



Short Communication

Microplastics release precursors of chlorinated and brominated disinfection byproducts in water

Mohamed Ateia ^{a, b, **, 1}, Amer Kanan ^{c, 1}, Tanju Karanfil ^{a, *}^a Department of Environmental Engineering and Earth Science, Clemson University, SC, USA^b Department of Chemistry, Northwestern University, Evanston, IL, 60208, United States^c Department of Environment and Earth Sciences, Faculty of Science and Technology, Al-Quds University, Palestine

HIGHLIGHTS

- MP in water released DBPs precursors under both light and dark conditions.
- DOC leaching ranges from ~30 to 1000 mg DOC per kg depending on the composition of MPs.
- Reactivity of leached DOC from MP was comparable to natural organic matter.
- Some MPs released Br⁻ that shifted the DBPs speciation towards brominated species.

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ABSTRACT

Microplastics (MPs) are prevalent global pollutants that are being detected in aquatic ecosystems and drinking water sources around the world. In addition to plastic polymers, MPs contain various chemical substances (known as “additives”) that can leach and risk water quality. In this paper, we investigated for the first time the potential release of disinfection byproducts (DBPs) precursors when MPs are exposed to hydrolysis and/or degradation by simulated sunlight. Seventeen MPs with seven different polymer types were collected either as commercial products (e.g. drinking water bottles, shopping bags, recycled plastics, etc.) or pure/virgin polymers. Results showed high release of dissolved organic carbon (DOC) from five MP samples and a significant increase in bromide concentrations from four MPs. DBPs formation potential (DBPFP) experiments with MPs' leachates showed higher concentrations of chlorinated trihalomethanes (THMs), haloacetonitriles (HANs), and total organic halogens (TOX) in three samples, while a significant shift to brominated DBPs was observed in samples containing bromide. Extending the leaching experiments to four consecutive cycles showed that the leaching of DOC and DBPs' precursor significantly decreased after the second leaching cycle. Further analysis revealed that the reactivity of the leached DOC – indicated by THMFP yields – was comparable to those of several raw waters that supply drinking water treatment plants. The leached THMs and TOX from MPs that were exposed to UVA irradiation were in general higher than MPs that were run under dark conditions.

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1. Introduction

The increasing worldwide production of plastics coupled with the poor waste management results in releasing ~300 million tons

of microplastics (MPs) per year to aquatic ecosystems (Lebreton et al., 2017). Once in water, MPs would undergo different degradation pathways: 1) biodegradation, 2) photodegradation by UV light, 3) thermooxidative degradation under low temperature, 4) thermal degradation at high temperature, and 5) hydrolysis in water (Andrady, 2011; Song et al., 2017). Various additives present in almost all plastic-derived materials can also contribute to marine pollution (Hahladakis et al., 2018). These chemical compounds, like plasticizers, can provide required properties to a plastic polymer or facilitate the manufacturing process (Hermabessiere et al., 2017). For instance, brominated flame retardants (BFR) are a class of

* Corresponding author.

** Corresponding author. Department of Environmental Engineering and Earth Science, Clemson University, SC, USA.

E-mail addresses: ateia@northwestern.edu (M. Ateia), tkaranfil@clemson.edu (T. Karanfil).¹ These authors contributed equally to this work.

additives (e.g. polybrominated diphenyl ethers and hexabromocyclododecan) that are being used to reduce flammability (Talsness et al., 2009). Other additives include bisphenol A (i.e. a monomer for polycarbonate plastics (65% of volume used)) (Crain et al., 2007), and antioxidants (e.g. Octadecyl 3-(3,5-ditert-butyl-4-hydroxyphenyl)propionate and 2,4-di-tert-butylphenol) which are used as additives in many synthetic polymers including polyolefins (Hahladakis et al., 2018; Lau and Wong, 2000).

There is a growing concern about toxicological risks associated MPs after the uptake of MPs by living organisms either directly (i.e. misidentification or indiscriminate consumption of MPs for feeding) or indirectly (i.e. trophic transfer along the food web) (Alimba and Faggio, 2019). Romera-Castillo et al. (2018) have tested the release of dissolved organic carbon (DOC) into artificial seawater from plastic supermarket packaging samples and estimated that the annual global DOC release from marine plastics can reach up to 23,600 metric tons. Isotopic analysis using labelled ^{13}C -polyethylene MPs suggested that organic carbon from MPs was partly mineralized and partly used for cell growth (Taipale et al., 2019). A recent study on the impact of Nano plastics on the quantification of total organic carbon (TOC) has also suggested that mixing river water with MPs would cause a significant increase in the TOC values (Hu et al., 2019).

Given the potential leaching of DOC, would MPs release precursors of disinfection byproducts (DBPs) into water? To answer this question, we designed a systematic study and investigated for the first time the release of DBPs precursors by hydrolysis of MPs under dark and UV-irradiation conditions. We used two different sets of MPs to compare their behavior in water side-by-side: 1) a large set of well-characterized MPs crushed from real plastic samples, and 2) a set of pure MPs from commercial vendors.

Collection and preparation of MPs: Seventeen MPs from different polymer types (i.e. polyethylene [PE], polypropylene [PP], polyethylene terephthalate [PET], polystyrene [PS], poly (methyl methacrylate) [PMMA], polylactic acid [PLA], polyamide [PA-66]) were collected either as commercial products (i.e. drinking water bottles, shopping bags, biodegradable cups, ropes, lab vial) or crushed recycled plastics from a local plastic recycling company in South Carolina, USA. All samples were washed with tap water followed by distilled de-ionized (DDI) water, dried at room

temperature and cut to pieces smaller than 1 cm. Then, the cut pieces were frozen in liquid nitrogen and crushed to $<500\ \mu\text{m}$ via a Fritsch Pulverisette-14 (Fritsch GmbH, Germany) (Ateia et al., 2020). The crushed samples were dried at room temperature and stored until further use. Pure PE (75–90 μm) and PMMA (27–45 μm) were purchased from Cospheric Co., CA, USA. Pure PE and PMMA were washed, dried and used without crushing. The sources of all MPs are listed in Table 1.

1.1. MPs released precursors for known and unknown DBPs

Experiments in dark conditions. 1 g of each MP used in this study was soaked in 250 mL of DDI water at pH 6.5 and room temperature in an amber brown bottle and the mixture was shaken on a tumbler for 3 days. Preliminary experiments with extended mixing time up to 10 days have shown that maximum increase in values for dissolved organic carbon (DOC) could be reached after one day, which agrees with previous observations by Romera-Castillo et al. (2018). Blank bottles without MPs were used as control. **Experiments in light conditions.** Open beakers with mixtures of MPs (1 g) and DDI (250 mL) were placed under UVA-340 light in a closed well-aerated incubator for 3 days. The incubator was a custom-made box with four UVA-340 nm fluorescent lamps (Q-Panel Co., Cleveland, OH, USA), which are commonly used to mimic sunlight for MPs aging tests (Nakano et al., 2001; Müller et al., 2018; Yang et al., 2019). After 3 days of irradiation, some evaporation was observed (less than 10 mL) and the water level was adjusted back to the original volume using DDI water. Blank beakers with only DDI water were treated in the same way as control. Then, all samples from dark and light experiments were filtered with 0.45 μm pore size Whatman™ Polycap 150 TC filters.

For all filtrates (i.e. MPs' leachates), Table 1 shows the measured DOC and dissolved nitrogen (DN) using TOC-V, Shimadzu Corp. and the released bromide (Br^-) using ICS-2100, Dionex Corp. The leached DOC from PE, PP, PLA, PMMA, and PS MPs were in the range of 0.3–2.8 mg/L (i.e. 75–700 mg organic carbon per one kg of MPs). This calculated range is in agreement with the previously reported DOC leach from three PE and PP samples in a simulated seawater (i.e. 30–940 mg DOC per one kg of MPs) (Romera-Castillo et al., 2018). Studies on the hydrolysis of plastics (e.g. PET) suggested

Table 1
Sources of all MPs used in this study and the released DOC, Br^- , and DN under dark and light conditions.

Polymer	Sample Code	Products	Potential DBPs Precursors					
			DOC (mg/L)		Br^- ($\mu\text{g/L}$)		DN (mg/L)	
			D	L	D	L	D	L
PE	PE-1	Shopping bags	0.9	2.6	ND	ND	0.1	0.3
	PE-2	Recycled Plastic ^a	0.4	0.9	85	95	0.1	0.1
	PE-3	Recycled Plastic ^a	0.3	0.9	ND	ND	0.1	0.1
PP	PP-1	Pure polypropylene polymer	0.3	0.9	ND	ND	ND	0.1
	PP-2	Recycled Plastic ^a	0.5	1.5	ND	ND	0.1	0.1
	PP-3	Lab vial	0.3	1.0	ND	ND	0.1	0.1
PA-66	Mix-1	Recycled Plastic ^a	1.0	0.9	51	84	0.1	0.1
	PA-1	Pure PA66	10.5	15.0	8	3	2.2	2.4
	PA-2	Nylon rope	11.9	12.6	840	1026	0.2	0.3
PLA	Mix-2	Recycled Plastic ^a	12.6	15.8	4325	4529	2.5	2.8
	PLA-1	Pure PLA polymer	0.3	1.2	ND	ND	0.0	0.1
	PLA-2	Biodegradable plastic cup	0.8	1.2	ND	ND	1.3	0.1
PET	PET	Plastic water bottles	0.4	0.9	ND	ND	0.1	0.1
PMMA	PMMA-1	PMMA polymer powder	2.5	2.8	6	37	2.2	0.1
	PMMA-2	PMMA pure polymer pellets	2.6	1.2	ND	ND	0.2	0.1
PS	PS-1	Takeaway cup	0.9	1.0	ND	ND	0.1	0.1
	PS-2	Recycled Plastic ^a	0.3	1.0	ND	ND	ND	0.1

^a Samples were provided by Residue Recycling, Inc., SC, USA. D: Hydrolysis in dark Conditions. L: Hydrolysis under UVA-340 nm irradiation. ND: Not detected (below the minimum reporting limits). Polyethylene [PE], polypropylene [PP], polyethylene terephthalate [PET], polystyrene [PS], poly (methyl methacrylate) [PMMA], polylactic acid [PLA], polyamide [PA-66].

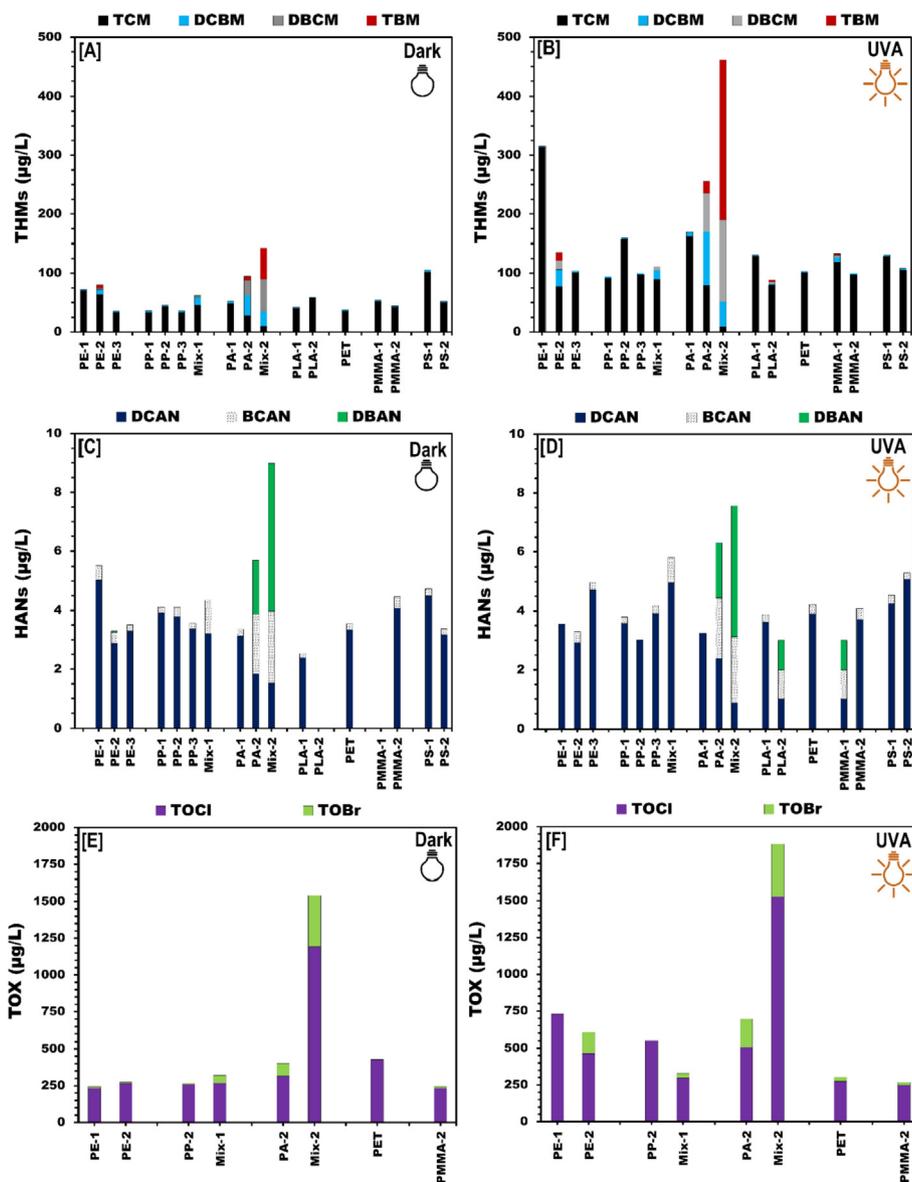


Fig. 1. Formation of THMs under [A] Dark condition, and [B] UVA-340 irradiation. Formation of HANs under [C] Dark condition, and [D] UVA-340 irradiation. Formation of TOX under [E] Dark condition, and [F] UVA-340 irradiation. Hydrolysis/UV-irradiation time = 3 d. Chlorine dose = 100 mg/L. Reaction time = 5 d at room temperature.

that MPs are potentially susceptible to hydrolytic cleavage of ester and/or amide bonds (Gewert et al., 2015; Enfrin et al., 2019). However, for the polyamide type MPs (PA-66 MPs) tested in this study, the average DOC release was 13.4 ± 2.4 mg/L (i.e. 3350 ± 700 mg organic carbon per one kg of MPs), which was significantly higher than all other tested MPs in this study. More research is needed to clarify the significant difference in leaching behavior of PA samples. Merdas et al. (2003) have tested the hydrolysis of PA and expressed the reaction by 'Amide + Water \rightarrow Acid + Amine'. The release of amines to the solution would explain the significant increase in DN from PA samples (Table 1). It should be highlighted that the hydrolysis is dependent on the experimental conditions and higher release would be expected at lower pH (Wen and Li Xy, 2015) and/or at higher water temperature (Liu et al., 2009). The results also showed that DOC release increased when most MPs were exposed to UVA light (Table 1). Photodegradation for e.g. PET MPs can occur via the cleavage of the ester bond forming a carboxylic acid end group

(COOH) and a vinyl end group ($-\text{CH}=\text{CH}_2$) (Gewert et al., 2015), or by a photo-induced autoxidation via radical reactions (Lambert et al., 2013).

We have also measured Br^- in all samples to monitor the inorganic DBP precursors (i.e., bromide) since the cytotoxicity results showed that the toxicity index of brominated DBPs are $>10^4$ times their chlorinated analogs (Plewa et al., 2017). Except for PE-2, Mix-1, Mix-2, PA 1–2, and PMMA-1, no detectable Br^- concentration was observed. Yet, PA-2 and Mix-2 release very high amounts of Br^- both in dark and light conditions with concentration range of 840–4529 µg/L.

All filtered samples were then chlorinated in amber brown glass bottles using an excess chlorine dose (100 mg/L) for 5 days at room temperature to determine the formation potential of trihalomethanes (THMs) and haloacetonitriles (HANs). Although HANs are not yet regulated, they have been reported to have the highest cytotoxicity index values among several classes of DBPs tested (Muellner et al., 2007). THMs and HANs were measured

using liquid-liquid extraction and gas chromatography with an electron capture detector (GC-ECD) (more details can be found in our previous work (Ateia et al., 2019)). Blank samples (i.e. before chlorination) were also extracted and no THMs or HANs were detected.

The total formation and speciation of THMs and HANs are shown in Fig. 1A–D. Two major observations were noticed. First, THMs and HANs were formed in all chlorinated samples, which indicate the release of DBPs precursors from all MPs under dark (THMs up to 150 µg/L) and light conditions (THMs up to 454 µg/L). The formation trend was consistent with the released DOC values, where the highest DBPs formations were for PA samples (Table 1). Second, the major formed specie from THMs and HANs in samples without Br⁻ was chloroform (TCM) and dichloroacetonitrile (DCAN), respectively. However, samples with Br⁻ have shown a remarkable shift towards brominated THMs (i.e. dichlorobromomethane (DCBM), dibromochloromethane (DBCm), and bromoform (TBM)) and brominated HANs (i.e. bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN)). The THMFY yields of MPs tested in this study in the presence of light ranged from 11.3 to 158.9 µg/mg DOC, which was comparable to the THMFY yields of raw waters of several drinking water treatment plants and other published results with a range of 15–149 µg/mg DOC (Golea et al., 2017).

Additionally, total organic halogens (TOX) were measured for selected samples including the ones that formed highest THMs, which can give insights on the formation of unknown DBPs. TOCl and TOBr were measured using an Analytic Jena Multi X 2500 TOX

Analyzer (Analytikjena, Jena, Germany) coupled with off-line Dionex ICS-2100 ion chromatography system (more details can be found in our previous work (Ateia et al., 2019)). As shown in Fig. 1E and F, TOX formed were $\times 2 - \times 4$ times higher than the measured known DBPs (i.e. THMs and HANs). These observations suggests that there are other halogenated DBPs formed in addition to THMs and HANs. The same shift towards brominated DBPs in the presence of Br⁻ was also confirmed in TOX analysis.

1.2. Hydrolysis was confirmed in four consecutive leaching cycles

Additional experiments with PE-1, PE-2, PP-2, PA-1, PA-2, and Mix-2 showed that DOC continued to leach after four consecutive leaching cycles. Experiments were performed by filtering MPs from the first cycle then placing MPs back in new batch of 250 mL of DDI water and shaking on a tumbler for 3 days. The same procedures were repeated for the third and fourth leaching cycles. All samples were run in duplicates. The concentrations of DOC, Br⁻, and THMs were measured using the same described methods in the previous section. The release of DOC and Br⁻ as well as the formation potential of THMs from the four cycles are shown in Fig. 2. Apparently, the precursors for brominated THMs were weakly bound to MPs and were washed out during the first cycle, as suggested by both of Br⁻ release data and the formation of brominated DBPs. This is consistent with previous observations that additives, in nearly all cases, are not chemically bound to the plastic polymer which make their leaching relatively easy (Hahladakis et al., 2018). Interestingly, the DOC release and THMs formations – except for Mix-2 – were higher in cycle 2 than cycle 1. It seems that MPs contained hydrolysis stabilizers (e.g. carbodiimides (Takahashi et al., 2008)) that were flushed during the first cycle and made MPs more susceptible to degradation by hydrolysis. This change in the hydrolysis rate need further investigations. Although MPs continued to release DOC, the hydrolysis rate slowed down after the second cycle.

2. Conclusions

- All MPs released precursors of DBPs under dark and UVA-irradiation conditions.
- The results from this study and others in the literature suggest that DOC leaching may range from ~30 to 1000 mg DOC per kg of MP, depending on the composition of MPs and the environmental conditions. However, some MPs tested in this study (i.e., polyamide) leached higher amounts of DOC (3,350 mg DOC per kg MP) and THM FP.
- Some MPs released Br⁻ that shifted the DBPs speciation towards the more toxic brominated DBPs.
- The leaching of DOC and DBPs' precursor significantly decreased after the second leaching cycle.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Mohamed Ateia: Conceptualization, Methodology, Writing - original draft. **Amer Kanan:** Conceptualization, Methodology, Writing - original draft. **Tanju Karanfil:** Supervision, Project administration, Conceptualization, Methodology, Writing - original draft.

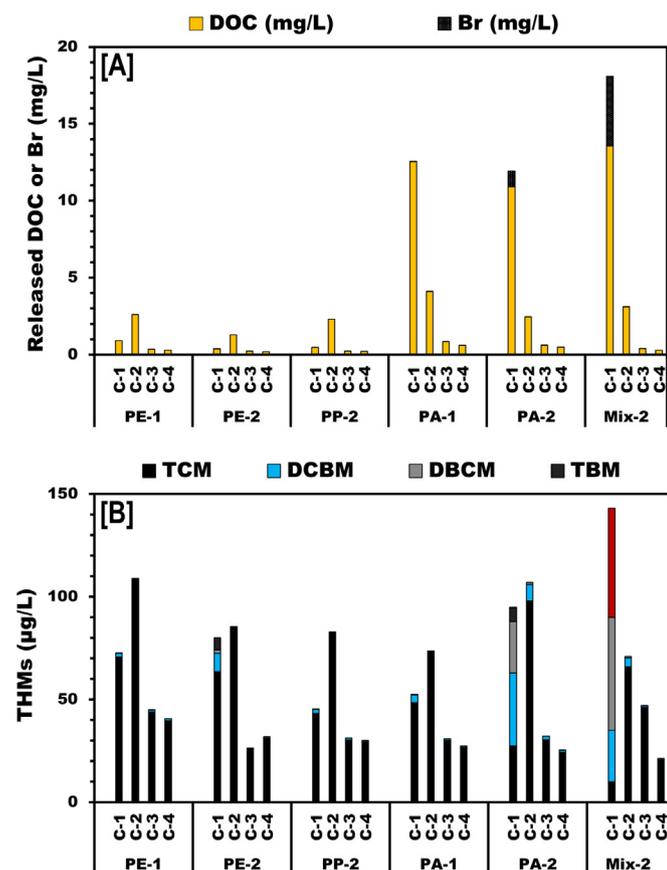


Fig. 2. [A] The release of DOC and Br⁻ during four consecutive leaching cycles. Each cycle was run for 3 days in dark and samples were shaken on a tumbler. [B] The formed THMs after chlorination of the filtered samples from each cycle. Chlorine dose = 100 mg/L. Reaction time = 5 d at room temperature.

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