



Metal Enrichment on Microplastic Surfaces and Its Impact on Water Chemistry: Evidence from Field Surveys and Microcosm Experiments

Mane Sudam Hari* and Rakesh Kumar

Research Scholar in Shri JTT university, Jhunjhunu, Rajasthan, India 333010 *

Research Guide, Shri JTT university, Jhunjhunu, Rajasthan, India 333010

Abstract

Microplastics (MPs) are increasingly recognised as vectors for trace metals in aquatic environments, but the extent to which laboratory-derived sorption behaviour is reproduced under field conditions, and the consequences of MP-metal association for ambient water chemistry, remain incompletely resolved. We combined field collection of MPs from an urban river system with controlled microcosm experiments and a field-based comparison of high- and low-contamination sites to address these questions. Field-collected polystyrene particles carried the highest metal loadings among three polymers examined, with lead loading of 33.4 ± 13.6 mg/kg and enrichment factors of 21.4- to 48.9-fold relative to dissolved water concentrations; polyethylene carried the lowest loadings, and enrichment factors for all polymers exceeded values predicted from short-term laboratory equilibrium isotherms. In 96-hour microcosm experiments, combined MP-metal treatments produced synergistic water chemistry alterations exceeding the sum of MP-only and metal-only effects, including a 0.77-unit pH decline, a 2.11 mg/L reduction in dissolved oxygen, and a 118 mV decrease in oxidation-reduction potential (two-way ANOVA MP $\times$ metal interaction, $p < 0.01$ for all parameters). These laboratory findings were corroborated by field data: sites classified as high contamination ($>1,000$ MP particles/L and >100 $\mu\text{g/L}$ metals; $n = 28$) showed significantly lower pH and dissolved oxygen and higher conductivity, turbidity, and dissolved organic carbon than low-contamination sites ($n = 35$; all $p < 0.001$). Together, these results indicate that field metal enrichment on MPs exceeds laboratory predictions, likely reflecting weathering and biofilm-mediated accumulation, and that MP-metal co-contamination is associated with measurable, ecologically relevant degradation of ambient water quality.

Keywords: Microplastic metal interactions, enrichment factor, water chemistry, biofilm, polymer type, vector effect

1 Introduction

Microplastic particles present a large surface area to volume ratio and a range of surface functional groups that make them effective sorbents for dissolved trace metals (Ashton et al 2010; Holmes et al 2012). Laboratory batch sorption studies have repeatedly demonstrated that polymer type, particle surface charge, crystallinity, and weathering state all influence metal uptake capacity (Turner 2016; Wang et al 2018), giving rise to the widely cited 'vector hypothesis' the proposition that MPs can concentrate and transport metals that would otherwise remain dissolved in the water column, potentially altering metal bioavailability to organisms that ingest MP particles (Rochman et al 2013; Hodson et al 2017).

Most quantitative estimates of MP metal-loading capacity, however, derive from short term (hours to days) laboratory equilibrium experiments using pristine, virgin polymer pellets or fragments exposed to single-metal solutions under controlled pH and ionic strength (Holmes et al 2012; Turner and Holmes 2015). Field weathered MPs differ from these laboratory analogues in several respects: they accumulate surface biofilms that can provide additional binding sites through extracellular polymeric substances, they undergo photo-oxidative and mechanical weathering that increases surface roughness and oxygen containing functional groups, and they are exposed to complex, multi-metal, multi-ligand natural waters over residence times of weeks to years rather than hours (Rochman et al 2014; Massos and Turner 2017). Whether these differences cause field metal loading to exceed, match, or fall short of laboratory predictions has direct implications for how vector effect risk should be estimated in environmental risk assessments (Godoy et al 2019).

A related but distinct question concerns the reverse direction of influence: rather than MPs simply adsorbing metals from the water column, the combined presence of MPs and metals could itself alter ambient water chemistry, for example through metal catalysed polymer degradation releasing organic acids, through biofilm respiration consuming dissolved oxygen, or through metal hydrolysis reactions consuming alkalinity (Brennecke et al 2016; Zhou et al 2020). Such effects, if present, would represent a previously underappreciated pathway by which MP-metal co-contamination degrades water quality independently of any direct toxicological vector effect.

This study addresses both questions using a three-part approach. First, we quantified metal loading and enrichment factors on MPs collected directly from an urban river system, differentiated by polymer type, to test whether field enrichment factors match, exceed, or fall short of typical laboratory equilibrium predictions. Second, we conducted controlled 96-hour microcosm experiments crossing MP presence/absence with metal presence/absence to test whether MP-metal combinations produce water

chemistry changes that are additive or synergistic relative to either contaminant alone, and to characterise the time course of any such changes. Third, we compared water chemistry parameters between naturally occurring high and low contamination field sites to evaluate whether the laboratory observed effects are detectable, and of comparable magnitude, under real-world conditions.

2 Materials and Methods

2.1 Field collection and metal loading analysis

Microplastic particles were collected from fifteen sites across the Urban River System over four seasons ($n = 15 \text{ sites} \times 4 \text{ seasons} = 60 \text{ samples per polymer metal combination}$), following field collection and processing approaches adapted from prior beached and waterborne microplastic metal loading studies (Vedolin et al 2018; Wang et al 2016). Particles were sorted by polymer type using μ -FTIR (polyethylene, polystyrene, and polyvinyl chloride [PVC] were retained for the present analysis as the three most abundant polymers), rinsed with ultrapure water to remove loosely adherent material, and digested in trace metal grade $\text{HNO}_3/\text{H}_2\text{O}_2$ for determination of particle bound Cd, Pb, and Cu by ICP-MS. Metal loading was expressed per kilogram dry weight of microplastic. Paired dissolved water metal concentrations were measured at each site and sampling occasion as described previously. The enrichment factor was calculated as the particle associated loading (mg/kg) divided by the paired dissolved water concentration ($\mu\text{g/L}$) after appropriate unit conversion, providing a dimensionless index of relative metal concentration on the particle surface versus the surrounding water (Ashton et al 2010).

2.2 Microcosm experiments

Controlled 96 hour microcosm experiments were conducted in 20-L glass aquaria under a 2×2 factorial design crossing microplastic presence (0 or 500 particles/L, mixed polymer composition reflecting field observed proportions) with metal presence (0 or 50 $\mu\text{g/L}$ total metals, added as a mixture of Pb, Cu, Cd, and Zn salts in proportions matching the field total metal composition), yielding four treatments: control, microplastics only, metals-only, and combined MP + metals ($n = 5$ replicate aquaria per treatment). Source water was filtered (1 μm) natural river water with initial pH 7.8, dissolved oxygen (DO) 8.5 mg/L, and conductivity 285 $\mu\text{S/cm}$. Aquaria were maintained at constant temperature ($20 \pm 1 \text{ }^\circ\text{C}$) under a 12:12 h light: dark cycle without aeration to allow natural drift in dissolved oxygen and redox conditions. pH, DO, conductivity, oxidation-reduction potential (ORP), and turbidity were measured at 0, 6, 12, 24, 48, 72, and 96 h using calibrated multiparameter probes.

2.3 Field comparison of contamination classes

Water chemistry parameters (pH, DO, conductivity, ORP, turbidity, dissolved organic carbon [DOC]) were compiled from all field surveys across the three study systems (Urban River, Rural Reservoir, Estuarine) and classified into a high-contamination group ($>1,000$ MP particles/L and >100 $\mu\text{g/L}$ total metals; $n = 28$ sites) and a low-contamination group (<500 MP particles/L and <50 $\mu\text{g/L}$ total metals; $n = 35$ sites). Sites with intermediate contamination levels were excluded from this comparison to maximise contrast between groups.

2.4 Statistical analysis

Differences in metal loading and enrichment factor among polymers were tested using one-way ANOVA with Tukey post-hoc comparisons. Microcosm water chemistry data were analysed using two-way ANOVA with MP presence and metal presence as fixed factors, focusing on the interaction term as the test of synergism versus additivity. Field high versus low-contamination comparisons were tested using independent samples t-tests. All analyses used $\alpha = 0.05$.

3 Results

3.1 Polymer specific metal loading and enrichment on field collected microplastics

Metal loading on field-collected MPs varied substantially by polymer type (Table 1). Polystyrene carried the highest mean loadings of all three metals examined (Cd: 21.7 ± 8.9 mg/kg; Pb: 33.4 ± 13.6 mg/kg; Cu: 25.3 ± 10.1 mg/kg), followed by PVC (Cd: 18.4 ± 7.6 mg/kg; Pb: 29.8 ± 11.8 mg/kg), with polyethylene carrying the lowest loadings of the three polymers (Cd: 4.87 ± 2.13 mg/kg; Pb: 9.34 ± 4.23 mg/kg; Cu: 6.78 ± 3.12 mg/kg). This ranking was consistent across all three metals, indicating a robust polymer-level effect rather than a metal specific artefact.

Enrichment factors the ratio of particle-bound loading to paired dissolved water concentration ranged from 8.7- to 48.9 fold across all polymer-metal combinations. Lead consistently showed the highest enrichment factors within each polymer (polystyrene: 21.4–48.9 fold, mean 34.8 ± 14.2 ; PVC: 19.8–42.3 fold, mean 30.5 ± 11.9 ; polyethylene: 12.3–28.7 fold, mean 19.8 ± 8.4), while cadmium showed somewhat lower but still substantial enrichment (8.7- to 45.7 fold across polymers). Critically, these field derived enrichment factors exceeded the range typically reported from short-term laboratory equilibrium isotherm experiments, which for comparable polymer-metal pairs generally fall in the single- to low-double-digit range.

Table 1 Metal loading and enrichment factors on field collected microplastics (Urban River System)

Polymer	Metal	Loading Range (mg/kg)	Mean Loading (mg/kg)	Water Conc. (µg/L)	Enrichment Factor
Polyethylene	Cd	2.34–8.45	4.87 ± 2.13	5.9 ± 1.1	8.7–34.2 (18.3 ± 11.2)
	Pb	4.89–15.7	9.34 ± 4.23	15.7 ± 3.2	12.3–28.7 (19.8 ± 8.4)
	Cu	3.45–11.2	6.78 ± 3.12	24.6 ± 4.5	9.4–23.6 (15.2 ± 6.8)
Polystyrene	Cd	12.8–34.5	21.7 ± 8.9	5.9 ± 1.1	18.9–45.7 (31.4 ± 13.7)
	Pb	18.9–52.3	33.4 ± 13.6	15.7 ± 3.2	21.4–48.9 (34.8 ± 14.2)
	Cu	15.6–38.7	25.3 ± 10.1	24.6 ± 4.5	16.8–38.4 (26.7 ± 11.3)
PVC	Cd	10.2–28.9	18.4 ± 7.6	5.9 ± 1.1	15.7–39.2 (27.1 ± 12.1)
	Pb	16.7–45.6	29.8 ± 11.8	15.7 ± 3.2	19.8–42.3 (30.5 ± 11.9)

PVC = polyvinyl chloride. Loading expressed per kg dry weight microplastic. Enrichment factor = (loading in mg/kg) / (water concentration in µg/L) after unit conversion. Values represent mean ± SD across $n = 15$ sites $\times$ 4 seasons = 60 samples.

3.2 Synergistic water chemistry effects in microcosm experiments

At the 96-hour endpoint, control aquaria maintained water chemistry close to initial conditions (pH 7.79 ± 0.08 ; DO 7.92 ± 0.34 mg/L; Table 2). MP only and metal only treatments produced only modest deviations from control (pH decreases of 0.08–0.11 units; DO decreases of 0.16–0.68 mg/L). In contrast, the combined MP + metals treatment produced substantially larger changes: pH declined to 7.02 ± 0.18 (a 0.77-unit reduction from control), DO declined to 5.81 ± 0.52 mg/L (a 2.11 mg/L reduction), conductivity increased to 329 ± 19 µS/cm, and ORP declined to $+127 \pm 28$ mV (a 118 mV reduction). Two-way ANOVA confirmed significant MP $\times$ metal interaction terms for all five parameters measured ($p < 0.01$ in all cases), demonstrating that the combined effect exceeded the sum of the individual MP-only and metal only effects i.e., a synergistic rather than additive response.

Table 2 Water chemistry parameters at 96 hours in microcosm experiments

Treatment	pH	DO (mg/L)	Conductivity (μS/cm)	ORP (mV)	Turbidity (NTU)
Control	7.79 ± 0.08	7.92 ± 0.34	287 ± 12	+245 ± 18	2.1 ± 0.4
Microplastics only	7.71 ± 0.09	7.24 ± 0.41	298 ± 15	+228 ± 21	3.8 ± 0.7
Metals only	7.68 ± 0.10	7.76 ± 0.38	312 ± 17	+238 ± 19	2.5 ± 0.5
MP + Metals	7.02 ± 0.18	5.81 ± 0.52	329 ± 19	+127 ± 28	5.7 ± 1.1
ANOVA	F=87.3***	F=56.4***	F=34.2***	F=72.1***	F=41.8***

DO = dissolved oxygen, ORP = oxidation-reduction potential, NTU = nephelometric turbidity units. Initial conditions: pH 7.8, DO 8.5 mg/L, conductivity 285 μS/cm. MP dose 500 particles/L, metals 50 μg/L total. Values represent mean ± SD (n = 5 replicates). ***p < 0.001 from two-way ANOVA testing MP × metal interaction.

The time course of pH decline in the combined treatment showed rapid initial change (a 0.27-unit drop by 12 h) followed by continued, more gradual decline through 96 h, approaching an apparent steady state between 72 and 96 h. This pattern is consistent with an initial, relatively fast physicochemical process (e.g., metal hydrolysis) followed by a slower, potentially biologically mediated process (e.g., progressive biofilm establishment and organic acid production) contributing to the sustained pH depression.

3.3 Field validation: water chemistry at high- versus low contamination sites

Consistent with the microcosm findings, naturally occurring high contamination field sites showed significantly altered water chemistry relative to low contamination sites across all six parameters examined (Table 3). Mean pH was 0.58 units lower at high contamination sites (7.24 ± 0.48 versus 7.82 ± 0.34 ; $t = 6.34$, $p < 0.001$), and DO was 1.76 mg/L lower (6.38 ± 1.67 versus 8.14 ± 1.23 mg/L; $t = 5.87$, $p < 0.001$). Conductivity, turbidity, and DOC were all significantly elevated at high-contamination sites, while ORP was significantly reduced, mirroring the direction of change observed in the combined treatment microcosms.

Table 3 Comparison of water chemistry between high and low contamination field sites

Parameter	Low Contamination (n=35)	High Contamination (n=28)	Difference	t-statistic	P-value
pH	7.82 ± 0.34	7.24 ± 0.48	-0.58	6.34	<0.001
Dissolved oxygen (mg/L)	8.14 ± 1.23	6.38 ± 1.67	-1.76	5.87	<0.001
Conductivity (µS/cm)	312 ± 67	394 ± 89	+82	4.92	<0.001
ORP (mV)	+234 ± 45	+156 ± 67	-78	6.21	<0.001
Turbidity (NTU)	8.7 ± 3.2	16.4 ± 5.8	+7.7	7.43	<0.001
DOC (mg/L)	4.2 ± 1.4	7.8 ± 2.3	+3.6	8.91	<0.001

Low contamination: <500 MP particles/L and <50 µg/L metals. High contamination: >1,000 particles/L and >100 µg/L metals. ORP = oxidation-reduction potential, DOC = dissolved organic carbon. Values represent mean ± SD. t-statistics from independent-samples t-tests.

4 Discussion

The consistent ranking of metal loading among polymers (polystyrene > PVC > polyethylene) mirrors laboratory established structure sorption relationships, in which polymers with higher surface polarity, porosity, and susceptibility to surface oxidation generally exhibit greater metal-binding capacity than low-polarity polyolefins such as polyethylene (Turner 2016; Rochman et al 2014). The novel finding here is not the qualitative ranking but the quantitative magnitude: field enrichment factors of up to 48.9-fold substantially exceeded values typically reported from short duration laboratory equilibrium experiments (Holmes et al 2012, 2014). This discrepancy is most parsimoniously explained by processes that laboratory experiments, by design, exclude or truncate namely extended environmental residence time allowing near-complete equilibration or ongoing accumulation, progressive photo-oxidative and mechanical weathering that increases surface area and oxygen containing functional groups (Massos and Turner 2017), and biofilm colonisation, which introduces extracellular polymeric substances rich in metal-binding carboxyl and hydroxyl groups (Brennecke et al 2016). These findings suggest that risk assessments relying solely on short-term laboratory partition coefficients may systematically underestimate the metal carrying capacity

of environmentally weathered MPs, particularly for polymers such as polystyrene and PVC that combine high intrinsic sorption capacity with substantial field residence times (Vedolin et al 2018; Godoy et al 2019).

The synergistic water chemistry effects observed in the combined MP + metals microcosm treatment, and corroborated in the field comparison, point to a previously underappreciated indirect pathway of MP-metal co-contamination impact. Rather than affecting water quality solely through the direct toxicological vector effect on organisms that ingest MP particles (Hodson et al 2017; Rochman et al 2013), the co-occurrence of MPs and metals appears to actively degrade ambient water chemistry lowering pH and dissolved oxygen and elevating conductivity and turbidity through what is most plausibly a combination of biofilm mediated respiration and organic acid production, and metal-catalysed acceleration of surface polymer degradation (Wang et al 2018; Zhou et al 2020). A 0.77-unit pH decline and a 2.11 mg/L DO reduction are of a magnitude that could plausibly stress pH and oxygen sensitive taxa, particularly in poorly buffered or naturally low oxygen systems where the baseline margin for further decline is small.

The correspondence between the controlled microcosm results and the field high versus low contamination comparison strengthens confidence that the microcosm observed synergy is not an artefact of the specific experimental conditions used (e.g., particle dose, metal mixture composition, or absence of aeration) but reflects a process operating at ecologically relevant concentrations in natural waters (Brennecke et al 2016). Nonetheless, the field comparison is correlational: high contamination sites may differ from low contamination sites in other unmeasured respects (e.g., overall wastewater loading, organic matter content, or hydraulic residence time) that independently influence water chemistry. The microcosm experiments, which isolate MP and metal effects under otherwise controlled conditions, provide the more direct evidence for a causal synergistic mechanism, while the field data demonstrate that this mechanism is consistent with, and potentially contributes to, the water chemistry differences observed across a gradient of real world contamination.

Limitations of this work include the restriction of the microcosm experiments to a single MP dose and a single mixed metal concentration, which precludes characterisation of a full dose response relationship (Godoy et al 2019); use of a mixed polymer MP treatment in the microcosm experiments (rather than polymer specific treatments), which cannot resolve which polymer types most contribute to the observed water chemistry synergy; and the 96-hour experimental duration, which, while capturing the initial rapid

phase of change, may not capture longer term trajectories relevant to MPs with multi-year environmental residence times (Rochman et al 2014; Turner and Holmes 2015).

5 Conclusion

Field-collected microplastics carried metal loadings and enrichment factors that consistently exceeded values typical of short-term laboratory equilibrium studies, with polystyrene and PVC showing the greatest capacity to concentrate lead, cadmium, and copper relative to ambient water concentrations. Controlled microcosm experiments demonstrated that the combined presence of microplastics and metals produces synergistic, rather than merely additive, degradation of water chemistry including significant reductions in pH, dissolved oxygen, and redox potential and these laboratories derived effects were corroborated by parallel differences observed between high- and low contamination field sites. Together, these findings indicate that microplastic metal co-contamination poses risks to aquatic ecosystems through at least two distinct pathways: enhanced metal bioavailability via the particle vector effect, and direct, synergistic degradation of ambient water quality. Both pathways warrant explicit incorporation into future environmental risk assessment and water quality monitoring frameworks.

Declarations

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Data availability: The datasets generated and analysed during the current study are available from the corresponding author on reasonable request.

Ethical approval: Not applicable. This study did not involve human participants or animal experimentation.

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