Metals and marine microplastics: adsorption from the environment versus addition during manufacture, exemplified with lead

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Abstract

There are two means by which metals associate with microplastics in the aquatic environment. Firstly, they may be adsorbed to the plastic surface or hydrogenous-biogenic accumulations thereon, and secondly, they may be present in the polymeric matrix as functional additives or as reaction or recyclate residues. In this study, the relative significance of these associations is evaluated with respect to Pb in beached marine microplastics. Thus, adsorbed Pb was determined in < 5 mm, neutrally-coloured polyethylene pellets that contained no detectable Pb added during manufacture by digestion in dilute aqua regia, while the bioaccessibility of this association was evaluated using an avian physiologically-based extraction test (PBET). Here, up to about 0.1 $\mu g\ g^{-1}$ of Pb was adsorbed to the plastic and between about 60 and 70% of the metal was accessible. Lead present as additive or residue was determined by x-ray fluorescence analysis of a wider range of beached plastics (polyolefins and polyvinyl chloride), with a selection of positive samples grated to mm-dimensions and subjected to the PBET. Here, total Pb concentrations up to 40,000 $\mu g\ g^{-1}$ and bioaccessibilities up to 16% were observed, with bioaccessible concentrations exceeding equivalent values for adsorbed Pb by several orders of magnitude. Ingestive exposure to Pb, and potentially other toxic metals, is more important through the presence of additives in historical plastics and recyclate residues in contemporary plastics than from adsorption, and it is recommended that future studies focus more on the environmental impacts and fate of metals bound in this form.

Keywords: microplastics; metals; lead; additive; adsorption; bioaccessibility

1. **Introduction**

Among the many and varied environmental impacts of marine microplastics is their ability to transport contaminants and act as a means of contaminant exposure to wildlife (Li et al., 2016; Karbalaei et al., 2018). Empirical studies have demonstrated that neutral organic contaminants, like polycyclic aromatic hydrocarbons and polychlorinated biphenyls, are readily sorbed by the hydrophobic microplastic surface from the surrounding aqueous medium (Velzeboer et al., 2014; Liu et al., 2019). However, recent calculations and considerations have questioned the significance of this route for exposure and bioaccumulation compared with natural pathways (Beckingham and Ghosh, 2017; Lohmann, 2017), with suggestions that ingested microplastics could even act as chemical cleansers in the digestive environment (Koelmans et al., 2016). More important in this respect appears to be the presence of organic chemicals in the plastic matrix as reaction or recyclate

residues or as functional additives, like plasticisers, antioxidants and flame retardants (Hermabessiere et al., 2017; Gallo et al., 2018). Because many residues and additives are not chemically but physically bound to the plastic matrix they are able to migrate, with experiments using fluids mimicking digestive conditions of fish and seabirds demonstrating considerable mobilisation of bisphenol A and various phthalate esters and flame retardants and evidence of enhanced bioaccumulation or biological estrogenicity (Tanaka et al., 2015; Coffin et al., 2019).

Many metals have also been shown to be associated with marine microplastics. Thus, laboratory and field studies have revealed that metal ions are able to adsorb directly to the plastic surface or to surficial accumulations of hydrogenous and biogenic matter (Rochman et al., 2014; Brennecke et al., 2016), while non-destructive x-ray fluorescence techniques have demonstrated the presence of historical and recycled additives within the polymeric matrix (Nakashima et al., 2012; Turner, 2016). What is less clear, however, is the relative significance of the two associations of metal (hereafter termed “adsorbed” and “matrix”) with regard to transport, fate and potential environmental impacts, like mobility in seawater or dissolution in the digestive system of a plastic-ingesting animal (Wang et al., 2017; Munier and Bendell, 2018).

In the present study, the associations of Pb with beached marine microplastics through adsorption from the environment and incorporation as a functional additive are quantified by appropriate analytical techniques and their mobilities compared by subjecting samples to a simulated avian physiologically-based extraction test (PBET). Lead was selected for study as, among trace metals, it has a relatively high affinity for plastic surfaces and accumulations thereon (Ashton et al., 2010; Holmes et al., 2014), it was historically important as a pigment for colour and a heat stabiliser in plastics (Hansen et al., 2013), and is highly toxic to seabirds (Finkelstein et al., 2003) with evidence that Pb derived from ingested plastic is able to accumulate (Lavers and Bond, 2016).

The two associations of Pb (or any metal) in microplastics and their mechanisms of release are conceptualised in Figure 1 and serve to assist the definitions and discussion below. Thus, firstly Pb is physically held in the plastic as a simple compounded additive, $(Pb\text{-}X)_{matrix}$, which is able to diffuse through the water-saturated matrix itself or on dissociation (with the rate of the latter pH-dependent). Secondly, Pb is bound at adsorption sites on the plastic or on a more reactive and charged coating that has accumulated on the plastic surface during suspension, Pb_{ads}, and is able to undergo release through desorption should environmental conditions change. While two distinctive associations and mechanisms of release are illustrated, it is likely that both processes occur simultaneously or successively in seawater or in the avian digestive environment.

2. Methods

2.1. Sampling

Samples of marine plastics were collected by hand from the strandlines of south- or south west- (i.e. Atlantic-) facing sandy beaches within 10 km of Plymouth, south west England. Sampling focussed on black, white and off-white pellets (and mainly pre-production pellets; n ~ 300), whose primary and secondary diameters ranged from about 2 to 4 mm and which are known to accumulate trace metals but are largely free from metallic additives (Ashton et al., 2010), and hard (thermoplastic) objects and fragments (i.e. excluding rubbers and foams) of a range of colours (n ~ 180) whose largest dimension ranged from < 10 mm to about 250 mm.

In the laboratory, plastic pellets were washed through a 1-mm mesh with the aid of a Nylon brush and subsequently ultrasonicated for five min in distilled water to remove extraneous (non-adsorbed) material. After drying at 40 ^{o}C, pellets were categorised by colour and morphology/shape and the five most abundant categories (namely, white discs, black discs, smooth white cylinders, rough white cylinders and translucent-amber ovoids) were retained in a series of screw-capped plastic jars for further characterisation and experimental work. Plastic objects and fragments were washed through a 2-mm mesh before being dried and stored in a series of polyethylene boxes.

2.2. XRF analysis

Plastic objects and fragments and selected plastic pellets were analysed for a range of elements contained in the matrix as additives, of which the main focus was Pb, by field portable X-ray fluorescence (XRF) spectrometry using a battery-powered Niton XL3t 950 He GOLDD+ XRF configured in a Thermo-Fisher Scientific shielded accessory (Turner and Solman, 2016). Measurements were made over the flattest surface of each sample, and with thickness correction applied, for counting periods of 40 s at 50 kV and 40 μA and 20 s at 20 kV and 100 μA. For quality assurance purposes, two reference polyethylene discs (PE-071-N and T-18) were analysed after every 15 samples, with concentrations returned for all elements, including Pb, within 15% of reference values and whose precisions (as relative standard deviations) were better than 10%. Median measurement detections limits, based on three counting errors for samples returning non-detects, were about 5 μg g^{-1} for Pb.

2.3. Avian PBET and residual Pb extraction

Five plastic samples whose added Pb concentrations exceeded 1000 μg g^{-1}, plus a control where Pb was undetected by the XRF, were micronized to < 3 mm in diameter using a stainless steel scalpel and grater in order to increase exposure of the internal structure and attain a size comparable with

the pellets. Aliquots of ~100 mg of each sample were then weighed into individual 60-mL screw-capped polypropylene centrifuge tubes. Meanwhile, 20 random pellets from each of the five categories, plus 20 virgin plastic pellets sourced from a local injection moulding facility (Algram Ltd, Plympton) were added to a series of centrifuge tubes and the total mass in each case (~500 mg) recorded.

In order to determine the reactivity or bioaccessibility of Pb in the plastic pellets and micronized plastics, samples were subjected to a physiologically-based extraction test (PBET) based on the digestive conditions present in marine birds, and in particular in Procellariiforms (Turner, 2018). Thus, 1 L of digestive solution containing 1% pepsin (lyophilised powder from porcine gastric mucosa; Sigma-Aldrich) in 0.1 M NaCl solution whose pH had been adjusted to 2.5 by addition of 1 M HCl was prepared in a glass volumetric flask, and 40 mL were added to each centrifuge tube, including three tubes without solids serving as procedural controls. The contents were then capped and incubated at 40°C in a shaking water bath set at 100 rpm for about 160 h, with subsamples of 1 mL pipetted (pellets) or 0.45 μm-filtered (micronized plastics) into individual Sterilin tubes after different time intervals and diluted to 5 mL in 2% HNO_3. The combined pellets from each tube were subsequently retrieved, rinsed in Millipore Milli-Q water (MQW) and dried under laminar flow before being extracted in 2.5 mL of 20% aqua regia for 16 h at room temperature. Lead removed here is defined as being residually adsorbed, or adsorbed to the plastic surface or hydrogeneous and biogenic coatings thereon but resistant to the PBET. Extracts were diluted to 10 mL in volumetric flasks using MQW pending analysis.

PBET digests and aqua regia extracts were analysed in triplicate for ^{208}Pb by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-Series II (Thermo Elemental, Winsford UK) operated in an ISO 9001-accredited laboratory. The instrument was calibrated externally using five mixed standards and five blanks prepared in 2% HNO_3 and internally through the addition of 100 μg L^{-1} of ^{115}In and ^{193}Ir to all samples, standards and blanks. The limit of detection for ^{208}Pb in extracts and diluted digests, based on three standard deviations arising from blank measurements, was about 0.02 μg L^{-1}, and precision, based on relative standard deviations of triplicate measurements, was usually better than 10%.

2.4. FTIR analysis

The polymeric composition of the samples used in the PBETs were determined by Fourier transform infra-red (FTIR) spectroscopy using a Bruker ALPHA Platinum attenuated total reflection QuickSnap A220/D-01 spectrometer. Thus, a selection of whole pellets (n = 30) and gratings of each micronized plastic object or fragment were clamped down on to the ATR diamond crystal before measurements,

consisting of 16 scans in the range 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1}, were activated via Bruker OPUS spectroscopic software. Polymer identification involved a comparison of sample transmittance spectra with libraries of reference spectra.

3. Results and Discussion

3.1. Sample characteristics

The characteristics of the six (combined) plastic pellet samples and six micronized plastics (selected from 180 samples retrieved) are shown in Table 1. All pellets analysed from each colour-morphology category were of polyethylene construction while gratings of the micronized plastics were more varied in polymeric makeup, and included two samples of polyvinyl chloride (PVC). No extractable Pb was detected by ICP-MS after acid extraction of the virgin (control) pellets, while in the beached pellets total adsorbed Pb concentrations, $[Pb_{ads}]$, are on the order of 0.1 $\mu g\ g^{-1}$ and represent metal acquired from the environment, calculated from the amount of Pb released at the end of the PBET on a weight-normalised basis plus that extracted by aqua regia once pellets had been recovered. (Where pellets were analysed by XRF, Pb was not detected and was below 10 $\mu g\ g^{-1}$.) Regarding micronized plastics, Pb was not detected by XRF in the sample serving as a control but in the remaining samples total concentrations present in the polymer as a functional additive or reaction or recyclate residue, $[Pb_{matrix}]$, range from a few thousand $\mu g\ g^{-1}$ to about 40000 $\mu g\ g^{-1}$. Specifically, co-association of Pb with Cr (also determined by XRF) in samples of polyethylene and polypropylene and in a mass ratio of about 4:1 suggests the presence of lead chromate particulates as a pigment for colour while Pb in samples of PVC is likely to be present in heat stabilising compounds (Hansen et al., 2013).

3.2. PBET results

Figure 2 shows the time-dependent concentration of Pb, normalised to sample weight (since the precise mass of plastic used in the experiment varied), that was released by desorption from plastic pellets during the avian PBET ($[Pb]_{des}$); note that Pb mobilisation was not detected from the virgin (control) pellets. Here, release represents desorption of Pb that is adsorbed to the plastic surface or to hydrogenous and biogenic accumulations on the pellets (Figure 1) and is largely dictated by the stability constants and site densities defining surface adsorption and the rate of diffusion in the aqueous medium. There is a general increase in Pb release over the time-course of the experiment and evidence of equilibrium attained for sample 3 but more complex distributions and secondary maxima in other cases, with no data conforming to a simple Fickian diffusion-based model (i.e. a

proportionality with the square root of time). Irregularities may reflect slight changes in experimental conditions over the time course of the experiment (e.g. particle mass to medium volume ratio) or the heterogeneity amongst the samples of a given classification and redistribution of Pb amongst plastic pellets with the progression of time. By the end of the time course, and as shown in Table 2, between 61 and 78% of total Pb adsorbed to the pellets is mobilised or "bioaccessible" (but not necessarily bioavailable), where bioaccessibility, BA, is computed as follows:

$$BA, \% = [Pb]^{e}_{des} * 100\%/([Pb]^{e}_{des} + [Pb]^{e}_{res})$$

Here, $[Pb]^{e}_{des}$ is the concentration of adsorbed Pb released at the end of the PBET, but which is not necessarily equal to the maximum or equilibrium concentration, $[Pb]^{e}_{res}$ is the concentration of residually adsorbed Pb that is not mobilised at the end of the PBET but is extracted in aqua regia, and $[Pb]^{e}_{des} + [Pb]^{e}_{res}$ is the total concentration of Pb acquired from the environment.

Figure 3 shows the time-dependent concentrations of weight-normalised Pb released by diffusion from the micronized plastics subject to the avian PBET ($[Pb]_{dif}$). In this case, release encompasses additives and reaction residues that are sufficiently small to diffuse through the matrix, as well as Pb ions and small complexes that have dissociated from additives and residues under the acidic conditions of the PBET (Figure 1; Town et al., 2018), and concentrations are orders of magnitude higher than those shown in Figure 2. Significantly, since (i) Pb release was not detected from the control sample prepared from plastic with no XRF-detectable Pb, and (ii) micronization exposes a greater proportion of the internal structure of the plastic relative to its original surface, the magnitude of desorption of the metal from the surface that had been acquired from the environment appears to be of minor importance here. The time courses of Pb release from the matrix are less complex than those defining release of Pb adsorbed to the plastic pellets but, as above, data did not conform to a simple diffusion model; specifically, there is evidence for secondary maxima in some cases (samples 1 and 2) suggesting that adsorption of mobilised Pb is possible at the micronized plastic surface or that there is some physical or chemical interaction between species diffusing through the plastic matrix. The concentrations of Pb released at the end of the time course, $[Pb]^{e}_{dif}$, are shown in Table 2, along with measures of bioaccessible Pb and where BA is now computed as follows:

$$BA, \% = [Pb]^{e}_{dif} * 100\%/[Pb]_{matrix}$$

BA ranges from < 1% in two polyolefin samples to about 16% for a sample of PVC where, presumably, organic stabilizers with higher diffusion coefficients than inorganic additives are present (Mercea et al., 2018).

3.3. Adsorbed versus added Pb

Overall, Pb bioaccessibility or reactivity is considerably greater when the metal is held at adsorption and exchange sites on the plastic surface or hydrogenous and biogenic coatings thereon than when bound as an additive or residue within the polymeric matrix. This is expected as diffusion coefficients defining Pb species traversing the plastic particle are orders of magnitude greater than those defining diffusion in the aqueous medium (Town et al., 2018). What is significant, however, and more than offsets differences in percentage bioaccessibility, is the difference in absolute concentrations of Pb released between the two associations that are many orders of magnitude. For plastics with no functionally added Pb, the quantity of adsorbed Pb largely depends on the surface area and length of time suspended in the water column (Rochman et al., 2014), and for microplastic pellets of the size and shape considered here, 0.05 $\mu g\ g^{-1}$ can be considered a representative bioaccessible concentration of adsorbed metal based on the PBET results (Figure 2). For micronized plastics of comparable dimensions containing leaded additives, bioaccessible concentrations range from about 20 to 1200 $\mu g\ g^{-1}$ in the PBET (Figure 3), or 10^2 to 10^4 times higher than bioaccessible Pb concentrations that are adsorbed.

3.4. Wider implications

Clearly, not all plastics contain leaded additives, but using the wider observations of samples made by XRF as part of the study may afford some indication of the quantity of added Pb that is bioaccessible more generally. Thus, despite Pb being restricted or phased out in consumer plastics, 28 beached samples out of 180 analysed by XRF were positive for Pb, presumably because of the presence of legacy plastics and the dilution of Pb through the recycling of older plastics (Nakashima et al., 2016; Rambabu et al., 2018), with a median concentration of $[Pb_{matrix}]$ of about 100 $\mu g\ g^{-1}$. Assuming that there is a similar abundance and concentration distribution of Pb among the (non-pellet) microplastic population that is amenable to ingestion and that 3% is a representative (median) bioaccessibility of added Pb (Table 2), an average concentration of bioaccessible Pb in microplastics would be about 0.5 $\mu g\ g^{-1}$, or an order of magnitude greater than adsorbed Pb that is bioaccessible on a similar size of microplastics. It would appear, therefore, that potential impacts on wildlife from exposure to Pb through ingestion is greater overall for metals present as additives or residues from manufacturing. Moreover, based on general reaction considerations and for a given plastic, risk is predicted to increase with decreasing particle size, gut acidity and length of digestion.

Although the focus of the present study has been on Pb, data garnered simultaneously or independently on Cd (albeit more limited owing to constraints on detection by both ICP-MS and XRF) reveal similar findings. Thus, compared with Pb, there were fewer Cd-positive plastics among the 180 beached samples analysed by XRF (n = 9) but a higher median concentration ($[Cd_{matrix}]$ ~ 900 μg g^{-1}), and greater bioaccessible concentrations as additive metal ($[Cd]^{e}_{dif}$ up to 30 μg g^{-1}) relative to bioaccessible concentrations when adsorbed to the surface of plastic pellets ($[Cd]_{des}$ < 0.001 μg g^{-1} throughout the time courses of the PBET).

4. Conclusions

In summary, the transport, exposure and accessibility of Pb (and other toxic metals) in the marine environment appears to be more important through the historical and contemporary disposal or recycling of legacy plastics than the gradual accumulation of metal ions on to plastic surfaces suspended in the water column. With the majority of studies to date addressing adsorbed metals (Ashton et al., 2010; Holmes et al., 2014; Rochman et al., 2014; Brennecke et al., 2016; Dobaradaran et al., 2018; Maršić-Lučić et al., 2018; Vedolin et al., 2018; Rivera-Hernandez et al., 2019) it is recommended that future research focus on the environmental and ecological impacts of metal additives in microplastics and the identification and characterisation of the sources and fates of legacy plastics.

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Table 1: Characteristics and total Pb content of the plastic samples used in the study. Note that total Pb was derived from extraction for the pellets ($[Pb]_{ads}$) and from XRF analysis for the micronized plastics ($[Pb]_{matrix}$).

sample		colour	polymer	$[Pb]_{ads}$ or $[Pb]_{matrix}$, $\mu g\ g^{-1}$
pellets	1	white	polyethylene	0.056
	2	black	polyethylene	0.060
	3	white	polyethylene	0.095
	4	white	polyethylene	0.037
	5	translucent-amber	polyethylene	0.062
	6 (control)	white	polyethylene (virgin)	<0.004
micronized plastics	1	red	polypropylene	4260
	2	yellow	polyethylene	3860
	3	green	polypropylene	6130
	4	blue	polyvinyl chloride	4090
	5	black	polyvinyl chloride	38200
	6	red	polypropylene	<8.6

Table 2: Concentration of Pb released from pellets ($[Pb]^e_{des}$) and micronized plastics ($[Pb]^e_{dif}$) at the end of each time course along with bioaccessibilities relative to total concentrations as reported in Table 1.

sample		$[Pb]^e_{des}$ or $[Pb]^e_{dif}$, $\mu g\ g^{-1}$	BA, %
pellets	1	0.043	77.7
	2	0.037	61.2
	3	0.066	70.2
	4	0.026	69.9
	5	0.039	62.9
micronized plastics	1	33.5	0.79
	2	19.9	0.52
	3	333	5.43
	4	657	16.1
	5	1230	3.22

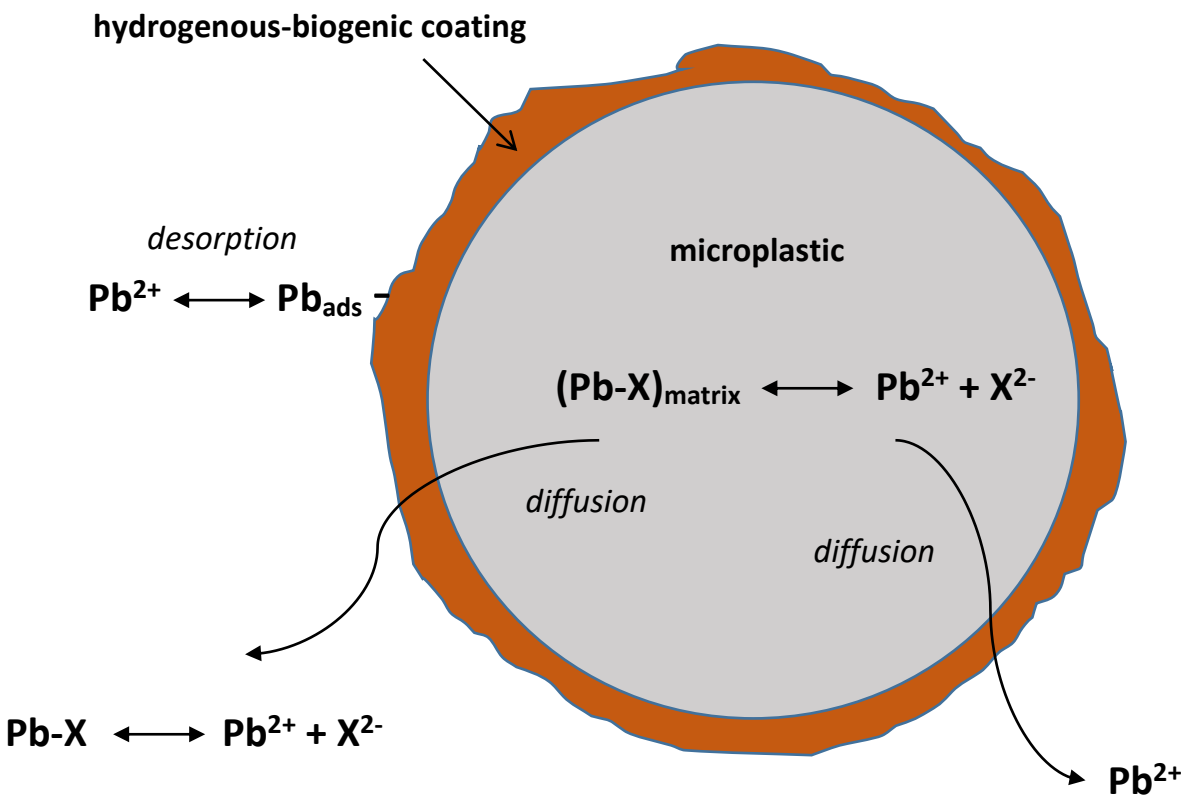
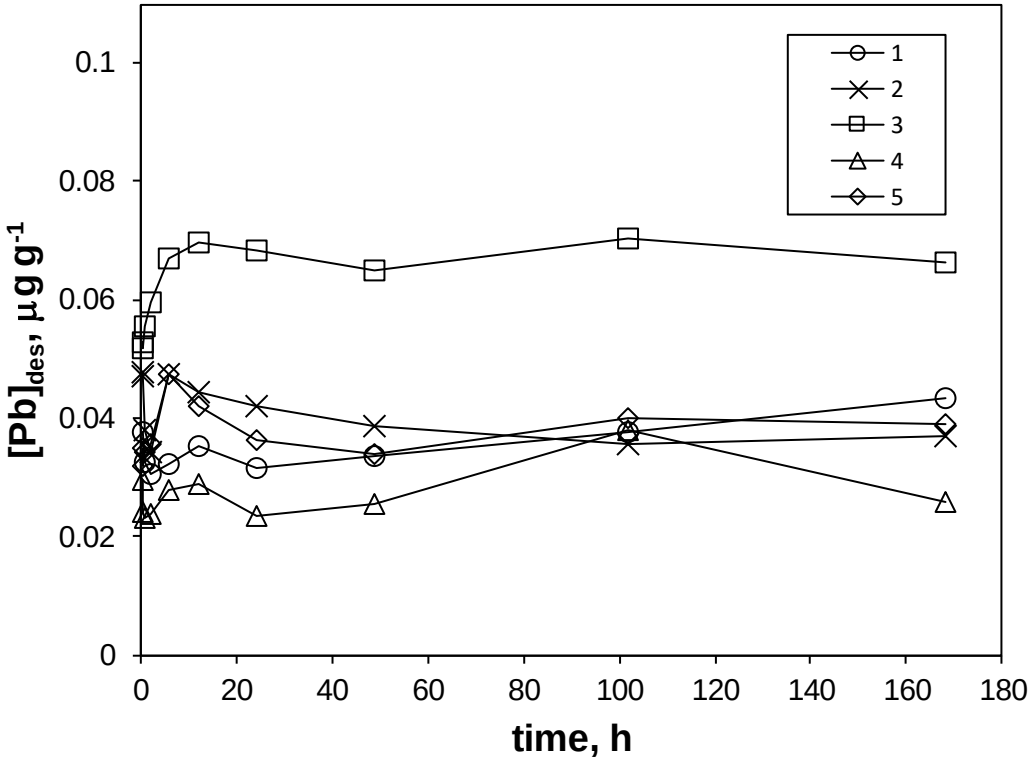


Figure 1: Associations of Pb (and other metals) with microplastics in the marine environment and mechanisms by which they are released. Note that Pb-X represents an additive or residue in the polymeric matrix.



375 Figure 2: Concentration of Pb adsorbed to five pellet types (defined in Table 1) that is released by an
376 avian PBET, $[Pb]_{des}$, as a function of time.

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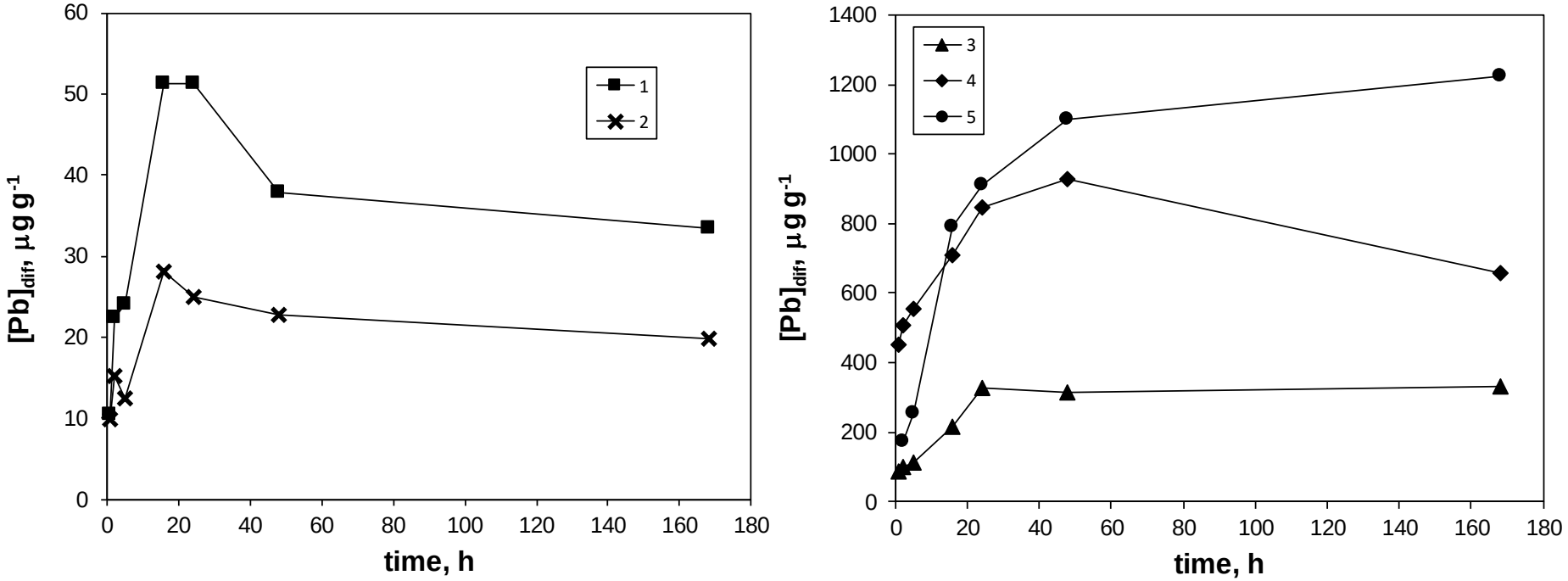

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379 Figure 3: Concentration of Pb as an additive in five micronized plastics (defined in Table 1) that is released by an avian PBET, $[Pb]_{dif}$, as a function of time.