



Polycyclic aromatic hydrocarbons affiliated with microplastics in surface waters of Bohai and Huanghai Seas, China[☆]

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ABSTRACT

Microplastics (MPs) sized between 0.33 and 5 mm were collected using Manta trawls from ten surface seawater sites in Bohai and Huanghai Seas, China. A total of 1024 (Bohai Sea) and 132 (Huanghai Sea) microplastic pieces were classified, including polystyrene foams, polyethylene films and lines, and other plastic pellets, with concentrations of MPs ranging from 3 to 162 particles per 100 m³ (0.012–2.96 mg m⁻³). A pretreatment of MPs with 30% H₂O₂ in water did not significantly lower polycyclic aromatic hydrocarbon (PAH) concentrations on MPs compared to no H₂O₂ pretreatment. Measurements of PAHs carried on the collected MPs indicated that the concentrations of the sum of 16 PAHs were in the range of 3400–119,000 ng g⁻¹. The sources of PAHs in Bohai and Huanghai Seas were highly similar, with petroleum and gasoline probably as the dominant sources. The present study shows the relative importance of MPs in regards to chemical transport in the marine environment. The combination of high concentrations of PAHs affiliated with MPs and the increasing magnitude of plastic pollution in the world's oceans demonstrates the considerable importance of MPs to the fate of PAHs in marine environments.

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1. Introduction

Plastic production has increased dramatically in recent decades, with a worldwide production of 269 million metric tons of plastic materials in 2015 (PlasticsEurope, 2016). Plastics enter the ocean through various pathways, such as riverine runoff, beach littering, and marine activities (Browne et al., 2011; Lebreton et al., 2017). Plastic pieces with sizes smaller than 5 mm were generally defined as microplastics (MPs), and this category of emerging contaminants in the marine environment has drawn increasing global concern (Thompson et al., 2004). Microplastics are known to ubiquitously distribute in the marine environment including sea water, sediment, and even biota (via ingestion) (Hirai et al., 2011; Law et al., 2014; Ng and Obbard, 2006). The ingestion of MPs by marine organisms is one of the serious consequences, which poses ecological risk to most marine organisms (Mallory, 2008; Mascarenhas et al., 2004).

Although much of the discussion pertaining to ecological risk of MPs has been concerning MPs themselves, they are also known to

carry chemicals either through addition or sorption. For instance, Van et al. (2012) found high concentrations of polycyclic aromatic hydrocarbons (PAHs) sorbed to unexposed commercial polystyrene (PS) packaging foam. Outside of chemicals that are purposely added to these plastics, these materials have also been reported to have the ability to sorb hydrophobic organic pollutants (HOCs) from the surrounding environment (Mato et al., 2001; Rios et al., 2007; Rochman et al., 2013a; Teuten et al., 2007). After long-term exposure in the environment, concentrations of chemicals sorbed to MPs can be several orders of magnitude higher than those in the aqueous phase (Rochman et al., 2013a). This is a concern as MPs can cause potential adverse effects if ingested by organisms, which can deliver sorbed chemicals into the organisms' bodies (Rochman et al., 2013a; Ziccardi et al., 2016). Although the effects of MPs alone are starting to be well-studied (Von et al., 2012), the relative importance of them to chemical transport in the marine environment is relatively unknown (Koelmans et al., 2016). Polycyclic aromatic hydrocarbons have widely been detected in the coastal water as well as in much of the biota in the food web found in Bohai Sea (Hong et al., 2016; Men et al., 2009; Wan et al., 2007). In addition, recent reports have also found high levels of MP pollution in beach sand and surface water of Bohai Sea (Yu et al., 2016; Zhang et al., 2017). As such it is highly likely that PAHs are bound to plastic

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materials as well, however this has not been evaluated to date.

As indicated by [Hidalgo-Ruz et al. \(2012\)](#), one of the major challenges in MP research is the effective extraction of MPs from environmental samples with rich organic matter. To address this issue, a H_2O_2 pretreatment step is generally applied to MP extraction from organics-rich samples ([Mai et al., 2018](#)), such as sediments ([Nuelle et al., 2014](#)) and wastewater treatment plant effluent ([Dyachenko et al., 2016](#)). Although the potential effects of H_2O_2 on infrared spectra as well as the size and morphology of MPs have been previously investigated, which showed that MPs remained unchanged even after 7 days of exposure to 30% H_2O_2 ([Mathalon and Hill, 2014](#); [Nuelle et al., 2014](#); [Tagg et al., 2015](#)), the effects of this treatment on sorbed contaminants, such as PAHs, remained unknown. Therefore, one of the objectives of the present study was to examine whether H_2O_2 pretreatment, a common approach for removing organic matter from MPs ([Nuelle et al., 2014](#); [Stolte et al., 2015](#)), would affect the quantification of PAHs on said particles.

Therefore, the aims of the present study were to 1) explore the effects of pretreatment with H_2O_2 on PAH concentrations in MPs; 2) investigate the occurrence of PAHs sorbed in MPs collected in surface waters of Bohai and Huanghai Seas; and 3) evaluate the relative concentrations of PAHs extracted from MPs, suspended particulate matter, and sea water, using Bohai Sea as a case study.

2. Experiment section

2.1. Field sampling

Sea surface waters at 10 sampling sites in Bohai and Huanghai Seas ([Fig. 1](#)) were collected during two research cruises on May 26–30 and June 14–17, 2017 under mild weather conditions (wind speeds between 3.0 and 7.2 m s^{-1} ; [Table S1](#)) using a documented trawling method ([Yamashita and Tanimura, 2007](#)). The manta trawl (made of silk; 0.90 m wide by 0.45 m high), similar to that used in a previous study ([Zhang et al., 2017](#)), was utilized. This trawl contains a 3-m long mesh bag (0.333 mm) and a removable cod-end with the same mesh size. Additionally, a digital flow meter (Hydro-Bios, Germany) was placed horizontally in the open mouth of the trawl frame to measure flow. The trawl was placed by the side of the boat during collection, with the towing distance and the amount of

filtered water calculated using information obtained from the digital flow meter. Depending on the sampling site, the trawling time ranged from 10 to 15 min at a cruising speed of about 2 knots. After each trawling, the manta net was rinsed with local seawater and all retained debris (as collected in the cod-end) were transferred to a 500 mL glass bottle. Meanwhile, for quality assurance and quality control purposes, commercially purchased MP particles (polyethylene (PE) standard purchased from Goodfellow, Cambridge, London, England) further preloaded with target compounds (16 PAHs mixture) in the laboratory were transferred into sample bottles to determine chemical losses during transportation. This action was carried out at each sampling site. Before each sampling event, the manta trawl was rinsed thoroughly with distilled water to minimize cross contamination. Samples were stored at 2–4 °C until laboratory analysis was conducted.

2.2. Analysis of microplastic particles

Based on previous studies ([Hidalgo-Ruz et al., 2012](#); [Van et al., 2012](#)), the sorted plastic particles were separated into several size fractions (333–500 μm , 500 μm –2 mm, and 2–5 mm) with stainless steel sieves of 10, 40, and 50 meshes (equal to pore sizes of 2 mm, 500 μm , and 300 μm), respectively. According to their morphology, samples were also divided into one of the following six categories: line, foam, fragment, pellet, and ‘others’. These samples were rinsed with distilled water, freeze dried, and covered with aluminum paper prior to instrumental analysis. The sorted plastic particles were confirmed using a Fourier transform infrared spectrometer with attenuated total reflectance (Shimadzu model 8300, Japan). Thirty sequential scans were made for each measurement at a spectral resolution of 4 cm^{-1} and wavenumbers from 4000 to 400 cm^{-1} . The spectrum of each particle was recorded and compared with the reference spectra of standard PS and polyethylene (PE) purchased from Goodfellow (Cambridge, London, England). Samples were subsequently kept covered with aluminum foil and stored at –18 °C until the measurements of PAHs could be conducted.

2.3. H_2O_2 pretreatment

To evaluate the effects of pretreatment with H_2O_2 on the target compounds sorbed on MPs, a 40-mL polytetrafluoroethylene tube was filled with MP particles from one of the sampling sites, BH-1. The particles from this site were immersed in 20 mL of 30% H_2O_2 (Tianjin Yongda Chemical Reagent, China) overnight based on a procedure by [Liebezeit and Dubaish \(2012\)](#), which reportedly obtained sufficient removal of natural organic matter without affecting the physical shape of target plastic particles. Upon incubating overnight, samples were briefly shaken and allowed to dry for 24 h. The treated particles were filtered through glass fiber membrane filters (Whatman International, Maidstone, UK), with a pore size of 0.7 μm . For comparison, untreated samples were also evaluated after being dried for 24 h. The dry masses of both the treated and untreated MP samples were recorded. Concentrations of PAHs in particles with and without pretreatment were measured (using procedures discussed below). Photographs of particles were also taken to visually compare the effects of the pretreatment. This experiment was performed in triplicate (50 mg of MPs for each performance).

2.4. Sample extraction

The target compounds in the present study were the commonly evaluated sixteen high priority PAHs, i.e., naphthalene (NAP), acenaphthylene (AC), acenaphthene (ACE), fluorene (FL),

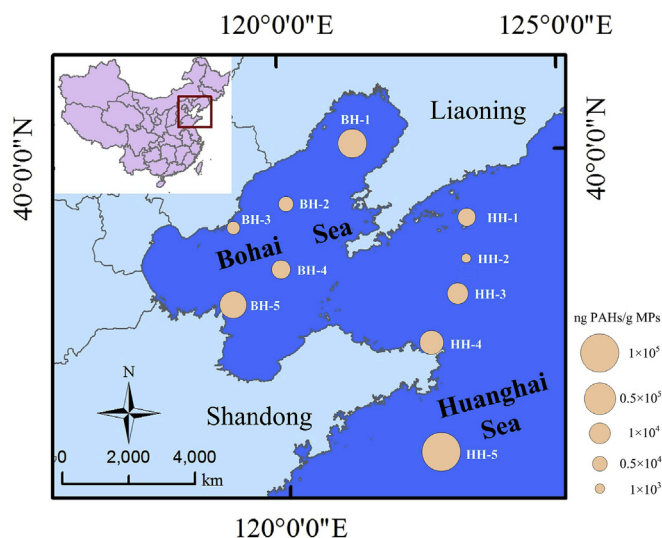


Fig. 1. Locations of sampling sites in Bohai Sea and Huanghai Sea, China. Circles mark the concentrations of microplastic-affiliated polycyclic aromatic hydrocarbons (ng g^{-1}) at sampling sites.

phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP). The freeze-dried plastic particles were spiked with 50 ng of the surrogate standards (i.e., naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12}) and extracted three times (30 min each time) in an ultrasonic bath, each with 20 mL of hexane. Three extracts were combined to form one sample and concentrated to approximately 1 mL with a rotary evaporator with a water bath temperature of 30 °C, and the extract was transferred onto a silica gel column (0.8 cm i.d. \times 25 cm) for purification. The column was filled with a small amount of cleaned degreasing cotton and 10 cm of 110 °C activated silica gel, and topped with 1 cm of dehydrated Na_2SO_4 (top to bottom). The target compounds were collected by elution with 10 mL of *n*-hexane/dichloromethane (3:1 in volume) mixture. The fraction containing PAHs was concentrated to 0.1 mL under a gentle stream of nitrogen. Internal standards (2-fluoro-1,1'-biphenyl, *p*-terphenyl- d_{14} , and dibenz[a,h]anthracene- d_{14} ; 100 ng each) were added to the final extract prior to instrumental analysis.

2.5. Instrumental analysis

The concentrations of target PAHs were determined with a Shimadzu gas chromatograph coupled with a QP 2010 and mass spectrometer, which was equipped with a 60 m \times 0.25 mm-i.d. (with a 0.25 μm film thickness) DB-5ms column. An auto injector was used to inject 1 μL of each extract. The column temperature was ramped from 65 °C (held for 1 min) to 200 °C (held for 5 min) at 10 °C min^{-1} , further increased to 250 °C (held for 5 min) at 5 °C min^{-1} , raised to 280 °C (held for 15 min) at 15 °C min^{-1} , and eventually ramped to 300 °C at 20 °C min^{-1} and held for 10 min. The temperatures of the transfer line and injection port were both maintained at 280 °C. The carrier gas, helium, was set at a flow rate of 2 mL min^{-1} , and splitless mode was applied and split after 1 min with a split ratio of 20. Electron ion full scan monitoring mode was used for collecting mass spectral data, with the ion source temperature set at 280 °C.

2.6. Quality assurance and quality control

Laboratory glassware was soaked in alkaline for 24 h, washed under water flow, oven-dried at 120 °C for 2 h, further baked in a furnace at 450 °C for 4 h, and carefully stored prior to use. Silica gels were Soxhlet extracted with methanol for 24 h and dichloromethane for 24 h, and vacuum dried before use. To ensure the measurements of the target compounds were accurate, three procedural blanks and five field-transportation loss control blanks were prepared for each sample site. Additionally, a second extraction was performed for a select number of field samples to monitor probable PAH residuals. Few PAHs (125 ng g^{-1} PHE, 45 ng g^{-1} FLU and 27 ng g^{-1} PYR in average) were detected in the blanks mentioned above, except for NAP, which showed comparable background values to samples. The recoveries of the six surrogate standards from various types of samples ranged from 61.1% to 127% (Table S2). The results of transportation loss control experiments showed no significant difference (*t*-test; $p > 0.05$) between pre-loaded standards in the laboratory and the sampling sites in Bohai and Huanghai Seas (Fig. S1). All concentrations in the present study were reported after blank samples were subtracted, but without the surrogate recovery correction.

2.7. Statistical analysis

The principle component analysis was conducted using IBM SPSS Statistics 22, and a two-sample *t*-test and analysis of variance were also run with IBM SPSS Statistics 22. The remaining statistical analysis was performed using SigmaPlot 10.

3. Results and discussion

3.1. Effects of H_2O_2 pretreatment

The concentration distributions of PAHs extracted from MPs, with and without 30% H_2O_2 treatment, are shown in Fig. 2, with visual evidence of 'purification' of the treatment being displayed in Fig. S2. Although the concentrations of PAHs extracted from untreated MPs were slightly higher than the treated ones (Fig. 2), no significant difference was observed between them (*t*-test; $p > 0.05$). Taken collectively, these results suggest that H_2O_2 treatment can purify MP samples without significantly affecting sorbed organic pollutants on the plastic itself (e.g., PAHs). We therefore suggest that a purification step can be taken when investigating organic pollutants on MPs from organics-rich samples. In the current literature, no chemical purification methods are available for extracting organic pollutants from MPs as acquired from sandy beach sediments (Van et al., 2012; Zhang et al., 2009) or collected from surface seawaters (Hirai et al., 2011; Rios et al., 2007).

As MP particles larger than 330 μm can be easily extracted from the mentioned environmental matrix without chemical pretreatment (instead only rinsing with water is required), any potential leftover organic matter particles would not affect FTIR identification of the polymer type for MP particles, as shown in the present study as well as in previous work by Tagg et al. (2015). As such, in the present study, concentrations of PAHs in MPs sampled from Bohai and Huanghai Seas were determined from MP particles which were rinsed with Milli-Q water only, with no H_2O_2 pretreatment.

3.2. Abundance and distribution of microplastics

The total number of MPs collected during the cruises was 1024

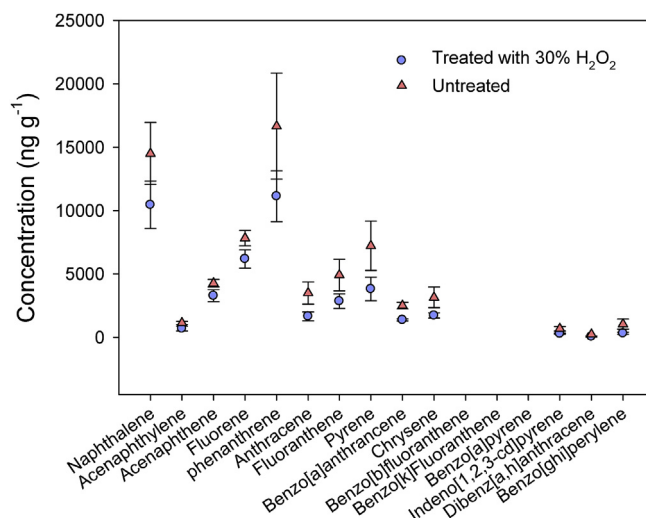


Fig. 2. The concentrations of polycyclic aromatic hydrocarbons in microplastic samples treated with (blue circles) and without (red triangles) 30% H_2O_2 for 24 h. Error bars represent the standard deviations. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and 132 (65 and 9 items per 100 m³) in Bohai Sea and Huanghai Sea, respectively, with the concentration of MPs from each sampling site being presented in Table S3. Microplastics were also found in the nearby beaches of Bohai Sea and Huanghai Sea, wherein 90 and 130 particles were found in Dongshan Beach and Zhengmingsi Beach, respectively (Zhang et al., 2015) indicating that MP pollution in the sea's surrounding environment might be related to that in the sea. These collected plastic particles were further identified and sorted into three categories: PS, PE, and 'other polymers'. Most of the plastic lines and all the plastic films were PE, while foams and pellets were identified as PS (Fig. 3). It is worth noting that the highest abundance of PS foam and PE line were found at sampling sites BH-1 and BH-4, respectively (Table S3). The most likely sources of MPs were fishing lines or nets for PE lines, while PS foams most likely came from broken foam containers used in the marine industry. The abundance of MPs at different sampling sites varied, ranging from 3 to 162 particles per 100 m³ (0.012–2.96 mg m⁻³) (Table S4), and the sites in Bohai Sea (an inner sea) had several times higher abundances of MPs than those in Huanghai Sea (an open sea). This finding suggests that anthropogenic plastic waste from inland or coastal activities may be the main sources of marine MPs, which coincides with previous findings by Jambeck et al. (2015), who emphasized the contribution of inland plastic waste to the ocean MP pollution.

3.3. Occurrence of PAHs in microplastics

The sum concentration of 16 PAHs (\sum_{16} PAH) was site-independent and ranged from 3400 ng g⁻¹ (site HH-2) to

120,000 ng g⁻¹ (site HH-5) (Table S5). The high concentration of PAHs at HH-5 was most likely caused by petroleum-based materials (which contain PAHs (Rochman et al., 2013b)) on the surface of PE lines (HH-5 in Fig. S3). The second highest concentration of PAHs occurred in the sample obtained from site BH-1, with an average of 68,000 ng g⁻¹ (Table S5). This site receives water from Daliao River, which was reported to have total PAH concentrations in surface waters ranging from 140 to 1700 ng L⁻¹ (Men et al., 2009), providing sorption availabilities for MPs. The main composition of MPs in BH-1 was identified as PS foam (Fig. 3), and these PS particles are known to contain PAHs from the manufacturing process of PS materials (Rochman et al., 2013b; Van et al., 2012; Wheatley et al., 1993). It is therefore not surprising that MP samples from site BH-1 showed elevated total PAH concentrations.

Although PAHs may have originated from PS particles (Rochman et al., 2013b), it is highly unlikely that the manufacturing process was the only source of PAHs on MP particles. High concentrations of PAHs have occurred in surface sediments (52.3–1870 ng g⁻¹ dry weight) (Jiao et al., 2012), coastal seawater (136–621 ng L⁻¹) (Hong et al., 2016), and marine organisms (60–129 ng g⁻¹ wet weight) (Hong et al., 2016) in Bohai and Huanghai Seas. As MPs (such as PS and PE) have a strong ability to sorb PAHs from the surrounding environment (Fries and Zarfl, 2012; Liu et al., 2016) behaving as a source and sink of PAHs (Rochman et al., 2013b), the high concentrations of PAHs in PS particles and other MPs were likely derived from the external environment.

Recent studies showed that MPs with sorbed PAHs were widely evident in open seas and beaches worldwide (Frias et al., 2010; Hirai et al., 2011; Rios Mendoza and Jones, 2015; Van et al., 2012;

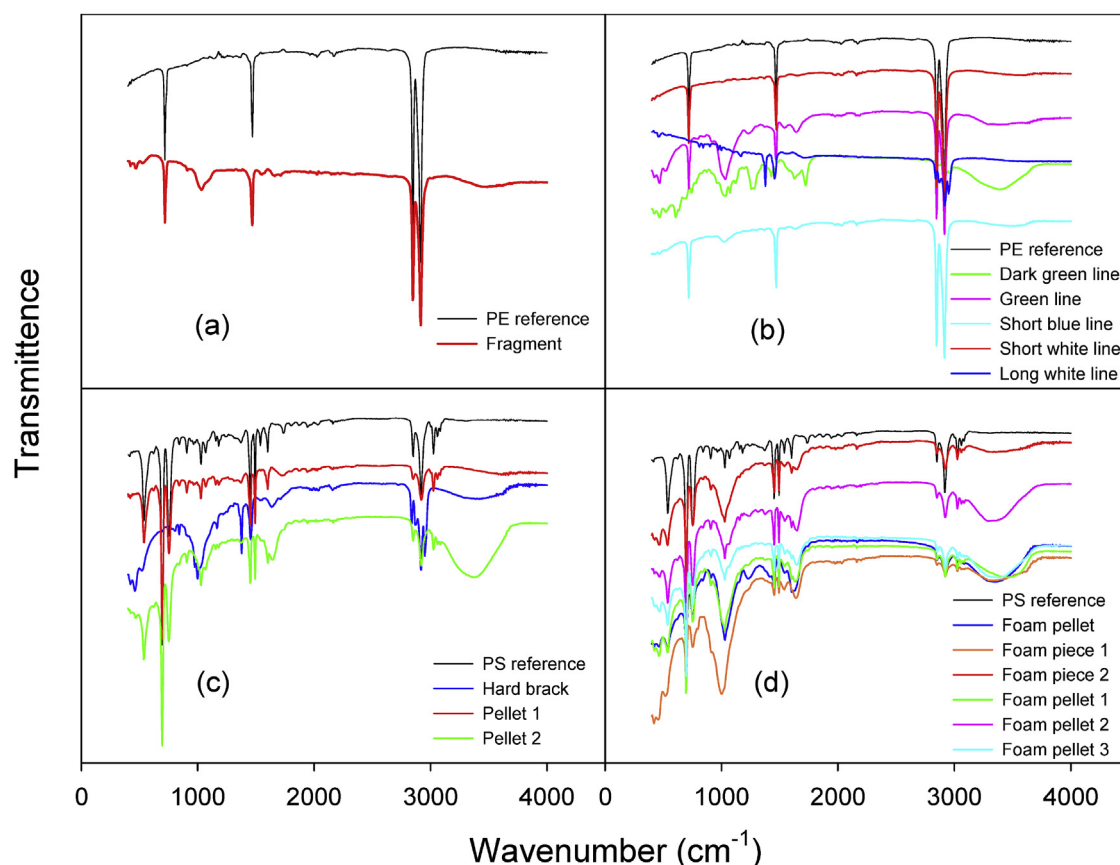


Fig. 3. Identification of microplastic samples using Fourier transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR): (a) spectra of fragments and a standard polyethylene (PE), (b) spectra of lines and the standard PE, (c) spectra of pellets and a standard polystyrene (PS) and (d) spectra of foams and the standard PS.

Zhang et al., 2015). Concentrations of PAHs found in the present study were 2–3 orders of magnitude higher than those in samples from the above-mentioned locations (Fig. 4). The large differences are most likely a combination of the heavy contamination present in both Bohai and Huanghai Seas (Jiao et al., 2012) and the strong sorption of MPs for PAHs (Fries and Zarfl, 2012; Liu et al., 2016). Besides, the sizes of collected MP samples varied with sampling sites (e.g., a few mm to a few cm in the study of Hirai et al. (2011)), which may result in different PAH concentrations. A recent study showed that the concentration of PAHs varied in different MP sizes and types, ranging from 1.2 to 194,000 ng g⁻¹ (Chen et al., 2017). Hence, although the results of the present study are alarming, they are perhaps not all that surprising.

3.4. Site variation of microplastic-affiliated PAHs

The concentrations of total PAHs extracted from MPs obtained from Bohai and Huanghai Seas were comparable to one another (Fig. S4 and Table S5), with no statistical difference between the two (*t*-test; *p* > 0.05). Sorption of individual PAH congeners behaved differently depending on the MP type (Rochman et al., 2013a), and the composition of PAHs also varied between sampling sites (Fig. S5 and Table S5), implicating different sources of sorbed PAHs. Low molecular-weight (2-ring and 3-ring) PAHs accounted for the majority of the components in all samples, which is consistent with the results achieved by Hong et al. (2016) in seawater of Northeast China. Lin et al. (2005) also observed high proportions of low molecular-weight PAHs in surface sediments of Bohai Sea, China. Principal component analysis showed that the top two components of PAH composition yielded 89% of the total variance, with P1 = 64% and P2 = 25%. The compositions of PAHs in the MP samples from Bohai and Huanghai Seas were similar to each other but clearly different from blank MPs (Fig. S6). Among the samples from Huanghai Sea, the PAH composition in site HH-5 was obviously different from those in the other four sites. Only slight differences in PAH composition were found in MP samples from the

Bohai Sea. The difference in PAH compositions imply that there are different sources of PAHs in MPs at many of these sites.

To track the potential sources of PAHs at each sampling site, molecular ratios of PAH congeners were used according to previously established methods (Yunker et al., 2002). The ratios of FLU/(FLU + PYR) and ANT/(ANT + PHE) have been used to examine the sources of PAHs. The FLU/FLU + PYR ratio of 0.50 and ANT/ANT + PHE ratio of 0.10 were generally used as the transition point for the PAH source of petroleum/combustion (Budzinski et al., 1997). The difference of FLU/(FLU + PYR) between Bohai and Huanghai Seas was not significant (paired *t*-test; *p* > 0.05), with respective averages of 0.45 (±0.20) and 0.53 (±0.28). The large standard deviations suggested a mixed origin of PAHs sorbed to MPs in both Bohai and Huanghai Seas, with 70% coming from a diesel source and 30% from a gasoline origin (Fig. S7). The ratio of ANT/(ANT + PHE) was also similar between the two seas (paired *t*-test; *p* > 0.05), averaging 0.131 (±0.085) and 0.123 (±0.049) for Bohai Sea and Huanghai Sea, respectively. These results suggested that PAHs were likely to derive from petroleum sources, similar to the finding of Zhang et al. (2015) that petroleum pollution contributed to PAHs sorbed to MPs in Zhengmingsi Beach. This is not surprising, as the sampling area at Huanghai Sea is heavily used for petroleum transportation. The sources of PAHs in beach MPs from the previous study (Zhang et al., 2015) and the nearby marine water MPs in the present study were both petroleum derived, and this similarity showed that PAHs were predominantly produced from the terrestrial environment (Zhang et al., 2009), as well as from marine transportation.

3.5. Significance of microplastics as a carrier of PAHs in marine environment

Although plastics are ubiquitously found in the world's oceans (Andrady, 2011; Eriksen et al., 2014), the calculated average mass abundance of plastics (~2 ng L⁻¹) in the oceans is negligible (i.e., several orders of magnitude less abundant than other media such as 0.5 mg L⁻¹ for dissolve organic carbon and 0.1 mg L⁻¹ for particulate organic carbon and colloids) (Cauwet, 1978; Koelmans et al., 2016). Koelmans et al. (2016) used the entire ocean volume in calculating the contribution of each environmental compartment to the total loading of PAHs. However, plastic concentrations decrease rapidly with increasing water depth (Reisser et al., 2015), so, in actuality, plastic concentration in surface sea waters may be orders of magnitude higher than that averaged throughout the entire ocean. Due to the strong sorption ability of MPs for HOCs (e.g., PAHs), the role of MPs carrying pollutants into these environments is considerably important. In the present study, to further understand the ramifications of MP materials in surface seawater to carry PAHs in the marine environment, they were compared to other media in Bohai Sea. Due to limited information, only three environmental compartments within Bohai Sea were evaluated including sea water, suspended particulate matter (SPM), and MPs that are present in the surface seawater (Fig. 5).

In the surface water of Bohai Sea, the concentrations of MPs ranged from 0.012 to 2.96 μg L⁻¹, which is 3 orders of magnitude higher than the estimated “whole ocean” average plastic concentration of ~2 ng L⁻¹ (Koelmans et al., 2016). Though the MP concentration in the surface water was high, MPs still accounted for only a small portion of the total mass compared to the other media evaluated. For instance, in one cubic meter of seawater, the mass of SPM was several orders of magnitude higher than that of MPs (Fig. 5(a)). Although, this might suggest that MPs are not as important as other media, the strong sorption ability of MPs (including nanoplastics) for HOCs suggests otherwise (Guo et al., 2012; Hüffer and Hofmann, 2016; Lee et al., 2014; Liu et al., 2016;

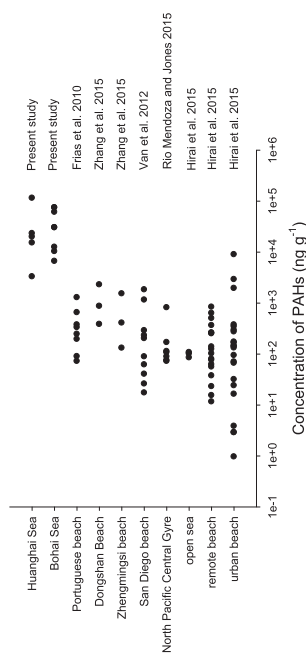


Fig. 4. Comparison of the logarithmic concentrations of polycyclic aromatic hydrocarbons (PAHs) in environmental microplastic samples from different regions around the world.

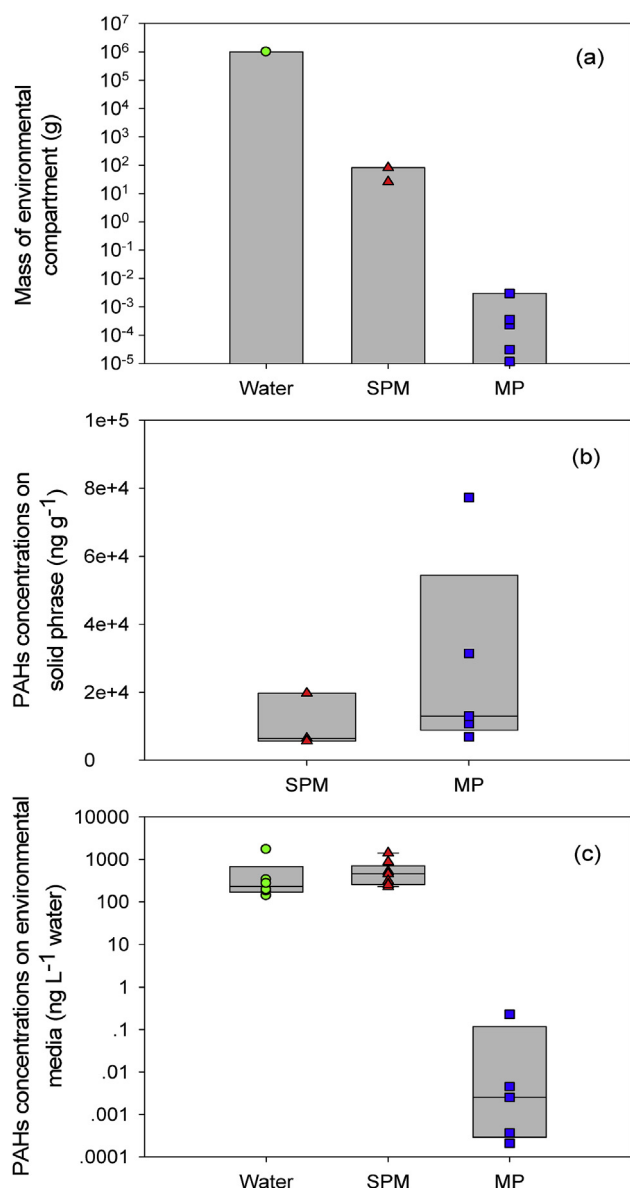


Fig. 5. Relative importance of environmental compartments, including water, suspended particulate matter (SPM) and microplastic (MP) in Bohai Sea: (a) Mass (g) of each environmental carrier in one cubic meter of sea surface water, and the corresponding, (b) mass concentrations (ng g^{-1}) of PAHs in SPM and MP, and (c) volume concentration (ng L^{-1}) of PAHs in SPM and MP in 1 L of sea surface water. Data of water (green circles) and SPM (red triangles) are adopted from Men et al., (2009) and data of MP (blue squares) obtained from the present study. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Velzeboer et al., 2014), as PAH concentrations sorbed by SPM ($5600\text{--}20,000 \text{ ng g}^{-1}$) is lower than those sorbed by MPs ($6900\text{--}77,000 \text{ ng g}^{-1}$) (Fig. 5(b)). These results revealed that the sorption ability of MPs was stronger than that of SPM, even though SPM may have larger specific surface area than MPs. Fig. 5(c) shows the mass distribution of PAHs in the environmental media under investigation in 1 L of seawater, i.e., less than 1 ng of PAHs were carried on MPs, whereas 100–1000 ng of PAHs were observed in both seawater and SPM (Men et al., 2009). This result was in agreement with the recent work of Koelmans et al. (2016), who estimated that plastics only bind about 0.0002% of all HOCs in the ocean, whereas seawater holds more than 98%. Given the low

abundance of MPs, it is likely that the importance of MPs on chemical transport in the aquatic environment is not substantial. However, Jambeck et al. (2015) predicted that the amount of available land-based plastic waste entering the ocean would increase ten times by 2025, if no proper waste management action is taken. A recent review estimated that the ocean receives 1.15–2.41 million tons of plastics from rivers every year (Lebreton et al., 2017). Other routes of exposure, such as ingestion of MPs by marine organisms, may also enhance the bioavailability of sorbed HOCs (e.g., PAHs) in the marine environment (Gouin et al., 2011; Koelmans et al., 2013). Overall, additional routes of exposure and an increase in the presence of MPs in the marine environment corroborate the importance of further understanding the effects of not only MPs alone, but also the compounds which may be sorbed onto MPs.

4. Conclusions

The present study suggested no need to pretreat MPs larger than $500 \mu\text{m}$, as attached organic matter showed no apparent influence on MP identification by Fourier transform infrared spectroscopy with attenuated total reflectance. For plastic particles larger than $500 \mu\text{m}$, pretreatment of MPs with 30% H_2O_2 did not significantly lower the concentrations of PAHs sorbed on MPs. Although this pretreatment did not affect the determination of PAHs in the present study, a disadvantage may occur in the analysis of other organic contaminants sorbed on MPs. These findings and improved methodologies would provide the foundation for future work on an extremely important topic, which was demonstrated by the successful application of the developed method in the present study.

Perhaps just as importantly, the present study also showed that levels of PAHs sorbed to MPs in surface seawater of Bohai and Huanghai Seas in China were considerably higher than any field measurements in the present literature. Additionally, we were able to determine the source of PAHs, which appeared to be petroleum residues. Amongst the environmental media in the ocean, MP accounted for only a small portion of the total mass of PAHs present because of the minimal mass abundance of plastics in the ocean. However, MPs (and associated sorbed contaminants) may adversely affect the health of aquatic organisms through ingestion, since high concentrations of PAHs were observed in the MP samples in the present study. Although the current knowledge about the role of MPs in transport of chemical contaminants is limited, the increasing input of plastics into the world's oceans is evident. The possible health effects brought by MPs and associated chemicals are an urgent matter and further efforts evaluating the biological effects of MPs and sorbed chemicals are highly encouraged.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2018.06.012>.

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