developmental phase could be more vulnerable to the adverse health effects of air pollutants due to their higher minute ventilation, immature immune system, incomplete lung development, and longer periods they spend outdoors (Buka et al., 2006). Thus, early exposure to microplastics could have many unintended consequences. Additionally, microplastics found in playgrounds could be enriched with pollutants such as lead, BPA's, cadmium, phthalates, or other chemical additives found in children's toys or playground structures (Becker et al., 2010). Thus, preferential emission of these contaminated microplastics by wind, owing to their lighter weight than other soil particles, may lead to the enrichment of these toxic chemicals. Thus, it is critical to understand the fate, accumulation, and release of microplastics, and their enriched chemicals, from the urban playgrounds.

4.5. Conclusion

Analyzing microplastic concentration from 19 playgrounds in Los Angeles, we confirmed an increased microplastic exposure to children inside the playgrounds. Children playing inside the playgrounds could be exposed to five times more microplastics than those who play outside the

designated play areas. The most common type of microplastics found on samples inside playgrounds (e.g., PE and PP) matched with the polymer composition of the playground structures, indicating that the dominant source of most microplastics accumulated in the playground is the built-in plastic structures in the playground that could release microplastics by physical and chemical weathering. Another source of microplastics in the playground could be food wrappers, toys, synthetic clothing, and those that are transported from urban hotspots by the wind. Increased microplastic concentration in the sand in the play area and their subsequent resuspension during playing activity could increase exposure risk to children.

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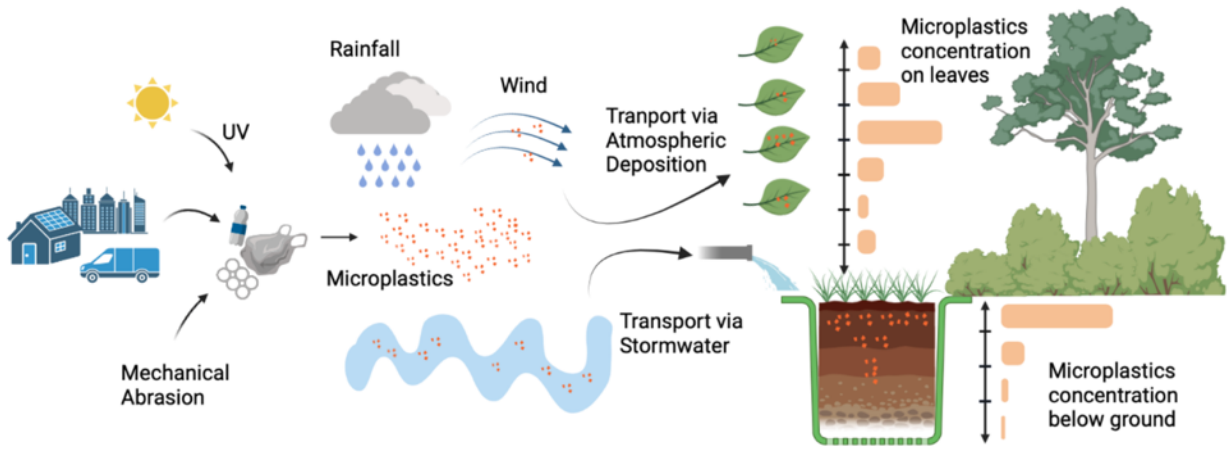
5. CHAPTER 5 – MICROPLASTIC RETAINED IN STORMWATER CONTROL MEASURES: WHERE DO THEY COME FROM AND WHERE DO THEY GO?



Koutnik, V.S., Leonard, J., Glasman, J.B., Koydemir, H.C., Novoselov, A., Brar, J., Bertel, R., Tseng, D., Ozcan, A., Ravi, S., Mohanty, S.K. (2022) Microplastics retained in stormwater control measures: Where do they come from and where do they go? *Water Research*. 118008. https://doi.org/10.1016/j.watres.2021.118008

Abstract

Stormwater control measures (SCM) can remove and accumulate microplastics and may serve as a long-term source of microplastics for groundwater pollution if downward mobility is not retarded. Furthermore, the number of microplastics accumulated in SCM may have been underestimated as the calculation typically only accounts for microplastics loading via episodic stormwater loading and ignores the contribution of continuous atmospheric deposition. To evaluate the source pathways of accumulated microplastics and their potential for downward mobility to groundwater, we analyzed spatial distributions of microplastics above ground on the canopy around SCM and below ground in the subsurface in and outside the boundaries of fourteen SCM in Los Angeles. Using an exponential model, we link subsurface retardation of microplastics to the median particle size of soil (D_{50}) and land use. Despite receiving significantly more stormwater, microplastic concentrations in SCM at surface depth or subsurface depth were not significantly different from the concentration at the same depth outside the SCM. Similar concentration in and outside of SCM indicates that stormwater is not the sole source of microplastics accumulated in SCM. The high concentration of microplastics on leaves of vegetation in SCM confirms that the contribution of atmospheric deposition is significant. Within and outside the SCM boundary, microplastics are removed within the top 5 cm of the subsurface and their concentration decreases exponentially with depth, indicating limited potential for groundwater pollution from the microplastics accumulated in SCM. Outside the SCM boundary, the subsurface retardation coefficient decreases with increases in D_{50}, indicating straining of microplastics as the dominant removal mechanism. Inside the boundary of SCM, however, the retardation coefficient was independent of soil grain size, implying that microplastics could have either moved deeper into the filter layer in SCM or that compost, mulch, or organic amendments

used in the filter media were pre-contaminated with microplastics. Overall, these results provide insights on microplastics source, accumulation, and downward mobility in SCM.

5.1. Introduction

Microplastics from urban compartments including trash or litter, roads (Knight et al., 2020; Kole et al., 2017b), biosolid applied land (Crossman et al., 2020a; Koutnik et al., 2021a), landfills (He et al., 2019b; Su et al., 2019b), and soils (Rafique et al., 2020; Su et al., 2020) are washed off by stormwater (Moruzzi et al., 2020; Müller et al., 2020; Piñon-Colin et al., 2020b), and enter surface waters (Leslie et al., 2017; Treilles et al., 2021). Thus, stormwater control measures (SCM), which are typically used to reduce runoff and remove stormwater pollutants including sediments, can capture these microplastics (F. Liu et al., 2019a; Smyth et al., 2021) and minimize pollution downstream. However, accumulated microplastics in SCM can also disintegrate over time (Andrady, 2011; K. Zhang et al., 2021), and the smaller microplastics could migrate downward through the subsurface to groundwater if their transport is not retarded by the filter media in SCM. The risk of groundwater pollution also depends on the total amount of microplastics accumulated in SCM and the fraction of which are available for downward mobilization. Thus, it is critical to account for all the pathways that contribute to microplastic inventory in SCM and examine their downward mobility potential towards groundwater.

Stormwater runoff is typically assumed to be the main source of microplastics in the SCM (F. Liu et al., 2019a; Werbowski et al., 2021), even though atmospheric deposition can be a significant source (Brahney et al., 2020a; Dris et al., 2016a). Unlike stormwater loading, which is episodic and happens a few times a year in response to precipitation events, atmospheric deposition is continuous throughout the year. Thus, net loading via atmospheric deposition could add up to a significant amount. Other studies have examined atmospheric transport of microplastics (Mbachu

et al., 2020; Roblin et al., 2020; X. Wang et al., 2021), and some of which could deposit in the SCM (Smyth et al., 2021). Several studies have examined microplastic concentration in soil or filter media in SCM (Boni et al., 2021; Gilbreath et al., 2019; Lange et al., 2021a; Smyth et al., 2021), but they did not examine the concentration of microplastics accumulated on the vegetation. Vegetation canopy can intercept microplastics (K. Liu et al., 2020; Sun et al., 2021) and contribute to the net inventory of microplastics in SCM. High concentrations of microplastics are frequently found in the dust (Abbasi et al., 2019; Koutnik et al., 2021b; J. Zhang et al., 2020), which can be transported by wind (Bullard et al., 2021; Rezaei et al., 2019) and redistributed in urban areas. As microplastics concentration in the canopy in SCM can serve as an indicator of microplastics deposition from the atmosphere, it is critical to estimate microplastic concentration trapped by vegetation on SCM.

The extent to which the accumulated microplastics can move downward in SCM in field conditions has not been evaluated, despite earlier evidence of subsurface mobility of microplastics during intermittent infiltration of rainwater (Mohanty et al., 2015a). Microplastic removal and transport processes in SCM can be inferred from the knowledge of particulate transport or removal mechanisms in the SCM (Tirpak et al., 2021). Microplastics, similar to particles or sediments, can be removed by settling, adsorption, and filtration from stormwater (Gavrić et al., 2019; Massoudieh et al., 2017). Although most microplastics, owing to their large size, are expected to be filtered out in topsoil (Luo et al., 2020), smaller microplastics could potentially migrate downward with infiltrating stormwater. Previous studies have shown that microspheres of size greater than 2 μm are retarded rapidly with limited transport potential (Gao et al., 2021; Zhou et al., 2020). Furthermore, PM10, or particulate matter with a size less than 10 μm, is relevant for air transport, as any larger particles are less likely to be relevant for long-range transport and

disposition on SCM by the wind. The hydraulic conductivity and porosity of the filter layer in SCM are typically high to facilitate a faster infiltration (Tirpak et al., 2021), which can also enhance the downward migration of microplastics. Furthermore, SCMs are exposed to intermittent infiltration of stormwater or dry-wet cycles, which could accelerate the downward migration of microplastics in the subsurface (Mohanty et al., 2015b; O'Connor et al., 2019). However, a lack of depth distribution data from SCM where microplastics have been accumulated for years precludes our understanding of the vertical migration of microplastics in SCM.

The study aims to evaluate the contribution of atmospheric deposition on the net accumulation of microplastics in SCM and examine the downward mobility potential of the accumulated microplastics. To achieve the objectives, we measured the below and above-ground distribution of microplastics in locations within and outside SCM boundary and fit below-ground distribution data to an exponential retardation model with the median particle size of soil (D_{50}) to evaluate the importance of straining on the removal of microplastics from infiltrating stormwater. The result informs the potential of SCM to serve as a long-term source or sink of microplastics.

5.2. Methods

5.2.1. Soil Sample collection from SCM

To compare the concentration of microplastics within and outside the physical boundary of SCM, we collected soils from fourteen SCM in Los Angeles on May 20th and 21st, 2021 (Figure 5-1), which was more than 2 months after the last recorded rainfall in the area. SCM are categorized for their type and the surrounding environment or land use (Table 5-1). The five location types were: driveways/parking lots, residential areas with single-family homes and low traffic neighborhood streets, commercial areas with medium traffic streets near business establishments, high traffic areas beside freeways, and a natural area beside a river drainage pipe

near clusters of trees and bushes. Locations outside the SCM boundary did not have stormwater inlets and were hydraulically disconnected from the SCM with a distance of 2 to 15 m away from the SCM boundary. Thus, most microplastics found outside the SCM boundary were assumed to be from atmospheric deposition. By comparing microplastics concentrations within and outside the SCM boundary, we evaluated the importance of atmospheric deposition.

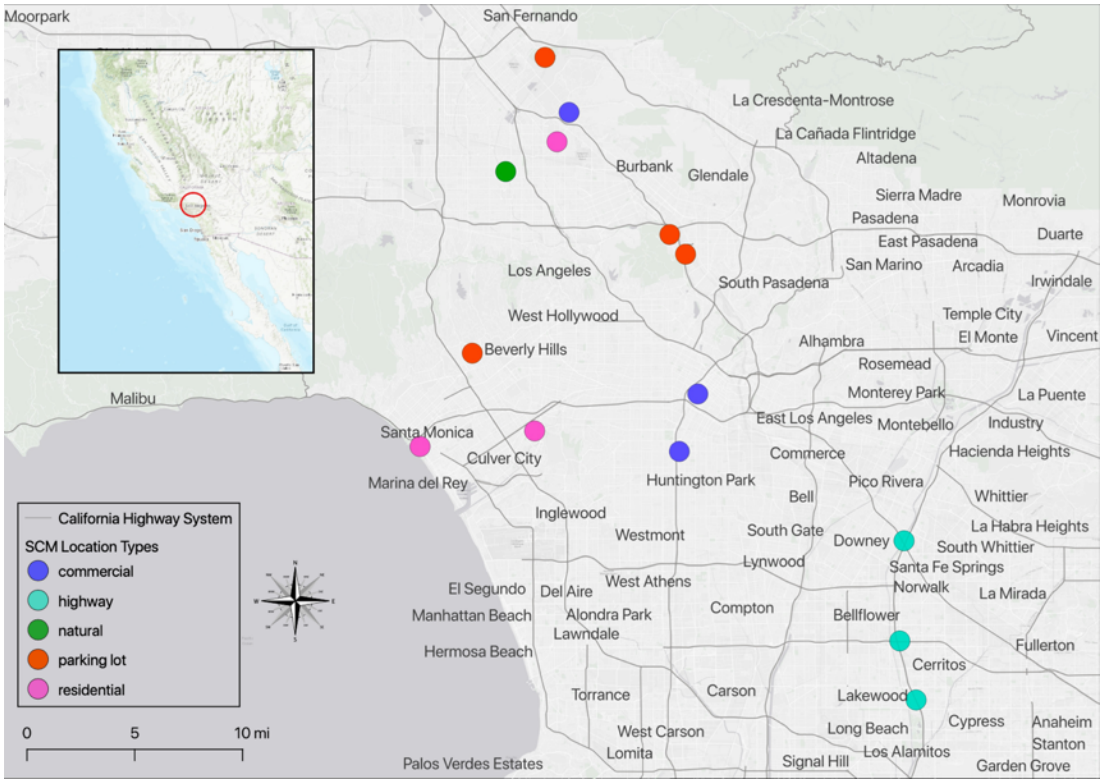


Figure 5-1. Sampling locations in Los Angeles. SCM is colored by the type of location: commercial, high-traffic, natural, parking lot, and residential. The GPS coordinates for each of the SCM are provided in Table 5-1.

The below-ground concentration of microplastics was estimated by collecting soil samples from the surface and subsurface. To collect soil samples, a stainless-steel hand auger with a diameter of 2.5 cm was inserted into the subsurface to a depth of 10 cm at three random spots inside and outside the boundary of SCM. From the auger, soils were extracted by a stainless-steel spatula into aluminum foil from two depths: 0-2 cm (surface) and 8-10 cm (subsurface). Wherever

the soil was impenetrable beyond the top layer due to rocks or hard-packed soil, only surface samples were collected. The core was thoroughly cleaned between sampling to prevent cross-contamination.

Table 5-1. Location and Characteristics of Stormwater Control Measures in Los Angeles sampled in this study.

Site	Name	Location Type	GPS longitude	GPS latitude	Picture of the SCM
A	Elmer Ave	Residential	34.210473	-118.376875	
B	Hansen Dam	Parking lot	34.26691118	-118.3865457	
C	Caltrans Bioswale (Santa Springs)	highway	33.94397523	-118.0969732	

D	Tujunga Wash Greenway	natural	34.190602	-118.4182163	
E	along the highway, Lakewood	highway	33.83741221	-118.0872803	
F	By Artesia Fwy and San Gabriel Freeway (Cerritos)	highway	33.87694412	-118.1003616	

G	Sidewalk bioswales downtown 11th + Hope	commercial	34.04212555	-118.2632089	
H	Glenoaks	commercial	34.2301655	-118.3671678	
I	Atwater Park Restoration	parking lot	34.1354333	-118.273087	

J	LA zoo	parking lot	34.14859972	-118.2859003	
K	Baldwin	residential	34.01744577	-118.3948878	
L	Broadway Greenway Project	commercial	34.00368118	-118.2781737	
M	Bickell Avenue	residential	34.00705466	-118.487221	

N	UCLA plaza	parking/ driveway	34.069516	-118.445083	

To determine the spatial distribution of microplastics at high resolution both under and above ground, one roadside bioswale was sampled extensively. This location was extensively sampled to compare the below-ground concentration profile in soil and above-ground on vegetation canopy. Leaves were collected at different elevations from 0.15 m to 2.5 m from two plant species at one location and wrapped individually in aluminum foil to prevent cross-contamination. To determine the spatial distribution of microplastics on the surface of the soil layer, samples were collected at 1, 2, 3, and 4 meters from the inlet. In addition, four 22.5 cm cores were collected near the inlet of the SCM, and soil samples were extracted from different depths at 2.5 cm increments. To examine how the particle size of subsurface soil can affect the downward migration of microplastics, we measured the particle size distribution of subsurface samples (8-10 cm). A portion of soil from subsurface samples at a site was mixed to create a composite sample, which was first sieved using a 2 mm sieve to remove any gravel. The sieved sample was mixed with water to create a slurry and the size distribution of soil particles suspended in a liquid (aqueous liquid module, ALM) was measured using a laser diffraction particle size analyzer (LS 13320, Beckman Coulter, Inc. CA, USA).

5.2.2. Extraction and quantification of microplastics in soil samples

Microplastics were isolated from soil samples by density separation (Cutroneo et al., 2021). Briefly, 1.0 gram of soil sample was mixed in 40 mL of 1.6 g mL^{-1} KI solution in a 50 mL centrifuge tube, and the mixture was centrifuged at 5000 rpm for 30 minutes to settle heavier soil particles from lighter (density < 1.6 g cm^{-3}) particles that include microplastics and organic debris (Mu et al., 2019). The supernatant was vacuum filtrated to trap floating debris on a filter paper (50 mm Whatman cellulose filter, 0.45 µm pore size), and the residue from the filter paper was diluted by washing off the debris from the first filter paper into a glass beaker using 100 mL of DI water. 10 mL of the samples were pipetted using glass pipettes onto a vacuum filtration setup fitted with a 24 mm glass fiber filter paper with 1.2 µm pore size (Thermo Fisher Scientific). A method blank was obtained where DI water was processed through all the steps to estimate any microplastics introduced from the materials used during the extraction steps.

The concentration of microplastics on the filter paper was quantified by coloring microplastics with Nile Red and counting the colored particles by image processing as demonstrated in many studies (Erni-Cassola et al., 2017; Shim et al., 2016; Tamminga et al., 2017). In this study, we stained the filters containing floating debris with 0.17 mL of 0.5 µg mL^{-1} Nile Red in chloroform solution (Maes et al., 2017) in a glass petri dish and air-dried with a glass cover for 24 hours in the fume hood. Dried filter membranes with floating debris including microplastics were transferred onto glass slides, covered with a glass coverslip to eliminate dust deposition, and imaged using a smartphone-based fluorescence microscope. The smartphone-based microscope includes an optomechanical attachment unit, which consists of four blue light-emitting diodes - LEDs (460-510 nm) powered with an external rechargeable battery, a long pass filter, an external lens, and a sample holder where the glass slide containing the membrane is inserted for imaging

(Figure 5-2). Similar smartphone attachments have been used previously for a variety of applications such as pathogen and bacteria identification and counting (de Haan et al., 2020; Ghonge et al., 2019; Koydemir et al., 2015; Müller et al., 2018). After inserting the glass slide into the sample holder, the LEDs were turned on and an image of the entire membrane was captured with a single shot using the regular application of the smartphone camera with an exposure of ⅕ s, ISO 100, and daylight settings. When the LEDs are turned on, the fluorophores on the microplastics are excited. The emitted light passing through the external lens and the emission filter is collected by the rear camera of the smartphone and converted to an image. This raw format image was then transferred to a PC for image processing with a custom-developed algorithm on MATLAB to automatically detect and count microplastics on the entire membrane (Figure 5-3). The microplastics detection limit was found as 10 µm. When analyzing the images, our analytical variance was ~4% of the mean.

It should be noted that optical detection relies on the sensitivity and selectivity of Nile Red to bind microplastics. Thus, the method is susceptible to all limitations discovered by other studies that have used Nile Red. Some microplastics (such as tire particles) may not have been detected if they do not absorb Nile Red. However, our preliminary study confirmed that our method was able to detect the most common microplastics in the mixture containing compost or mulch, which are the primary source of organics in the biofilter. We did not analyze the size or shape distribution of microplastics detected. The method can detect microplastics as small as 10 µm due to a large field of view of 490 mm^2. The largest size observed in our study is 2.25 mm.

Figure 5-2. The prototype used for imaging of the membranes with microplastics samples

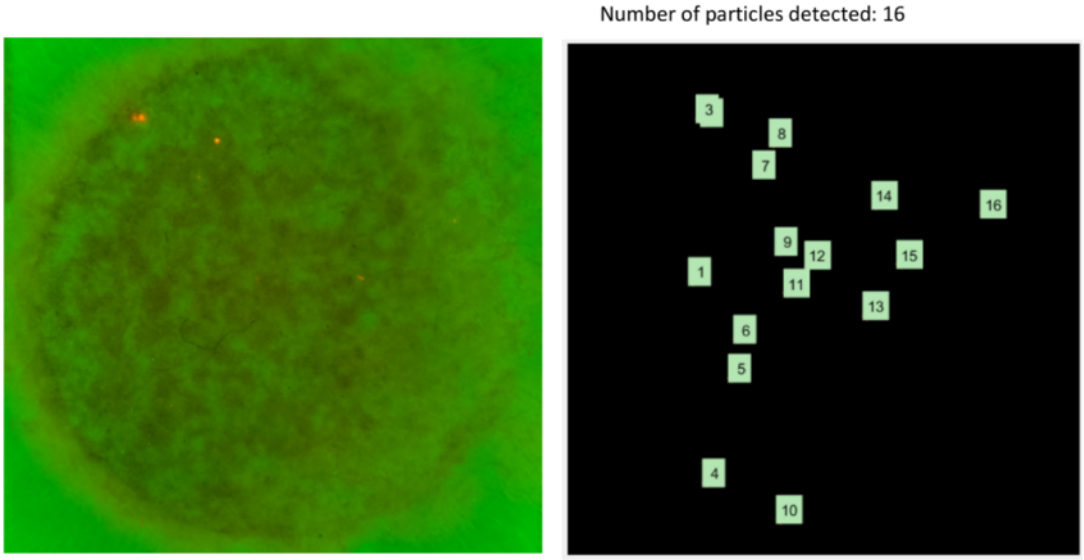


Figure 5-3. Images of a membrane, contaminated with microplastics and the count from the MATLAB algorithm.

5.2.3. The concentration of microplastics on leaves

To quantify the number of microplastics per unit surface area of leaves, collected leaves were cut using metal scissors into a rectangular shape so that surface area could be measured. The debris from the leaves was washed with 100 mL of DI water into a glass beaker, and each leaf was sonicated inside the respective beaker in 100 mL of water for 30 min. After sonication, the

microplastics suspension was vacuum filtrated onto a 24 mm G4 glass fiber membrane. The membranes were then dyed with Nile Red and dried as described above. Blank or pre-washed leaves were also dyed to ensure there are no fluorescent particles on the leaves without microplastics.

5.2.4. Quality assurance and quality control

For sampling, storage, and processing, pre-washed non-plastic containers were used. All clean glassware and containers were rinsed with DI water three times. The DI water was analyzed for possible microplastic contamination. Triplicate samples from 14 sites were collected to get a wide distribution of data. Each sample was mixed thoroughly, and a representative 1 gram of each of those samples was analyzed for microplastics concentration. A total of 140 environmental soil samples were analyzed including replicates. No field blanks were collected as the samples were taken from the subsurface using clean tools. We have performed laboratory blanks to account for any cross-contamination. In addition, during every day of analysis, a method blank was run, following the same lab procedure as sample analysis. The mean laboratory blank for sediment samples was 5 pieces and the mean for leaf samples was 6 pieces (Table 5-2). The mean of laboratory blanks for each method was subtracted from the measured concentration of samples to account for any microplastics introduced from any material used. We performed a recovery test using our method, where water samples containing a known number of microplastics were processed (Table 5-3). The test resulted in an average recovery rate of 93.7% ± 13.7% (Table 5-4). To check how different processing steps influence the quantification result, two variability tests were performed. Human processing variation was found to be 6.8% of the mean, and the sample processing variation was 9.1% (Table 5-4). Therefore, the total maximum error for each of the microplastic measurements was estimated to be 22.2%.

Table 5-2. Laboratory blank data for each sampling day.

Sample	Microplastics detected	Volume Analyzed
DI Water Blank	0	100 ml
Sediment Procedure Blank	6	40 ml
Sediment Procedure Blank	5	40 ml
Sediment Procedure Blank	10	40 ml
Sediment Procedure Blank	14	40 ml
Sediment Procedure Blank	8	40 ml
Sediment Procedure Blank	0	40 ml
Sediment Procedure Blank	4	40 ml
Sediment Procedure Blank	3	40 ml
Sediment Procedure Blank	4	40 ml
Sediment Procedure Blank	2	40 ml
Sediment Procedure Blank	3	40 ml
Sediment Procedure Blank	2	40 ml
Sediment Procedure Blank	5	40 ml
Leaf Procedure Blank	7	100 ml
Leaf Procedure Blank	3	100 ml
Leaf Procedure Blank	8	100 ml
Avg Sediment Procedure Blank	5.08	40 ml
Avg Leaf Procedure Blank	6.00	100 ml

Table 5-3. Microplastics recovery and methodology variations tests

Sample	Picture	Analyzed by	Microplastics Count	Microplastics Expected
Sample 1	1	Person 1	7	10
Sample 1	2	Person 1	10	10
Sample 2	1	Person 1	22	24
Sample 2	2	Person 1	25	24
Sample 3	1	Person 1	34	30
Sample 4	1	Person 1	180	200
Sample 4	2	Person 1	198	200
Sample 4	3	Person 1	193	200
Sample 5	1	Person 1	94	100
Sample 5	2	Person 1	107	100
Sample 5	3	Person 1	98	100
Sample 1	1	Person 2	6	10
Sample 1	2	Person 2	7	10
Sample 2	1	Person 2	21	24
Sample 2	2	Person 2	20	24
Sample 3	1	Person 2	33	30
Sample 4	1	Person 2	184	200
Sample 4	2	Person 2	188	200
Sample 4	3	Person 2	197	200
Sample 5	1	Person 2	99	100
Sample 5	2	Person 2	109	100
Sample 5	3	Person 2	90	100

Table 5-4. Results of microplastics recovery and methodology variations tests

Microplastics Recovery Rate	93.7% ± 13.7%
Human Processing Variation	7%
Sample Processing Variation	9.10%

5.2.5. Subsurface microplastics retention profile

Microplastics removal can be modeled similarly to the removal of colloids or sediments. Large articles (> 5 µm) are typically removed by settling or straining, and removal of particles larger than 10 µm is dominated by straining as they are blocked by narrow pores. The typical pore size in biofilter is around 30 µm and the minimum size microplastics that can be detected were of 10 µm size, we assumed straining to be the dominant mechanism and thus used an empirical equation with an exponential function, similar to (Gao et al., 2021): $C(z) = C_0 e^{-K z}$, where C and C_0 are microplastic concentrations ($p\ g^{-1}$) at depth *z (cm)* and on the surface respectively, and *K* is the retardation coefficient. Thus, K is estimated by the fitting depth and concentration data into the model. The retardation coefficient is different from the commonly used retardation factor, which is estimated by comparing the velocity of water with the velocity of contaminant based on the breakthrough curves. In our case, breakthrough curves were not obtained due to the complete filtration of microplastics in the biofilter. Thus, estimated K includes absorption, straining, gravity settling, and removal by any other mechanism. Microplastics are expected to be removed by physical filtration or straining, where the removal or straining rate can increase with increasing colloid size and decreasing median grain size (D_{50}) (Bradford et al., 2003). The exponential model was verified at one site, and the same was assumed for other sites. The assumption is based on the result of a previous study that found that microplastic penetration depth is sensitive to the ratio of the size of microplastics and grain diameter in biofilter and that 10 µm or larger microplastics would have shallow penetration depth in porous media relevant for stormwater biofilter (Waldschläger and Schüttrumpf, 2020). As the size detection limit of microplastics in our study is 10 µm, our observation is limited to larger (>10 µm) microplastics. Thus, caution should be

maintained when extrapolating our results to smaller microplastics (< 1 μm), which can be more mobile.

5.2.6. Statistical analysis

To calculate the statistical difference in concentration of microplastics in and outside the SCM, a Wilcoxon rank-sum test was performed (R version 4.0.0), with ∗ notation signifying p-value < 0.05, ∗∗ meaning p-value < 0.01 and ns showing the data is not statistically significant. We use a linear model (lm function in R) to estimate the standard error. The 95% confidence interval was estimated by using t-statistics.

5.3. Results

5.3.1. Microplastic concentrations inside and outside of SCM are similar

The spatial distribution of microplastics within and outside of SCM reveals that the concentration of microplastics within the SCM boundary is similar ($p > 0.05$) to the concentration outside the boundary (Figure 5-4). Microplastic concentrations in samples varied between 0 to 2784 particles per gram of soil (p g^{-1}) based on location and depth of soil. In particular, the concentration decreased with subsurface depth in all locations. Concentration in surface samples was significantly higher than the concentration in subsurface samples irrespective of the locations: within or outside SCM boundary. The mean microplastic concentration outside SCM was 283 p g^{-1} for the top surface and 82 p g^{-1} for subsurface samples. Inside SCM, the mean concentration was 472 p g^{-1} for the top surface and 149 p g^{-1} for subsurface samples.

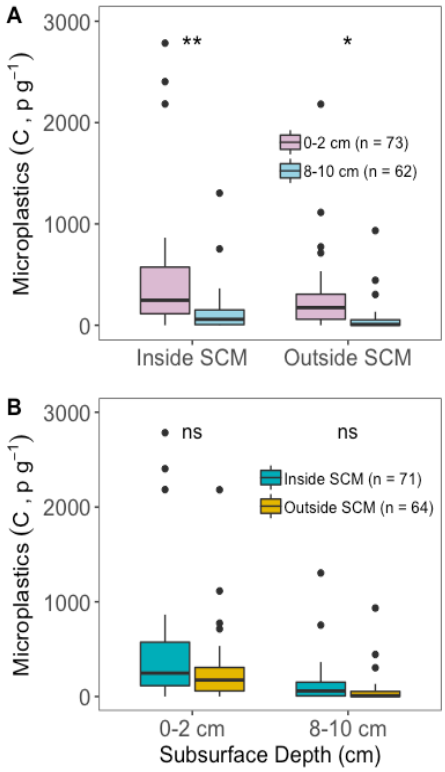


Figure 5-4. (A) Microplastics concentration inside and outside SCM at two depths, 0-2 cm and 8-10 cm from 14 locations in Los Angeles. (B) Microplastics concentration of samples collected at two depths (0-2 cm and 8-10 cm) is plotted against the location of the sample: inside and outside SCM. Statistical difference was calculated using the Wilcoxon rank-sum test, $*$ p-value < 0.05, $**$ p-value < 0.01, ns not statistically significant. n is the number of samples analyzed.

5.3.2. Subsurface microplastic concentration decreases exponentially with depth

Analysis of microplastic concentration at five depths at one SCM reveals that microplastic concentration decreases exponentially with depth (Figure 5-5). Based on the exponential fit with the mean concentration of microplastics at different depths, we estimated the mean retardation coefficient K at this location to be 0.13. K value from the whole data set is 0.18 with a standard error of 0.64 and a 95% Confidence Interval from 0.11 to 0.50.

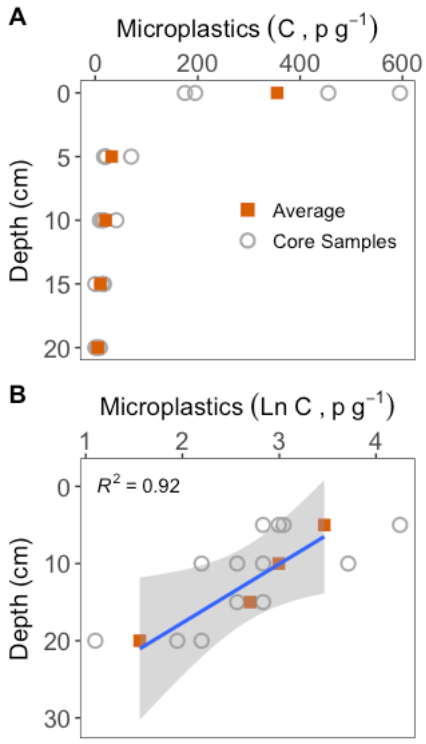


Figure 5-5. (A) Microplastics concentrations from four core samples collected at site by depth. Average values per depth are shown in orange shaded squares. (B) Relationship between the natural log of concentration and depth. The linear fit equation is $\boldsymbol{ln(C) = 4.32 - 0.13z}$ with $R^2 = 0.92$, where z is depth in cm and C is concentration in particles per gram. Gray shading is showing the 95% confidence interval for the linear fitting.

5.3.3. Plant leaves around SCM contained a high concentration of microplastics

Leaves collected at different heights from the ground contained high concentrations of microplastics ranging from 0 to 66 p cm^{-2} (Figure 5-6). The concentration on leaves initially increased with height, reaching maximum values around 1.5 m above the ground. Above this height, an increase in height decreased the concentration of microplastics.

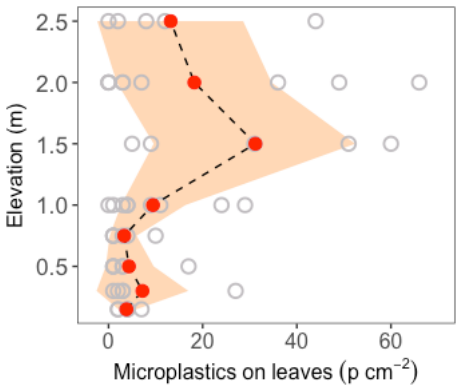


Figure 5-6. Microplastics concentrations on leaves were collected at varying heights around SCM by the driveway/parking, with red dots showing the average and the orange shading showing the 95% confidence interval for the concentration at each height.

5.3.4. Retardation coefficients are similar between location types.

Assuming an exponential decrease in the concentration of microplastics with depth in all other locations, we calculated retardation coefficients (K) for all locations and the retardation coefficients were independent of location type or land use (Figure 5-7A). To check if the median particle size (D_{50}) affects the retardation coefficient, as it does for straining coefficient (Bradford et al., 2003), we compared the correlation of retardation coefficient with D_{50} inside and outside SCM. With an increase in soil particle size (D_{50}), retardation coefficient decreases outside the SCM, indicating filtration or straining is the dominant retention mechanism outside SCM. In contrast, inside SCM, no such correlation was observed (Figure 5-7B).

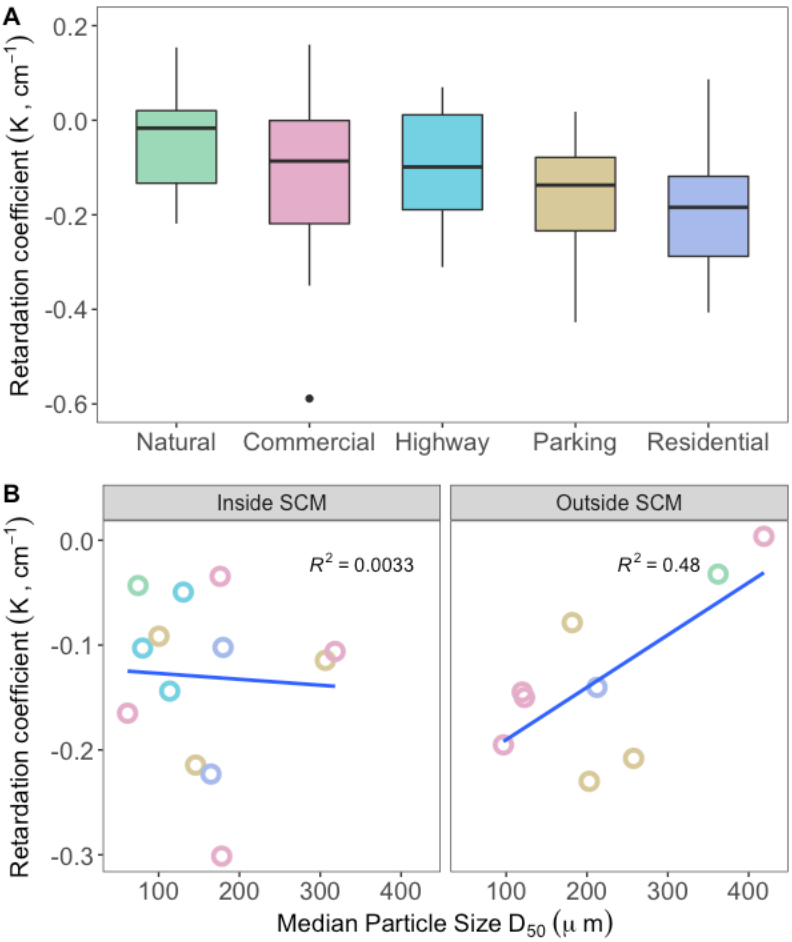


Figure 5-7. (A) Graph of retardation coefficient (K) for each of the samples by location type, (B) Graph of median particle size D50 versus average retardation coefficient K for each of the collected samples, colored by the location type.

5.4. Discussion

5.4.1. Microplastics are retained within the top 5cm of subsurface

Vertical profiles of microplastic concentrations in SCM reveal that SCM is effective in filtering most microplastics from stormwater, and the majority are retained within the top 5 cm layer (Figure 5-4). The trend is consistent in locations outside the SCM, indicating subsurface soil is an effective barrier to filter microplastics from runoff and could prevent groundwater pollution with microplastics. The result is expected based on the previous understanding of particle mobility in the subsurface soil: particles greater than 10 µm are expected to be filtered out in soil by settling

and straining or physical filtration (Bradford et al., 2003; Chu et al., 2019; Tong et al., 2020; Waldschläger and Schüttrumpf, 2020). However, microplastics accumulated on the surface can become disintegrated by UV radiation (Song et al., 2017a; Weinstein et al., 2016) or biodegradation (González-Pleiter et al., 2019; Kalogerakis et al., 2017), releasing much smaller microplastics that may have higher mobility (Pelley and Tufenkji, 2008; Sirivithayapakorn and Keller, 2003) than the ones detected in most studies. Furthermore, microplastics are of different shapes such as rod, fragment, and sphere, which can influence their transport (Huilian Ma et al., 2020; Waldschläger and Schüttrumpf, 2020). Future studies should examine the influence of microplastic shapes on their mobility in stormwater treatment systems.

We estimated the retardation coefficient in all locations assuming an exponential decrease in the concentration of microplastics with depth. We also observed that the mean retardation coefficient in SCM is slightly lower than the mean retardation coefficient outside of SCM (Figure 5-8A), indicating some microplastics are more likely to transport deeper into the subsurface in SCM than outside SCM. We attributed this to the pore size distribution of subsurface media and the infiltration rate of stormwater. Infiltration-based SCM typically uses sand or sandy soil, which has a higher porosity and hydraulic conductivity than the native soil (Tirpak et al., 2021). However, D_{50} outside SCM was slightly higher than inside SCM although not statistically significant (Figure 5-8B). Thus, it is expected that the microplastics will move deeper into the subsurface in SCM than they would outside SCM. Furthermore, microplastic transport in subsurface soil can be enhanced by intermittent infiltration of stormwater (Mohanty et al., 2015b), which typically occurs in SCM. Recent studies show that dry-wet cycles accelerate the downward migration of microplastics (Gao et al., 2021; O'Connor et al., 2019), although most microplastics are found within a depth of up to 7.5 cm even after extensive weathering and dry-wet cycles (O'Connor et

al., 2019; Rillig et al., 2017). In our study, the SCM are 5 years or older and have been subjected to various weathering cycles, and have accumulated microplastics for many years. Thus, we assume that the concentration profile is at a semi-steady state. Overall, our results show that the top 5 cm of soil in SCM removes microplastics from stormwater and potentially prevents groundwater pollution. However, this finding could have other unexplored consequences. For instance, accumulated microplastics can adsorb pollutants from stormwater (Aghilinasrollahabadi et al., 2021) and become suspended by wind, thereby posing an inhalation risk (Borthakur et al., 2021a). In addition, a high concentration of microplastics in the top 5 cm of subsurface where roots are concentrated could affect biochemical processes in the root zone (de Souza Machado et al., 2018; van Weert et al., 2019b). Thus, future studies should quantify the impact of accumulated microplastics on the functions of SCM.

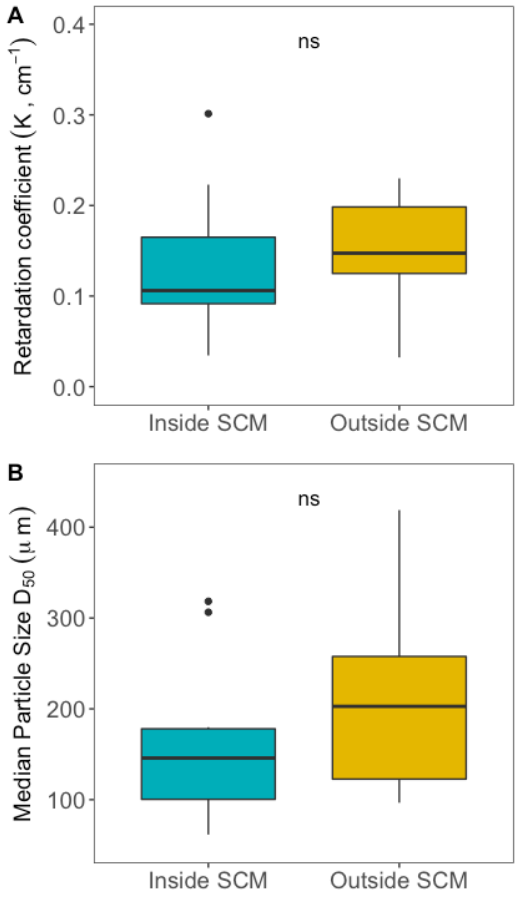


Figure 5-8. (A) Retardation Coefficient K (cm^{-2}) for samples collected inside and outside the SCM. (B) Soil particle size (D_{50}) for samples collected inside and outside of the SCM boundary.

5.4.2. Straining is the dominant removal mechanism for microplastics outside SCM

Filter medium composition, particularly particle size distribution, varies widely in the SCM (Tirpak et al., 2021), which can affect the removal of microplastics or their downward mobility. In this study, we compared how the retardation coefficient changes with mean particle size (D_{50}) both inside and outside SCM. An increase in retardation coefficient with a decrease in D_{50} of soil outside SCM indicates that straining is a dominant removal mechanism for microplastics in subsurface soil (Figure 5-7A). Straining is particularly expected for large particles, where the passage of particles through narrow pores is blocked (Auset and Keller, 2006; Bradford et al.,

2006). There is no exception for microplastics. The size detection limit of this study is nearly 10 μm. SCM are typically composed of sandy soil with a mean pore radius of 32 μm (Ding et al., 2019), indicating microplastics in the same size range can be filtered out by straining. Unlike soil, coarse sand could permit the passage of large microplastics due to large pore size. Analyzing sediment size distribution in influent and effluent of model biofilter packed with the sand column, a previous study found that nearly 99% of the sediments with size 10 μm were filtered out by straining (Valenca et al., 2020). For the same reason, the penetration depth of 10 μm size microplastics was observed to be below 10 cm (Waldschläger and Schüttrumpf, 2020). Thus, we assumed that the probability of microplastics passing through the entire filter layer is very small. The retardation coefficient did not decrease with an increase in particle size of filter media in SCM (Figure 5-7B). The results suggest that the concentrations of microplastics in deeper layers of SCM are higher than that predicted by the exponential retardation model. There could be several reasons for this discrepancy. First, SCM are typically designed by using mulch, compost, or other organic amendments that may contain microplastics (Watteau et al., 2018; Weithmann et al., 2018). Thus, the microplastics found in deeper layers may have been introduced by the amendments used during the installation of the SCM. Second, bioturbation could play a significant role in moving nanoplastics in SCM via injection (Heinze et al., 2021) and microplastics via the preferential flow paths created by earthworms (Yu et al., 2019). The extent of these processes in different SCM could vary. Third, the infiltration rate in the SCM is high to prevent overland flow, which could facilitate the relocation of microplastics from the surface layer into deeper layers if pore sizes are bigger than microplastic size. Previous studies demonstrated enhanced transport of colloids or particles with an increase in flow rate through porous media (Kretzschmar et al., 1999). A similar process could also enhance the transport of microplastics in SCM. Most SCM are designed by

replacing soil with sand to increase hydraulic conductivity (Tirpak et al., 2021), which could increase relative pore size and enhance the transport of small microplastics. In our study, we could not distinguish whether enhanced transport in filter media or pre-contamination from filter media is the cause of a relatively high concentration of microplastics in deeper subsurface layers. Thus, future studies should screen the typical amendments for microplastic contamination before their use in the SCM and examine the subsurface distribution profile of microplastics after many years of stormwater infiltration.

5.4.3. The atmosphere is a significant source of microplastics accumulated in SCM

Understanding the source and the processes by which microplastics may accumulate in SCM can help assess whether SCM can become a long-term source of microplastics for groundwater pollution and be an effective strategy to prevent retribution of microplastics in the environment. While it is typically assumed that stormwater is the dominant source of microplastics found in SCM, our study shows that contribution of atmospheric deposition is just as important. Although the mean microplastic concentration appears to be higher inside SCM than outside of SCM, the difference is not statistically significant (Figure 5-4). Thus, despite receiving more stormwater runoff, SCM did not accumulate more microplastics than the location outside SCM. This result indicates that stormwater is not the only source of microplastics accumulated in the SCM, and atmospheric deposition, both wet and dry, is also a significant source of microplastics in urban areas. This result confirmed the finding of another study where field blanks were found to have a high concentration of microplastics (Smyth et al., 2021). Atmospheric dry deposition is particularly significant in dry climates (Abbasi and Turner, 2021). The Los Angeles area, where the sampled SCM are located, does not receive regular or frequent rainfall, which could result in SCM receiving lower amounts of stormwater than the SCM located in wet climates (Sadeghi et

al., 2019). Thus, most microplastics deposited on land could be via dry deposition or wind, which occurs throughout the year. Transport of waterborne microplastics is event-based and is associated with intense rainfall, while deposition of airborne microplastics is continuous throughout the year. Thus, we surmise that continuous deposition of microplastics in dry seasons throughout the year may have overshadowed any high amount of microplastics deposited in sporadic runoff events. One may argue that flooding after high-intensity rainfalls could redistribute microplastics beyond the SCM by overflow (Daly et al., 2012; Sanders and Grant, 2020). In many of the sampling sites in our study, however, the locations outside the boundary are at a higher elevation, above the curb, where floodwater would rarely reach.

Our result indicates that atmospheric deposition or wind-blown microplastics could be a significant source of microplastics accumulated in SCM. The presence of microplastics on leaves of vegetation around SCM further confirmed this hypothesis. Dust can be deposited on leaves via dry deposition (falling off from the sky), interception of wind (horizontal transport), or rain splash from the ground surface (Gonzales et al., 2018). The same processes are also relevant for the transport and deposition of airborne microplastics. If dry deposition is the dominant process, the concentration of microplastics should be higher on leaves at high elevations. In contrast, we found that the concentration on leaves was lower at the 2.5 m height and was the highest at 1.5 m height (Figure 5-6). The size of microplastics, similar to any other airborne particles, could dictate the relative importance of different atmospheric transport mechanisms (Raupach et al., 2001). Small airborne particles are transported mainly by deposition rather than rain splash, while larger particles are typically moved vertically due to horizontal transport within the 1–2 m range, where we found the highest concentrations of microplastics. The same processes are relevant for airborne microplastics. Thus, the variation in microplastic concentration on canopy near SCM could be a

result of changes in wind flow patterns induced by the canopy (Beckett et al., 2000) and from the variation in trapping efficiency of the different vegetation types (Chaudhary and Rathore, 2018; Sæbø et al., 2012; Wang et al., 2013). These differential velocity patterns can result in the differential deposition of particles at different heights along with the canopy (Gonzales et al., 2018).

5.5. Conclusions

Analyzing the distribution of microplastics in and around SCM at fourteen locations in Los Angeles we show that microplastic concentrations inside and outside of SCM are not statistically different, indicating that, in addition to stormwater, the atmospheric deposition could be a dominant source of microplastics in urban areas. A high concentration of microplastics in vegetation around SCM confirmed this theory. The results reveal the importance of wind transport and dry deposition on the accumulation of plastics in urban areas, which have implications on the source proportion of microplastics at any location. Thus, an accurate inventory of microplastics accumulated in SCM must account for both stormwater and atmosphere as sources of microplastics. Irrespective of the source of accumulated microplastics in SCM, most microplastics were trapped in the top 5 cm subsurface layers of the SCM, and their concentration exponentially decreased with depth. The retardation coefficient, which was estimated from the exponential fitting parameter, increased with a decrease in median particle size (D_{50}) of subsurface soil. This result indicates that straining is the dominant removal process of the microplastics outside the SCM. The retardation coefficient, however, did not change with changes in D_{50} within SCM boundary, indicating pre-contamination of filter media with microplastics and/or enhanced downward transport of microplastics in filter media in SCM may have moved the microplastics deeper into the subsurface. Overall, the study not only offers the first critical analysis of microplastic

concentrations both within and outside of SCM that reveals straining as the dominant removal process in subsurface but also provides evidence confirming the significant contribution of atmospheric deposition on the accumulation of microplastics in SCM. However, there are a few limitations of the study, which are largely derived from the assumptions made in identifying microplastics and using the exponential models. Microplastics identified in the method excluded any plastic particles that do not absorb Nile Red or glow after absorbing the dye. Similarly, the empirical exponential model used here to compare retardation or retention of microplastics between SCM may not be applied to small microplastics (< 1 μm) due to their increased transport without straining. The optical method used in this study has a size detection limit of 10 μm. Thus, the conclusions are applied to microplastics larger than 10 μm.

5.6. References

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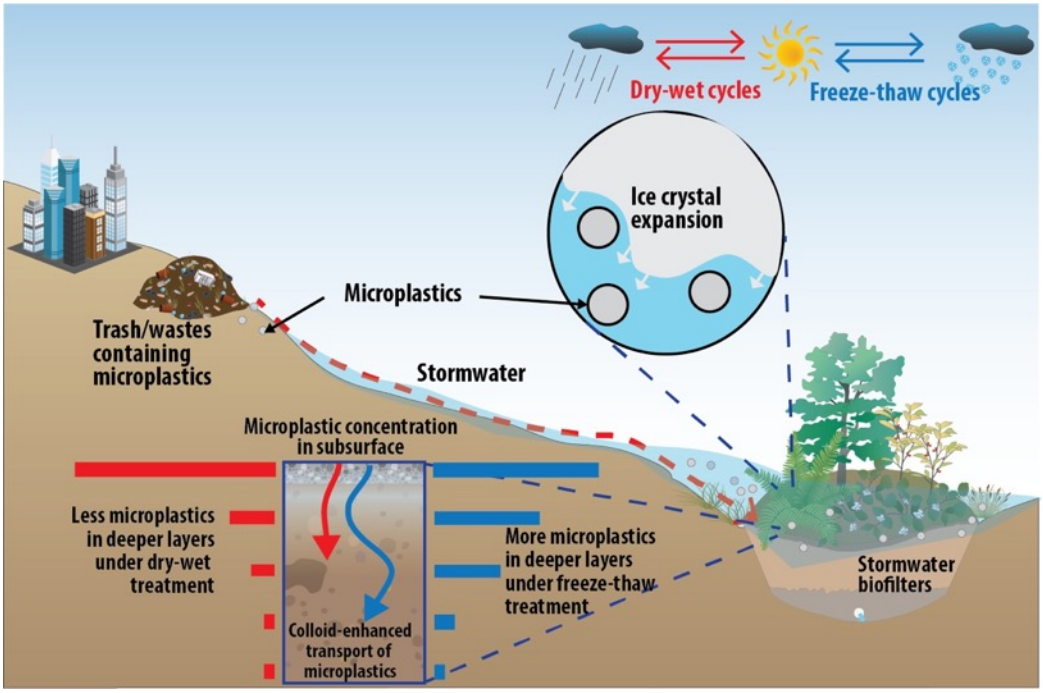
6. CHAPTER 6 – MOBILITY OF POLYPROPYLENE MICROPLASTICS IN STORMWATER BIOFILTERS UNDER FREEZE-THAW CYCLES



Koutnik, V.S., Borthakur, A., Leonard, J., Alkidim, S., Koydemir, H.C., Tseng, D., Ozcan, A.,Ravi, S., Mohanty, S.K. (2022) Mobility of polypropylene microplastics in stormwater biofilters under freeze-thaw cycles. *Journal of Hazardous Materials Letters.* 100048. https://doi.org/10.1016/j.hazl.2022.100048

Abstract

Stormwater biofilters naturally experience dry-wet and freeze-thaw cycles, which could remobilize deposited particulate pollutants including microplastics. Yet, the effect of these natural weathering conditions on the mobility of deposited microplastics has not been evaluated. We deposited microplastics on columns packed with sand or a mixture of sand with soil (25% by volume), subjected them to intermittent infiltration events punctuated by either freeze-thaw cycles or drying cycles. Comparing the vertical distribution of microplastics in biofilters after both treatments, we showed that more than 90% of microplastics were retained within the first 3 cm of filter media but the distribution in deeper layers varied with media type and treatment conditions. Freeze-thaw cycles were more effective than dry-wet cycles in increasing the downward mobility of deposited microplastics. We attributed these results to the disruption of filter media by expanding ice crystals, which could release deposited colloids and associated microplastics. An increase in natural colloid concentration in the effluent following freeze-thaw treatments confirmed the hypothesis. The results are useful in predicting microplastic transport in the root zone in stormwater biofilters or contaminated land experiencing natural freeze-thaw cycles.

6.1. Introduction

Stormwater is one of the major conveyors of microplastics in urban areas (Boni et al., 2021; F. Liu et al., 2019b; Lutz et al., 2021; Werbowski et al., 2021). Stormwater treatment systems such as biofilters remove microplastics similar to sediments or colloids from the stormwater (Gilbreath et al., 2019; Lange et al., 2021b; Smyth et al., 2021) and retain them in the media. However, a fraction of colloids could move downward during intermittent infiltration of stormwater (Mohanty et al., 2015a). Understanding the microplastic transport processes in biofilters can help predict their distribution in the root zone (Yuyue Huang et al., 2021) and the potential of groundwater pollution (Selvam et al., 2021). However, only a few studies have examined the transport of the deposited microplastics in stormwater biofilters (Kuoppamäki et al., 2021; Lange et al., 2021a), and they did not account for weathering treatments such as drying or freeze-thaw cycle that all biofilters experience naturally.

Transport processes relevant for microplastics in stormwater biofilters can be inferred from earlier studies on natural soil colloids or other particulate pollutants (DeNovio et al., 2004). Plastic microspheres have been used as a tracer for pathogens in numerous studies for the last 3 decades (Becker et al., 1999; Burkhardt et al., 2008; Mohanram et al., 2012; Yu et al., 2013). These studies provide insights into the behavior of spherical microplastics in saturated soil under a steady infiltration of water. However, microplastics typically found in stormwater are of irregular shape (Sang et al., 2021; Sutton et al., 2016; Werbowski et al., 2021). Furthermore, the stormwater infiltration events are intermittent, typically followed by drying or freeze-thaw cycles based on seasons. Dry-wet and freeze-thaw cycles have been shown to increase mobilization of natural colloids (Mohanty et al., 2014) and pollutants accumulate in biofilters (Borthakur et al., 2021b; Mohanty and Boehm, 2015). Recent studies found that dry-wet cycles could increase the

penetration depth of microplastics in soil (Gao et al., 2021; O'Connor et al., 2019). In contrast to dry-wet cycles, freeze-thaw cycles could either increase mobility by disrupting the deposited microplastics during the expansion of ice crystals (Mohanty et al., 2014) or decrease mobility by increasing their aggregation (Alimi et al., 2021). Thus, the net effect of freeze-thaw cycles on microplastics transport is unclear.

This study aims to evaluate the effect of freeze–thaw cycles on the mobilization of previously deposited microplastics in biofilter media. We hypothesize that freezing would disrupt filter media, mobilizing deposited microplastics through the filter layer. To test the hypothesis, we subjected pre-contaminated model biofilter columns to intermittent infiltration events separated by drying or freeze-thaw cycles. Microplastic concentrations in the effluent and filter media were analyzed to quantify the effect of freeze-thaw cycles on microplastic mobility.

6.2. Materials and Methods

6.2.1. Microplastics preparation

To obtain irregular-shaped microplastics, polypropylene test tubes were abraded using a mechanical orbital sander. Sanding created irregularly shaped polypropylene (PP) particles such as fragments and fibers, similar to what was found in stormwater (Piñon-Colin et al., 2020a). We chose polypropylene because it is the most common type of microplastic found in stormwater (Lange et al., 2021b). The PP microplastics were uniformly mixed in a glass container to create a homogeneous mixture, of which 0.1 g of microplastics were added to each biofilter later.

6.2.2. Biofilter design

Biofilter media are typically composed of a mixture of sand and soil from the vicinity of the sites to reduce the overall cost (Tirpak et al., 2021). To simulate biofilter design, we used two

types of filter media: sand (20-30 Standard Sand, Certified MTP) and a mixture of sand and soil (25% by volume). The soil was collected from the roadside in Los Angeles and sieved to size between 0.42 mm and 2 mm. Each medium was packed in transparent PVC columns (2.54 cm in diameter and 30 cm in height), where the bottom of the column was filled with glass wool and pea gravel to create a drainage layer. The smaller size columns have been previously used to examine the transport of particulate pollutants (Ghavanloughajar et al., 2021), where preferential flow near the wall was not observed. The sand or soil mixture was packed to a height of 15 cm in 2-3 cm increments to ensure uniform packing. Four columns were packed with each media type for a total of 8 columns (Figure 6-1, Table 6-1). After packing, the columns were saturated with DI water from the bottom to estimate the pore volume based on the weight difference between saturated and dry columns.

Figure 6-1. Photograph of the experimental set up of the biofilter columns in the laboratory.

Table 6-1. Experimental Set Up of the Biofilter Columns

Column #	Media	Weathering Treatment
1	Soil Media	Dry Wet Cycle
2	Soil Media	Dry Wet Cycle
3	Soil Media	Freeze Thaw Cycle
4	Soil Media	Freeze Thaw Cycle
5	Sand Media	Dry Wet Cycle
6	Sand Media	Dry Wet Cycle
7	Sand Media	Freeze Thaw Cycle
8	Sand Media	Freeze Thaw Cycle

6.2.3. Mobility of microplastics by freeze-thaw cycles

The experiments were conducted in 3 phases: conditioning, contamination, and weathering. The purpose of the conditioning phase is to estimate the leaching of background microplastics from the setup by freeze-thaw or dry-wet cycles. In the conditioning phase, 4 pore volumes (PV) or 100 mL of synthetic stormwater (6 mM NaCl in DI water) were applied to the column at a rate of 5 mL min^{-1} using a peristaltic pump. The effluent samples for each column were collected and analyzed for absorbance (Ghavanloughajar et al., 2020) and background microplastics concentration. Then, duplicate columns of each media type were subjected to either drying or freeze-thaw cycles. During freeze-thaw cycles, columns were frozen at -20 ºC for 6 h followed by thawing at 22 ºC for 17 h. To simulate dry-wet cycles, the same types of columns were drained by gravity and air-dried at 22 ºC. The conditioning phase was repeated for 5 injection cycles. During the contamination phase, 0.1 g of polypropylene (PP) microplastics were dry deposited on the top of each column to simulate microplastic accumulation on biofilters for many years. The weathering treatment phase was initiated by subjecting the contaminated columns to either dry-wet or freeze-thaw cycle followed by injection of 4 PV of synthetic stormwater at 5 mL min^{-1} or 0.96 cm min^{-1}. The stormwater application rate was below the hydraulic conductivity of the packed sand (7.3 cm min^{-1}) and soil (2.3 cm min^{-1}) columns, thereby resulting in no overflow

during the experiment. The cycle was repeated at least 40 times, and the effluents were analyzed for UV absorbance and microplastic concentrations after 1, 5, 10, 15, 20, 25, 30, 35, and 40 cycles. To account for any microplastics that were already present in soil or sand before the contamination stage, we packed additional two columns of each type and subjected them to dry-wet or freeze-thaw cycles without adding any microplastics.

All columns were dismantled, and the bottom caps were removed. A steel spatula was used to scrape media from specific depths, starting from the bottom-most depth (near effluent). Samples were collected in aluminum foil from 0.5, 1, 2, 4, 8, and 12-cm depths to measure depth distribution. To quantify the retardation of microplastics in soil with depth, we used an exponential model (Gao et al., 2021): $C(z) = C_0 e^{-K z}$, where C and C_0 are microplastic concentrations (p g^{-1}) at depth z (cm) and on the surface respectively, and K is the retardation coefficient. K includes absorption, straining, gravity settling, and removal by any other mechanism. We compared the K value between columns subjected to dry-wet or freeze-thaw cycles to compare the effect of each type of cycle on the downward mobility of the deposited microplastics.

6.2.4. Analysis of effluent and filter media samples

The particle size distributions of soil media and the polypropylene abrasives were measured using a laser diffraction particle size analyzer (LS 13320, Beckman Coulter, Inc. CA, USA) (Figure 6-2). To compare the colloid concentration mobilized during injection of stormwater following drying or freeze-thaw treatment, effluent water samples were analyzed for absorbance at 890 nm using UV–Vis spectrophotometer (Lambda 365, PerkinElmer). To estimate microplastics concentration in effluent, water samples were first vacuum filtered through 24 mm glass fiber filter membranes with 1.2 µm pore size (Thermo Fisher Scientific), and then 0.17 mL of 0.5 µg mL^{-1} Nile Red in chloroform solution (Maes et al., 2017) was added on filters inside a

glass petri dish. Filters were air-dried with a glass cover and imaged using a smartphone-based fluorescence microscope. The method permits the counting of microplastics that can adsorb Nile Red dyes and doesn't differentiate between different types of plastic polymers. The filters containing particles including microplastics were dyed with Nile Red and dried. Dried filters were transferred onto glass slides, covered with a glass coverslip to eliminate dust deposition and imaged using a smartphone-based fluorescence microscope. The smartphone-based microscope was built with the optomechanical attachment unit, which consists of four blue light emitting diodes - LEDs (460-510 nm) powered with an external rechargeable battery, a long pass filter, an external lens and a sample holder where the glass slide containing the membrane is inserted for imaging (Figure 5-2). Similar smartphone attachments have been extensively used before for a variety of applications such as pathogen and bacteria identification and counting (de Haan et al., 2020; Ghonge et al., 2019; Koydemir et al., 2015). Prior to capturing the image, the LEDs were turned on and the glass slide with the filter paper was inserted into the sample holder. Prior to capturing the image, the settings were checked on the smartphone camera to be: exposure of ⅕ s, ISO 100 and daylight setting. Once ready, the image of the entire membrane was captured with a single shot using the regular application of the smartphone camera while focusing on the particulates in the zoomed view. The raw format image captured of the filter with fluorescent microplastics was then transferred to a PC for image processing with a custom-developed algorithm on MATLAB to automatically detect and count microplastics on the entire membrane (Figure 5-3). Microplastics detection limit of this smartphone-based device with an optical attachment is estimated to be 10 μm. When analyzing the images, our analytical variance was ~4% of the mean.

To estimate the concentration of microplastics in different filter layers, 1 g of oven-dried sample from each depth was analyzed using density separation (Cutroneo et al., 2021). Briefly, 1.0-gram dry filter medium was mixed in 40 mL of 1.6 g mL^{-1} KI solution in a 50 mL centrifuge tube, and the mixture was centrifuged at 5000 rpm for 30 minutes to settle soil or sand particles, leaving the lighter (density < 1.6 g cm^{-3}) particles such as microplastics and organic debris to float on the supernatant surface (Mu et al., 2019). The supernatant was filtered to isolate plastics, stained using Nile Red, and analyzed for microplastics concentration.

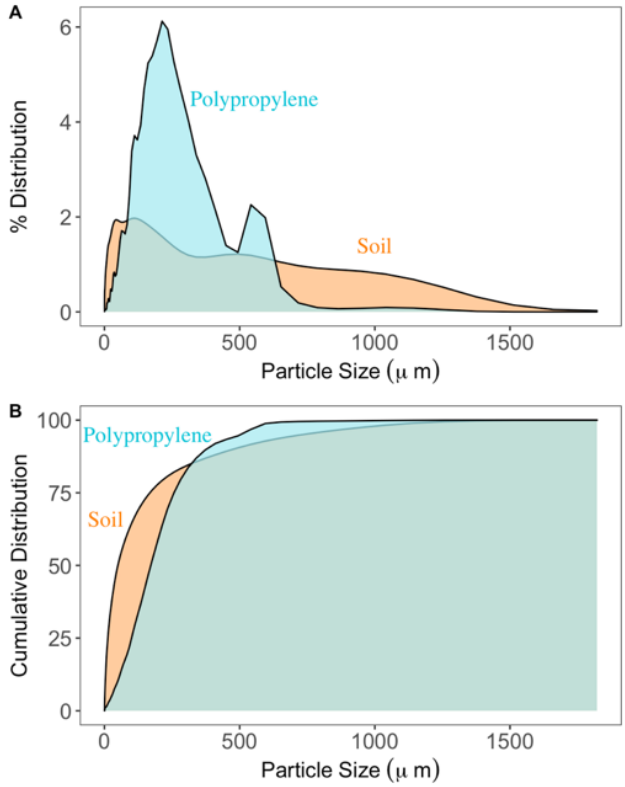


Figure 6-2. Particle size distribution for polypropylene abrasive microplastics and soil by (A) % distribution and (B) cumulative distribution.

The concentrations were reported as the number per L of effluent or g of filter media. To analyze difference and similarity between the measured concentrations between column or treatment types, we performed a Wilcoxon rank-sum test (R version 4.0.0), where ∗, ∗∗, ∗∗∗, and ∗∗∗∗ denote p-values less than 0.05, 0.01, 0.001, and 0.0001 respectively.

6.2.5. Quality assurance and quality control

All lab surfaces were wiped down every day and before and after usage. For sampling, storage, and processing, laboratory glassware was used. All glassware and containers were washed first with soap and water and then rinsed with DI water three times. Glass covers or clean aluminum foil were used to prevent airborne contamination during the sample processing. The filter media was analyzed for microplastics background concentration and this concentration of microplastics at each depth in uncontaminated columns was subtracted from the concentration of microplastics at the same depth in contaminated columns to estimate the true penetration depth of added polypropylene microplastics. The DI water was analyzed for possible microplastic contamination. The contribution of plastic tubing for pumping, PVC plastic columns, centrifuge polypropylene test tubes, and plastic pipette tips to microplastics in samples was estimated using appropriate blanks. In addition, during every day of analysis, a method blank was run, following the same lab procedure. The mean of laboratory blanks for each method was subtracted from the measured concentration of samples to account for any microplastics introduced from procedural steps.

6.3. Results and Discussion

6.3.1. Freeze-thaw cycles enhanced microplastics concentration in deeper subsurface layers

The addition of polypropylene microplastics did not increase the concentration in the effluent, indicating all added microplastics remained inside the columns (Figure 6-3). Freeze-thaw cycle did remobilize microplastics inside the columns and increased the concentration of microplastics in the effluent. The concentration of microplastics in effluent was negligible compared to the number of plastics used to contaminate the biofilters. Freeze-thaw treatment increased microplastic the concentration in the effluent from sand columns, whereas it has no impact with no significant effect on microplastic the concentration in effluent from soil columns

(Figure 6-4). The effluent concentration before and after the addition of microplastics in soil remained on the same level of magnitude.

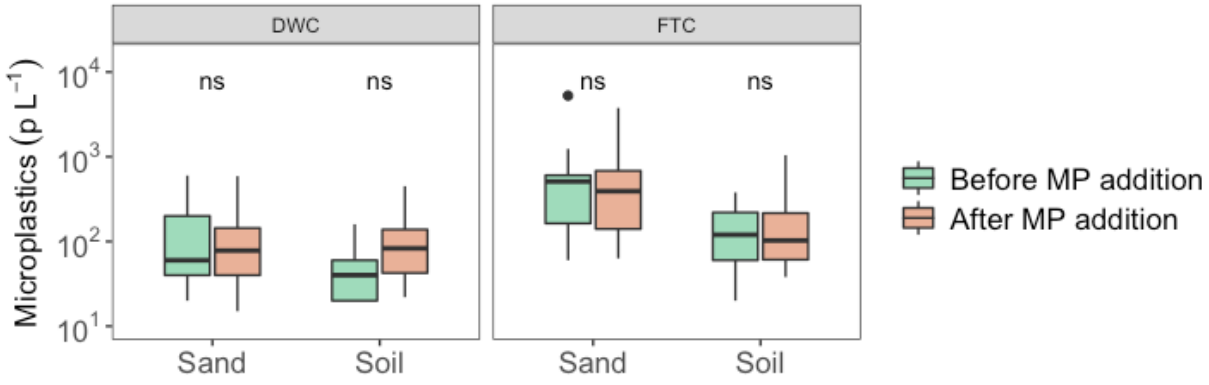


Figure 6-3. The concentration of microplastics before and after the addition of microplastics is not statistically different in the effluent of the columns.

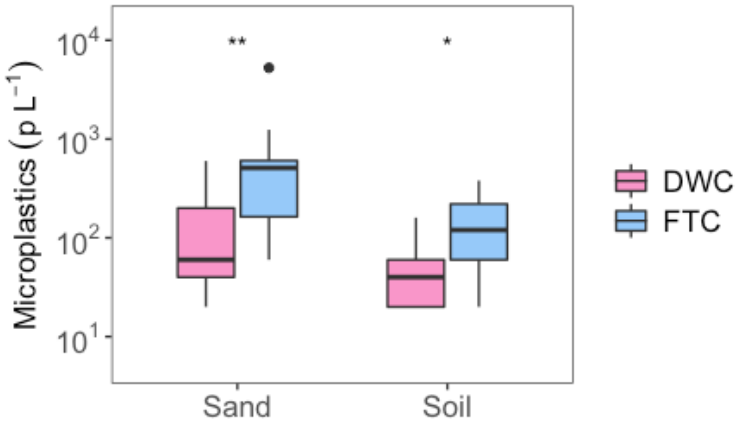


Figure 6-4. Difference of microplastics concentration in the effluent before the addition of microplastics.

In sand columns, the effluent microplastic concentration after freeze-thaw cycles were significantly ($p<0.0001$) higher than the concentration after dry-wet cycles, indicating freeze-thaw cycles was more effective in mobilizing microplastics in sand columns (Figure 6-5). In soil columns, however, the microplastic concentrations after both treatments were similar.

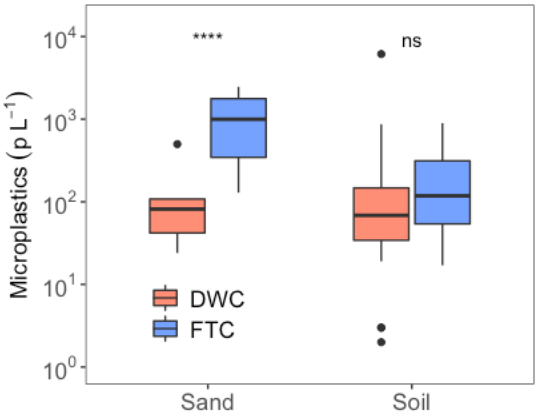


Figure 6-5. Concentration of microplastics in the effluent shown as a comparison between DWC and FTC. Wilcoxon rank-sum test was performed (R version 4.0.0), with $*$ notation signifying p-value < 0.05, $**$ meaning p-value < 0.01 and "ns" showing the data is not statistically significant.

Analyzing the vertical distribution of deposited microplastics, we found that the majority of added microplastics were retained in the top 5 cm (Figure 6-6). In both columns, freeze-thaw cycles increased the concentration of microplastics below the surface layer. After 40 freeze-thaw cycles, the microplastic concentration at 5 cm depth was more than 25% compared to the columns subjected to the drying cycle (Figure 6-6). Microplastics distributions were found to follow an exponential distribution in sand and soil columns after freeze-thaw treatments (Figure 6-7) and did not have a clear relationship after dry-wet cycle (Figure 6-8). Retardation coefficient calculated for the two media types showed no statistically significant difference between weathering treatment (Figure 6-9). The results indicate that freezing and subsequent thawing of pore water in biofilters remobilized the previously deposited microplastics and accelerated their downward migration and that the freeze-thaw cycles were more effective than dry-wet cycles at disrupting the deposited microplastics and moving them downward. We attributed several mechanisms for the accelerated migration of microplastics by freeze-thaw cycles. First, freeze-thaw cycles have been shown to release colloids from soil (Borthakur et al., 2021b) and biofilter amendments (Mohanty and Boehm, 2015). Since microplastics could adsorb onto these colloids or pore walls

containing these colloids, the released colloids could enhance the downward movement of microplastics.

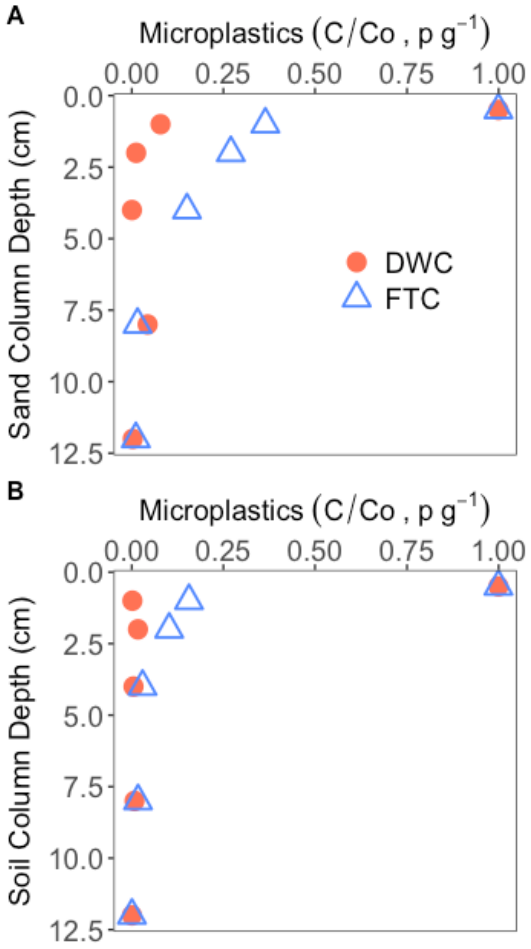


Figure 6-6. Average microplastic concentration (C) normalized to the concentration at the surface (Co) as a function of depths of filter media subjected to freeze-thaw cycles (FTC) and dry-wet cycles (DWC) in (A) sand columns and (B) soil columns.

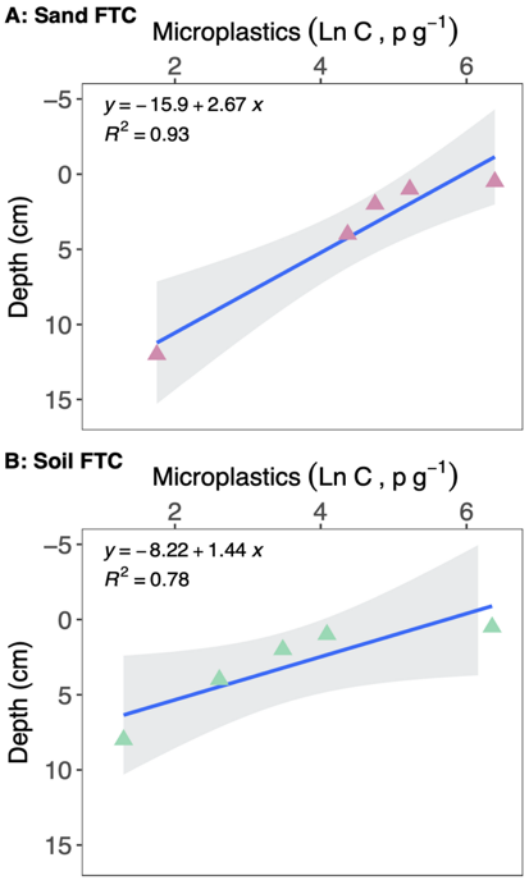


Figure 6-7. Logarithmic depth distribution of microplastics in (A) sand column undergoing FTC, and (B) Soil column undergoing FTC.

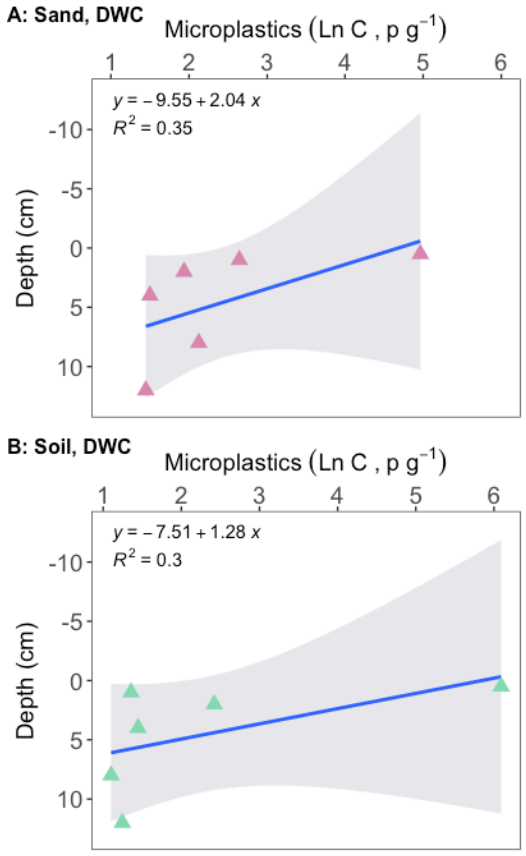


Figure 6-8. Showing the relationship between the natural log of concentration inside the columns and depth where z is depth in cm and C is concentration in particles per gram for (A) Sand column undergoing DWC, (B) Soil column undergoing DWC.

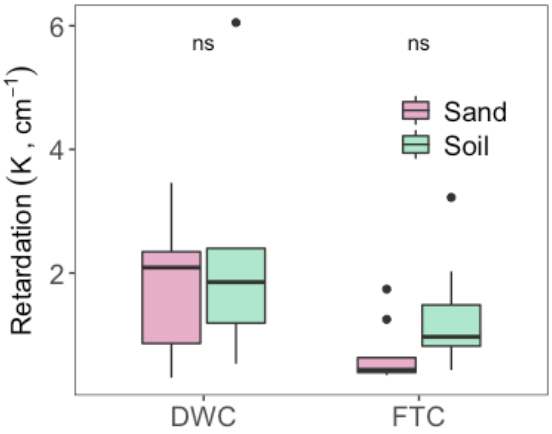


Figure 6-9. Retardation Coefficient of the two media types subjected to FTC and subjected to DWC weathering treatment. Wilcoxon rank-sum test was performed (R version 4.0.0), "ns" showing the data is not statistically significant.

Second, freezing of ice could also exert positive pressure on pore walls and create additional preferential flow paths (Mohanty et al., 2014), thereby easing the passage of microplastics through the biofilter media. Thus, even though most microplastics are retained at the top 5 cm of biofilters, repeated freeze-thaw cycles cause microplastics to migrate further downwards in biofilters. Our result is in contrast with a recent study that showed that FTC could increase the aggregation of nano plastics and decrease their transport (Alimi et al., 2021). In our study, we used microplastics that are at least 10 times larger. Thus, aggregation with other microplastics is less likely compared to nano plastics. Furthermore, any loosely bound microplastics-soil hetero-aggregates could break down under stress exerted by expanding ice crystals during freezing. In this study, we measured the distribution of microplastics after 40 cycles. In each winter season, the surface could experience many more freeze-thaw cycles. Thus, the net effect of freeze-thaw cycles after several years could result in accelerated transport of deposited microplastics deeper into biofilter media. This process would eventually push microplastics downwards into the subsurface. However, exact mechanisms could not be proved in column experiments due to the limitation of the experimental design. Thus, future studies should use direct visualization methods to improve the mechanistic understanding of microplastics' mobility under dynamic freeze-thaw cycles. Furthermore, the transport of colloids in porous media is known to be affected by the density of colloids (Waldschläger and Schüttrumpf, 2020). Thus, we expect that the results may vary for other types of microplastics with different densities.

6.3.2. The cause of enhanced microplastic mobility by freeze-thaw treatment is disruption of filter media and release of colloids

Freeze-thaw cycles resulted in an increase in the leaching of colloids, mostly non-plastic particles, through the columns (Figure 6-10). The colloid concentration in the effluent was higher

following freeze-thaw treatment than drying treatment. SEM images of the effluent confirmed a higher concentration of colloids in the effluent of sand and soil columns following freeze-thaw treatments than drying treatments (Figure 6-10, Figure 6-11). This is in agreement with an earlier study that observed that freeze-thaw cycles released twice as many colloids as dry-wet cycles (Mohanty et al., 2014). Intermittent infiltration events followed by drying typically disrupt air-water interfaces that bind some colloids. Thus, a collapse of the air-water interface during wetting events could mobilize these released colloids into pore water (Flury and Aramrak, 2017; Shang et al., 2008), from where they can move downward assuming microplastic transport is not restricted by the size of flow paths. On the other hand, freeze-thaw cycles could release colloids from the biofilter media by expanding ice crystals that fracture the pore walls (Mohanty et al., 2014) and release pollutants in association with soil colloids (Borthakur et al., 2021b). In our study, colloids and microplastics could be attached to each other forming heteroaggregates. Ice expansion during freezing can break those aggregates if ice pushes them through the pores in each cycle. An increase in the number of freeze-thaw cycles could push these colloids and microplastics downwards into deeper layers in the biofilters.

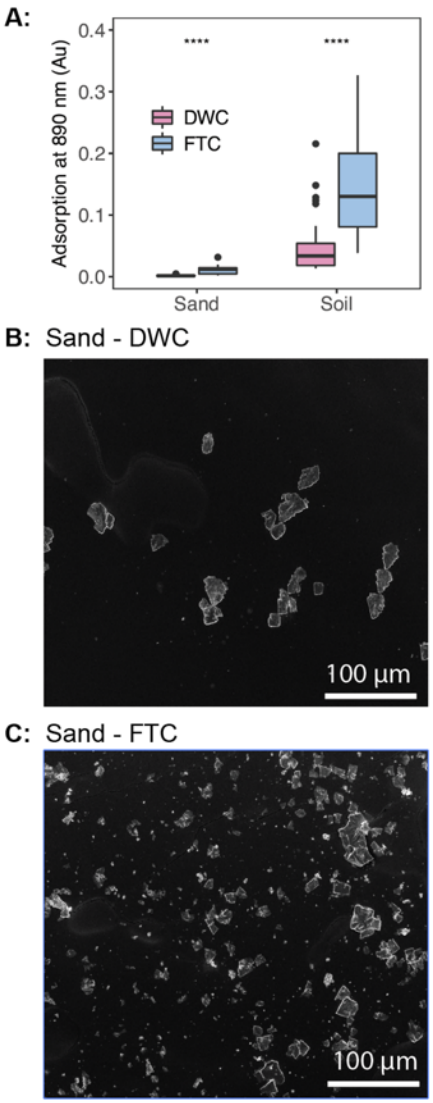


Figure 6-10. (A) Adsorption at 890 nm of the effluent samples, (B) SEM image of the colloid selected for EDS analysis from the effluent sample of a sand column without freeze-thaw cycles, and (C) after freeze-thaw cycles. Wilcoxon rank-sum test was performed (R version 4.0.0), with **** notation signifying p-value < 0.0001.

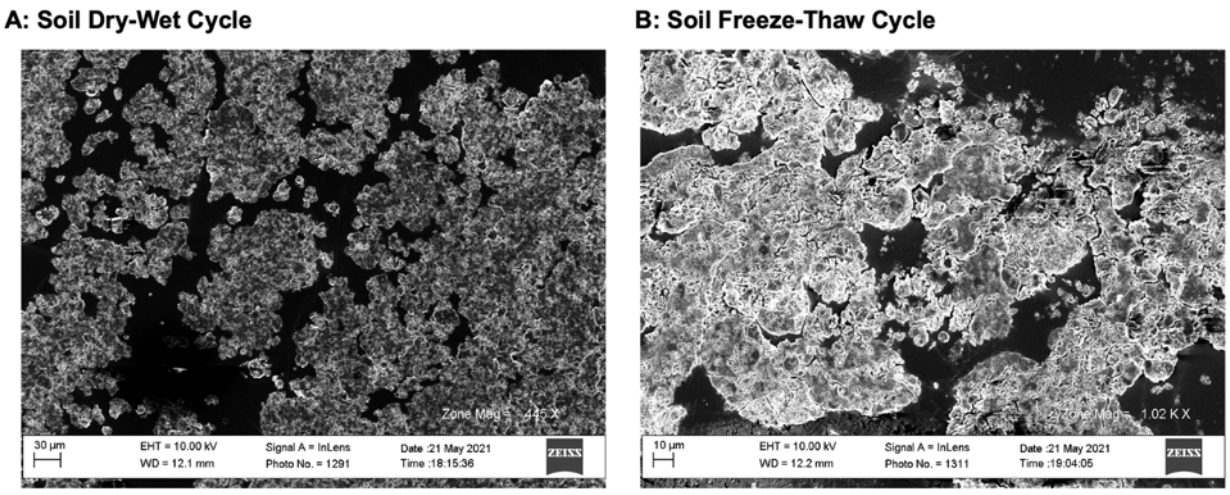


Figure 6-11. SEM image of the colloid selected for EDS analysis from effluent sample from (A) soil column without freeze-thaw cycles and (B) after freeze thaw cycle.

In our study, sand columns released fewer colloids than soil columns. The sand medium was composed of quartz particles of size ranging between 0.65 mm to 0.85 mm. Thus, it is difficult for the freeze-thaw cycles to break up the quartz particles to generate < 1 µm size colloids. On the other hand, the soil is composed of a variety of siliceous and carbonaceous minerals of various sizes such as sand, clay, silt, and even organic matter in a homogeneous mixture (Graham and O'Geen, 2010; Schulze, 2002). Our results show that the effect of freeze-thaw cycles on microplastic mobility was amplified in sand biofilters despite releasing fewer colloids than soil columns. We attribute the results to limited transport of microplastics through soil columns where the pore size could be smaller than that in sand-only columns. The colloids released are predominantly within 2 µm whereas the microplastics used were larger than 10 µm. Thus, microplastics were more restricted in their mobility than soil colloids where pore paths are narrower.

6.3.3. FTC cycle effect on microplastic mobility is more pronounced in biofilters with more sand

Biofilter media composition such as sand content could vary between stormwater treatment systems to achieve different infiltration capacities (Tirpak et al., 2021). Our study shows that the impact of freeze-thaw cycles on the downward mobility of the deposited microplastics is more prominent in sand-only biofilters than the biofilters containing sand and soil mixture (Figure 6-6, Figure 6-7). We attributed the results to the inability of microplastics to move through inter-particle gaps between sand grains if soil particles block the pore paths. Based on the particle size distribution of microplastics, around 75% of microplastics were larger than 100 μm and more than 98% of particles were larger than 10 μm. The typical pore size in biofilter media is 32 μm (Ding et al., 2019), indicating most of the added microplastics have low mobility due to straining. The pore size in sand columns was expected to be larger than the pore size in soil columns. Thus, the mobility of microplastics was more pronounced in the sand column. Although soil columns release more colloids than sand columns (Figure 6-10), large microplastics appear to be effectively filtered by biofilters with soil. The result indicates that the presence of soil in biofilters limits the mobility of microplastics by simply blocking the pore paths. Thus, freeze-thaw cycles would have a more prominent effect on microplastic mobility in filter media where transport is not limited by flow path size. Overall, the result indicates that media choice could play an important role in preventing the downward transport of microplastics irrespective of weathering treatments.

6.3.4. Environmental implications

Our results confirmed that most microplastics are likely retained in the top layer of biofilters from where they slowly migrate downward during intermittent infiltration of stormwater. As stormwater contains metals and organic pollutants that can also bind with accumulated

microplastics (Aghilinasrollahabadi et al., 2021; T. Wang et al., 2020). If most of the microplastics remained on the surface, they can be re-entrained into the atmosphere by wind (Rezaei et al., 2019) and pose inhalation risk (Borthakur et al., 2021a; Gasperi et al., 2018). While other studies on biofilters reported net removal of microplastics by measuring influent and effluent concentration of microplastics(Gilbreath et al., 2019; Lange et al., 2021b; Smyth et al., 2021), our study examined the fate of the microplastic removed or their slow migration within biofilters. Our results show that microplastics penetration depth in biofilters is sensitive to weather conditions. That is, compared with dry-wet cycles, freeze-thaw cycles would likely increase the downward mobility of microplastics in biofilters. This is particularly relevant because most parts of the terrestrial surface in the northern hemisphere experience freeze-thaw cycles. We used only polypropylene microplastics to demonstrate the effect of freeze-thaw cycles on the downward mobility of microplastics. The results are expected to be similar for other microplastics of similar density. Microplastic density could vary between 0.96 to 1.4 (Koutnik et al., 2021b) with some lighter and other heavier than water. Thus, future studies should examine the effect of density on microplastics' downward mobility. The size distribution of added microplastics in our study is large. In the field, they could be smaller than 2 μm and thus could be more mobile. Thus, the penetration depth of smaller microplastics could be much higher than observed in this study(Waldschläger and Schüttrumpf, 2020).

6.4. Conclusions

We measured depth distribution of microplastics in model biofilters loaded with microplastics on the top surface after subjecting the biofilters to dry-wet or freeze-thaw cycles and found that nearly all PP microplastics were retained. Comparing the penetration depth between biofilters subjected to dry-wet cycles and freeze-thaw cycles, we showed that freeze-thaw cycles

increased the penetration depths, and this effect was more prominent in biofilters with more sand content. This is particularly significant considering most added microplastics were larger than the mean pore size expected in biofilters. We attributed these results to the disruption of media aggregates by expanding ice crystals during freezing and the release of microplastics along with colloids during the thawing process. Overall, the results of the effect of freeze-thaw cycles in winter on the distribution of microplastics should be accounted for in order to accurately predict the extent of downward mobility of microplastics in soil or stormwater biofilters.

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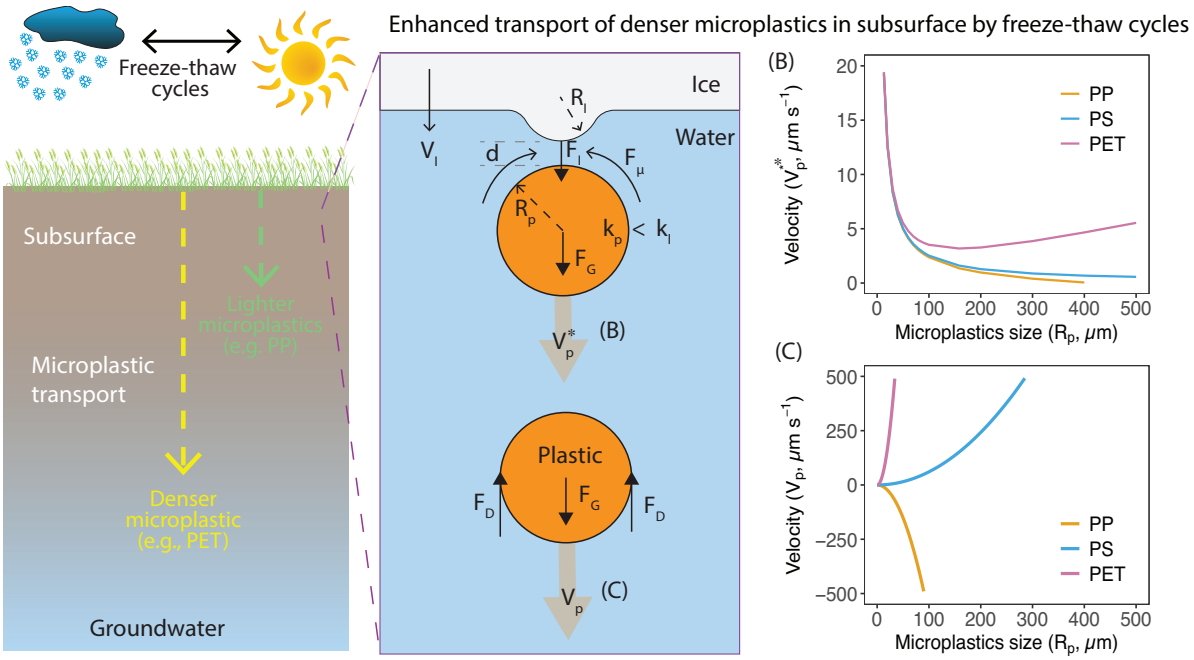
7. CHAPTER 7 – MICROPLASTIC TRANSPORT IN THE SUBSURFACE BY OSCILLATING ICE-WATER INTERFACE: CRITICAL ROLE OF THE PLASTIC DENSITY



Koutnik, V.S., Leonard, J., Brar, J., Cao, S., Glasman, J.B., Cowger W., Ravi S., Mohanty, S.K. (202X) Microplastic transport in the subsurface by oscillating ice-water interface: Critical role of the plastic density. *Environmental Science and Technology*. [In review March 2022]

Abstract

Subsurface soils accumulate most of the microplastics from surface runoff, but some microplastics can be remobilized by natural freeze-thaw cycles. Yet, it is unclear whether or how microplastic properties could affect the extent to which the oscillating ice-water interfaces transport microplastics into the subsurface. We deposited microplastics with densities smaller, similar, and greater than water on the top of sand columns and subjected them to intermittent infiltration events punctuated by freeze-thaw cycles. The distribution of microplastics in vertical water columns with and without porous media confirmed that freeze-thaw cycles could disproportionally accelerate the downward mobility of denser microplastics. We used a force balance approach to estimate the downward velocity of microplastics near and far from the moving ice interface. The analysis reveals that smaller microplastics (<50 μm) are pushed at higher velocity by the ice-water interface, irrespective of the density of microplastics. However, density becomes critical when the size of microplastics becomes larger than 50 μm. The coupled experimental studies and modeling effort improved the understanding of why denser microplastics such as PET and PVC may move deeper into the subsurface and consequently elevate groundwater pollution risk.

7.1. Introduction

Terrestrial soil surface and subsurface are major sinks of microplastics in the environment (Li et al., 2021; Nizzetto et al., 2016; Scheurer and Bigalke, 2018) from where they can either move deeper into the ground (Viaroli et al., 2022) or be transported away by wind (Bullard et al., 2021; Rezaei et al., 2019) or stormwater (Piñon-Colin et al., 2020; Werbowski et al., 2021). In particular, stormwater biofilters remove most microplastics from stormwater, (Gilbreath et al., 2019; Lange et al., 2021; Smyth et al., 2021) which is a major conveyor of microplastics in the terrestrial environment (Boni et al., 2021; Lutz et al., 2021; Werbowski et al., 2021). These accumulated microplastics could have several health and environmental impacts (Li et al., 2022; Prata et al., 2020). For instance, airborne microplastics could pose inhalation health risks (Prata, 2018) due to their suspension via wind in agricultural land (Borthakur et al., 2021a), where contaminated biosolids have been applied (Crossman et al., 2020; Koutnik et al., 2021a). Microplastics retained in the subsurface could affect root systems and crop productivity (Chen et al., 2022; Huang et al., 2021; Khalid et al., 2020). Nano- and microplastics could carry some of the pollutants into groundwater aquifers if their mobility in the subsurface is not retarded (Samandra et al., 2022; Zhou et al., 2022). Thus, it is critical to understand the processes that affect the mobility of microplastics in subsurface systems.

Accumulated microplastics in the surface or subsurface environment could disintegrate into smaller particles by photochemical or bio-degrading processes (Sørensen et al., 2021; Zumstein et al., 2018) and move downward during intermittent infiltration of stormwater (Gao et al., 2021; Koutnik et al., 2022a; Mohanty et al., 2015; O'Connor et al., 2019). Subsurface soil naturally experiences dry-wet and freeze-thaw cycles, which could increase the transport of the deposited microplastics (Dong et al., 2022; Gao et al., 2021; Koutnik et al., 2022a; O'Connor et

al., 2019). Compared to numerous studies that have examined the mechanism of particle transport by dry-wet cycles (Borthakur et al., 2021b; Gu et al., 2018; Mohanty et al., 2015; O'Connor et al., 2019; Seiphoori et al., 2020), fewer studies have examined the mechanism of particle transport by freeze-thaw cycles (Alimi et al., 2021; Koutnik et al., 2022a; Mohanty et al., 2014). Freeze-thaw cycles could either increase microplastic mobility by disrupting the deposited microplastics during the expansion of ice crystals (Mohanty et al., 2014) or decrease the mobility by increasing their aggregation (Alimi et al., 2021). Both aggregation or transport in pore water or porous media depends on particle properties such as density, size, and surface properties (Bennacer et al., 2013; Bradford et al., 2003, 2002; Zhang et al., 2014). Yet, none of the previous studies on microplastics examined whether and how the properties of microplastics could affect their mobility by oscillating the ice-water interface during freeze-thaw cycles.

Many studies have examined the dynamics of colloids at freezing interfaces (Asthana and Tewari, 1993; Azouni et al., 1997; Hattori et al., 2020; Körber et al., 1985; Lin et al., 2020; Rempel and Worster, 2001, 1999; Saint-Michel et al., 2017; Shangguan et al., 1992; Tyagi et al., 2020), and they can help explain the behavior of microplastics in subsurface subjected to freeze-thaw cycles. During freeze-thaw cycles, colloids in pore water could experience three types of forces: gravitational force owing to particle size and density, buoyancy owing to the density of the water displaced by the submerged particle, and the interfacial force exerted by moving ice-water interfaces when the interface comes close to within few nanometer distances of the colloid (Azouni et al., 1997; Spannuth et al., 2011; Tyagi et al., 2020). The interfacial force can be sensitive to colloid surface properties (Körber et al., 1985; Shangguan et al., 1992; Thompson and Wettlaufer, 1999). The resulting force balance determines the velocity of colloids near ice font. At a close distance (~ few nm) between the particle and ice front, the drag force also changes due to the

movement of water molecules from bulk to the interface, where the curvature of the ice surface near the particle could change based on the thermal conductivity of the particle (Rempel and Worster, 2001). Microplastics are insulators with thermal properties different from water. The particle thermally shields the local interface underneath the particle, creating a cooler spot where the ice interface grows faster to create a convex protuberance that prevents the engulfment of microplastics (Asthana and Tewari, 1993). Thus, convex protuberance could push microplastics and accelerate their mobility in the subsurface (Asthana and Tewari, 1993). Consequently, the transport of microplastics by these forces could depend on the density, thermal and surface properties of microplastics. Thus, their mobility by freeze-thaw cycles could vary with density and other properties. Yet, no study to date has examined the effect of microplastic size and density on their mobility in porous media under freeze-thaw cycles.

We examine how the density of microplastics could affect their mobility in the subsurface subjected to freeze−thaw cycles. We hypothesize that freeze-thaw cycles could disproportionately move denser microplastics downward. To test the hypothesis, we quantified the mobility of microplastics with different densities in water columns with and without porous media during freeze-thaw cycles. Comparing the difference in the depth distribution of microplastics following many freeze-thaw cycles, we demonstrate that freezing disproportionately affects the mobility of microplastics denser than water. Using the force balance on microplastic near the ice interface, we estimated how the transport velocity of microplastics could change as a function of plastic size and density. The results could help predict the fate of microplastics in subsurface or stormwater biofilters subjected to freeze-thaw cycles.

7.2. Materials and Methods

7.2.1. Microplastics preparation and characterization

We selected three polymers based on their densities lower than (polypropylene or PP, $\rho_{PP} = 920\ kg\ m^{-3}$), similar to (polystyrene or PS, $\rho_{PS} = 1{,}015\ kg\ m^{-3}$), and greater than (polyethylene terephthalate or PET, $\rho_{PET} = 1{,}350\ kg\ m^{-3}$) the density of water ($\rho_W = 1{,}000\ kg\ m^{-3}$ at 12 ºC) (Koutnik et al., 2021b). These three plastic types are commonly used in single-use plastic products and have been extensively found in natural environments (Koutnik et al., 2021b). To create irregular-shaped microplastics, plastic objects made from one of the three types of polymers were abraded using a mechanical orbital sander (Figure 7-1), following the method described elsewhere (Koutnik et al., 2022a). Sanding created irregularly shaped microplastic particles such as fragments and fibers, similar to what has been found in stormwater (Piñon-Colin et al., 2020).

Figure 7-1. Creation of microplastics using an orbital sander with an attachment to catch created particles.

Microplastics were characterized for their size distribution, shape, and for polymer types using Thermo Scientific Nicolet™ iN10 Fourier Transform Infrared spectroscopy (FTIR) in the reflectance mode. First, the microscope was calibrated using an in-house reference standard of high-density polyethylene to ensure that the device was functioning in a reproducible way. Then, sample particles were placed onto a clean gold-coated slide and dispersed with ethanol. A particle map of ~1 cm^2 area was analyzed using the particle analysis wizard included in the PICTA™ software (Brahney et al., 2020). A portion of the particle map with even particle spacing and a low amount of overlapping particles was selected for FTIR analysis to yield individual spectra for each particle. Default image analysis settings were used in the particle wizard to differentiate particles from the gold slide. Spectra were measured using a resolution of 0.124 cm^{-1} and 1 scan, over a spectral range of 4000 - 675cm^{-1}. The background was collected immediately after the samples at a reference point made of reflective gold. Spectra were automatically converted to absorbance intensities from reflectance in the software. To identify particle composition and frequency of various polymers, the collected spectra were compared across all available commercial libraries. The OMNIC correlation routine was used to compare each particle to the reference database. The criteria for reporting a match in the spectra libraries was set to a 15% match score. Matches were confirmed if above 60%.

FTIR microscope can identify the size distribution of microplastics based on image analysis of particles within 1 cm^2 area with a limited number of particles dispersed in that area. Under the current setting to scan 1 cm^2 area on the slide, the iN10 could not reliably detect microplastics' size and shape below 20 µm diameter. Thus, we also used the laser diffraction method to analyze the size distribution of microplastics at a wider range (0.1 µm to 2 mm). Briefly, the particle size distributions of three microplastics polymer types were measured using a laser

diffraction particle size analyzer (LS 13320, Beckman Coulter, Inc. CA, USA). As dispersion of microplastics in water can be difficult due to density difference, dry microplastics were injected into the analyzer where the Tornado Dry Powder System dispersed the dry microplastics in the chamber where the diffracted laser beams were analyzed to calculate the particle size distribution assuming a spherical equivalent of the microplastics. Thus, the size distribution obtained by this method does not provide information related to the shape of the microplastics. To analyze the size distribution of microplastics at a wider size range (0.1 μm to 2 mm), we used a laser diffraction particle size analyzer (LS 13320, Beckman Coulter, Inc. CA, USA), where dry microplastics were dispersed by the Tornado Dry Powder System in the chamber where the diffracted laser beams from microplastics were analyzed.

7.2.2. Sand filter design

Quartz sand (20-30 Standard Sand, Certified MTP) was packed in transparent PVC columns (2.54 cm in diameter and 30 cm in height) to create model biofilters for the simulation of microplastic transport in porous media filters, similar to a previous study (Koutnik et al., 2022a). Briefly, sand was packed in 2-3 cm increment layers to a total filter media height of 15 cm above the bottom drainage layer that consisted of glass wool and pea gravel. The columns were saturated with DI water from the bottom, and the pore volume was estimated based on the weight difference between saturated and dry columns. A total of 20 columns were packed to compare the mobility of 3 types of microplastics by either dry-wet (control) or freeze-thaw treatment. Triplicate columns were used per one type of microplastics per treatment (Table 7-1).

Table 7-1. Experimental setup of sand columns using different plastic types and treatment conditions.

No. of columns	Microplastic added	Treatment type
3	PET	Dry-wet cycle
3	PET	Freeze-thaw cycle
3	PS	Dry-wet cycle
3	PS	Freeze-thaw cycle
3	PP	Dry-wet cycle
3	PP	Freeze-thaw cycle
1	No plastic	Dry-wet cycle
1	No plastic	Freeze-thaw cycle

7.2.3. Distribution of microplastics in the water column without porous media during freezing

Microplastic suspensions were prepared by mixing a specific amount of each of the three microplastics in 100 mL of DI water in a 1L pre-cleaned glass bottle. The suspension was poured into pre-washed transparent PVC columns, which were placed in a freezer at -15 ºC at an up-right position overnight for 18 h. The frozen columns were placed in a warm water bath for 1-2 min to melt ice near the wall and loosen the ice core. The ice core was laid on an aluminum foil and sliced into segments of 3 cm in length with a heated iron knife. Each segment was melted in a clean glass bottle and weighed before filtering the water samples through a 24 mm G4 glass fiber filter paper with 1.2 µm pore size (Thermofisher Scientifc, 09-804-24C) to isolate microplastics in each ice core segment.

7.2.4. Transport of microplastics in saturated sand columns by freeze-thaw cycles

The transport experiments were conducted following the method outlined elsewhere (Koutnik et al., 2022a). Briefly, packed sand columns were conditioned to remove any colloids or

particulates by injecting 4 pore volumes (PV) or ~100 mL of synthetic stormwater (6 mM NaCl in DI water) at 5 mL min^{-1} using a peristaltic pump. The effluent samples for each column were collected and analyzed for background microplastic concentration (ranging from 0.01 p mL^{-1} to 0.18 p mL^{-1}). To simulate microplastic accumulation on biofilters for many years (Koutnik et al., 2022a), 0.1 g of each polymer type of microplastics was deposited on the top of 6 columns, of which 3 columns were subjected to drying treatment (control) and the other 3 columns were subjected to freeze-thaw cycle treatment. The weathering treatment phase was initiated by subjecting the contaminated columns to either dry-wet or freeze-thaw cycle followed by the injection of 4 PV of synthetic stormwater at 5 mL min^{-1} or 0.96 cm min^{-1} for 20 min. The stormwater application rate was below the hydraulic conductivity of the packed sand (7.3 cm min^{-1}) columns, thereby resulting in no overflow during the experiment. To simulate freeze-thaw treatment, columns were frozen at -20 ºC for 6 h and thawed at 22 ºC for 17 h. To simulate dry-wet treatment, the columns were drained by gravity and air-dried at 22 ºC for 23 h. The cycles were repeated 36 times, and the effluents were analyzed for microplastic concentrations after 1, 8, 15, 22, 26, 31, and 36 cycles to estimate potential breakthroughs in deposited microplastics. To account for any microplastics that were already present in the sand before the contamination stage, uncontaminated sand columns were subjected to dry-wet or freeze-thaw cycle treatments, and effluents were analyzed for microplastics.

At the end, all columns were dismantled to sample sand from different depths from specific depths (0.5, 1, 2, 3, 4, 5, 8, 12 cm), starting from the bottom-most depth (near effluent). As straining is the dominant removal process of microplastics, the depth distribution was fitted to an empirical equation (Eq. 7-1):

$$\boldsymbol{C(z) = C_0 e^{-Kz}} \qquad \text{(Eq. 7-1)}$$

where $C(z)$ and C_0 are microplastic concentrations ($p\ g^{-1}$) at depth z *(cm)* and on the surface respectively, and K is the retardation coefficient. Thus, K is estimated by the fitting depth and concentration data into the model and includes effects of absorption, straining, gravity settling, and removal by any other mechanism.

7.2.5. Analysis of effluent and filter media samples

To isolate microplastics from effluent, water samples were vacuum filtered through 24 mm glass fiber filter membranes with 1.2 µm pore size (Thermo Fisher Scientific), and the filtered microplastics were stained by adding 0.17 mL of 0.5 µg mL^{-1} Nile Red in chloroform solution on filters inside a glass petri dish (Koutnik et al., 2022b). Filters were air-dried with a glass cover and imaged using a smartphone-based fluorescence microscope (Koutnik et al., 2022b). The method permits the counting of microplastics that can adsorb Nile Red dyes and does not differentiate between different types of plastic polymers. To estimate the concentration of microplastics retained at different depths of the sand filters, 1 g of oven-dried sand sample was mixed in 40 mL of 1.6 g mL^{-1} KI solution in a 50 mL centrifuge tube, and the mixture was centrifuged at 5000 rpm for 30 min to settle sand particles, leaving the lighter (density < 1.6 g cm^{-3}) particles including microplastics to float on the supernatant surface (Mu et al., 2019). The supernatant was filtered to isolate plastics, stained using Nile Red, and analyzed for microplastic concentration as described earlier. The concentrations were reported as the number per L of effluent or g of filter media. To analyze the difference and similarity between the measured concentrations between contaminated plastic or treatment types, we performed a Wilcoxon rank-sum test (R version 4.0.0).

7.2.6. Quality assurance and quality control

All lab surfaces were wiped down every day and before and after usage. Samples were collected, stored, and processed using pre-washed laboratory glassware. All glassware and containers were washed with soap and water and then rinsed with DI water three times to remove any background microplastics. Glass covers or clean aluminum foil were used to prevent airborne contamination during the sample processing. Uncontaminated filter media was analyzed from each column depth for any background concentration of microplastics, which was subtracted from the concentration of microplastics at the same depth in contaminated columns to estimate the true penetration depth of added microplastics. The DI water used in this study was analyzed for possible microplastic contamination. The contributions of microplastics from plastic tubing for pumping, PVC plastic columns, centrifuge polypropylene test tubes, and plastic pipette tips were estimated using appropriate blanks. During every day of analysis, a method blank was run, following the same lab procedure. The mean of laboratory blanks for each method was subtracted from the measured concentration of samples to account for any microplastics introduced from procedural steps.

7.3. Results

7.3.1. Characterization of microplastics used

The grinding of plastic objects resulted in particles with a range of shapes and sizes. FTIR analysis confirmed that more than 97% of the particles analyzed matched with the plastic polymer designated in the plastic object (Figure 7-2A-C). The shape of the microplastics varied widely from fiber (aspect ratio > 3) to fragment shape (Figure 7-2D-F). Between 11-20% of the particles created were fibers (Figure 7-3). The size distribution of the plastic mixtures varied by plastic types (Figure 7-2G-I). 54% of the PS microplastics were sized between 100 - 250 μm, whereas a similar

majority for PET and PP were sized between 50 - 100 µm. A laser diffraction analyzer recorded a slightly different size distribution than that observed using an FTIR microscope (Figure 7-4).

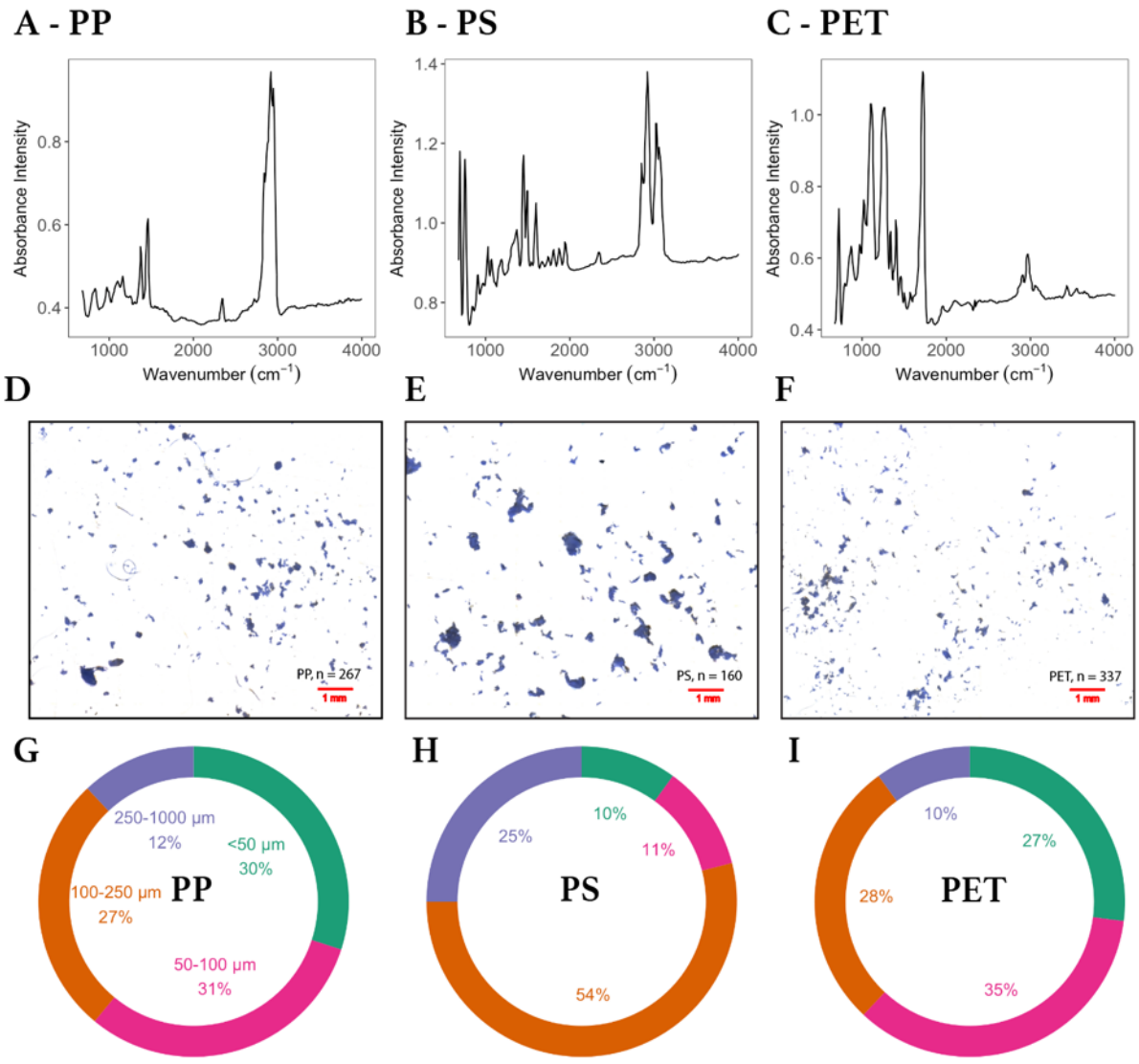


Figure 7-2. Size distribution of the microplastics used in the experiment. Plastic types were identified using FTIR spectra (A-C). The shapes and sizes of each plastic type were estimated using images from the microscope (D-F). The size distribution of microplastics varied based on polymer types (G-I).

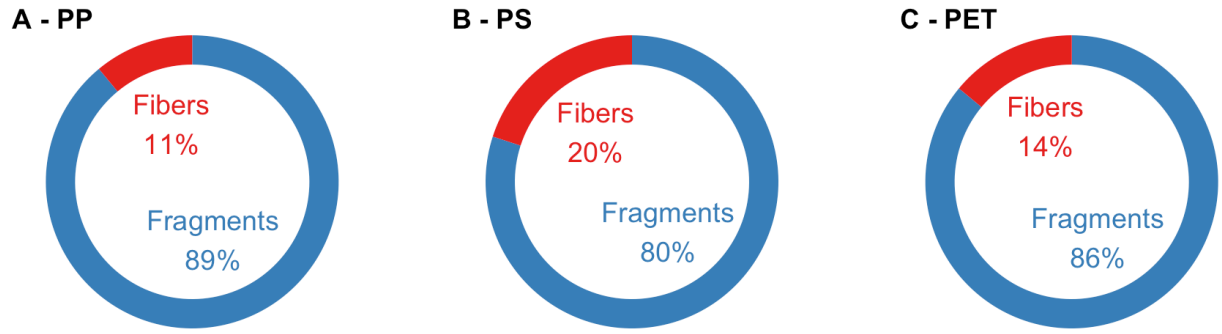


Figure 7-3. The shape distribution of the plastics used in the experiment for (A) PP, (B) PS, (C) PET.

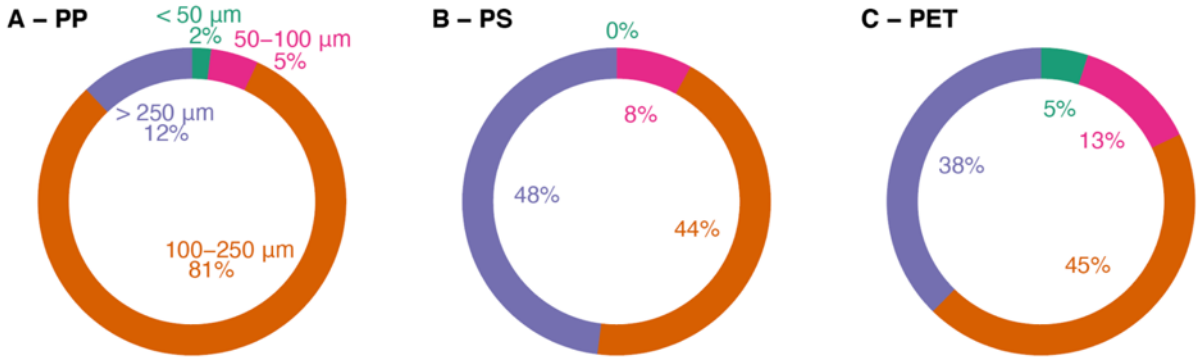


Figure 7-4. Particle size distribution using a laser diffracted particle size analyzer for (A) PP, (B) PS, (C) PET.

7.3.2. Distribution of microplastics in frozen water columns without porous media

Analysis of the distribution of microplastics in frozen water columns without sand media revealed that the distribution varied with microplastic density (Figure 7-5). More than 60% of PP microplastics were found at the surface, with their concentration decreasing with depth. In contrast, PET concentration was higher at lower depths. Around 20% of PET particles were found at the surface despite being expected to sink due to their greater density than water.

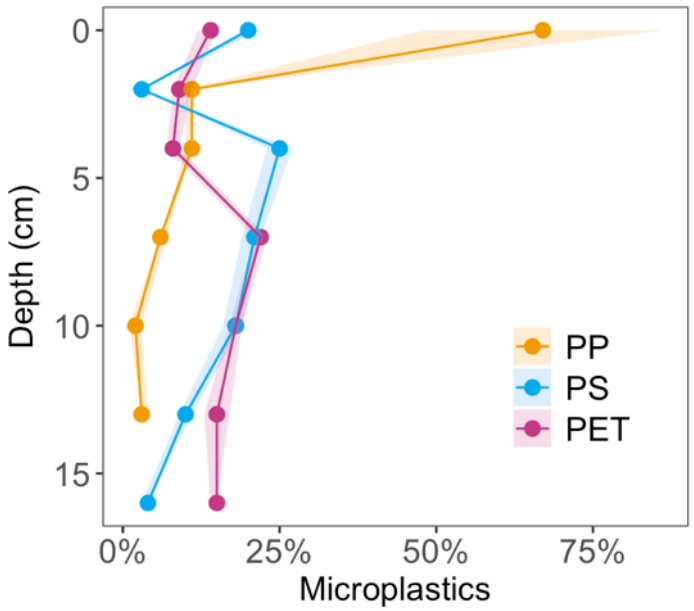


Figure 7-5. Fraction of total microplastics in water found at each depth of the frozen water column for three plastic polymer types: polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET). The shaded area shows the 95% confidence interval for the data due to the variance between multiple measurements.

7.3.3. Distribution of microplastics in sand columns subjected to freeze-thaw cycles

Depth distribution of microplastics in columns packed with sand showed that freeze-thaw cycles increased the penetration depth of microplastics compared to dry-wet cycles (Figure 7-6). Irrespective of treatment methods, the downward mobility was more pronounced for denser microplastics such as PET. The distribution was sensitive to the density of microplastics. For all the columns subjected to dry-wet cycles, the microplastic concentration near the outlet was similar to the background concentration (0 - 7 p g^{-1}) irrespective of microplastic density. In contrast, for the columns subjected to freeze-thaw treatments, microplastic concentration near the outlet was similar to background concentration only for columns contaminated with two types of plastics: PP and PS. Regardless of the weathering, PET microplastics moved deeper into columns than the PP and PS particles.

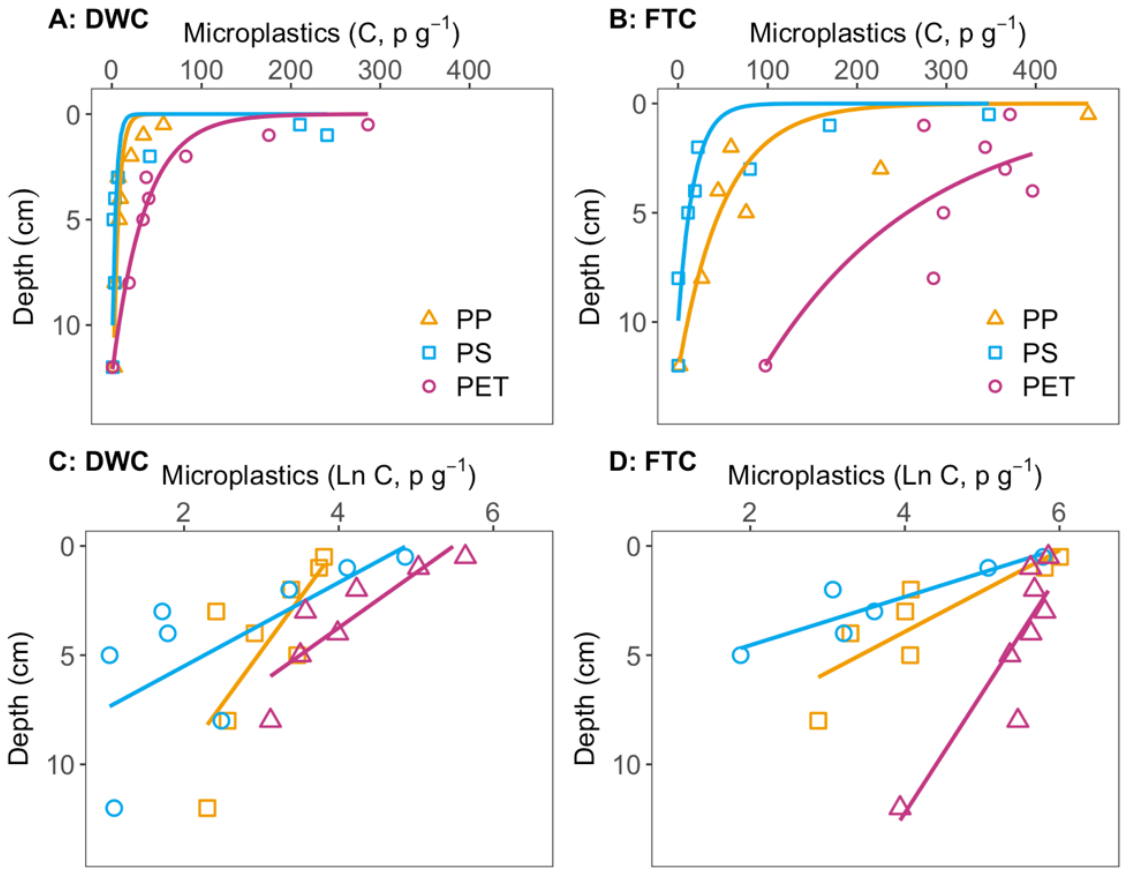


Figure 7-6. Microplastics concentration by depth for columns contaminated with three types of plastics subjected to either (A,C) dry-wet cycles or (B,D) freeze-thaw cycles. Each point represents an average of the experiment data points beween three columns, and the lines represent best fitting exponential model (Equation 1). C and D showing logarithmic concentration of microplastics varying with depth and weathering.

Fitting the distribution of microplastics with the exponential model (Eq. 7-1) (Koutnik et al., 2022b, 2022a), we showed that retardation of microplastics in sand biofilters varied with microplastic density irrespective of treatment types, but the density had a more pronounced effect on microplastic retardation under freeze-thaw cycles (Figure 7-6B). Specifically, the retardation coefficient, which we estimated based on the slope of the graphs in Figure 3C-D, ranges from 1.11 to 5.49, with the highest retardation coefficient corresponding to PET in columns subjected to freeze-thaw cycles (Table 7-2).

Table 7-2. Summary of the logarithmic equations and R^2 values for different plastic and weathering types.

Plastic	Treatment	Linear Fit Equation	R^2
PP	DWC	y = 4.84x - 19.3.	0.57
PP	FTC	y = 1.86x - 11.4	0.72
PS	DWC	y = 1.92x - 9.34	0.49
PS	FTC	y = 1.11x - 6.77	0.82
PET	DWC	y = 2.52x - 13.8	0.76
PET	FTC	y = 5.49x - 34.2	0.77

7.3.4. The concentration of microplastics in the effluent

Analysis of microplastic concentration in the effluent from all columns revealed that transport of PP and PS microplastics was negligible and statistically insignificant irrespective of the treatment types (Figure 7-7). The 15-cm deep sand media was sufficient to prevent the transport of PP and PS microplastics out of the columns via effluent. In contrast, PET microplastics were found in higher concentrations than the background concentration from uncontaminated or blank columns. The background concentrations were 0.023 p mL^{-1} and 0.075 p mL^{-1} for blank columns with dry-wet and freeze-thaw cycles, respectively. The higher effluent concentration of PET microplastics in contaminated columns subjected to freeze-thaw cycles further confirmed the finding that PET microplastics were disproportionately moved by freeze-thaw cycles.

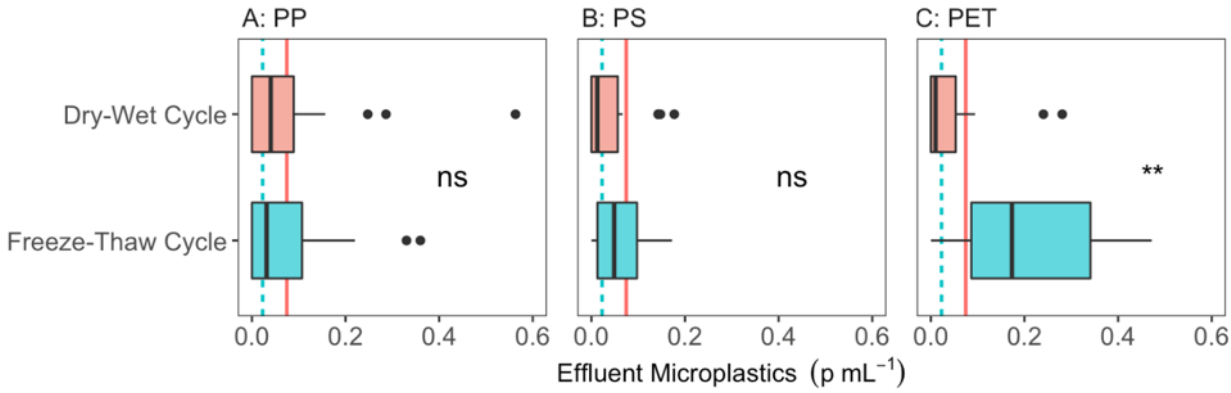


Figure 7-7. Concentration of (A) PP, (B) PS, and (C) PET microplastics in the effluent of the columns subjected to dry-wet cycles and freeze-thaw cycles. ns and * indicate no statical difference and significant statistical difference with $p < 0.05$, respectively. The solid and dashed vertical lines correspond to the background concentrations of the effluent from control samples for columns subjected to dry-wet and freeze-thaw treatments, respectively.

7.4. Discussion

7.4.1. Retention of microplastics in sand columns.

All deposited microplastics, with the exception of PET microplastics in columns subjected to freeze-thaw cycles, were retained in sand columns. Among the three types of microplastics used, PET is heavier than water. Freeze-thaw treatment decreased the retention of PET microplastics and enhanced their mobility more than that of PP and PS microplastics. The results indicate that in most conditions, microplastics with densities lighter than water can be effectively retained in the subsurface. The results are similar to previous studies that showed the removal of microplastics in sand columns (Gao et al., 2021; Koutnik et al., 2022a; O'Connor et al., 2019; Rong et al., 2022; Waldschläger and Schüttrumpf, 2020). Most microplastics were removed in sand columns due to physical straining (Koutnik et al., 2022b, 2022a), which is sensitive to size of microplastics and pore size of the media (Bradford et al., 2003). Straining occurs when larger particles are blocked by the narrow pores (Auset and Keller, 2006). In our study, the mean size of microplastics was larger than 100 μm, which is bigger than the mean pore size (40 μm) of sand columns (Minagawa et al., 2008), indicating straining could be a significant removal mechanism. PS particles used in

this study were larger than PE or PET particles (Figure 7-2). Therefore, PS microplastics are expected to be removed by sand by straining to a greater extent than the other two types of microplastics. Larger microplastics blocked at narrow pore throats between sand grains could not move further, irrespective of dry-wet or freeze-thaw cycles. This partially explained why PS microplastics were retained to a greater extent (smaller retardation coefficient or K) than the other two types of microplastics irrespective of weathering treatments.

Among plastic types, PET microplastics were found in greater concentration than the background level in the effluents of columns subjected to freeze-thaw cycles (Figure 7-7). The depth distribution data (Figure 7-6) also confirmed the enhanced mobility of PET microplastics by freeze-thaw cycles. The result indicates that the density of microplastics plays a critical role in the remobilization of microplastics by freeze-thaw cycles compared to dry-wet cycles. Previous studies (Mohanty et al., 2015, 2014) have compared the remobilization colloids by dry-wet and freeze-thaw cycles, but they did not vary the density of colloids. Only one study (Chrysikopoulos and Syngouna, 2014) has examined the role of gravity on the transport of colloids in sand columns by comparing the transport of bacteria (specific gravity similar to PET~ 1.4), and natural clay colloids (specific gravity ~2.6) and observed that an increase in specific gravity of colloids increased in colloid transport velocity in vertical sand columns. Collectively, the results confirmed that denser colloids are more susceptible to transport than lighter colloids.

7.4.2. Enhanced transport of microplastics by freeze-thaw cycles compared to dry-wet cycles

For the same microplastic type, freeze-thaw cycles transported more microplastics than dry-wet cycles did within the columns (Figure 7-6). This result agreed with a previous study that compared the transport of PP microplastics in sand and soil columns under dry-wet or freeze-thaw cycles (Koutnik et al., 2022a). Our study provides additional evidence that the effect of freeze-

thaw cycles on the transport of microplastics is sensitive to the density of microplastics. In particular, the effect of freeze-thaw cycles is more pronounced for denser microplastics. We attributed the results to fundamental differences in processes by which dry-wet or freeze-thaw cycles could mobilize deposited microplastics in porous media. Advancing or receding wetting fronts during dry-wet cycles typically disrupt solid-water and air-water interfaces where colloids were typically deposited (DeNovio et al., 2004). Thus, the shear force of the rapidly moving air-water interfaces could scour microplastics or colloids from their deposited locations and mobilize them into pore water (Flury and Aramrak, 2017; Shang et al., 2008). The interaction of air-water interfaces on colloids depends on the hydrophobicity of colloids (Keller and Auset, 2007). Thus, hydrophobicity of microplastics may play a greater role than density in the remobilization of microplastics by dry-wet cycles. In contrast to dry-wet cycles, freeze-thaw cycles involve the transition of the water phase to ice. During freezing, deposited microplastics can either be pushed or engulfed by the ice front based on the free energy change to replace particle-liquid (pl) and liquid-solid (lp) interfaces with a solid-particle (sp) interface (Asthana and Tewari, 1993; Shangguan et al., 1992). Ice front engulfs the particle if the free energy change is negative. As all plastics are insulators, which block the heat energy from water to ice near the interface, the ice formation could accelerate near the microplastics, creating a convex-shaped interface that would be more likely to push microplastics along the direction of ice-interface propagation (Asthana and Tewari, 1993). A moving ice front can be more disruptive than rewetting of the pore by liquid water because expanding ice during freezing can exert more pressures than capillary pressures on pore walls during drying (Koutnik et al., 2022a; Mohanty et al., 2014). The ice crystals can also fracture or expand the pore walls, thereby creating flow paths conducive to the transport of large colloids (Borthakur et al., 2021b).

7.4.3. Mechanisms of microplastic transport by freeze-thaw cycles

Our results confirmed that the extent to which freeze-thaw cycles could accelerate the downward mobility of microplastics is dependent on the density of microplastics. However, the microplastics used in our study are >50 µm, and the detection method used in our study could not reliably detect microplastics < 10 µm. To understand the effect of density on the mobility of microplastics within all size ranges (0.1 µm to 1000 µm), we estimated the velocity of suspended plastic particles at far and close (within a few nm) distances from the moving ice interface using a force balance approach (Shangguan et al., 1992). The velocity of a plastic particle (V_p) far from the moving ice-water interface, as shown in Eq. 7-2, can be derived by force balance where gravitational force based on the density difference between particle and water ($F_G = \frac{4}{3}\,\pi\,R_p^3\,\Delta\rho\,g$) acts against the drag force ($F_D = 6\,\pi\,\mu\,R_p\,V_p$). Here, $\Delta\rho$ is the difference in the density of the particle (ρ_p) and water (ρ_L), μ is the viscosity of water, g is the acceleration due to gravity, and $R_p$is the radius of the particle.

$$\boldsymbol{V_p = \frac{2}{9}\,R_p^2\,\Delta\rho\,g\,\mu^{-1}} \qquad \text{(Eq. 7-2)}$$

The particle moves at constant flotation velocity in a direction based on the sign of $\Delta\rho$ (Figure 7-8C). Thus, most PP microplastics are expected to float and stay near the surface of the water column, whereas most PET microplastics are expected to settle at the bottom of columns after sufficient time has passed. Our results (Figure 7-5) confirmed the overall trend: more than 60% PP microplastics and less than 15% PET microplastics moved to the top of the water column after freeze-thaw cycles. As the initial position of microplastics in a well-mixed suspension and the time taken to freeze the water column was unknown, Stoke's law could not be used to predict the occurrence of the microplastics present at different depths.

The force balance on the suspended microplastics would change at close proximity (within a few nanometers) to the ice-water interface, where molecular interactions become relevant. If the particle is denser than water, the interaction between the particle and ice interface would occur only if the velocity of the ice-water interface (V_S) is greater than the settling velocity (V_p) (Figure 7-8A). At a distance of the order of the atomic spacing, the particle would experience an interfacial molecular force (F_I) or the Van der Waals force or the force due to a change in the interfacial energy. In this case, the standard Stokes' equation for the drag force is no longer valid as the flow of liquid is perturbed by the ice front. At this close proximity, the particle experiences a drag force or cryosuction force (F_μ) because water moves from the suspension towards the interface to support ice growth, thereby attracting the particle towards the interface (Figure 7-8A). At equilibrium, the net force on the particle would be zero ($F_G + F_I - F_\mu = 0$) as shown in Eq. 7-3:

$$\frac{4}{3}\,\pi\,R_p^3\,\Delta\rho\,g + 2\,\pi\,R_p\,\Delta\sigma_0\left(\frac{a_0}{a_0+d}\right)^n\alpha - 6\,\pi\,\mu\,V_p^*\,\frac{R_p^2}{d}\,\alpha^2 = 0 \qquad \text{(Eq. 7-3)}$$

where a_0 is the sum of the radii of atoms in the surface layers of the particle and the solid, d is the gap between particle and ice-water interface, and $\Delta\sigma_0$ ($= \sigma_{SP} - \sigma_{LP} - \sigma_{SL}$) is the net free energy changes for the particle to be engulfed by ice, which occurs when free energy between the ice and particle (σ_{SP}) exceeds the free energy between water and particle (σ_{LP}), and ice and water (σ_{SL}). α is a function of the curvature of the ice-water interface near the particle, which is the ratio of the radius of curvature of the ice-water interface (R_I) and the difference between the radius of interface curvature and particle radius ($R_I - R_p$). As the curvature is created by the melting of ice due to a difference in thermal conductivity of water and particle, α can be calculated as the ratio of thermal conductivity of particle (k_p) and water (k_L). As the thermal conductivity of microplastics is smaller than water, a convex shape ice hump would form near the interface between the particle and ice,

which can push microplastics further. Solving Equation 7-4, the velocity of the particle near the ice-water interface would

$$\boldsymbol{V_p^*} = \frac{\boldsymbol{d}}{\boldsymbol{3\mu\alpha}}\left(\frac{\boldsymbol{\Delta\sigma_0}}{\boldsymbol{R_p}}\left(\frac{\boldsymbol{a_0}}{\boldsymbol{a_0+d}}\right)^{\boldsymbol{n}} + \frac{\boldsymbol{2R_p\,(\rho_p-\rho_L)\,g}}{\boldsymbol{3\alpha}}\right) \qquad \text{(Eq. 7-4)}$$

Estimating the velocity of plastic particles with a radius between 0.1 to 1000 μm near the ice-water interface, we show that the velocity is sensitive to plastic density if the size of microplastic is bigger than 10 μm (Figure 7-8B). The contribution of interfacial force on microplastic mobility was prominent when the particle size was smaller than 10 μm. However, our method is inadequate to detect microplastics within these size ranges. Thus, the velocity of smaller microplastics (< 10 μm) is expected to increase dramatically with a decrease in size due to push from the ice interface irrespective of the density of microplastics. In contrast, the velocity of larger microplastics, such as the ones used in this study, would be much small near the ice-water interface, and the velocity would be affected by the density of microplastics. The theoretical prediction that PET velocity would be much higher than PP and PS near the ice interface is confirmed by our experimental data, where PET microplastics were relocated deeper into the water columns (Figure 7-5) followed by PS and PET. Most PP particles are expected to float on the surface, so they were not affected by ice propagation from top to bottom of the columns.

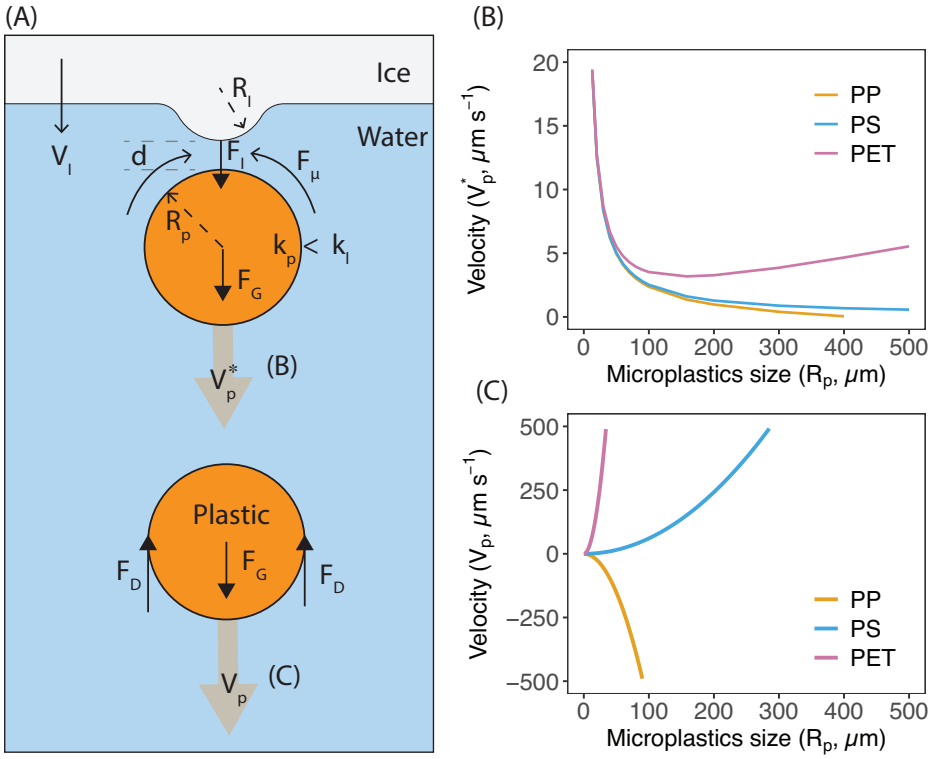


Figure 7-8. (A) Force balance on microplastic particles near (~ few nm) and far from the moving ice-water interface. (B) The velocity of suspended microplastics away from the ice interface using Stokes' law. (C) The velocity of particles near the ice interface. The velocity of microplastics from three polymer types at the interface was calculated using the following assumption: $a_0 = 0.2\ nm$; $d = 1\ nm$; $n = 2$; $\Delta\sigma_0 = 10\ mN/m$; $\mu = 0.0018\ N\ s/m^2$, $\rho_{PP} = 920\ kg\ m^{-3}$), $\rho_{PS} = 1{,}015\ kg\ m^{-3}$, $\rho_{PET} = 1{,}350\ kg\ m^{-3}$, $\rho_{H_2O} = 1{,}000\ kg\ m^{-3}$, $k_{p\ or\ H_2O} = 0.561$, and $k_p = 0.115$.

7.4.4. Conceptual processes of microplastic transport in the subsurface by freeze-thaw cycles

Based on the experimental evidence and theoretical framework, we suggest the following conceptual processes that could describe the subsurface transport of microplastics in soil or other porous media subjected to freeze-thaw cycles. Suspended microplastics move through the porous media through the flow paths and can be retained by physical straining if their particle size is larger than the pore size. Microplastics smaller than the pore size can pass through the pores, where some of them can be adsorbed on water-air or water-solid interfaces, and the remaining particles will stay suspended in the pore space. In this case, denser particles are expected to travel deeper into the subsurface because gravitational force coincides with the advective force exerted by the flow

of water. Thus, particles with lower density than water are expected to remain near the surface, and particles with higher density than water would move deeper into the subsurface. The gap between penetration depths of lighter and heavier microplastics is expected to increase by freeze-thaw cycles, which can disproportionately push denser microplastics deeper into the subsurface. In addition, freeze-thaw cycles can create more preferential flow pathways by expanding cracks in subsurface soil (Mohanty et al., 2014), which could further increase their downward migration.

7.4.5. Environmental Implications

The results of this study provide the first quantitative and experimental evidence showing accelerated transport of microplastics by freeze-thaw cycles as a function of the particle density. The theoretical framework provided here can be applied across all plastic polymers with other densities. Understanding the effects of freeze-thaw cycles is critical due to the prevalence of these seasonal weather patterns across all of northern America and Europe. Furthermore, these results are useful to predict microplastic movement in freshwater lakes or ponds that undergo freezing during winter. As freezing cycles and conditions are expected to vary during climate changes, the results can later be used to understand a change in microplastic distribution in the subsurface under different climates. Predicted climate change scenarios suggest an increase in the frequency and severity of soil freeze-thaw cycles in many northern temperate regions of the world (Henry, 2008), with implications of transport rates of different emerging contaminants in the subsurface, including microplastics. The results can also help predict microplastic distribution in the soil in the agricultural fields and urban areas and the potential transport pathways to ground water (Henry, 2008; Pauli et al., 2013). Understanding how far some microplastics would move near the root zone can help predict their impact on root function or crop productivity (Boots et al., 2019; de Souza Machado et al., 2019). Plants growing in microplastic-contaminated soils are predicted to

have decreased nutrient contents and increased toxicity as nano plastics can be uptaken by plant roots and soil microbiota (Li et al., 2020; Seeley et al., 2020; Sun et al., 2021). Downward migration also has the potential for groundwater contamination, which serves as a source of freshwater for at least two billion people worldwide (Panno et al., 2019; Samandra et al., 2022; Viaroli et al., 2022). Recent anecdotal evidence showed a greater abundance of denser plastics such as PET and PVC in the groundwater samples, but the cause of such abundance was unknown (Samandra et al., 2022). Our study provided a theoretical basis to predict the increased abundance of denser microplastics in deeper subsurface soil or groundwater aquifers.

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8. CHAPTER 8 – CONCLUSIONS AND RECOMMENDATIONS

8.1. Conclusions

Distribution of microplastics in terrestrial environments: The analysis of microplastic concentration reported in 196 studies from 49 countries yields the following conclusions: The concentration of microplastics can vary up to 8 orders of magnitude depending on the location. The concentration decreases by up to two order magnitude from urban areas inland to estuaries in coastal areas or terrestrial boundary. The concentration of microplastics is the highest in urban soil/water mediums where usage and disposal of plastics are high. Remote glaciers contain higher concentrations of microplastics than urban hotspots, indicating that wind-driven transport is significant. Our analysis reveals that the shape of microplastics affects their transport and distribution in the environment. The fiber fraction is enriched in the sediment in coastal areas or estuaries and on the glacier, indicating fibers are preferentially transported from the source. The abundance of microplastics varies with plastic polymer type. PP, PE, PET, and PS were most commonly identified.

Unaccounted microplastics in WWTP: The study shows that biosolids could contain a much higher amount of microplastics than previously estimated, and these microplastics could be released back to the environment based on sludge disposal methods. the results reveal that more than 94% of microplastics entering wastewater treatment plants are not accounted for. The cause of unaccounted microplastics could be a lack of uniform protocols in the sampling and analysis of microplastics, lack of influent, effluent and sludge data in all treatment plants, inconsistent reporting of the size, shape, and types of microplastics found in sludge or wastewater.

Microplastics in Urban Playgrounds. Analyzing microplastic concentration from 19 playgrounds in Los Angeles, we confirmed an increased microplastic exposure to children inside

the playgrounds. Children playing inside the playgrounds could be exposed to five times more microplastics than those who play outside the designated play areas. The most common type of microplastics found on samples inside playgrounds (e.g., PE and PP) matched with the polymer composition of the playground structures, indicating that the dominant source of most microplastics accumulated in the playground is the built-in plastic structures in the playground that could release microplastics by physical and chemical weathering.

Microplastics in Stormwater Control Measures. Analyzing the distribution of microplastics in and around SCM at fourteen locations in Los Angeles we show that microplastic concentrations inside and outside of SCM are not statistically different, indicating that, in addition to stormwater, the atmospheric deposition could be a dominant source of microplastics in urban areas. A high concentration of microplastics in vegetation around SCM confirmed this theory. The results reveal the importance of wind transport and dry deposition on the accumulation of plastics in urban areas. Most of the microplastics were trapped in the top 5 cm subsurface layers of the SCM, and their concentration exponentially decreased with depth. The retardation coefficient, which was estimated from the exponential fitting parameter, increased with a decrease in median particle size (D_{50}) of subsurface soil. This result indicates that straining is the dominant removal process of the microplastics outside the SCM. The retardation coefficient, however, did not change with changes in D_{50} within SCM boundary, indicating pre-contamination of filter media with microplastics and/or enhanced downward transport of microplastics in filter media in SCM may have moved the microplastics deeper into the subsurface.

Freeze–Thaw Effect on Microplastics Transport in Biofilter Media. A comparison of the penetration depth between biofilters subjected to dry-wet cycles and freeze-thaw cycles showed that freeze-thaw cycles increased the penetration depths, and this effect was more

prominent in biofilters with more sand content. The result was attributed to the disruption of media aggregates by expanding ice crystals during freezing and the release of microplastics along with colloids during the thawing process.

Density impact on microplastic transport under freeze-thaw cycle. The distribution of microplastics in vertical water columns with and without porous media confirmed that freeze-thaw cycles could disproportionally accelerate the downward mobility of denser microplastics. A force balance analysis reveals that smaller microplastics (<50 μm) are pushed at higher velocity by the ice-water interface, irrespective of the density of microplastics. However, density becomes critical when the size of microplastics becomes larger than 50 μm. The coupled experimental studies and modeling effort improved the understanding of why denser microplastics such as PET and PVC may move deeper into the subsurface.

8.2. Recommendations for future studies

Effect of deposited microplastics in biochemical processes in the subsurface. One of the primary functions of stormwater biofilters is to degrade pollutants removed from stormwater, thereby recharging the filter media. Microbial communities near the root zone, especially, play a critical role in carrying out the biochemical processes, which are responsible for nutrient cycling, pollutant decay, and heath of the biofilter. Microplastic accumulation, based on the concentration, in the biofilter, could affect soil bulk density, water-holding capacity, and hydraulic conductivity of the soil (Machado et al., 2018). Additionally, microplastics can directly interfere with the biochemical processes in the subsurface. Microplastics could inhibit extracellular enzymatic activities in the subsurface by adsorbing the enzymes (Yu et al., 2020). For instance, recent studies have shown that microplastics can reduce degradation of the antibiotics, leading to soil microorganisms developing antibiotic resistance (Fan et al., 2021; Wang et al., 2020). However,

these studies use unnaturally high microplastic concentrations to show a noticeable impact on the processes. The threshold microplastic concentration required to cause any effect has not been evaluated and thus the environmental implications of previous studies are limited (Lozano and Rillig, 2020; Rillig et al., 2019). Furthermore, the previous study rarely answers why the presence of microplastics affects biochemical processes. A recent study examines the effect of microplastics on nitrogen fixation processes in the soil. Microplastics could counteract the activities of microorganisms that promote denitrification (Huang et al., 2021) and reduce the abundance of nitrifying and denitrifying bacteria in the soil (Yang et al., 2020). Microplastics could also adsorb dissolved organic carbon (DOC) or influence the quality of DOC (Ateia et al., 2020a; Chen et al., 2019; C. Liu et al., 2019). Therefore, the link between pore water DOC altered by microplastics and denitrification needs further evaluation.

Microplastic-facilitated transport of stormwater pollutants. Stormwater contains a wide range of pollutants, which can accumulate in biofilters, where most microplastics reside. Thus, microplastic buried in biofilters may become more toxic by adsorbing pollutants such as heavy metals, polychlorinated biphenyl (PCBs), polybrominated diphenyl ethers (PBDEs), dichlorobiphenyl trichloroethane (DDTs), hexachlorocyclohexanes (HCHs), and polycyclic aromatic hydrocarbon (PAHs) (Menéndez-Pedriza and Jaumot, 2020; Ziccardi et al., 2016). Recent studies have shown adsorption of emerging pollutants such as pharmaceutical active compounds (PhACs), antibiotics, and PFASs on microplastics (Bank et al., 2020; Fan et al., 2021; Llorca et al., 2018; Magadini et al., 2020; Puckowski et al., 2021). These co-contaminants can be significantly enriched on polymer surfaces, exceeding over 100 times their ambient concentrations in stormwater (Beck and Birch, 2012; Menéndez-Pedriza and Jaumot, 2020).The extent and mechanisms of adsorption in conditions relevant for stormwater biofilter design has not been

studied. Stormwater biofilters are subjected to drying and freezing treatment, which can affect the concentration of pollutants in pore water. For instance, freezing of soil has been shown to increase heavy metals on soil colloids (Mohanty et al., 2014b; Naqash et al., 2020). The same process could enrich pollutants on microplastics. Additionally, previous studies primarily focus on heavy metal adsorption on pristine microplastics, even though most microplastics in biofilters are weathered. Weathering causes fracturing and pitting, which can increase the surface area and the number of active adsorption sites (Vedolin et al., 2018; Zhu et al., 2020). Weathering can affect surface properties such as charge, contact angle, and hydrophilicity (G. Liu et al., 2019; Liu et al., 2020b) and reduce crystallinity (Ateia et al., 2020b; Hüffer et al., 2018). These changing structural and surface properties could affect the sequestration of stormwater pollutants on microplastic surfaces. Thus, is critical to further understand how weathering of microplastic through freeze-thaw cycles might affect their preferential adsorption of co-contaminants also present in stormwater biofilters.

Effect of weathering and shape of microplastics on their transport in subsurface. Plastic microspheres have been used in numerous studies as a tracer to examine colloid and pathogen transport in soil (Becker et al., 1999; Burkhardt et al., 2008; Close et al., 2006; Harvey et al., 1993; Knappett et al., 2008; McCarthy et al., 2002; Mohanram et al., 2012, 2010; Mondal and Sleep, 2013, 2012; Yu et al., 2013; Zhuang et al., 2005). However, majority of microplastics have been shown to be fibers or fragments and not be of perfectly spherical shape. Future studies should update the models for microplastics with different shapes and sizes, particularly fibers. In nature, microplastics are often weathered under natural conditions such as temperature fluctuation, UV light, and biodegradation (Ding et al., 2020a; Shah et al., 2008; Song et al., 2017). In particular, environmental UV exposure can weather microplastics, which can decrease the material surface toughness, elasticity, rigidity, and uniformity (Iniguez et al., 2018; Moezzi and Ghane, 2013; ter

Halle et al., 2017; Weinstein et al., 2016) and can affect microplastics hydrophobicity. All the chemical and physical changes that microplastics undergo in natural environments could affect their transport potential in the subsurface soil. Future study should examine the transport of weathered microplastics with a wide range of shapes in subsurface.

Improved method to detect microplastics in wastewater. Our results reveal that more than 94% of microplastics entering wastewater treatment plants are not accounted for, and we attribute the discrepancy to several factors, which should be explored in future studies. First, a lack of uniform protocols in the sampling and analysis of microplastics makes it difficult to compare results between different studies. The concentration should be reported in similar units. Second, comparison of removal of microplastics in WWTP between studies is difficult because studies rarely reported concentration of microplastics in all three inlets and outlets: influent, effluent and sludge. Furthermore, most studies have not reported the size, shape, and types of microplastics found in sludge or wastewater. Microplastics smaller than 50 μm are harder to detect in sludge, which we attributed as the main reason for unaccounted microplastics in sludge. Future studies should focus on improving methods of detection of smaller microplastics and nanoplastics in wastewater sludge, untreated wastewater influent and treated effluent. Loss of microplastics by biodegradation could also explain some of the unaccounted microplastics. Thus, future studies should examine the biodegradation of microplastics in conditions relevant to wastewater treatment plants and quantify the fragmentation rate as a result of biodegradation.

8.3. References

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