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Sorption of PAHs to microplastic and their bioavailability and toxicity to marine copepods under co-exposure conditions[☆]

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ABSTRACT

Organic chemical pollutants associated with microplastic (MP) may represent an alternative exposure route for these chemicals to marine biota. However, the bioavailability of MP-sorbed organic pollutants under conditions where co-exposure occurs from the same compounds dissolved in the water phase has rarely been studied experimentally, especially where pollutant concentrations in the two phases are well characterized. Importantly, higher concentrations of organic pollutants on ingested MP may be less bioavailable to aquatic organisms than the same chemicals present in dissolved form in the surrounding water. In the current study, the sorption kinetics of two model polycyclic aromatic hydrocarbons (PAHs; fluoranthene and phenanthrene) to MP particles in natural seawater at 10 and 20 °C were studied and the bioavailability of MP-sorbed PAHs to marine copepods investigated. Polyethylene (PE) and polystyrene (PS) microbeads with mean diameters ranging from 10 to 200 μm were used to identify the role of MP polymer type and size on sorption mechanisms. Additionally, temperature dependence of sorption was investigated. Results indicated that adsorption dominated at lower temperatures and for smaller MP (10 μm), while absorption was the prevailing process for larger MP (100 μm). Monolayer sorption dominated at lower PAH concentrations, while multilayer sorption dominated at higher concentrations. PE particles representing ingestible (10 μm) and non-ingestible (100 μm) MP for the marine copepod species *Acartia tonsa* and *Calanus finmarchicus* were used to investigate the availability and toxicity of MP-sorbed PAHs. Studies were conducted under co-exposure conditions where the PAHs were also present in the dissolved phase (C_{free}), thereby representing more environmentally relevant exposure scenarios. C_{free} reduction through MP sorption was reflected in a corresponding reduction of lethality and bioaccumulation, with no difference observed between ingestible and non-ingestible MP. This indicates that only free dissolved PAHs are significantly bioavailable to copepods under co-exposure conditions with MP-sorbed PAHs.

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1. Introduction

Microplastic (MP) is ubiquitous in all marine environmental compartments and its widespread occurrence has been reported in marine organisms representing most trophic groups, sizes and life stages (Barboza et al., 2019; Booth et al., 2018; GESAMP, 2015; Lusher, 2015). While most studies report MP in the digestive tracts of heterotrophic species, increasing evidence suggests smaller MP

and nanoplastic can transfer across biological barriers and accumulate in organs and tissues (Brennecke et al., 2015; Collard et al., 2017; Ribeiro et al., 2019). The potential for ingestion and accumulation of MP is influenced by particle size, with larger organisms (e.g. fish and mammals) ingesting MP passively from contaminated food and the water column and smaller organisms (e.g. zooplankton and juvenile stages) actively ingesting MP particles by mistaking them for food items.

Planktonic filter feeding organisms have been predicted to be particularly vulnerable to MP pollution due to their feeding modes and the similarity in the size of their natural food and MP. Ingestion of MP has been proven for several species of copepods (summarized by Barboza et al., and Lusher et al., (Barboza et al., 2019;

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Lusher, 2015)), and includes *Acartia* spp. and *Calanus* spp. (Cole et al., 2019; Cole et al., 2013). However, there is limited knowledge on the actual size range of MP that is ingestible by planktonic organisms, which is likely to vary between species (Cole et al., 2013).

The sorption of organic contaminants present in the marine environment to plastic and MP has been investigated in detail in recent years. Studies have shown that both sorbent (e.g. polymer type) and sorbate properties (e.g. molecular size and polarity), as well as extrinsic environmental conditions influence the sorption process (Ziccardi et al., 2016). Several studies have emphasized the importance of polymer type on sorption of organic chemicals to microplastic particles (Bakir et al., 2014b; Hüffer and Hofmann, 2016; Rochman et al., 2013b; Teuten et al., 2007; Wang and Wang, 2018a, b). Polyethylene (PE) and polystyrene (PS) have been identified as the plastic polymer types with highest sorption capacity for hydrophobic, organic contaminants. To our knowledge, little is known about the effect of particle size on the sorption of organic contaminants in the natural environment, although existing knowledge on intraparticle diffusion in polymer matrices may provide some insight. Furthermore, seawater temperature, known to vary greatly with location, will influence the sorption capacity of organic contaminants to MP.

The ingestion of MP in organisms has raised the issue of MP pollution influencing the bioavailability of organic contaminants to aquatic organisms (Barboza et al., 2019; Hartmann et al., 2017; Koelmans, 2015; Koelmans et al., 2016; Ziccardi et al., 2016). Of particular concern has been the possibility that MP-sorbed organic pollutants are desorbed in organisms after MP ingestion and that this can result in much higher levels of pollutant exposure than through exposure to the same compounds present in the dissolved form in natural waters. In recent years, various studies have attempted to investigate the bioavailability of MP-sorbed contaminants.

Several studies have demonstrated that gut and biological fluid conditions may increase desorption of both additive chemicals and environmental contaminants (Bakir et al., 2014a; Coffin et al., 2019; Wang et al., 2018). In the case of contaminants inherently associated with plastics, namely plastic additive chemicals, several field investigations have demonstrated a positive correlation between the occurrence of plastic particles in the animals and additive chemicals found in animal tissues (Franzellitti et al., 2019).

In the case of chemicals that are ubiquitous contaminants in the marine environment, understanding the potential added impact of exposure through ingestion of contaminated plastic or MP is more challenging. An increasing number of laboratory studies have reported the bioavailability of MP-sorbed organic chemicals to aquatic organisms, leading to transfer into tissues and accumulation (González-Soto et al., 2019; O'Donovan et al., 2018), transfer to the next generation (Batel et al., 2018) and toxicological effects (González-Soto et al., 2019; Rainieri et al., 2018; Rochman et al., 2013a; Rochman et al., 2014). However, drawbacks related to environmental relevance and the comparability of studies have recently been presented and discussed (Burns and Boxall, 2018). Crucially, most laboratory studies used clean organisms exposed to contaminated MP placed in clean water, which creates conditions that promote chemical transfer to the tested organisms (Koelmans, 2015). Under more environmentally relevant exposure scenarios, modelling studies suggest that the MP-exposure route for organic contaminants is negligible with respect to the combined intake from food and water (Koelmans et al., 2016). Furthermore, the body burden of these chemicals may actually decrease if they have opposing concentration gradients between plastic and biota lipids (Herzke et al., 2016; Koelmans et al., 2013).

Using polycyclic aromatic hydrocarbons (PAHs) as a model for toxic hydrophobic organic contaminants, the current laboratory study investigates the relative bioavailability of dissolved and MP-sorbed phenanthrene and fluoranthene under co-exposure conditions representing of those occurring in the marine environment. Upon determination of sorption capacity and mechanisms of model PAHs to model MP (PE and PS), the influence of particle size (surface area), seawater temperature and pollutant hydrophobicity on sorption is determined. A size cut-off for copepod MP ingestion was determined and used as the basis for selecting both ingestible and non-ingestible MP to help elucidate mechanisms of PAH exposure and bioavailability. Finally, bioavailability and toxicity of MP-sorbed PAHs towards two marine copepods; *Calanus finmarchicus* and *Acartia tonsa*, was investigated.

2. Materials and methods

2.1. Chemicals and materials

Ultrapure (MilliQ) water was supplied by a Millipore® filtration system. Analytical grade solvents were used, and purity was verified in-house. Dichloromethane (DCM) was supplied by Rathburn, *n*-hexane by Fluka Analytical, acetonitrile (ACN) and methanol (MeOH) were supplied by Honeywell, Riedel-de-Häen. Hydrochloric acid (HCl) was supplied by Sigma Merck and diluted in MilliQ water to 15%. Fluoranthene and phenanthrene (>98% purity) were purchased from Sigma-Aldrich. Deuterated PAHs were supplied by Chiron AS (Trondheim, Norway). Stock and calibration solutions of PAHs were prepared in MeOH or DCM and stored in the dark at 4–5 °C.

Polystyrene (PS) microspheres (mean particle size 10 µm) were purchased as an aqueous dispersion from Polysciences Europe GmbH (www.polysciences.com). High density polyethylene (PE) microspheres were purchased from Cospheric LLC (www.cospheric.com) in dry powder form, in the following size ranges: 3–16 µm ('PE-10'), 45–53 µm ('PE-50'), 90–106 µm ('PE-100') and 180–221 µm ('PE-200'). The physicochemical properties of the particles are summarized in Table S1 of the Supplementary Information (SI) together with scanning electron microscopy images (Fig. S1). The particles were used as supplied, without further pre-treatment. The commercial PS dispersions were shaken vigorously to re-suspend particles before addition to water samples.

2.2. Preparation of PAH seawater solutions

To produce PAH solutions at their maximum seawater solubility without using co-solvents, phenanthrene or fluoranthene were dissolved in DCM and applied to 4 × 8 cm tetrafluoroethylene and ethylene polymer monofilament grids (Fluortex™, Sefar AG., Heiden, Switzerland) (Lofthus et al., 2016). The amount of PAH applied exceeded the theoretical seawater solubility by at least two-fold. After complete evaporation of the solvent (room temperature, ~30 min), the pads were suspended in sterile filtered (Sterivex cartridge filter, 0.22 µm) natural seawater sourced from a depth of 80 m in Trondheim Fjord and acclimatized to either 10 or 20 °C. After equilibration with the seawater (pre-determined: 3 days), the solubility of the PAHs was determined by direct liquid chromatography coupled to ultraviolet detection (LC-UV) (see SI for analytical details). The generated PAH solutions were transferred to sterile glass bottles and stored in the dark at 10 or 20 °C until used in sorption or toxicity studies.

2.3. PAH sorption dynamics

PAH sorption equilibrium times were first determined at both 10 °C and 20 °C. To keep concentrations comparable and below the solubilities of fluoranthene and phenanthrene at both experimental temperatures, stock solutions were diluted to approximately 20 µg/L in 250 mL glass bottles using sterile filtered seawater, leaving approximately 10% headspace. MP were added (Tables S2 and SI) and the samples shaken on a horizontal shaking table. The temperatures were recorded to 10 ± 2 °C or 20 ± 1 °C throughout the sorption studies. For determination of sorption kinetics, small volumes of water (<2 mL) were removed for analysis at each sampling interval (day 0, 1, 2, 3, 4, 7, 9, 11 and 14) to determine when equilibrium had been achieved. Control samples (triplicate) of PAHs without MP were collected at each sampling interval. Water samples were filtered to remove MP from the water prior to analysis by LC-UV (method described in SI). An empty glass SPE-column (2 mL) was used as a sample reservoir, connected by luer-lock to a 13 mm PTFE syringe filter (0.45 µm). Samples were passed through the filter using the plunger from a BD Plastipak® 2 mL syringe.

2.4. PAH sorption isotherms

To determine PAH-MP isotherms, the saturated fluoranthene and phenanthrene solutions were diluted to seven concentrations ranging from 5 to 100% of their individual maximum solubility (at 10 °C). These were transferred to vials (22 mL) containing a fixed amount of MP sufficient to result in a reduction of dissolved PAH concentration (C_{free}) of 30–70% (Tables S2 and SI), leaving 10% volume headspace in the vial. Control samples at each test concentration consisted of diluted PAH solutions without MP. Each sample of a given MP-PAH (or no MP) combination was sampled after equilibrium was reached (determined as described above), and samples filtered immediately (as described above, but here the entire volume of sample was filtered). Samples where the PAH concentration was too low to be accurately measured by LC-UV were acidified (pH~2, using HCl), and stored dark and cool (~4 °C) until they were extracted and analyzed by GC-MS (method described in SI). The comparability of LC-UV and GC-MS analyses was verified using a range of solutions of both PAHs.

Sorbed concentrations of the PAHs were determined indirectly from the reduction in C_{free} after accounting for losses in control (no MP) samples. Sorption parameters were calculated and isotherms fitted by a trial and error procedure using the solver add-in for Microsoft Excel 2017 (Wang and Wang, 2018b). Non-linear isotherm models (Linear, Freundlich, Langmuir, Dual Langmuir, Redlich-Peterson and Dubinin-Astakhov) were fitted to the MP-PAH sorption data. An overview of the different isotherm models is provided in the SI. The sum of squared errors (SSE) function (Kumar et al., 2008) was used to evaluate the fit of the isotherm models. When F-tests of similar SSE-values gave inconclusive results, the best fit was determined by the lowest values of sum of squared error function (SSE), the coefficient of correlation (R^2), and a visual inspection of the fit of the model to the experimental data. Equations for the tested isotherm models are given in Tables S3 and SI. It should be noted that the indirect approach used to quantify the sorbed PAH concentrations may contain a degree of error that is propagated during the calculation of partition coefficients (K_{pw}).

2.5. Copepod toxicity assays

The test procedure used to determine the LC₅₀ for the copepods (*Acartia tonsa* Dana and *Calanus finmarchicus* (Gunnerus)) followed ISO guideline ISO 14669:1999, with some species-specific

adaptations as described in the SI. All dilutions and controls were performed with sterile filtered seawater (Opticap XL cartridge filter, Durapore® 0.22 µm; MerckMillipore). A 7-point dilution series representing 100%–4% of the PAH stock solutions was applied in all studies, and concentrations verified using LC-UV.

2.6. PAH toxicity modulation assays

A pre-study was performed to determine the ingestible and non-ingestible MP particle sizes for both *A. tonsa* and *C. finmarchicus* (described in SI). PAH exposure solutions with and without MP were prepared in either 40 mL glass vials (*A. tonsa*) or 1 L bottles (*C. finmarchicus*) using fully saturated solutions of phenanthrene or fluoranthene and a sufficient amount of MP particles calculated to reduce PAH C_{free} by ~50%. Additionally, control samples containing only MPs (no PAHs) were prepared in the same way using clean seawater. The 40 mL vials were gently shaken in the dark for 7 days and the 1 L bottles were shaken for 9 days to achieve equilibrium before use in experiments. After shaking, 7-8 adult *A. tonsa* of mixed sex were transferred to each 40 mL vial, which were then mounted on a custom-made rotating plankton wheel immersed in a water bath (20 °C) for 48 h. For *C. finmarchicus*, 10 adult non-ovulating female copepods were transferred to each 1 L bottle, which were then mounted on a custom-made rotating plankton wheel immersed in a water bath (10 °C) until the end of the exposure at 96 h. The exposure duration for each species was in line with ISO guidelines. Every 24 h, the 40 mL vials were checked under a dissecting microscope and the 1 L bottles were visually checked to determine the viability of the organisms. The test animals were not fed during exposure. PAH C_{free} was measured before addition of MP, as well as at the start (0 h) and end (48 h or 96 h) of the exposure study. At the end of exposure, viable *C. finmarchicus* (5–10 copepods) were sampled for body burden analysis, kept frozen at –80 °C until extraction following a procedure described in Øverjordet et al. (2018), followed by analysis with GC-MS (as described in SI).

2.7. Data treatment and statistical analysis

For the effect studies, LC-values were calculated by a non-linear sigmoidal dose-response model with variable slope (four-parameter logistic equation) using Prism version 5.0b for Macintosh (GraphPad Software, San Diego, CA, US). Comparisons between treatments were done by one-way ANOVA test followed by Tukey's multiple comparisons test in the R software (R Development Core Team, 2008).

3. Results and discussion

3.1. PAH solubility

The obtained seawater solubilities at 10 and 20 °C are given in Table 1. As expected, phenanthrene was more soluble than fluoranthene, whilst both PAHs were more soluble at 20 °C than at 10 °C. Given that these values correspond well to those reported in the literature (0.6 and 0.1 mg/L at 22 °C for phenanthrene and fluoranthene, respectively) (Verschuere, 2001), experimental solubility values were used for the fitting of isotherms.

3.2. Sorption of PAHs to PE and PS MP particles

MP-PAH equilibration times were faster for fluoranthene (5 days at both 10 and 20 °C, Fig. S2 and SI) than for phenanthrene where equilibrium was achieved faster at higher than at lower temperatures (7 days at 20 °C, 9 days at 10 °C, Fig. S2 and SI). Both by mass

Table 1
Obtained seawater solubility and lethality (LC_{50}) of fluoranthene and phenanthrene towards *Calanus finmarchicus* (96-h assay, 10 °C) and *Acartia tonsa* (48-h assay, 20 °C).

	Seawater solubility [$\mu\text{g/L}$]		<i>Calanus finmarchicus</i>		<i>Acartia tonsa</i>	
	10 °C	20 °C	LC_{10} [$\mu\text{g/L}$]	LC_{50} [$\mu\text{g/L}$]	LC_{10} [$\mu\text{g/L}$]	LC_{50} [$\mu\text{g/L}$]
Fluoranthene	28 ± 1	84 ± 1	> solubility	> solubility	49.84 (43.35–57.30)	80.65 (77.18–84.26)
Phenanthrene	159 ± 1	415 ± 5	70.52 (57.88–85.93)	> solubility	234.9 (220.3–250.4)	316.7 (301.0–333.1)

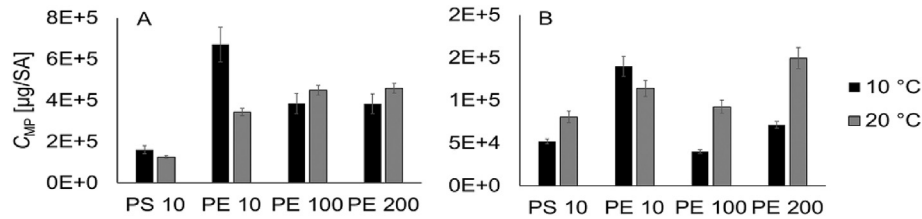


Fig. 1. Surface area normalized sorption (μg PAH per m^2 of MP) of A) fluoranthene (FLA) and B) phenanthrene (PHE). Nominal C_{free} was 20 $\mu\text{g/L}$ PAH.

(Fig. S3 and SI) and estimated surface area (Fig. 1) of the particles, the sorption of PAHs was higher for PE MP than for PS MP of the same size. The findings of the current study are in line with previous studies where sorption of PAHs to PS and PE particles of comparable sizes and shapes has been investigated (Wang and Wang, 2018a, b). The higher PAH sorption capacity of PE than PS may be due to the greater segmental mobility and free volume in its molecular segments, which can facilitate solute diffusion into the polymer (Karapanagioti and Klontza, 2008; Pascall et al., 2005). Although there were small differences in the morphology and size distributions of the PE and PS particles used in the current study,

with PS MP being slightly more spherical and having a narrower size distribution (Fig. S1 and Table S1), these variations do not appear to have played a significant role in the outcome of the current study.

On a surface area basis, both polymer types showed a higher sorption capacity for fluoranthene than phenanthrene, reflecting the difference in hydrophobicity and expected polymer affinity between the two compounds. Consequently, PS and PE have the potential to sorb and transport higher amounts of more hydrophobic organic contaminants. While isotherm model fit (Fig. 2, Table 2) varied with seawater temperature and MP polymer type

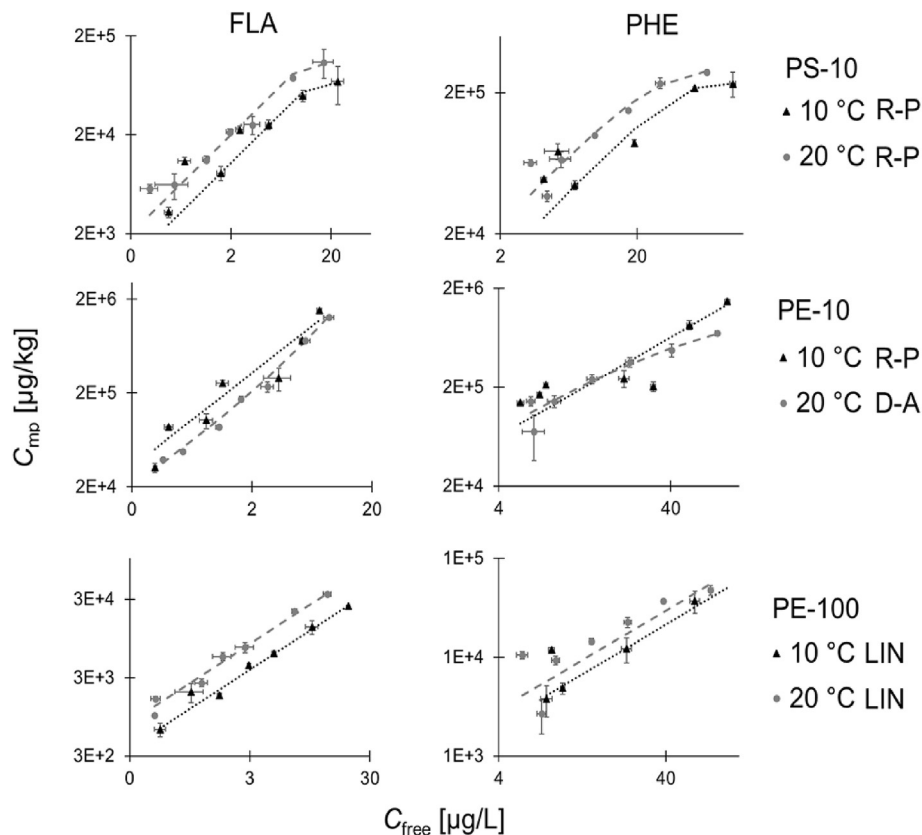


Fig. 2. Sorption data and fitted isotherms for all combinations of fluoranthene (FLA) and phenanthrene (PHE) with the MP. Data generated at both 10 °C (black triangles) and 20 °C (grey circles) is presented in each case, and the isotherm model is indicated (R–P = Redlich–Peterson, D–A = Dubinin–Astakhov, LIN = Linear).

Table 2

Fitted parameters of the Dubinin-Astakhov, Redlich-Peterson and linear models for adsorption isotherms of fluoranthene and phenanthrene to three types of MP at 10 and 20 °C. Equations and explanations of parameters are presented in Table S3 and SI.

Dubinin-Astakhov	Log Q^0 [$\mu\text{g}/\text{mg}$]	E [kJ/mol]	b	R^2	SSE
PE-10 20 °C					
Fluoranthene	730	0.767	0.512	0.9946	0.0836
Phenanthrene	1.12	10.2	1.76	0.9793	0.0363
Redlich-Peterson	a_r	K_R [L/mg]	B	R^2	SSE
PE-10 μm 10 °C					
Fluoranthene	0.0007	0.163	11.3	0.9996	0.607
Phenanthrene	0.0007	0.0319	0.000	0.9999	0.455
PS-10 μm 10 °C					
Fluoranthene	0.0410	0.00520	11.8	0.9999	9.00E-04
Phenanthrene	0.0135	0.00630	1.79	0.9999	0.0131
PS-10 μm 20 °C					
Fluoranthene	0.0526	0.00990	7.67	0.9999	1.40E-03
Phenanthrene	0.0222	0.0117	1.45	0.9999	0.00590
Linear	K [L/mg]		R^2	SSE	
PE-100 μm 10 °C					
Fluoranthene	1.3E-04		0.9999	4.26E-05	
Phenanthrene	5.0E-04		0.9999	6.00E-04	
PE-100 μm 20 °C					
Fluoranthene	2.7E-04		0.9999	8.07E-05	
Phenanthrene	7.0E-04		0.9999	8.00E-04	

and size, the same best fit model was found for both phenanthrene and fluoranthene where conditions were otherwise similar, indicating that sorption mechanisms for 3- and 4-ring PAHs are the same. Although surface normalization rather than mass was used to present the data, this does not imply that sorption occurred only at the surface.

Larger (100 μm) PE MP had PAH sorption isotherms that could best be described by linear regression, suggesting that absorption of PAHs is the main sorption process for larger PE MP. Partition coefficients of phenanthrene and fluoranthene between PE-100 and seawater (log K_{PW}) were determined as 3.1 (10 °C) and 3.4 (20 °C) for fluoranthene and 2.7 (10 °C) and 2.9 (20 °C) for phenanthrene. These values are typically lower than literature values reported for PAH-PE partitioning, where log K_{PW} at 20 °C is around 4.8–4.9 for fluoranthene and 4.0–4.3 for phenanthrene (Choi et al., 2013). In the literature studies conducted to obtain these values, larger low-density PE (LDPE) sheets are utilized rather than the high-density PE (HDPE) micron-sized particles used in the current study. While some discrepancies between the effect of PE density on sorption of PAHs exist in literature, the general observations suggest that lower density PE exhibits higher diffusion coefficients for hydrophobic contaminants, leading to higher sorption capacities and higher K_{PW} values (Fries and Zarfl, 2012; Muller et al., 2001), thereby explaining the discrepancies between K_{PW} values in the current study and literature values.

For smaller particles (10 μm PE and PS), the sorption mechanism was generally best explained by the Redlich-Peterson model, with the exception of PE-10 at 20 °C. The fit of the Redlich-Peterson model, being a hybrid between the Langmuir and Freundlich equation, suggests a combined monolayer and multilayer adsorption process, with monolayer sorption dominating at lower PAH concentrations and multilayer sorption dominating at higher concentrations. Given that the concentrations applied in the current study (even the lower range values) are well above expected environmental concentrations, PAHs are thus expected to be found adsorbed in monolayers to these small particles in the environment. The transition from absorption to adsorption with decreasing particulate size has previously been reported in a study looking into

the sorption of polychlorinated biphenyl (PCB) congeners to PE microspheres (10–180 μm) and PS nanospheres (70 nm) (Velzeboer et al., 2014). The authors report that linear sorption was observed for larger PE spheres, whilst non-linear sorption was observed for smaller particles, in line with the findings of the current study. It is important to note that the Redlich-Petersen model is likely to give good fits for both the combined bulk partitioning and for the initial surface sorption. To fully understand the relative importance of each process, more detailed studies with a bigger range of particle sizes, including into the nano-scale, and an increased number of data points are therefore required to test a broader range of sorption models.

In general, the sorption capacity of PE and PS MP for PAHs was higher at 20 °C than at 10 °C, with the exception of sorption to PE-10, where the trend was opposite (Fig. 1). When assessing the change in sorption partition coefficient between the two temperatures according to the van 't Hoff equation, the sorption of PAHs to PE-10 is an exothermic process, while the sorption processes for PS-10 and larger PE MPs appears to be endothermic. This would explain why sorption to PS-10 and larger PE particles is favored at higher temperatures, while the opposite is the case for PE-10. With only two experimental temperatures, the temperature independence of entropy and enthalpy could not be determined and therefore further discussion of the sorption thermodynamics is not possible for the current study. The good fit of the Dubinin-Astakhov model for PAH sorption to PE-10 at 20 °C indicates that PAHs are increasingly able to transition into the micropores of PE particles with increasing temperature, which is consistent with previous studies (Gil and Grange, 1996). This transition process is known to be temperature dependent (Foo and Hameed, 2010), and may reflect changes in adsorption behavior observed for PE-10 MP between 10 °C and 20 °C. The same effect was not observed for PS particles and may be the result of differences in the phase of the two polymer types at the temperatures studied. The phase of a polymer is known to influence organic contaminant adsorption (Brandup et al., 1989; Teuten et al., 2009). While PE has a glass transition temperature (T_g) of approximately -68 °C meaning it is considered 'rubbery' at temperatures used in the current study, PS is 'glassy' (T_g approximately 100 °C) – supporting the idea that sorption would only occur at the particle surface.

Wang et al. (Wang and Wang, 2018a, b) studied the sorption of pyrene and phenanthrene dissolved in synthetic freshwater to PE and PS MP (100–150 μm , 200 mg/L) at ambient temperature. A best fit of the Langmuir isotherm was observed for both chemicals, indicating predominantly monolayer sorption of PAHs to the MP, which is not consistent with the current study in seawater. Here, it is important to note that the current studies were conducted in seawater (salinity $\sim 33\%$) to simulate a marine environment. While some studies have suggested salinity has little effect on PAH sorption to polymers (Bakir et al., 2014b; Choi et al., 2013), differences between the results in the current study and comparable studies conducted in synthetic freshwater indicate that salinity does influence sorption. In line with the current study and with the Setschenow equation describing the salting-out effect of solutes, salinity has been shown to increase the sorption of other organic contaminants to both PE and PS, and a multilayer sorption model of PCBs to micron-sized PE particles in seawater has been previously suggested (Velzeboer et al., 2014).

3.3. Copepod ingestion of MP

A cut-off size for MP ingestion by copepods was determined, allowing selection of both ingestible and non-ingestible particles for studying modulation of PAH bioavailability. *C. finmarchicus* readily ingested PE MP with an average size of 10 μm diameter, as



Fig. 3. *Calanus finmarchicus* (A) surrounded by non-ingestible 90–106 μm PE particles showing the relative size to the animal, as well as feces of *Calanus finmarchicus* demonstrating excretion of encapsulated PE particles sizes 3–16 μm (B) and 45–53 μm (C). Scale bar A: 500 μm . B–C: 100 μm Photos: Dag Altin, BioTrix.

well as to some extent MP particles up to ~ 50 μm diameter (Fig. 3) but were not able to ingest MP particles of 100 μm diameter. A size cut-off could not be visually confirmed for *A. tonsa* as the small size and transparency of the MP particles, combined with the partial opacity of the copepods, prevented an unequivocal identification of the particles inside the organisms (data not shown). For the purposes of the current study, 100 μm particles were used to represent non-ingestible MP and 10 μm particles (mean size) used to represent ingestible MP for both species, the latter falling within the size range of natural algae prey. The results highlight that only a limited size range of MP particles are ingestible by copepods, and that the specific cut-off size may vary from species to species. Although determination of ingestion and excretion rates were not a focus of the current study, ingested particles were clearly observed encapsulated in feces from *C. finmarchicus* demonstrating both ingestion and egestion in this species for solid particles up to 50 μm (Fig. 3). No increase in mortality (relative to seawater controls) was observed in copepods exposed to PE MP of either size.

3.4. Modulation of PAH-induced mortality through sorption to MP

Previous studies have used MP particles that are pre-loaded with the organic pollutant to be tested. However, as soon as the MPs are transferred to the pristine aqueous exposure media used in toxicity tests the organic pollutant will begin to dissolve directly into the water as the systems tries to achieve equilibrium. This process initially proceeds very quickly as the system is far from equilibrium and can lead to high concentrations of the target chemical in the dissolved at the start of an exposure. As a result, exposure to organisms will then proceed via a combination of conventional aqueous exposure and exposure through ingestion of contaminated MP. However, most studies fail to consider this issue and do not directly measure the dissolved concentration of the organic pollutant, nor factor this into the interpretation of the results of the study. Ultimately, this means that such studies may well be overestimating the bioavailability of organic pollutants sorbed to MP and therefore preventing a direct link between any observed accumulation or effects and the MP-sorbed contaminants only.

The reduction in C_{free} with addition of MP in the present study is an intended artefact of the experimental design that specifically allows investigation of the bioavailability of MP-sorbed PAHs under simulated environmental conditions where co-exposure of an organism to a known concentration of freely dissolved PAHs also occurs. By allowing a quantified proportion the PAHs in the dissolved phase to naturally partition to the added MP and establish an equilibrium, the experimental design prevents overloading of the MP and creates a more environmentally relevant exposure. Furthermore, the approach allows the quantifiable co-exposure of MP-sorbed PAHs and dissolved PAHs to organisms and the

opportunity to study the relative bioavailability of the PAHs through these two exposure pathways. While the presence of PAH contamination in the test materials was not determined directly, PAH levels in the seawater from the MP-only control exposures were below the instrumental limit of detection suggesting this did not influence the results obtained.

The addition of the copepods had the potential to change the system dynamics and begin shifting the equilibrium due to a proportion of the PAH partitioning to the surface of the copepods. Given the relatively short exposure time (48–96 h), it is unlikely that a new, steady-state equilibrium would be established. However, results show that there was a negligible change in C_{free} during the exposure periods used in the current study, suggesting that redistribution of the PAHs is slow or that presence of the organisms did not significantly affect the established equilibrium of the system.

As expected, the PAHs used in the current study did not elicit an acute effect in *C. finmarchicus* (96 h assay, 10 $^{\circ}\text{C}$), even at the highest dose (equal to maximum solubility), owing to their large lipid store and documented tolerance towards lipophilic contaminants (Hansen et al., 2018; Øverjordet et al., 2018). Thus, the estimated LC_{50} values for phenanthrene and fluoranthene to *C. finmarchicus* were above the maximum seawater solubilities of both chemicals (Table 1). In this study, the presence of PE-10 MP reduced PAH C_{free} by $56 \pm 5\%$ for fluoranthene and $47 \pm 2\%$ for phenanthrene, while the PE-100 MP reduced C_{free} by $49 \pm 6\%$ for fluoranthene and $36 \pm 2\%$ for phenanthrene. The reduction in C_{free} resulted in 0% observed mortality for *C. finmarchicus* in all MP-PAH exposures (Fig. 4B). This indicates that exposure of *C. finmarchicus* to PAHs via ingestion of contaminated MPs does not result in the PAH being sufficiently bioavailable to elicit acute effects in the organisms.

The LC_{50} values for freely dissolved phenanthrene and fluoranthene to *A. tonsa* (48 h assay, 20 $^{\circ}\text{C}$) were determined at approximately 317 and 81 $\mu\text{g}/\text{L}$, respectively. While the addition of the MP caused a reduction in C_{free} , the total concentration of each PAH used in the exposure systems remained above the determined LC_{50} value for *A. tonsa*. In PAH exposures without MP, mortality remained above 50% for both PAHs as expected (Fig. 4A). In the fluoranthene exposures, MP addition reduced C_{free} by $66 \pm 22\%$ (PE-10) and $67 \pm 18\%$ (PE-100), which resulted in no *A. tonsa* mortality. A $37 \pm 6\%$ (PE-10) and $41 \pm 6\%$ (PE-100) reduction in phenanthrene C_{free} from addition of MP also led to a corresponding reduction of *A. tonsa* mortality to 0% in both cases (Fig. 4A). The reduced C_{free} concentration for phenanthrene represents approximately the LC_{10} value for *A. tonsa*. In the case of the non-ingestible PE-100 MP, the results indicate that the sorbed PAHs are no longer bioavailable given the time-scale of exposure. This indicates that PAHs sorbed to ingestible MP are not a significant contributor to toxicity under typical gut residence times in copepods. Although not sufficiently

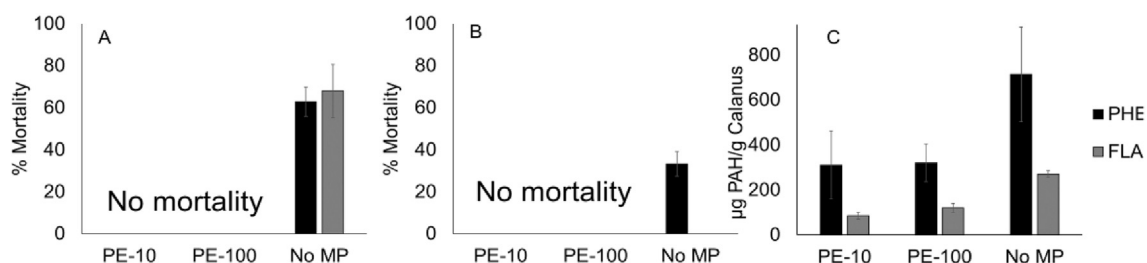


Fig. 4. Modulation effect of MP presence on PAH toxicity and bioaccumulation in copepods. A) Reduction in mortality in *Acartia tonsa* exposed to MP modulated PAHs. B) Reduction in mortality in *Calanus finmarchicus* exposed to MP modulated PAHs. C) Reduction in PAH body burden in *C. finmarchicus* exposed to MP modulated PAHs. Values are given with standard deviation, n = 4 (*A. tonsa*) or n = 3 (*C. finmarchicus*).

bioavailable to *A. tonsa* to reach or exceed the lethal body burden, it is possible that MP-sorbed PAHs were partially bioavailable. This highlights a limitation of using LC₅₀ as an endpoint in such studies. In contrast to *A. tonsa*, lipid-rich copepods such as *C. finmarchicus* permit a direct quantification of PAH body burden and therefore a more detailed investigation of MP-sorbed PAH bioavailability.

3.5. Bioavailability of MP-sorbed PAHs

The reduction in C_{free} due to MP sorption caused a comparable reduction in *C. finmarchicus* body burden of both fluoranthene and phenanthrene after 96 h exposure (Fig. 4C). Bioaccumulation factors (wet weight basis), were calculated based on measured body burden concentrations and the C_{free} measured at the end of the exposure period. The obtained values (log BAF 3.6 ± 0.1 and 4.2 ± 0.1 for phenanthrene and fluoranthene, respectively) in PAH-only (no MP) solutions were in line with those reported in previous studies into PAH bioaccumulation in *C. finmarchicus* (Jensen et al., 2012). The calculated BAF values for the MP-PAH exposures were based on C_{free} values determined experimentally at the end of exposure period (96 h). The values were comparable to those calculated for the PAH-only solutions (3.5 ± 0.2 and 3.5 ± 0.1 for phenanthrene with PE-10 and PE-100; 4.0 ± 0.1 and 4.1 ± 0.1 for fluoranthene with PE-10 and PE-100), and no statistical difference (one-way ANOVA, p > 0.05) was observed. This indicates that only the C_{free} fraction of PAHs in the exposure system has contributed to the observed accumulated PAH fraction in *C. finmarchicus*. Furthermore, the results suggest that MP-sorbed contaminants such as PAHs do not contribute significantly to body burden and detrimental effects in seawater copepods under conditions where co-exposure of the chemicals in the dissolved phase also occurs. This is in line with a recent study which determined negligible effects on the BAFs of PCBs in lugworms exposed to PE MPs and PCBs in sediments (Besseling et al., 2017). In future studies, it would be interesting to conduct exposures where the volume of PAH-contaminated seawater is sufficiently large that a negligible reduction in C_{free} occurs when MPs are introduced. However, this would require a much lower concentration of MP and would result in a reduced encounter rate with the test organisms.

Although several laboratory studies have demonstrated the potential for transfer of organic contaminants to organisms via ingestion of contaminated MP, other studies have shown that MP-sorbed organic contaminants may not be readily bioavailable (reviewed by Ziccardi et al. (2016)). For example, PCB concentrations in lugworm (*Arenicola marina*) tissues were higher in organisms exposed to PS MP mixed with PCB-containing sediment compared with exposure to the PCB-containing sediment alone (Besseling et al., 2013). Mean concentrations of organic contaminants in fish lipids from organisms exposed to PE MP with chemicals sorbed from the marine environment were found to be 1.2 to

2.4 times greater than those in the negative control (Rochman et al., 2013a). It should be noted that the unrealistic contaminant gradient between the pellets and the exposure water in the study prevents differentiation between desorption in water and subsequent uptake or via internal gut releases (Burns and Boxall, 2018). In contrast, the addition of PE MP particles to PCB-contaminated sediment reduced the bioaccumulation of PCBs by 80–98%, depending on the concentration of PE (Koelmans et al., 2013). Furthermore, a negligible impact of ingested MP on tissue concentrations of organic contaminants has been reported in seabirds (Herzke et al., 2016).

From the current study and available literature, it is evident that species-dependent factors, such as lipid store and gut residence time of MP play a crucial role in the potential for desorption and transfer of MP-sorbed organic contaminants to organismal tissue, which again determines an eventual toxicological influence of these chemicals. Importantly, the bioavailability of MP-sorbed organic contaminants appears to be significantly influenced by the presence of the same chemicals dissolved in the aqueous phase. This is important when considering the bioavailability of MP-sorbed organic contaminants under real environmental conditions, where such co-exposure is more likely to occur and where organisms may already contain accumulated pollutants. In the natural environment, organisms exposed to MP-sorbed pollutants via ingestion are most likely to already contain levels of the same pollutants in their tissues taken up from the surrounding media. This 'pre-contamination' of an organism may significantly influence the bioavailability of MP-sorbed pollutants, even resulting in decontamination or 'cleaning' as chemicals partition from the organism to the ingested plastic (Gouin et al., 2011; Herzke et al., 2016; Koelmans et al., 2013). As the current study employed 'clean' test organisms, it would be interesting to investigate the bioavailability of MP-sorbed pollutants to 'pre-contaminated' copepods in future studies.

4. Conclusions

The current work represents one of the first experimental studies to investigate the bioavailability MP-sorbed organic chemicals to aquatic organisms under co-exposure conditions with the same chemicals in the dissolved phase. Results confirmed the importance of polymer type, particle size and temperature as determining factors for the degree and mechanism of hydrophobic organic contaminant sorption from seawater to MP. Salinity is proposed as a parameter that may also influence this process. By including both ingestible and non-ingestible MP in exposure systems, it was possible to identify if ingestion of MP represents a viable exposure route for MP-sorbed PAHs. The acute toxicity and bioaccumulation studies indicate that MP-sorbed PAHs do not significantly accumulate nor contribute to toxicity in marine

copepods when co-exposed with the same chemicals in the dissolved phase. Furthermore, there were no observable differences in toxicity or bioaccumulation between ingestible and non-ingestible PAH-loaded MP. The relative importance of MP as an exposure route for PAHs to marine organisms must be considered in the context of other simultaneously occurring exposure routes such as passive uptake from seawater or ingestion through food.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.113844>.

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