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UV exposure to PET microplastics increases their downward mobility in stormwater biofilters undergoing freeze-thaw cycles

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1 **Water Impact Statement**

2 Microplastics accumulated on stormwater biofilters are naturally exposed to sunlight and
3 other transient weather conditions such as drying, wetting, and freezing based on seasons. Yet,
4 the coupled effect of UV weathering and weather conditions on microplastic transport has not
5 been evaluated. This study shows that UV weathering of PET microplastics increases their
6 downward mobility in subsurface soil under freeze-thaw cycles.

UV exposure to PET microplastics increases their downward mobility in stormwater biofilters undergoing freeze-thaw cycles

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Abstract

Stormwater conveys microplastics and accumulates them in stormwater treatment systems such as biofilters, where they are exposed to sunlight and natural weather conditions such as drying, freezing, and wetting cycles. Thus, the mobility of microplastics through biofilters could depend on the interactive effects of the weather conditions. Yet, how weathering of microplastics under UV light affects their mobility during freeze-thaw cycles has not been

evaluated. This study estimates to what extent UV weathering could affect the rate of microplastic transport through sand filters during freezing and thawing cycles. To compare the mobility of unweathered and weathered microplastics based on their concentration at different depths, PET microplastic particles weathered to different degrees under a UV light were deposited on sand-packed columns and subjected the columns to freeze-thaw cycles. Our results confirm that an increase in exposure to UV light alters the surface properties of microplastics, particularly contact angle, leading to increased surface hydrophilicity. Additionally, the depth distribution of microplastics varies with weathering of microplastics, with most weathered microplastics moving farthest into the subsurface. We attribute these results to a combination of changes in surface properties due to weathering and changes in the interaction of weathered plastics with either ice or water interfaces, resulting in a net increase in the downward mobilization of microplastics over time. The results imply that UV weathering, in conjunction with the freeze-thaw cycle process, could substantially increase the mobility of microplastics in subsurface soil, and should be considered when predicting the transport of microplastics in subsurface systems.

1 Introduction

Microplastics are increasingly found in surface water bodies, affecting their ecosystem functions and threatening aquatic lives (1). Ingestion and inhalation of microplastics from the environment could also cause adverse health effects in humans (2). Thus, removing microplastics from their transport pathways could protect these aquatic systems and limit their adverse effects. Among non-point sources, stormwater runoff is a significant pathway for microplastics to enter

aquatic systems (3). These microplastics originate from various urban compartments, including trash or litter, roads, biosolid-applied land, landfills, and soils (4,5). As rainwater washes over urban areas, it collects these microplastics and carries them through stormwater drainage systems and into nearby water bodies (3,6). Thus, it is important to intercept the microplastics from stormwater before they reach the aquatic systems.

Stormwater treatment systems such as biofilters are designed to remove suspended sediments from stormwater, and they have been shown to effectively filter microplastics as well (7–9). The deposited microplastics on biofilters are naturally exposed to variable weather conditions including sunlight or drying, rainfall, and freeze-thaw cycles based on the seasons. These conditions could not only alter the surface properties and size of microplastics (10–14) but also affect their migration into and distribution in the subsurface soil, (15,16) with implications on rhizosphere functions in stormwater biofilters and agricultural systems (17–19) and groundwater contamination (20,21). Thus, it is critical to determine how local climate could influence microplastic mobility in the subsurface.

Microplastics accumulated on the surface of biofilters are typically exposed to UV radiation in sunlight, which could alter the surface chemistry of plastic polymers and disintegrate them based on how long they are exposed to UV light (22). These weathered microplastics could move downward during wetting events by advection and dispersion (23–26). The transport of microplastics can be accelerated by natural dry-wet (24,25,27–29) and freeze-thaw cycles (26,30), although freeze-thaw cycles are shown to have a greater effect on microplastic mobility than dry-wet cycles (26). Previously deposited microplastics are remobilized into pore water and pushed downward during dry-wet and freeze-thaw cycles due to disruption caused by the

movement of water-air and water-ice interfaces. The interfacial interaction with the plastic surface can be sensitive to plastic surface properties, which change naturally based on sunlight exposure and oxidants present in the environment (31–33). Thus, the coupled effect of weathering of microplastics and their transport during dry-wet or freeze-thaw cycles should be evaluated to accurately predict microplastic distribution in the root zone and their eventual mobility to groundwater.

Only a few studies examined the transport of UV-weathered microplastics in porous media in saturated and continuous flow conditions (16,34), and they did not account for intermittent weather conditions such as freeze-thaw cycles. Those studies that examined the effect of freeze-thaw cycles only used pristine or unweathered microplastics (35,36,26). In stormwater biofilters, the accumulated microplastics are rarely pristine due to their prolonged exposure to sunlight and other natural oxidants (37). Weathering of microplastics can alter their surface charge and decrease their surface hydrophobicity (38). A few studies show that a decrease in hydrophobicity could increase the downward mobility of microplastics in porous media during intermittent infiltration of water (23,39,30). However, the interaction of hydrophilic microplastics with the wetting front is different from that of their interaction with the ice front. The interaction of ice-water interface with plastic surface or change in free energy when expanding ice crystal either push or engulf particle depends on the surface properties of the particles (30,40). Thus, any changes in microplastic surface properties due to weathering could affect the extent to which the freezing front could move microplastics in biofilters. Yet, no study to date has examined the effects of weathering on the mobility of microplastics by freezing front.

The objective of the study is to examine the effect of the UV-weathering microplastics on their mobility in the subsurface filter media subjected to freeze–thaw cycles. We hypothesize that weathering of microplastics would make them more susceptible to downward transport under freeze-thaw cycles. To test the hypothesis, we quantified the mobility of microplastics weathered under UV light for different durations in sand columns subjected to many freeze-thaw cycles. The results could help predict the distribution of microplastics in subsurface or stormwater biofilters in natural conditions.

2 Materials and Methods

2.1 Preparation and characterization of PET microplastics

To simulate irregular microplastic shapes found in the natural environment, a mechanical orbital sander (*BOSCH Palm Sander 2.5 Amp, 80 grit, 9 speed*) was used to abrade PET beverage bottles for 15 minutes each, following methods outlined elsewhere (26). PET is chosen because it is one of the most commonly used plastic polymers in the packaging and textile industries (41) and is increasingly found in natural environments and groundwater (33) potentially due to higher mobility as a result of their higher density (30,42). Compared to other plastic polymers, PET is also highly susceptible to degradation under UV radiation (43). Additionally, we selectively chose one plastic type (PET) so that only surface properties change without varying the density of plastic particles to examine whether freezing front can affect the mobility of microplastics as a function of the surface hydrophobicity changed during weathering.

This method typically produced microplastics within a size up to 500 μm (26). To confirm the size distribution and shape of the prepared microplastics and verify their polymer type, a Fourier Transform Infrared or FTIR microscope (Thermo Scientific Nicolet™ iN10) was

used in the reflectance mode (Brahney et al., 2020) using the particle analysis wizard included in the PICTA™ software. A minimum 50% match criteria was used to identify the particle. The details of the method were described in previous studies (30,44). The PET particles were spread on a 1 cm² area of a slide, and images of particles and FTIR spectra were collected to measure their size distribution. The detection limit for FTIR was nearly 20 μm. FTIR measurement confirmed the size distribution of microplastics between 20μm to 520μm (Figure 1).

2.2 *Weathering of microplastics*

Improperly disposed of PET plastics used in the packaging industry typically undergo UV weathering under sunlight (42). To simulate the UV radiation of PET microplastics, the prepared microplastics were weathered in a UV chamber (Novascan PSD-UV Ozone System) emitting UV light at both 185nm and 254nm. 0.15 g of microplastics was first placed on a glass petri dish as a single uniform layer to minimize the overlap of plastic particles and then exposed to UV radiation for either 0, 15, 30, or 60 minutes. For uniform exposure to all particles, the microplastics were mixed for 15 seconds every 5 min of exposure to UV radiation.

2.3 *Effects of UV radiation on PET hydrophobicity*

UV radiation can cause oxidation of plastic surface chemistry, and thus cause the plastic to become more hydrophilic (46). The contact angle measurement has been used to indicate changes in the hydrophobicity of a material (46). To examine changes in surface hydrophilicity of the exposed plastic surface, the contact angle was measured using a Contact Angle Goniometer (Rame-Hart 500) after UV exposure for 0, 15, 30, and 60 minutes. The contact angle was measured by placing a 3 μL water droplet onto the weathered surface of the plastic and measuring the angle 10 times using DropImage Advanced software. This process was repeated for 10 droplets on each sample to determine the average contact angle per sample type.

2.4 *Biofilter column design*

Although stormwater biofilters typically contain a mixture of sand, compost, and/or soil, this experiment solely utilized quartz sand (20-30 Standard Sant, Certified MTP) to minimize the likelihood of microplastic contamination from locally collected soil or compost and isolate the effect of weathering on microplastics mobility in a controlled environment without interferences from the confounding factors. To simulate a stormwater biofilter in the natural environment, sand columns were packed and tested for microplastic mobility following the method described in previous studies (26,30). Briefly, sand was packed up to a 15 cm layer in transparent PVC pipes (2.54 cm in internal diameter and 30 cm in height) in 2-3 cm increments to ensure uniform packing. The columns were then saturated with DI water to measure the average pore volume (26 mL) of the sand medium.

2.5 *Testing the mobility of weathered microplastics by freeze-thaw cycles*

To simulate natural seasonal conditions, the biofilter columns were subjected to freeze-thaw cycles following the methods outlined in a previous study (30). Briefly, 4 pore volumes (PV) or about 100 mL of synthetic stormwater (6 mM NaCl in DI water) were applied on sand columns at 5 mL min⁻¹ to remove any colloids or particulates from the sand. The effluent collected from this initial injection was analyzed to measure the background concentration of microplastics in the sand columns. Then, 0.1 g of unweathered or weathered PET microplastics were deposited on the surface of the packed sand layer in each column. This amount is equivalent to 0.01% of filter media weight, which could represent microplastic concentration in highly contaminated surface soil (47) due to the accumulation of microplastics over several decades. A high concentration on the top layer also ensured the concentration of microplastics in subsurface layers can be detected to compare the change in mobility due to freeze-thaw cycles.

Triplicate columns were used to deposit microplastics subjected to a specific duration of weathering (0 - 60 min). All 12 columns underwent freeze-thaw cycles. During each cycle, the columns were frozen at $-20\text{ }^{\circ}\text{C}$ for 6 h and thawed at $22\text{ }^{\circ}\text{C}$ for 17 h followed by injection of ~ 4 pore volumes (100mL) of synthetic stormwater at 5 mL min^{-1} for 20 min. This process was repeated for 28 cycles. During the last few cycles, the effluent was measured for the concentration of microplastics. It should be noted the temperature variation in winter is more moderate ($-5\text{ }^{\circ}\text{C}$ to $+5\text{ }^{\circ}\text{C}$) than the range used in this study. We assumed that microplastics experience force from ice crystal growth during temperature ranges when water can turn into ice. Any decrease in temperature after ice formation would not have any effect on the mobility of microplastics due to the entrapment of microplastics by ice crystals. However, a slower rate of temperature change can affect the size and structure of ice crystals (Wu et al. 2015), which could affect the distribution of microplastics. Future studies should use a confocal microscope and controlled variation of temperatures at different ranges to examine if the rate of change in temperature or temperature ranges affects how ice crystal interacts with microplastics and affects their distribution.

2.6 *Quantification of microplastics*

The effluent was filtered through a 24 mm glass filter with a $1.2\text{ }\mu\text{m}$ pore size using a vacuum filtration setup. The filter containing microplastics was analyzed using a smartphone method that counts microplastics dyed with Nile Red (48). The method is rapid compared to other traditional methods, but Nile Red is known to bind organic residues which may contribute to false positives (49). However, we used pre-washed clean sand without organic particles. The use of control columns in our previous study and analysis of background microplastic concentration that may be released from sand and column materials before the addition of

microplastics on top of filter media confirmed the negligible contribution of false positives (5). Therefore, we assume that the use of Nile Red did not significantly affect the outcome of the current study. However, no organic materials were used in this study, and thus any interference from organic particles is not expected. Briefly, the method involved placing the filter with microplastics on a petri dish and staining it with 0.17 mL of $0.5 \mu\text{g mL}^{-1}$ Nile Red dye in a chloroform solution. The petri dish covers were placed over the stained filters to prevent air deposition of microplastics in ambient air and were left to dry. To quantify the microplastic count, the filter was imaged using a smartphone fitted with an external casing to illuminate the filter, and the images were analyzed using a Matlab algorithm (48).

After the completion of the freeze-thaw cycles, each column was dismantled, and the sand layer was extracted from various depths: 0.5, 1, 2, 3, 4, 5, 8, and 12 cm. To estimate the concentration of microplastics at various depths, 40 mL of 1.6 g mL^{-1} KI solution was mixed with 1 g of oven-dried sand. The resulting solution was centrifuged at 5000 rpm for 30 min. This process allowed the sand particles to settle, while the lighter-density particles (density $< 1.6 \text{ g cm}^{-3}$) remained floating. The supernatant was filtered to isolate floating microplastics, and the microplastics are analyzed using the same method as described earlier.

2.7 Data Analysis

The statistical analysis for this study was performed using R (version 4.3.0). To analyze the data, a one-way analysis of variance (ANOVA) was employed. The significance of differences between two specific means was assessed with Tukey HSD post-hoc comparison, where the difference is assumed to be significant if the p-value < 0.05 .

2.8 *Quality assurance and quality control*

To enhance quality assurance and control, a controlled and sterile workspace was maintained. Laminar flow hoods ensured a continuous flow of filtered air, effectively minimizing the risk of airborne contamination during sample handling and preparation. Strict adherence to appropriate personal protective equipment (PPE) protocols was followed, including the use of gloves and cotton lab coats. These measures aimed to minimize the introduction of external contaminants and prevent cross-contamination between samples, safeguarding the integrity of the experimental process. All laboratory surfaces were thoroughly cleaned and wiped down before and after each experimental session to remove any potential sources of contamination. Glassware materials were preferred for sample processing, as they offer superior resistance to leaching and contamination, reducing the risk of introducing external particles or impurities. Before use, all glassware and tools were meticulously washed three times using deionized (DI) water, ensuring their cleanliness and minimizing the potential for contamination. To prevent unintended contamination during periods of inactivity, samples were covered with glass or aluminum covers when not actively being processed. This protective measure shielded the samples from airborne particles and potential cross-contamination, preserving their integrity until further analysis.

Blank control experiments were conducted for the lab space in a previous study. These experiments involved processing samples without the inclusion of microplastic components, allowing for the identification and evaluation of any inadvertent contamination or experimental artifacts that could impact the accuracy and interpretation of the results. By implementing these comprehensive quality assurance and control measures, the study maintained a controlled and

contamination-limited environment. These practices ensured reliable and accurate results while upholding the integrity and validity of the research findings.

The detailed quality control for blanks and cross-contamination was carried out in the laboratory and was described in our previous studies (5). Blank columns were used to quantify the number of microplastics that might be released from sand and columns and found the insignificant contribution of those materials compared to the added microplastics (5). Furthermore, the sand column was flushed with DI water before the experiment to remove any potential impurities. We analyzed the background wash solution to analyze for microplastics, and no microplastic was detected in the wash effluent samples, indicating an insignificant contribution of any residues that contribute to false positives. Recovery tests were performed to account for variation in microplastic concentration based on user (Table S1) and the recovery rate was found to be $93.7\% \pm 13.7\%$ (Table S2).

3 Results and Discussion

3.1 UV effect on the hydrophilicity of the microplastic surface

Our results confirmed that an increase in exposure to UV light alters microplastic surface properties such as contact angle (Figure 2). An increase in UV exposure decreased the contact angle of the PET plastics, but the effect appears to be non-linear. After exposure to UV for 15, 30, and 60 minutes, the contact angle decreased from 88° (control, no UV exposure) to 58° , 55° , and 52° , respectively, which is significantly different from that observed for unweathered plastics ($p < 0.001$). The results indicate that most changes in contact angle occurred within the first 15 minutes of the UV exposure. We attributed the results to changes in molecular properties of the plastic surface under UV radiation. When exposed to UV radiation, PET plastic surfaces could undergo a series of free radical chain reactions, which include the breaking of the C-C

bonds and formation of hydroxyl (OH, $\sim 3300\text{ cm}^{-1}$) and carbonyl (C=O, $\sim 1700\text{ cm}^{-1}$) groups (50). These groups increase the polarity of the plastic surface and make them less hydrophobic. Our result is consistent with other studies (43,46,50–52) that examined the chemical changes on the plastic surface during UV irradiation.

In our study, the contact angle of PET decreased by 41% after 15 min exposure to UV radiation, but any additional increase in UV exposure did not decrease the contact angle at the same rate. Increasing exposure from 15 to 30 min resulted in a 5% decrease in contact angle, and a further increase in exposure from 30 to 60 min resulted in a 6% decrease in contact angle. This trend indicates that most changes on plastic surfaces occur within the first few minutes of UV exposure, and any subsequent increase in UV exposure decreases the contact angle to a lesser degree. We attributed this result to a lack of penetration of UV light beyond a few nanometers into the surface. UV light interacts with the top atomic layer of plastics and oxidizes them to form hydroxyl or carbonyl groups (53–55), which can no longer be oxidized further. UV light could not penetrate deep into the plastic surface, thereby limiting further changes in the plastic atomic composition (56). Any longer exposure to UV light can only physically alter the surface by forming cracks, rough surfaces (57), or breakdown to nanoplastics (52,53,58). However, physical alteration by UV light takes many hours, exceeding the UV exposure that occurred in our study. Thus, we rule out physical alteration of PET surface during our weathering in our experiments. This explained why the contact angle did not decrease at a higher rate after the first 15 min of the exposure. Other studies agree with this finding, demonstrating that a decrease in contact angle due to UV weathering follows a more exponential pattern (43,46). Collectively, these results imply that UV light would alter the surface properties of plastics very quickly and make them more hydrophilic. As the hydrophobicity of particles affects their mobility in soil

(23), future studies on microplastic transport should preferably use weathered microplastics, not the pristine microplastic created in lab conditions.

3.2 Mobility of weathered microplastic in sand columns subjected to freeze-thaw cycles

We show that the depth distribution of microplastics varies with the extent to which they were exposed to UV radiation (Figure 3). Microplastics pre-exposed to UV light for 60 min transported a greater distance in sand filters than the unweathered microplastics. An increase in UV exposure increased the mobility of microplastics deeper into the subsurface, but the mobility was more apparent within the first 3 cm below the surface during the experimental time frame. Most microplastics did not move beyond 5 cm depth and resided in the top 5 cm of the column. Comparing the increase in the concentration of weathered microplastics at 1 and 2 cm depths (Figure 3-E), we proved that an increase in weathering time significantly ($p < 0.05$) increased the mobility of microplastics (Table S3). For instance, a 15-min UV exposure to microplastics increased their concentration relative to control (no exposure) by 93% at 1 cm and 73% at the 2 cm depth. A 60-min UV exposure increased their concentration by 254% at 1 cm and 172% at 2 cm depth. The increase in the transport of weathered microplastics is further confirmed by a higher concentration of microplastic in the effluent in the columns containing weathered microplastics (Figure 4). There was a significant increase in the mobility of microplastics in effluent samples as the weathering time increased from 0 to 30 and 60 minutes ($p < 0.05$), (Table S4). However, no significant difference ($p > 0.05$) in mobility was observed at a weathering time of 15 minutes.

Previous studies showed that freeze-thaw cycles could facilitate the transport of microplastics in porous media (36,30,5,26). The mechanism of microplastic transport near a moving ice front is similar to our study. As the ice-water interface approaches within a few

nanometers from the suspended microplastics, microplastic particle as insulator blocks warmer water flow and heat transport from bulk liquid to the ice front, thereby rapidly cooling the interface (30). Thus, ice crystals grow more rapidly near the interface forming a convex perturbation between ice and plastics, which pushes the microplastic downward in the direction of ice crystal growth. This theory explained why freeze-thaw cycles could accelerate microplastic mobility in pore water, but it did not explain why weathering would increase the effectiveness of freeze-thaw cycles to push microplastics even deeper into the subsurface as observed in this study. We attributed the results to a decrease in free energy for pushing microplastics into the water and a decrease in net attractive interactions or an increase in net repulsive interactions with porous media surface. While at one end, ice pushes the microplastics downward, the other end of the plastic surface must break the hydrogen bonds between water molecules and displace them to move downward. The energy required to replace the water molecules with mostly carbon atoms in plastic polymers depends on the surface properties of plastic particles. If the surface is more hydrophobic (less H-bond forming functional groups), the energy required will be higher. If the surface is less hydrophobic, which is the case for weathered microplastics due to the formation of polar functional groups, the energy required to push microplastics will be lower. Measurement of contact angle confirmed that an increase in UV exposure decreased hydrophobicity or increased hydrophilic properties of plastic surface. This result indicates that water offers less resistance to hydrophilic microplastics than hydrophobic particles to move in the water column. A previous batch study (46) observed a similar trend: the dispersivity of polyethylene microplastics in water increased with an increase in UV exposure. Increased mobility of UV-weathered polystyrene nanoplastics was also observed in saturated loamy sand without dynamic freeze-thaw or dry-wet cycles (16). Calculating interaction energy

between nanoplastics and sand surface using extended DLVO theory, they proved that a decrease in hydrophobic attraction and an increase in hydrophilic repulsion between sand and microplastics due to weathering increased nanoplastics mobility. The same theory is also applied in our study. Thus, UV-weathered microplastics are more susceptible to moving in the subsurface under freeze-thaw cycles.

Our results confirmed that microplastics are pushed into biofilters by freeze-thaw cycles, and weather particles are pushed deeper than unweathered microplastics. As most microplastics are filtered by porous media in the biofilter, the size of microplastics exerts the primary control on what fraction of total microplastics could be removed by straining (59). Thus, we speculate that smaller microplastics, which are less likely to be removed by straining, could be susceptible to downward mobility by freeze-thaw cycles. This is particularly important because the smallest size microplastics pose the greatest risk due to the accumulation of pollutants and enhanced mobility in aquatic systems and the human body (60). However, we did not measure the particle size distribution of trapped microplastics at different depths to confirm if size fractionations occurred during the transport of microplastics by freeze-thaw cycles. Future studies should examine the size fractionation of microplastics during their mobility through porous media or biofilters subjected to natural dry-wet and freeze-thaw cycles.

3.3 Environmental Implications

Most particles are exposed to sunlight in terrestrial environments, which can oxidize their surface and make them less hydrophobic. Our study confirms that the UV exposure and weathering of microplastics could disproportionally increase their mobility in the subsurface soil during freeze-thaw cycles. The results would help predict the distribution of microplastics in the top 3 cm of subsurface soils, which has implications for crop productivity and root function (61).

Our data shows that most microplastics were retained within the top 3 cm of soil because of the short duration of the experiment. In nature, freeze-thaw cycles occur many more times over decades. In the long run, weathered microplastics or nanoplastics could move much deeper into the subsurface and end up in the groundwater (23,62,63). As climate change is expected to spur more drastic fluctuations in freezing cycles in future years, the results from this study could help estimate the transport of microplastics in subsurface soil by accounting for the local weather effects on both microplastic surface properties and their mobility.

4 Conclusions

This study examines the transport of weathered microplastics in stormwater biofilters during freeze-thaw cycles and proves that freeze-thaw cycles could preferentially increase the mobility of UV-weathered microplastics compared to unweathered microplastics. Most microplastics were retained within the top 5 cm of the sand layer indicating the shallow subsurface could become the reservoir of microplastics from where they can be mobilized downward based on the conditions in the subsurface. Two of those conditions that can increase microplastic transport are: (1) an increase in the UV weathering of microplastics deposited on the earth's surface and (2) an increase in the frequency of freeze-thaw cycles. Our study confirmed that an increase in UV exposure decreased the hydrophobicity of PET surface potentially due to the formation of polar functional groups via oxidation of plastic polymer. Increased mobility of weathered microplastics is attributed to a decrease in free energy required to push microplastics into the water and a decrease in net attractive interactions or an increase in net repulsive interactions with porous media surface. Thus, future studies should use weathered microplastics instead of pristine microplastics and transient weather conditions to predict the microplastic transport in subsurface soils or stormwater treatment systems.

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