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Importance of size and polymer type

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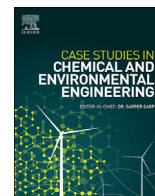
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Sorption of PCBs to environmental plastic pollution in the North Atlantic Ocean: Importance of size and polymer type



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ABSTRACT

Plastic pollution is a great threat to the marine environment. Owing to its low density, a substantial fraction of plastic debris is transported across ocean surfaces by currents. Consequently, plastic debris has been concentrated in oceanic gyres such as the North Atlantic subtropical Gyre (NASG). This study presents data that describes plastic abundances and the concentrations of adhered PCBs (polychlorinated biphenyls) from 15 surface trawls conducted within and outside the NASG. Abundance of plastic pieces was significantly higher inside the gyre than outside supporting earlier findings about the importance of the gyres as accumulation zones for plastic debris. Concentrations of PCBs were comparable among different sizes fractions when measured per plastic piece but significantly higher on smaller pieces when measured per weight unit. Polyethylene pieces furthermore had higher concentrations of PCB than polypropylene pieces. These findings highlight the importance of accounting for particle size and polymer type when assessing sorbed contaminants to environmental plastic pollution.

1. Introduction

The release of plastic into the marine environment is recognized as a problem of global concern [1]. Owing to slow degradation rates and low density of plastics, a significant proportion of marine plastic debris is transported by oceanic currents and concentrated in accumulation zones in oceanic gyres, such as the North Atlantic subtropical gyre (NASG) [2, 3]. The concentrations of plastic debris within these gyres have been shown to be orders of magnitude higher than concentrations outside of these specific locations [1] as predicted by Ekman dynamics. For instance, Lusher et al. [4] demonstrated that plastics were present in 94% of samples collected in 470 trawls conducted in the North Atlantic. They further showed, that 89% of these samples contained plastics < 5 mm in length or diameter, defined as microplastics (MPs) [5]. This percentage is in accordance with other studies, such as [6].

Plastics may act as a 'vector' that transports other contaminants altering the environmental fate and effects of those contaminants [7]. This mechanism is a function of the individual plastics' ability to

adsorb or absorb (collectively termed as 'sorption' hereafter) hydrophobic organic compounds (HOCs) [8,9]. Contaminant groups such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) have all been isolated from plastic debris sampled in the marine environment [10]. PCBs are ubiquitous in the marine environment, making them suitable for studying HOC sorption to marine plastic debris. PCBs are further considered chemicals of high concern due to their hazardous properties [11]. The toxic effects of PCBs due to transportation by MPs have been documented under controlled experimental conditions [12]. There are several physical and chemical properties that govern the sorption of contaminants to MPs including polymer type and particle size [8,9]. For example, polyethylene (PE) has a higher amorphous-to-crystalline ratio than polystyrene (PS) and therefore offers lower resistance to the sorption of HOCs since the HOCs more readily diffuse into the polymer's amorphous regions. Since PE and polypropylene (PP) comprise saturated hydrocarbon units, resulting in nonpolar surfaces, they can also absorb hydrophobic contaminants by polar sorption [13]. Since initial sorption processes

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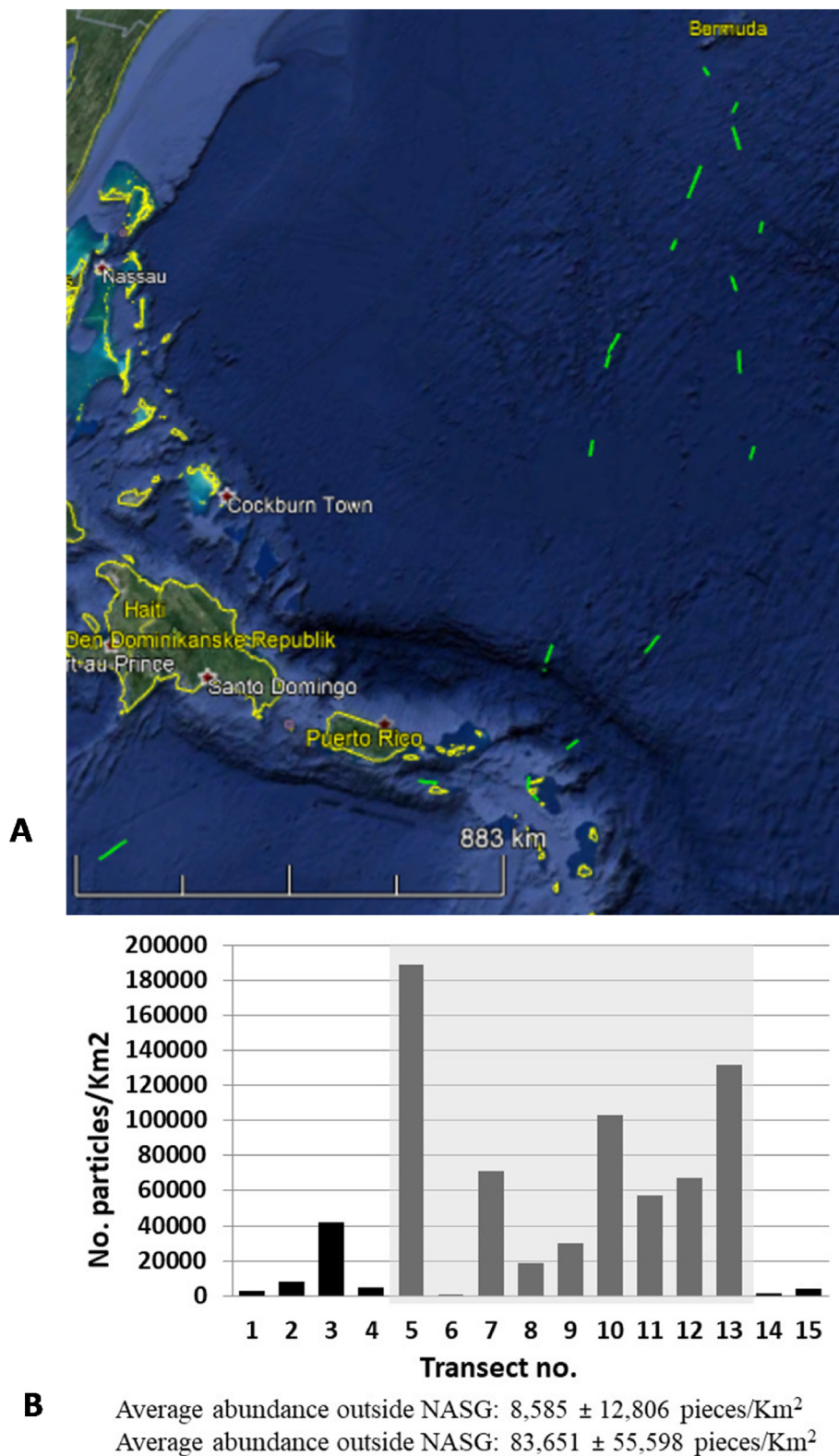


Fig. 1. Distribution of plastic particles along sample transects.

increase with larger surface area, sorption is highly governed by the size:volume ratio of the plastic particle. Even though several papers have addressed the sorption between contaminants and MPs, the empirical evidence of sorption on plastic sampled in the gyre zones is still limited. Such information is imperative to better understand the

importance of the vector effect in the accumulation zones. Here we report on the abundance of meso-/microplastics down to 0.33 mm as well as adhered PCBs for macro/meso (>5 mm) and larger microplastic (1–5 mm) sampled from the North Atlantic Ocean.

2. Materials and methods

2.1. Sample collection

Samples were collected during an expedition from Caribbean Sea to Bermuda on board the SY Christianshavn as part of the "Expedition Plastic" carried out by Plastic Change in April–May 2015. Fifteen surface trawls were conducted, covering a total distance of 633,922 m with a trawling area of 88,749 m² (Fig. 1). The average distance of the trawls was 42.26 ± 17.75 m (mean ± SD). All trawls were conducted with a Manta trawl with a width of 14 cm and a net mesh size of 0.335 mm.

Fig. 1 a) Map of coordinates for each trawl. Transects can be separated into two distinct regions: outside the NASG (transects 1–4 + 14–15) and within the NASG (transects 5–13). b) Abundance (MPs/km²) of plastic particles in the 15 trawls conducted. Samples collected within the NASG are marked with grey background. Abundance was calculated as particle/km² and average MP concentration within samples collected in- and outside of the NASG are provided. The small abundance in sample 6 was due to some of the samples being lost during transportation.

Each sample was sorted by size immediately after sampling into three size categories: macro/meso (Ma/Me) (>5 mm), Large microplastics (LMP, 1–5 mm s) and small microplastics (SMPs, 0.33–1 mm) based on [3] and in accordance with [5]. Sorting was conducted using metal meshes of 5 mm, 1 mm and 0.2 mm, and samples were stored in glass containers for later analyses. Samples were kept in a cooler with controlled light and temperature (around 5 °C) as recommended by Ref. [15]. Samples treated with 10% KOH for 24 h in the laboratory to remove any organic matter adhered to the plastic pieces. Samples were thereafter dried at 40 °C for 24 h before being categorized based on shape, (fragments, foam, film, line and pellets) using a magnifying lens and/or dissection microscope (Zeiss Stemi 2000-CS). This procedure was based on [3] and in accordance with [5].

2.2. Characterization of polymer composition

Compositions of the surfaces (1–2 µm) of plastic particles were determined non-destructively with Attenuated Total Reflection -Fourier Transform Infrared (ATR-FTIR) spectroscopy. A single bounce diamond internal reflectance element (2 × 2 mm) was employed to run 20 scans at a resolution of 2 cm⁻¹ between 4000 and 650 cm⁻¹ using a PerkinElmer Spectrum two spectrometer. Characterization was based on at least a 90% match with reference spectra as well as manual assessment of compliance with peaks within the 1400–4000 cm⁻¹ part of the spectra.

2.3. Extraction of sorped contaminants

Particles <1 mm were too small to obtain reliable extractions of PCBs, therefore only particles larger than 1 mm were included in the analysis of sorbed chemicals. PCBs were extracted from plastic particles using a modified SW-846 Test Method 3550C: Ultrasonic Extraction -GC/MS [15]. The modification consisted of two changes in which pure hexane was used as the extraction medium and ultrasound treatment of samples comprised 5 × 30 min instead of 2 × 60 min. Previously, this modified method has resulted in extraction efficiencies higher than 95% [16]. Analyses were made for 15 PCB Congeners (PCBs 8, 18, 28, 31, 44, 52, 70, 101, 105, 138, 151, 153, 180, 194, 195). PCB 52 with 12 C¹³ was used as internal standard. Standards were obtained from Dr. Ehrenstorfer (PCB-mix17) and the C¹³ standard from Greyhound Chromatography (MBP-52). Each sample was weighed (Mettler, AE 200) and transferred to a glass bottle. Hexane (10 mL) was added and the sample was subsequently placed in an ultrasonic bath for 30 min. This last step was repeated 5 times – each time collecting the extraction phase before adding a new aliquot of hexane. The recovery from spiked polyethylene samples were tested and was around 70% - a little lower than that recorded by Hirai et al. [17]. The extraction phases were combined and afterwards evaporated to complete dryness. Each sample was then

reconstituted in 10 mL hexane together with 100 µL of the internal standard. The sample was run through a coated silica column (Thermo Scientific, Florisil SPE column) and eluted with 10 mL of hexane. The eluent was evaporated to dryness, re-dissolved in 200 µL hexane and transferred to a vial for Gas Chromatography-Mass Spectrometry (GC-MS).

2.4. GC-MS analyses

All analysis was performed using a GC-MS in single ion monitoring (SIM) mode (Agilent Technologies, 5975 MS detector 6890 N GC system, quadrupole), using a Zebron Inferno (ZB-5HT, Phenomenex) column with dimensions of 20 m × 0.18 mm × 0.18 µm. The PCB concentrations were so low, that only SIM mode was used, so the identification of the PCBs was based on their retention times only. Initial temperature was 110 °C, which was maintained for 10 s. The temperature was subsequently increased by 20 °C per minute until a temperature of 210 °C was reached. Afterwards, the temperature was raised by 10 °C per minute until it reached 320 °C, where it was held for 3 min before completing the program. The program runtime was 19min6sec minutes. The retention time for the last standard (PCB 195) was 12min40sec. Blank runs were in the range of 1 ng/g and were subtracted from the sample measurements. Comparing with Gandhi et al. [18], our PCB sum may account for about 75% of the total PCB concentration.

2.5. Statistical analyses

Mann-Whitney *U* test conducted with SYSTAT (version 13.0) was used for analysis of variance of abundance data and associated PCB concentrations with a 95% significance level (*p* = 0.05).

3. Results and discussion

3.1. Abundance

Concentrations of plastic particles were significantly higher (*p* < 0.01) in samples from within the area earlier defined as NASG [2], even though sample sizes varied markedly within these two regions. Average concentrations (mean ± SD) were 83,651 ± 55,598 pieces/km² within the NASG and 8585 ± 12,806 pieces/km² outside the NASG. Highest and lowest observed abundance were 188,788 pieces/km² and 1714 for trawl 1 (outside NASG) and trawl 5 (inside NASG) respectively. The LMP fraction of trawl 6 was lost at sea resulting in markedly lower reported abundance than actual sampled for this transect (Fig. 1). These concentrations are comparable to those reported in other studies of the region for the same size range [2,6]. The high variation is a function of large spatial heterogeneity both within and outside of the NASG (Fig. 1). The data thus contributes to the documentation of oceanic converging zones as hotspots for plastic contamination [3,6].

We found an inverse relationship between size and abundance throughout the samples. Eighty-five percent of the particles were categorized in the LMP + SMP fraction (*n* = 1337 + 2083) whereas only 15% of the samples were larger than 5 mm (Ma/Me) (*n* = 230). Our findings are in accordance with those reported in other studies. Eriksen et al. [6] found that MPs in the 1.01–4.75 mm size (LMPs in this study) were most abundant, followed by MPs in the 0.33–1.00 mm range (SMPs in this study). Larger plastic particles above 4.75 mm (Ma/Me in this study) were least abundant. Lusher et al. [4] also found that LMPs were the most abundant in their survey of MPs in the NASG.

3.2. Characteristics of plastic samples

Polyethylene (PE) was the most abundant polymer comprising 90.3% of all plastics found. Polypropylene (PP) plastics constituted 9.7%, Polymethylmethacrylate (PMMA) and polyethylene terephthalate (PET) were also identified but contributed <0.1% each. Whilst most of both PE

Table 1
Sorped contaminant concentrations on different size fractions of particles.

A						
Size	No. Items (n)	Weight (g.)	PCB (ng)	PCB (ng/Pieces)	PCB (ng/g dw plastic)	
Macro/Mesoplastics (Ma/Me) (>5 mm)	170	3.49	24.39	0.14	6.99	
Large MP (LMP) (1–5 mm)	520	2.13	84.19	0.16	39.51	
ratio (LMP:Ma/Me)	–	0.61	4.45	1.14	5.65	
B						
PCB (ng/g plastic)						
PCB 8	PCB 18	PCB 28 + 31	PCB 44	PCB 52	PCB 70	PCB 101
15.44	2.82	2.99	2.82	17.88	47.09	14.07
PCB 105	PCB 138	PCB 151	PCB 153	PCB 180	PCB 194	PCB 195
5.44	2.36	9.76	15.27	4.83	0	0

and PP MPs were fragments (81% and 68% respectively), only PE was found in granulate form (0.28% of total PE fraction). Fibres constituted 15% of PE and 20% of PP microplastics. Finally 3.5% of the PE microplastics were in the form of film compared with 11.84% for PP. Since both PE and PP are the most commonly produced plastics and have densities below that of seawater, this finding is not surprising and other authors sampling the North Atlantic have reported similar results. Similar to our results Morét-Ferguson et al. [19] found that 19 samples collected in North Atlantic consisted of HDPE, LDPE (high- and low density PE respectively) and PP.

3.3. Adhered PCB – importance of composition and size

The measured concentration of the 15 PCB congeners analyzed in this study were in the ranges 6.8–80.5 ng PCB/g dw plastic for the LMPs, and 3.3–18.6 ng PCB/g dw plastic for the Ma/Me fraction. These findings are in the same range as those presented in previous similar studies [13,17,20] even though some variation could be associated with a difference in the congeners analyzed. Sorped concentrations are likely to be controlled by the complex competition between sorption and desorption processes in the ocean [17] but will also be governed by aspects such as plastic residence time and polymer specific sorption kinetics [9,20].

In the present study concentrations of adhered PCBs were 6.99 ng/g and 39.51 ng/g dw PE for Ma/Me and LMP respectively (Table 1), whereas the concentration on PP particles were below detection limits, highlighting the importance of polymer type when considering the capacity of HOC sorption.

A: Total number of pieces in the two size fractions (n), total dry weight (g dw), concentration of contaminants (ng), concentration of contaminants per plastic pieces (ng/pieces) and concentration of contaminants per weight unit (ng/g dw plastic) are provided, together with ratios calculations between the two size fractions. B: concentrations of the 15 different PCB congeners analyzed. Concentrations are shown as ng/g plastic and account for all analyzed plastic pieces.

There was no difference in sorbed PCB concentrations between the different size categories when expressed as ng PCB/pieces (LMP:Ma/Me ratio = 1.14). However, when expressed as ng PCB/g dw plastic the LMP fraction had 5.6 times more PCB than the larger Ma/Me fraction (Table 1). This illustrates the importance of surface area for adhesion, since LMPs had a distinctly higher surface area/volume ratio than the larger Ma/Me. Our findings thus demonstrate the importance of the unit that the HOC concentration is expressed in (i.e. per plastic item or per weight) since different units provide different concentrations and in turn changes the HOC distribution between the different size categories. This

issue of how best to express particles concentrations has been raised previously with regard to dosing MP exposures [21] but is equally relevant when assessing the importance of plastic pieces as a vector for HOCs.

In conclusion, our data adds to the weight of evidence of gyres acting as accumulation zones for plastic debris. Furthermore, even though our samples only contained two types of polymers (PE and PP) our data illustrates that attempts to quantify environmental importance of sorption of HOCs on plastic pollution must account for both composition and sizes of the plastic pieces. These two aspects are currently not well documented, especially for the smallest sizes range that could relatively be most important in this context.

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.

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