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Experimental Evidence from the Field that Naturally Weathered Microplastics Accumulate Cyanobacterial Toxins in Eutrophic Lakes

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Abstract: Freshwater ecosystems with recurring harmful algal blooms can also be polluted with plastics. Thus the two environmental problems may interact. To test whether microplastics influence the partitioning of microcystins in freshwater lakes, we examined the sorption of four microcystin congeners to different polymers of commercially available plastics (low-density polyethylene, polyethylene terephthalate, polyvinyl chloride, and polypropylene). We conducted three experiments: a batch sorption experiment in the laboratory with pristine microplastics of four different polymers, a second batch sorption experiment in the laboratory to compare pristine and naturally weathered microplastics of a single polymer, and a 2-month sorption experiment in the field with three different polymers experiencing natural weathering in a eutrophic lake. This series of experiments led to a surprising result: microcystins sorbed poorly to all polymers tested under laboratory conditions (<0.01% of the initial amount added), irrespective of weathering, yet in the field experiment, all polymers accumulated microcystins under ambient conditions in a eutrophic lake (range: 0–84.1 ng/g). Furthermore, we found that the sorption capacity for microcystins differed among polymers in the laboratory experiment yet were largely the same in the field. We also found that the affinity for plastic varied among microcystin congeners, namely, more polar congeners demonstrated a greater affinity for plastic than less polar congeners. Our study improves our understanding of the role of polymer and congener type in microplastic–microcystin sorption and provides novel evidence from the field, showing that naturally weathered microplastics in freshwater lakes can accumulate microcystins. Consequently, we caution that microplastics may alter the persistence, transport, and bioavailability of microcystins in freshwaters, which could have implications for human and wildlife health. *Environ Toxicol Chem* 2022;41:3017–3028. © 2022 SETAC

Keywords: Absorption; adsorption; algal toxins; biofilm; freshwater toxicology; microplastics

INTRODUCTION

Plastic pollution is increasingly common in freshwater ecosystems with pervasive harmful algal blooms (HABs; Earn et al., 2021; Egessa et al., 2020; Zhang et al., 2020). The interplay between these globally important environmental issues (i.e., plastic pollution and eutrophication) is critical to understand because plastics, particularly microplastics (smaller than 5 mm), could potentially exacerbate the problem of freshwater HABs. For example, microplastics may act as a dispersal vector for bloom-forming cyanobacteria (Masó et al., 2003; Naik et al., 2019; Oberbeckmann et al., 2014; Yokota et al., 2017; Zettler et al., 2013), expanding the spatial and temporal extent of HABs. Furthermore, microplastics may influence the growth of toxin-producing cyanobacteria or the production and release

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of toxins by these cyanobacteria (Sánchez-Fortún et al., 2021; Wan et al., 2021; Wu et al., 2021; Zhou et al., 2021). An emerging concern and focus of the present study is whether microplastics can influence the environmental fate of waterborne algal toxins released by cyanobacteria. Microplastics are known to act as sinks and vectors for environmental contaminants (Bellasi et al., 2020; Caruso, 2019; Hartmann et al., 2017) and have the potential to change a number of environmental behaviors of algal toxins (e.g., partitioning, transport, persistence, and bioavailability). If this is indeed the case, plastic pollution in freshwater ecosystems could alter the exposure of humans and wildlife to these harmful toxins.

One mechanism by which microplastics can influence the fate of waterborne contaminants is through the process of sorption. This interaction has been documented for a wide range of environmental contaminants, including polycyclic aromatic hydrocarbons (Frias et al., 2010; Rios et al., 2007; Rochman et al., 2013), polychlorinated biphenyls (Endo et al., 2005; Frias et al., 2010; Mato et al., 2001; Rios et al., 2007; Rochman et al., 2013), metals (Ashton et al., 2010; Richard et al., 2019; Rochman et al., 2014), and pharmaceuticals (Magadini et al., 2020). Recent research demonstrates that microplastics can sorb microcystins (Moura et al., 2022; Pestana et al., 2021; Qu et al., 2019), which are potent hepatotoxins produced by freshwater HABs that can have deleterious health effects on humans (Carmichael, 2001) and wildlife (Gene et al., 2019; Shahmohamadloo et al., 2021).

Microcystins are a family of over 300 monocyclic heptapeptides (Bouaïcha et al., 2019). The pervasive success of microcystins in eutrophic freshwaters can be attributed to various factors, including their structural diversity and physicochemical properties (Ortiz et al., 2017; Puddick et al., 2014; Zastepa et al., 2014). Microcystins vary in polarity depending on their amino acid composition (e.g., number of arginine moieties conferring polarity), which in turn dictates their sorption potential to surfaces including sediments (Harada & Tsuji, 1998; Miller et al., 2001; Wu et al., 2011; Zastepa et al., 2014, 2017) as well as glass and plastics (Altaner et al., 2017; Hyenstrand et al., 2001). Cation-bridging, hydrogen-bonding, and electrostatic interactions are some of the sorption mechanisms responsible for the interaction between microcystins and hydrophobic phases in water (Altaner et al., 2017; Newcombe et al., 2003; Wu et al., 2011), mechanisms that are also responsible for the sorption of waterborne hydrophilic contaminants, such as antibiotics, to microplastics (Li et al., 2018; Liu et al., 2019; Zhang et al., 2018). Because freshwater HABs are projected to increase in duration under a warming climate (Chapra et al., 2017), the frequency and occurrence of microcystins in global freshwaters may likewise increase, affording more opportunities for interaction with microplastics.

Although recent research has demonstrated that microcystin congeners quickly adsorb to pristine microplastics in artificial freshwater laboratory assays (He et al., 2022; Moura et al., 2022; Pestana et al., 2021), to our knowledge, no study has resolved the question of do weathered microplastics affect the environmental fate of microcystins in surface waters of natural ecosystems. Once plastics enter the aquatic environment, their properties immediately begin to change as a result of weathering processes (Arp et al., 2021), which include abiotic and biotic weathering, as well as mechanical degradation and fragmentation. Weathering processes can significantly change the physicochemical properties of plastics (e.g., specific surface area, crystallinity, and oxygen content of surface functional groups), thereby influencing their sorption behavior and other interactions with co-pollutants (Duan et al., 2021; Liu et al., 2020). Biofilm formation may likewise influence the kinetics of uptake and release of contaminants by microplastics (Rummel et al., 2017). Consequently, it is prudent to resolve whether the natural weathering of microplastics modifies their sorption capacity for microcystins in freshwater ecosystems afflicted by HABs.

In the present study, we assessed the sorption of four structurally diverse and recurring microcystins (microcystin–arginine–arginine [MC-RR], microcystin–tyrosine–arginine [MC-YR], microcystin–leucine–arginine [MC-LR], and microcystin–leucine–alanine [MC-LA]) to four types of polymers of commercially available plastics (low-density polyethylene [LDPE], polyethylene terephthalate [PET], polyvinyl chloride [PVC], and polypropylene [PP]). Because microplastic-contaminant sorption is influenced by the physicochemical properties of both the microplastic and the contaminant as well as the conditions of the ambient environment (Hartmann et al., 2017), we conducted two batch sorption laboratory experiments, one with unweathered microplastics of four different polymers (Experiment 1) and one with a single polymer exposed to different weathering conditions (Experiment 2), as well as a sorption field experiment with three different polymers in a eutrophic lake (Experiment 3). We wanted to test the following hypotheses: that sorption capacity for microcystins differs among polymer types (H1), that affinity for plastic varies among microcystin congeners (H2), and that weathered microplastics have a greater sorption capacity for microcystins compared with unweathered microplastics (H3).

MATERIALS AND METHODS

Laboratory batch sorption experiment with unweathered microplastics (Experiment 1)

The first experiment was conducted at the Ontario Ministry of the Environment, Conservation and Parks (MECP; Etobicoke, ON, Canada) and consisted of five experimental groups (six replicates/group): four treatments of different polymers (LDPE, PET, PVC, and PP) and a negative control (no added microplastics). Thirty 1-L deactivated borosilicate clear glass bottles were filled with 500 ml of ultrapure water (conductivity <2 mS/cm at 25 °C, total organic carbon <2 ppm) and 500 microplastic particles, measured gravimetrically. Each bottle was spiked with 2.5 µg each of MC-RR, MC-YR, MC-LR, and MC-LA (all 95% or more pure; Enzo Life Sciences) to achieve a final concentration of 20 µg/L total microcystins, which is representative of the guideline value of the World Health Organiation (WHO) for maximum acceptable levels of total microcystins (expressed as MC-LR equivalent) in recreational waters (WHO, 2020). Bottles were rotated continuously at 20 °C throughout the experiment

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for 48 h. An exposure period of 48 h was chosen because 1) a pilot study showed that the microplastic–microcystin equilibrium was reached within 48 h (data not shown), and 2) many other laboratory-based microplastic-contaminant sorption studies employ a similar exposure period (Guo et al., 2018; Liu et al., 2019; Zhang et al., 2018). At 0, 1, 2, 4, 8, 16, 32, and 48 h, 5 ml of solution and 50 microplastics were collected from each bottle for microcystin analysis. Solution subsamples were stored in PP tubes at −40 °C and microplastic subsamples were stored in PP tubes with 10 ml of methanol at room temperature (20 °C).

Laboratory batch sorption experiment with weathered microplastics (Experiment 2)

The second experiment, also performed at the MECP laboratory, consisted of five experimental groups (6 replicates/group): three treatments of one polymer under different weathering conditions (weathered LDPE in filtered lake water, unweathered LDPE in filtered lake water, and unweathered LDPE in ultrapure water), a negative filtered lake water control, and a negative ultrapure water control. Filtered lake water (nylon mesh, 100 μm) obtained from Buck Lake (44°32′51.4″N 76°26′09.8″W, ON, Canada) was used to increase the environmental relevance of the experiment. The LDPE microplastics were chosen because they demonstrated sorption capacity for all microcystin congeners tested in Experiment 1. Microplastics were weathered from July 1 to September 15, 2019 in Buck Lake, a small (surface area: 755 ha, volume: 25.9×10^6 m^3), deep (depth: mean 11.9 m, maximum 40.9 m) mesotrophic lake that is not prone to cyanobacterial HABs; thus microcystin-contaminated microplastics or lake water samples were unlikely to interfere with the laboratory exposure. We confirmed that there were no microcystins in weathered microplastics and lake water samples. Microplastics were enclosed in a wooden frame wrapped in a black fiberglass mesh screen (1 mm^2), which was suspended from stainless steel wire fixed to two floating docks and submerged approximately 0.1 m below the surface of the water (Supporting Information, Figure S1). Microplastics were retrieved from Buck Lake 36 h prior to the experiment and transported to the MECP laboratory in lake water at ambient temperature. This experiment followed the same procedure as Experiment 1 (i.e., microplastics were exposed to 20 μg/L total microcystins consisting of MC-RR, MC-YR, MC-LR, and MC-LA), except subsamples were collected at 0, 1, 2, 4, 8, 16, 32, 64, and 128 h to ensure that a state of sorption equilibrium was reached because the pilot study referenced in the previous section, *Laboratory sorption experiment with unweathered microplastics (Experiment 1)*, was conducted with unweathered microplastics only.

Field-based sorption experiment (Experiment 3)

The third experiment was conducted in Dog Lake (44°23′43.9′N 76°21′50.0′W, ON, Canada), a small eutrophic lake (surface area: 964 ha, volume: $55.4 \times 1\,0^6$ m^3). This lake has a deep northern basin (depth: maximum 50 m) and a shallow southern basin (depth: <3 m), where HABs are pervasive during warmer months. In the past decade, total microcystins in surface water concentrations of this lake have ranged from <0.05 to >7 μg/L (E. Korenkova, personal communication, August 26, 2022). This experiment was conducted at two sites in the littoral zone of the southern basin where HABs are known to recur.

Experiment 3 consisted of four experimental groups (three replicates/group): three treatments of different polymers (LDPE, PET, and PVC) and a control (water with no microplastics). Following the same weathering set-up as Experiment 2, 18 wooden frames (3 frames × 3 polymer × 2 sites) were deployed in Dog Lake on August 21, 2019 and 250 microplastics were collected from each wooden frame weekly for microcystin analysis between August 29 and October 24, 2019 (excluding September 25 and October 2 and 16 due to adverse weather). Therefore, the microplastics used in Experiment 3 were weathered for a similar period of time (9 weeks) compared with the microplastics used in Experiment 2 (10 weeks). After collection, microplastics were rinsed with reverse-osmosis water and gently dried with a Kimwipe™ to remove lake water droplets. Subsurface (0.5 m) water samples were collected in 1-L amber glass bottles in triplicate at the time of microplastic collection and stored on ice for return to the laboratory. Water samples were homogenized by manual agitation, and a 40-ml aliquot of whole water was collected for microcystin analysis. Microplastic and water samples were stored in PP tubes at −20 °C. Collection bottles were sterilized between sampling events.

Plastic polymers and characterization

All experiments used recycled LDPE, PET, PVC, and PP (Kal-Polymers). These plastics were made from recaptured postconsumer waste to create preproduction plastic pellets used to make plastic products and likely contained a complex blend of chemical additives (see Brosché et al. (2021) for a recent global study). Polymers had different morphologies (Table 1), and identifications were confirmed by Fourier transform infrared (FT-IR) spectrometry (Agilent Cary 630 device; Figure 1A and Supporting Information, Table S1). Surface areas of each polymer were determined by the Brunauer–Emmett–Teller (BET) method from ultra-high-purity nitrogen gas adsorption isotherms at 77 K using an ASAP 2000 surface area and porosity analyzer (Micrometrics; Table 1). The FT-IR and BET analyses were performed at the Metrology Research Centre, National Research Council Canada. Surface morphology of each polymer was observed by scanning electron microscopy (SEM; FEI Quanta 250) at Queen's University.

Microcystin analysis

Microcystins sorbed to microplastics were extracted in triplicate with 10 ml of methanol. Microcystins are highly soluble in methanol (Altaner et al., 2017), which is why this solvent was

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TABLE 1: Physical characterization of polymers used for Experiments 1–3

Polymer[a]	Shape	Largest dimension (mm)	Weight (mg)	Specific surface area[b] (m^2/g)
Low-density polyethylene (LDPE)	Disc-shaped	3–5	18.7 ± 1.4	2.0 ± 1.1
Polyethylene terephthalate (PET)	Fragmented	5	54.7 ± 7.4	0.3 ± 0.1
Polyvinyl chloride (PVC)	Cylindrical	3	18.5 ± 0.3	3.4 ± 0.3
Polypropylene (PP)	Cylindrical	3	25.1 ± 0.1	0.3 ± 0.1

[a]Polymer as confirmed by Fourier transform infrared spectroscopy (see Figure 1).
[b]Specific surface area as measured by the Brunauer–Emmett–Teller method.
Weight and surface area are shown as mean ± standard deviation ($n = 3$).

chosen to both store and extract the microplastic samples. Samples were sonicated for 15 min and left to sit at room temperature (20 °C) for 30 min, after which extracts were transferred to new PP tubes. Extracts were evaporated to near dryness (<0.5 ml) under a stream of nitrogen gas at 50 °C. Microcystins were resuspended in a 4.5-ml mixture of ultrapure water/methanol (75:25, v/v). Final solutions were filtered through a hydrophilic PP membrane (0.45 μm), and 2 ml was collected for microcystin analysis. Extracts from microplastic samples collected from Dog Lake were diluted 1:4 in a mixture of ultrapure water/methanol (75:25, v/v) after filtration. Water samples were filtered through a hydrophilic PP membrane (0.45 μm), and 2 ml was collected for microcystin analysis. Water samples from Dog Lake required three freeze/thaw cycles (at −40 °C and 50 °C, respectively) before filtration to ensure recovery of cell-bound microcystins.

Concentrations of MC-RR, MC-YR, MC-LR, and MC-LA in microplastic extract and water were determined by on-line solid-phase extraction coupled to liquid chromatography-quadrupole time-of-flight mass spectrometry (Water Xevo

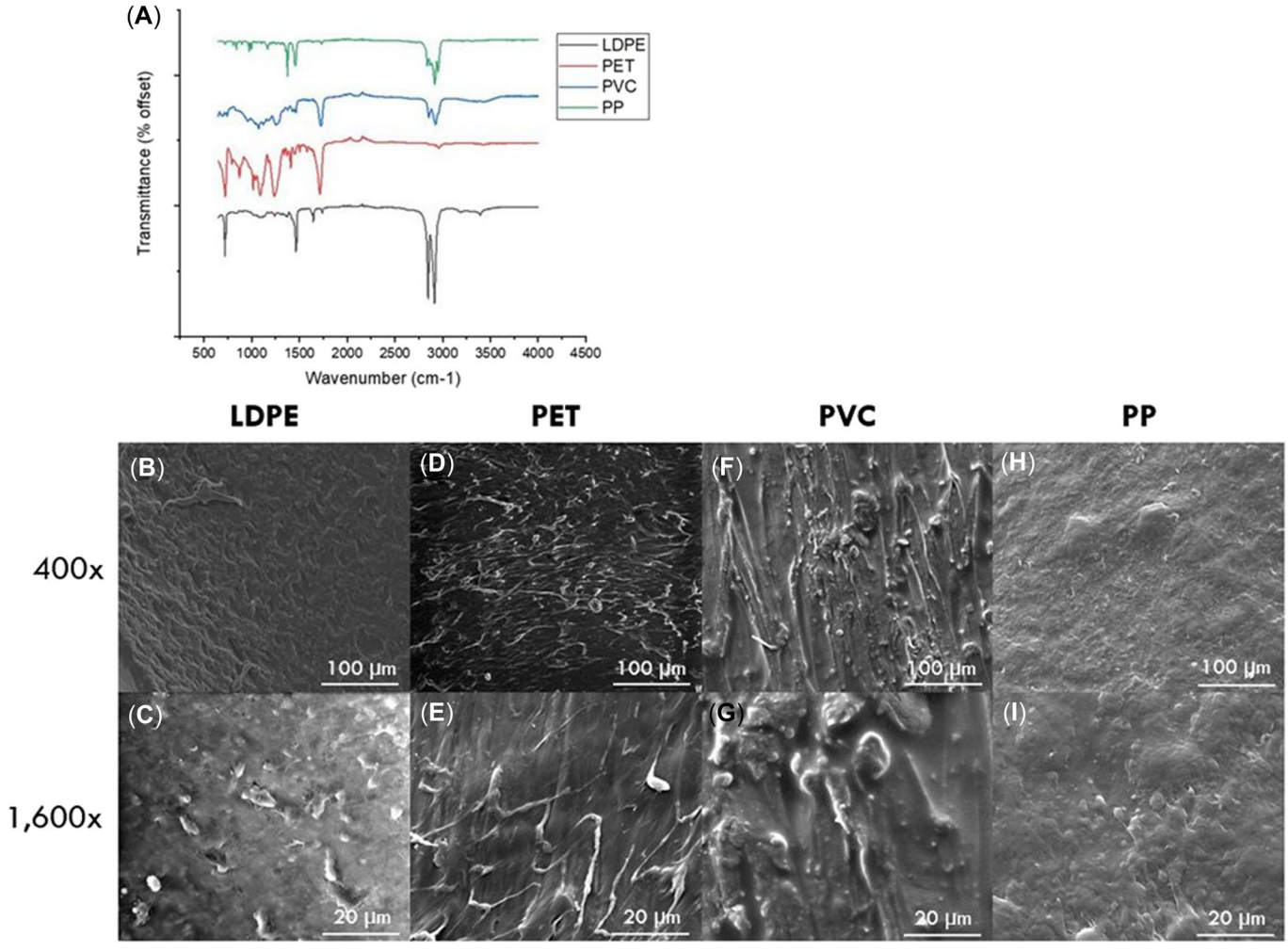

FIGURE 1: Fourier transform infrared spectra (**A**) of low-density polyethylene (LDPE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polypropylene (PP). Characteristic peaks were identified and match respective polymer types (Supporting Information, Table S1). Scanning electron microscopy images at ×400 and ×1600 magnification of LDPE (**B** and **C**), PET (**D** and **E**), PVC (**F** and **G**), and PP (**H** and **I**).

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G2-XS; Ortiz et al., 2017). Nodularin (95% or higher purity; Enzo Life Sciences), an algal toxin with a monocyclic pentapeptide structure like that of microcystin but not commonly present in fresh water, was used as an internal standard. In Experiments 1 and 2, changes in aqueous microcystin concentration were undetectable. Microplastic extract and water from Experiment 3 were also tested for microcystin–homotyrosine–arginine (MC-HtyR), microcystin–homoisoleucine–arginine (MC-HilR), microcystin–tryptophan–arginine (MC-WR), microcystin–leucine–tryptophan (MC-LW), microcystin–leucine–phenylalanine (MC-LF), microcystin–leucine–tyrosine (MC-LY), microcystin–Dha^7–leucine–arginine (MC-Dha^7-LR), and microcystin–Dha^7–arginine–arginine (MC-Dha^7-RR). In Experiments 1 and 2, total microcystins ($\sum_4$MCs) was defined as the sum of the concentrations of MC-RR, MC-YR, MC-LR, and MC-LA. In Experiment 3, total microcystins ($\sum_{12}$MCs) was defined as the sum of the concentrations of MC-LR, MC-YR, MC-RR, MC-HtyR, MC-HilR, MC-WR, MC-LW, MC-LA, MC-LF, MC-LY, MC-Dha^7-LR, and MC-Dha^7-RR. To account for the different morphologies of polymers (Table 1), microcystin concentrations were standardized in two different ways: ng microcystin/gram of microplastic (ng/g) and ng microcystin/surface area of microplastic (ng/m^2).

Statistical analyses

Data analyses were performed using Sigma Plot Ver 14.5 (SYSTAT Software). For Experiment 3, differences among polymer types were tested by one-way analysis of variance (ANOVA) on each sampling date. Post hoc Bonferroni tests were used to distinguish significantly different mean values ($\alpha = 0.05$). Normality and homogeneity of variance were verified by Shapiro–Wilk and Brown–Forsythe tests, respectively. If assumptions were not met, data were analyzed by Kruskal–Wallis one-way ANOVA on Ranks. Post hoc Dunn's tests were used to distinguish significant differences among experimental groups ($\alpha = 0.05$).

RESULTS

Laboratory batch sorption experiment with unweathered microplastics (Experiment 1)

In the 48-h sorption experiment, microcystins sorbed poorly, or not at all, to all four polymers. Concentrations of $\sum_4$MCs ($n = 8$ sampling events) sorbed to microplastics ranged from 1.1 to 4.1 ng/g for LDPE, 0.2 to 1.0 ng/g for PET, 0.0 to 0.3 ng/g for PP, and 0.0 to 0.2 ng/g for PVC (Figure 2 and see Supporting Information, Figure S2, for concentrations standardized to surface area). Maximum concentrations of $\sum_4$MCs sorbed to microplastics were reached within 1 h, and generally declined thereafter, whereas microcystins in water samples remained at the initial concentration of 20 µg/L (Supporting Information, Table S2). The final masses of $\sum_4$MCs sorbed to LDPE, PET, PP, and PVC after 48 h were approximately 0.008%, 0.005%, 0.0005%, and 0.00005%, respectively, of the initial amount added.

Microcystins with higher polarity (Table 2) demonstrated a greater affinity for microplastics than those with lower polarity

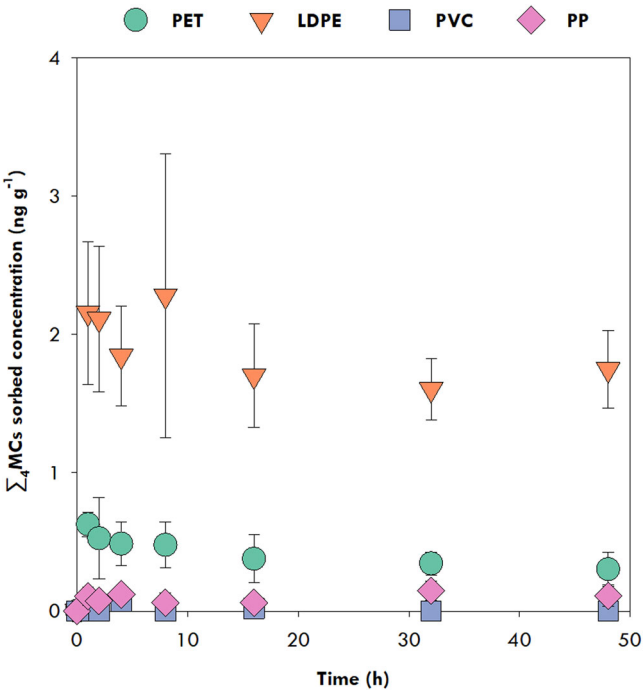

FIGURE 2: Sorption kinetics of total microcystins (∑4MCs; the sum of microcystin–arginine–arginine [MC-RR], microcystin–tyrosine–arginine [MC-YR], microcystin–leucine–arginine [MC-LR], and microcystin–leucine–alanine [MC-LA]) by polyethylene terephthalate (PET), low-density polyethylene (LDPE), polyvinyl chloride (PVC), and polypropylene (PP) at $t = 0$, 1, 2, 4, 8, 16, 32, and 48 h. Each marker represents the mean sorbed concentration (ng/g) ± standard deviation ($n = 6$). Data from Experiment 1 (see *Laboratory batch sorption experiment with unweathered microplastics [Experiment 1]*).

(Figure 3 and see Supporting Information, Figure S3 for concentrations standardized to surface area). Affinity of microcystins for all microplastics followed the general trend: MC-RR > MC-YR > MC-LR > MC-LA. Sorption of MC-RR, MC-YR, MC-LR, and MC-LA by LDPE and PET increased within 1 h, after which MC-RR, MC-YR, and MC-LR appeared to reach equilibrium, whereas MC-LA desorbed. Sorption of all microcystins by PP and PVC was largely negligible, barring the sorption of MC-RR by PP, which marginally increased within 1 h, after which MC-RR appeared to reach equilibrium.

Laboratory batch sorption experiment with weathered microplastics (Experiment 2)

In the 128-h sorption experiment with LDPE only, microcystins sorbed poorly to microplastics, irrespective of weathering. Concentrations of $\sum_4$MCs ($n = 9$ sampling events) sorbed to microplastics ranged from 0.0 to 3.0 ng/g for weathered LDPE in filtered lake water, 0.2 to 4.6 ng/g for unweathered LDPE in filtered lake water, and 0.0 to 2.6 ng/g for unweathered LDPE in ultrapure water (Figure 4 and see Supporting Information, Figure S4, for concentrations standardized to surface area). The final masses of $\sum_4$MCs sorbed to weathered LDPE in filtered lake water, unweathered LDPE in

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TABLE 2: Physical and chemical properties of microcystins used for Experiments 1 and 2

Congener	Name	Molecular weight[a] (Da)	Net charge, pH 7[a]	Log(D_{ow}), pH 7[b]	Hydrophobicity
MC-RR	Microcystin–arginine–arginine	1037	0	0.72 ± 0.05	Least
MC-YR	Microcystin–tyrosine–arginine	1044	–1	—	↓
MC-LR	Microcystin–leucine–arginine	994	–1	–1.2 ± 0.2	
MC-LA	Microcystin–leucine–alanine	909	–2	0.16 ± 0.05	Most

[a]Newcombe et al. (2003).
[b]McCord et al. (2018).
D_{OW} = octanol–water distribution ratio.

filtered lake water, and unweathered LDPE in ultrapure water after 128 h were approximately 0.006%, 0.005%, and 0.003%, respectively, of the initial amount added.

Microcystins with higher polarity (Table 2) demonstrated a greater affinity for weathered LDPE microplastics than less polar ones (Supporting Information, Figure S1 and Figure S5, for concentrations standardized to surface area). Sorption of MC-RR, MC-YR, and MC-LR by weathered LDPE in lake water, unweathered LDPE in lake water, and unweathered LDPE in ultrapure water increased from 1 to 4 h, after which point sorption capacity of weathered LDPE in lake water and unweathered LDPE in ultrapure water reached equilibrium. Unweathered LDPE in lake water, however, continued to increase. Sorption of MC-LA followed no apparent trend.

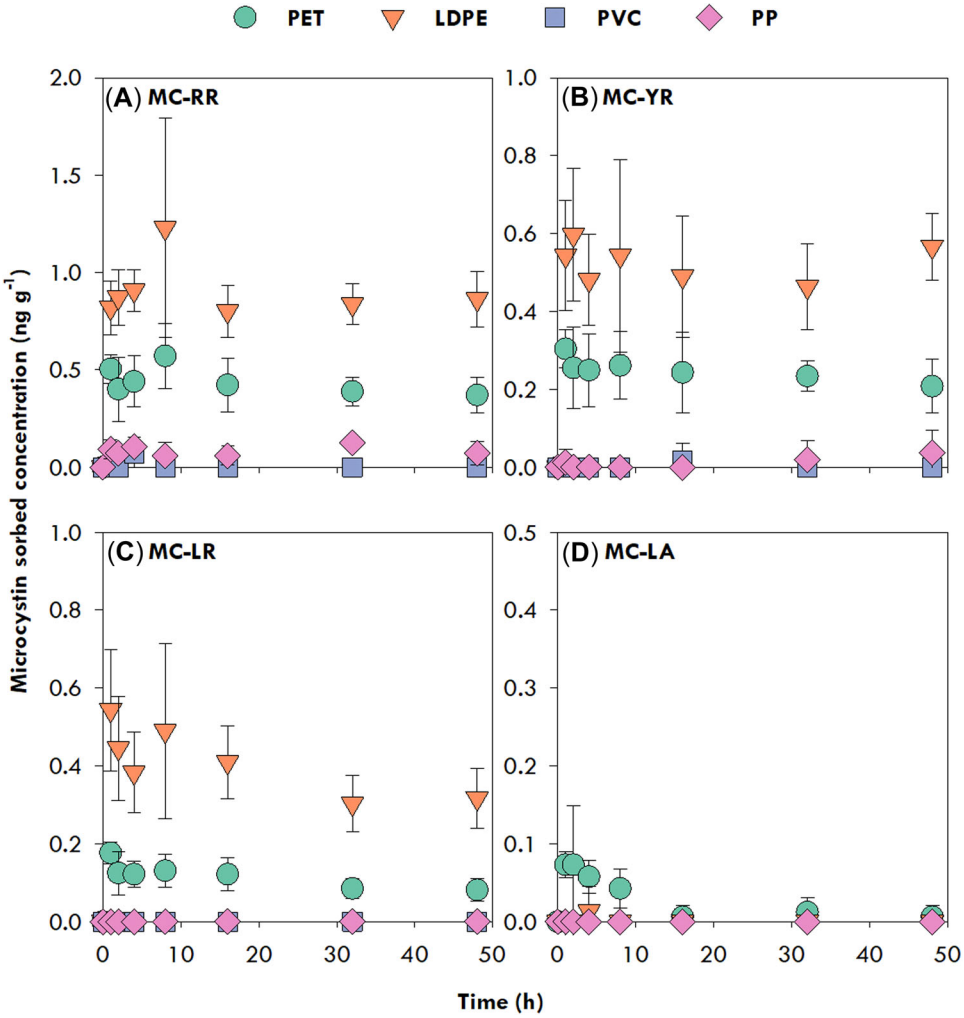

FIGURE 3: Sorption kinetics of microcystin–arginine–arginine (MC-RR; **A**), microcystin–tyrosine–arginine (MC-YR; **B**), microcystin–leucine–arginine (MC-LR; **C**), and microcystin–leucine–alanine (MC-LA; **D**) by polyethylene terephthalate (PET), low-density polyethylene (LDPE), polyvinyl chloride (PVC), and polypropylene (PP) at $t = 0$, 1, 2, 4, 8, 16, 32, and 48 h. Each marker represents the mean sorbed concentration (ng/g) ± standard deviation ($n = 6$). Vertical axes differ among panels. Data from Experiment 1 (see *Laboratory batch sorption experiment with unweathered microplastics [Experiment 1]*).

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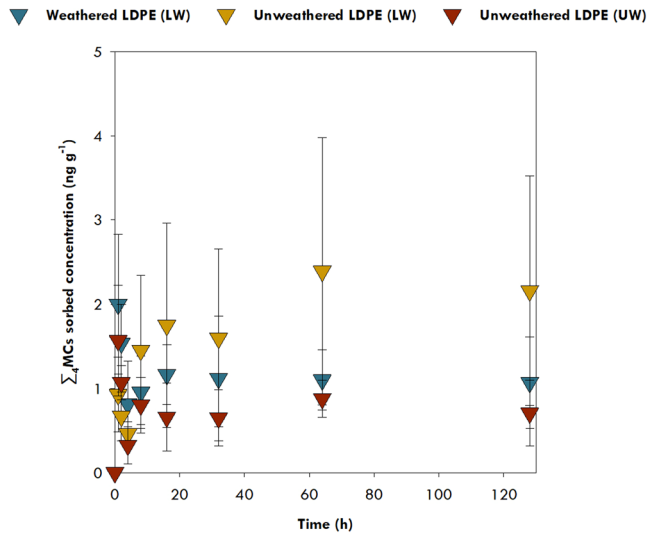

FIGURE 4: Sorption kinetics of total microcystins (∑4MCs; the sum of microcystin–arginine–arginine [MC-RR], microcystin–tyrosine–arginine [MC-YR], microcystin–leucine–arginine [MC-LR], and microcystin–leucine–alanine [MC-LA]) by weathered low-density polyethylene (LDPE) in filtered lake water (LW), unweathered LDPE in filtered lake water (LW), and unweathered LDPE in ultrapure water (UW) at $t = 0$, 1, 2, 4, 8, 16, 32, 64, and 128 h. Each marker represents the mean sorbed concentration (ng/g) ± standard deviation ($n = 6$). Data from Experiment 2 (see *Laboratory batch sorption experiment with weathered microplastics [Experiment 2]*).

Field-based sorption experiment (Experiment 3)

Surface water concentrations of $\sum_{12}$MCs in Dog Lake during the field experiment ($n = 8$ sampling events) ranged from 0.1 to 3.6 µg/L, with maximum concentrations observed in early October (Supporting Information, Figure S7). On average, Site 2 had concentrations of $\sum_{12}$MCs three times greater than those of Site 1. The dominant congener was MC-LA, accounting for more than 88% and more than 53% of $\sum_{12}$MCs measured in surface waters of Sites 1 and 2, respectively. The congener MC-LR was detected at both sites, but MC-RR and MC-YR were detected at Site 2 only.

In the field experiment, microcystins were detected in 100% of PET, 92% of LDPE, and 86% of PVC samples. Concentrations (ng/g) of sorbed $\sum_{12}$MCs on microplastics ranged from 0.2 to 84.1 for PET, 0.0 to 76.5 for LDPE, and 0.0 to 66.1 for PVC (Figure 5 and see Supporting Information, Figure S8, for concentrations standardized to surface area). On average, Site 2 had concentrations of accumulated $\sum_{12}$MCs three times greater than those of Site 1. The mean concentration of accumulated $\sum_{12}$MCs for PET was 14.3 ± 20.0 ng/g (47.7 ± 66.6 ng/m^2), for LDPE was 18.7 ± 24.1 ng/g (9.4 ± 12.1 ng/m^2), and for PVC was 14.4 ± 18.0 ng/g (4.2 ± 5.4 ng/m^2). There was a significant difference in sorption capacity among polymer types at Site 2 on only two sampling dates: LDPE microplastics accumulated significantly more microcystins than PET microplastics on October 10 ($F_{(2,6)} = 7.182$, $p = 0.027$) and October 24 ($F_{(2,5)} = 15.414$, $p = 0.009$).

All microcystins measured in the surface waters of Dog Lake were also measured on microplastic samples collected at the same time (Supporting Information, Figures S9 and S10, for concentrations standardized to surface area). Accumulated concentrations of microcystins on all polymers followed the trend: MC-LA > MC-LR > MC-RR > MC-YR. Of the microplastic samples collected at Sites 1 and 2 ($n = 18$/site), MC-LA was detected in 86% and 96% and MC-LR was detected in 29% and 94%, respectively, and Site 2 also detected MC-YR and MC-RR in 20% and 63% of samples, respectively.

DISCUSSION

Sorption capacity for microcystins differs among polymer types (H1)

The present study demonstrates that the sorption capacity for microcystins differed among polymers in the laboratory experiment (Experiment 1) yet were largely the same in the field (Experiment 3). Under laboratory conditions, LDPE and PET consistently sorbed more microcystins than PP and PVC (Figure 2 and Supporting Information, Figure S2), and therefore, we accept the hypothesis that sorption capacity for microcystins differs among polymer types (H1).

We anticipated differences in sorption capacity among the microplastics tested (Table 1) because sorption behavior is partly driven by the distinct physicochemical properties of each polymer type. Crystallinity, the proportion of crystalline to amorphous regions in a polymer, may explain some of the responses seen in Experiment 1. Sorption occurs predominantly in amorphous regions, where greater sorption is typical in flexible rubbery polymers because rigid glassy polymers are more condensed and cross-linked, and thus have lower permeability (Alimi et al., 2018). Some previous studies on waterborne contaminants support this rule (Wang & Wang, 2018), but others do not (Li et al., 2018). Given that LDPE and PP are considered rubbery, and PET and PVC are considered glassy (Alimi et al., 2018), crystallinity may therefore explain the enhanced sorption capacity of LDPE and the reduced sorption capacity of PVC but neglects to explain the responses of PP and PET.

Pestana et al. (2021) also found that some glassy polymers (polystyrene [PS] and PVC) had a greater sorption capacity for microcystins compared with their rubbery counterpart (PE). This exception to the rule is likely explained by the presence of other more dominant drivers of the interaction, such as some microplastics having a rougher surface, resulting in more sites for adsorption (Pestana et al., 2021). In our case, the poor response of PP may be better explained by the microplastic's low specific surface area (Table 1), which can be an important factor in governing the sorption of hydrophilic contaminants to microplastics (Godoy et al., 2020; Liu et al., 2020). Enhanced sorption capacity of PET may also result from the polarity of the polymer, something seen by Moura et al. (2022) between PET and the more hydrophilic congener MC-WR.

In contrast, sorption capacity was similar among the polymer types tested when microplastics were exposed to microcystins in a eutrophic lake. Although LDPE accumulated

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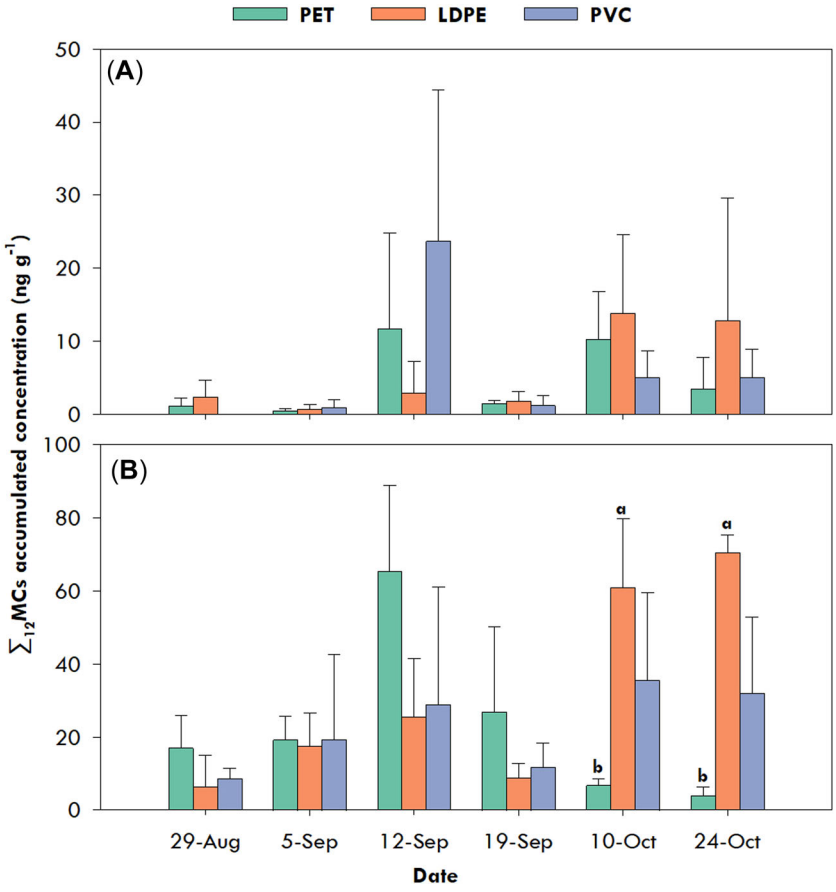

FIGURE 5: Temporal variation in concentration of total microcystins (∑12MCs; the sum of MC-LR, MC-YR, MC-RR, MC-HtyR, MC-HilR, MC-WR, MC-LW, MC-LA, MC-LF, MC-LY, MC-Dha7-LR, and MC-Dha7-RR) accumulated by each polymer type (polyethylene terephthalate [PET], low-density polyethylene [LDPE], and polyvinyl chloride [PVC]) from August 29 to 24 October 24 2019 at Sites 1 (**A**) and 2 (**B**) in Dog Lake, Ontario, Canada. Each bar represents the mean accumulated concentration (ng/g) ± standard deviation ($n = 3$). Vertical axes differ among panels. Lowercase letters represent significant differences across polymer types within locations at each sampling timepoint. Data from Experiment 3 (see *Field-based sorption experiment [Experiment 3]*). MC-HtyR, microcystin–homotyrosine–arginine; MC-HilR, microcystin–homoisoleucine–arginine; MC-WR, microcystin–tryptophan–arginine; MC-LW, microcystin–leucine–tryptophan; MC-LF, microcystin–leucine–phenylalanine; MC-LY, microcystin–leucine–tyrosine; MC-Dha^7-LR, microcystin–Dha^7–leucine–arginine; MC-Dha^7-RR, and microcystin–Dha^7–arginine–arginine. For other abbreviations, see Figure 2 legend.

more microcystins on average in the field compared to PET and PVC, the difference was considerably smaller than the response under laboratory conditions, and the greatest accumulation within each sampling period alternated between each polymer type (6× LDPE, 3× PET, and 3× PVC). This discrepancy in findings between Experiment 1 and Experiment 3 is interesting, albeit somewhat expected, because the factors governing the interaction between microplastics and microcystins will differ between these two environments (see the later section, *Weathered microplastics have a greater sorption capacity for microsystins (H3)*, for further discussion).

Affinity for plastic varies among microcystins (H2)

Experiments 1 and 2 showed that affinity for plastic varies among microcystin congeners when exposed under laboratory conditions. Specifically, more polar microcystins (i.e., congeners with one or two arginine residues—denoted by "R" in the naming scheme—such as MC-RR, MC-YR, and MC-LR) demonstrated a greater affinity for plastic than less polar congeners (i.e., congeners with no arginine residues such as MC-LA; Figure 3 and Supporting Information, Figures S1, S3, and S5). Therefore, we accept the hypothesis that affinity for plastic varies among microcystins (H2).

The chemical structure of the four congeners studied differed only in the amino acid residues present in the variable positions X^2 and Z^4, which are known to govern differences in sorption behavior among microcystins (Altaner et al., 2017). For instance, surface electrostatic interactions are a dominant mechanism in microplastic-contaminant sorption (Elizalde-Velázquez et al., 2020; Godoy et al., 2020; Guo et al., 2018) and likely explain the trend in affinity for plastic among the congeners tested. Microplastics commonly carry a net negative surface charge and are likely to attract positively charged species and repel negatively charged species (Godoy et al., 2019).

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Microcystins also primarily exist in anionic form but can contain both negatively and positively charged groups. For example, at neutral pH, MC-RR has two negatively charged groups and two positively charged groups, MC-YR and MC-LR each have two negatively charged groups and a single positively charged group, and MC-LA has two negatively charged groups (Newcombe et al., 2003; see net charge at pH 7 in Table 2). Consequently, simultaneous surface electrostatic attraction and repulsion likely influence the microplastic–microcystin interaction, an idea supported by MC-RRs strong affinity for plastic compared with MC-LAs poor affinity for plastic. The pH of our laboratory experiments was 7.0 whereas the pH of our field experiment ranged between 7.2 and 9.2, indicating that for the duration of our experiments, MC-RR was net neutral, MC-YR and MC-LR carried a –1 charge, and MC-LA carried a –2 charge.

Other studies examining the microplastic–microcystin interaction observed the opposite trend, namely, as congener hydrophobicity increased, affinity for plastic also increased (Moura et al., 2022; Pestana et al., 2021). This suggests that hydrophobic interactions are a leading force driving the sorption capacity of plastics for microcystins. However, given that microcystins are predominantly hydrophilic molecules, others have noted that hydrophobic interactions are unlikely to play a significant role in their sorption to hydrophobic phases in water and instead have suggested that mechanisms including cation-bridging, hydrogen-bonding, and surface electrostatic interactions are more likely (Wu et al., 2011). The discrepancies in affinity for plastic among congeners between our study and others (Moura et al., 2022; Pestana et al., 2021) further bolster the notion that the interaction between microplastics and microcystins is a multifactor process that is context dependent.

Weathered microplastics have a greater sorption capacity for microcystins (H3)

The present study further demonstrates that although there is no apparent difference in sorption capacity for microcystins between unweathered and weathered LDPE when exposed under laboratory conditions (Experiment 2; Figure 4 and Supporting Information, Figure S4), polymers accumulated more microcystins in the field. Therefore, we accept the hypothesis that weathered microplastics have a greater sorption capacity for microcystins compared with unweathered microplastics (H3). The latter result is likely due to biofilm formation on the microplastics' surface when left to weather under ambient conditions in a eutrophic lake.

Biofilms can increase microplastic surface polarity, hydrophilicity, and specific surface area, contributing to greater sorption capacity, especially for polar and hydrophilic contaminants (Rummel et al., 2017) like microcystins. Biofilm formation across all polymer types could explain why PVC demonstrated sorption capacity for microcystins in the field but not in the laboratory. Furthermore, the accumulation of metals and pharmaceuticals on plastic can be mediated by a biofilm (Magadini et al., 2020; Rochman et al., 2014). Thus, the sorption capacity for microcystins among different polymers may be comparable in the field but noticeably different under laboratory conditions because the biofilm, whose composition can be similar among polymer types within a given location (Ye & Andrady, 1991; Zettler et al., 2013), is the dominant layer for sorption. This hypothesis has recently been tested for one polymer type (PS) and a single microcystin congener (MC-LR) under laboratory conditions (He et al., 2022). In their study, these authors found that PS had enhanced sorption capacity for MC-LR after biofilm formation due to an alteration of the microplastic's surface properties, specifically the addition of oxygen-containing functional groups increasing polar interactions (He et al., 2022). Together, these findings have important implications for studies that assess the interaction between microplastics and microcystin in the laboratory using pristine microplastics. Thus, we recommend that future studies include the influence of biofilm formation on sorption capacity.

In addition, the biofilm itself may contain toxin-producing cyanobacteria. A growing body of evidence demonstrates that microplastics interact with primary producers, including bloom-forming algae such as dinoflagellates and cyanobacteria (Kettner et al., 2019; Masó et al., 2003; Oberbeckmann et al., 2014; Yokota et al., 2017; Zettler et al., 2013). For example, Oberbeckmann et al. (2014) identified cyanobacteria as a dominant constituent of the plastisphere on PET drinking bottles submerged in the North Sea and PS, PP, and PE microplastics collected from the same area. Similarly, in a laboratory-based experiment, Yokota et al. (2017) exposed two microcystin-producing freshwater cyanobacteria, *Microcystis aeruginosa* and *Dolichospermum flos-aquae*, to microplastics and found colonial and filamentous cyanobacteria to be a dominant part of the plastisphere. In our study, it is probable that the microplastic-associated microcystins detected in the field included extracellular (i.e., waterborne) toxins sorbed from the ambient environment and intracellular (i.e., cell-bound) toxins from cyanobacteria colonizing the microplastic's surface. The latter additional, more indirect microplastic–microcystin interaction mechanism may also explain why we measured greater accumulated concentrations in the field (Experiment 3) than in the laboratory (Experiments 1 and 2) despite a considerably lower aqueous microcystin concentration in Dog Lake (Supporting Information, Figure S7).

CONCLUSIONS

A comprehensive understanding of the combined effects of microplastic pollution and HABs in freshwater ecosystems is vital for assessing environmental risk. Recent studies on nanoplastics and microcystins offer insights into these potential synergies. For example, amino-modified PS nanoparticles can promote microcystin synthesis and extracellular release from *Microcystis aeruginosa* (Feng et al., 2020); PS nanoplastics can weaken inhibitory effects of hydrogen peroxide, a control measure for HABs (Guo et al., 2021); and prolonged exposure to PS nanoparticles can enhance MC-LR toxicity in the nematode *Caenorhabditis elegans* (Qu et al., 2019). In terms of the

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latter concern regarding adverse impacts on aquatic life, organisms at every level of the food web have been shown to ingest or interact with microplastics (Bucci et al., 2020), and biofilm formation can increase their likelihood of doing so (Rummel et al., 2017), potentially increasing the possibility of microcystins causing a toxic insult. Still, the role of microplastic ingestion as a dominant pathway for contaminant transfer to biota is contested. Some researchers argue that the fraction of a given contaminant associated with microplastics is negligible compared with other natural media such as water, sediment, and food (Bakir et al., 2016; Koelmans et al., 2016). However, given that this idea is often discussed in reference to legacy contaminants, which waterborne microcystins are not, whether microplastics act as a vector for exposure to microcystins in biota should be investigated further.

Our findings also indicate that microplastics may influence the persistence and facilitate the transport of microcystins in freshwater ecosystems. Unlike legacy contaminants, the concentration of waterborne microcystins is in constant flux. Microcystins typically persist in the water for weeks to months after a bloom event, contingent on natural detoxification routes such as dilution, sorption to sediment, thermal decomposition, photolysis, and biological degradation (Chorus & Welker, 2021). Microplastics may aid in microcystin removal from the water column via accumulation, as was seen by He et al. (2022). However, microplastics may also make microcystins more persistent in surface waters if accumulated microcystins are more stable than waterborne microcystins or if microplastics carry microcystins to new areas within a waterbody with no or low aqueous concentrations. Again, these scenarios merit further investigation to determine the risk posed by both microplastics and microcystins when they are present in the same freshwater ecosystem.

Supporting Information—The Supporting Information is available on the Wiley Online Library at https://doi.org/10.1002/etc.5485.

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Conflict of Interest—The authors declare no conflict of interest.

Author Contributions Statement—**Eden K. Hataley**: Conceptualization; Formal analysis; Investigation; Methodology; Resources; Visualization; Writing—original draft; Writing—review & editing. **René S. Shahmohamadloo**: Investigation; Writing – original draft; Writing—review & editing. **Xavier Ortiz Almirall**: Conceptualization; Formal analysis; Investigation; Methodology; Resources; Supervision; Writing—original draft; Writing—review & editing. **Anna L. Harrison**: Conceptualization; Formal analysis; Writing—review & editing. **Chelsea M. Rochman**: Conceptualization; Formal analysis; Writing—review & editing. **Shan Zou**: Formal analysis; Investigation; Writing—review & editing. **Diane M. Orihel**: Conceptualization; Formal analysis; Funding acquisition; Methodology; Project administration; Supervision; Writing—original draft; Writing—review & editing.

Data Availability Statement—Data produced in this study is available in the Supporting Information.

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