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

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15

16 **Abstract**

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

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

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36

37 **1. Introduction**

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

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

54 Many metals have also been shown to be associated with marine microplastics. Thus, laboratory and
55 field studies have revealed that metal ions are able to adsorb directly to the plastic surface or to
56 surficial accumulations of hydrogenous and biogenic matter (Rochman et al., 2014; Brennecke et al.,
57 2016), while non-destructive x-ray fluorescence techniques have demonstrated the presence of
58 historical and recycled additives within the polymeric matrix (Nakashima et al., 2012; Turner, 2016).
59 What is less clear, however, is the relative significance of the two associations of metal (hereafter
60 termed “adsorbed” and “matrix”) with regard to transport, fate and potential environmental
61 impacts, like mobility in seawater or dissolution in the digestive system of a plastic-ingesting animal
62 (Wang et al., 2017; Munier and Bendell, 2018).

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

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

80

81 **2. Methods**

82 *2.1. Sampling*

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

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

97 *2.2. XRF analysis*

98 Plastic objects and fragments and selected plastic pellets were analysed for a range of elements
99 contained in the matrix as additives, of which the main focus was Pb, by field portable X-ray
100 fluorescence (XRF) spectrometry using a battery-powered Niton XL3t 950 He GOLDD+ XRF
101 configured in a Thermo-Fisher Scientific shielded accessory (Turner and Solman, 2016).

102 Measurements were made over the flattest surface of each sample, and with thickness correction
103 applied, for counting periods of 40 s at 50 kV and 40 μ A and 20 s at 20 kV and 100 μ A. For quality
104 assurance purposes, two reference polyethylene discs (PE-071-N and T-18) were analysed after
105 every 15 samples, with concentrations returned for all elements, including Pb, within 15% of
106 reference values and whose precisions (as relative standard deviations) were better than 10%.
107 Median measurement detection limits, based on three counting errors for samples returning non-
108 detects, were about 5 μ g g^{-1} for Pb.

109 *2.3. Avian PBET and residual Pb extraction*

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

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

118 In order to determine the reactivity or bioaccessibility of Pb in the plastic pellets and micronized
119 plastics, samples were subjected to a physiologically-based extraction test (PBET) based on the
120 digestive conditions present in marine birds, and in particular in Procellariiforms (Turner, 2018).
121 Thus, 1 L of digestive solution containing 1% pepsin (lyophilised powder from porcine gastric
122 mucosa; Sigma-Aldrich) in 0.1 M NaCl solution whose pH had been adjusted to 2.5 by addition of 1 M
123 HCl was prepared in a glass volumetric flask, and 40 mL were added to each centrifuge tube,
124 including three tubes without solids serving as procedural controls. The contents were then capped
125 and incubated at 40°C in a shaking water bath set at 100 rpm for about 160 h, with subsamples of 1
126 mL pipetted (pellets) or 0.45 µm-filtered (micronized plastics) into individual Sterilin tubes after
127 different time intervals and diluted to 5 mL in 2% HNO₃. The combined pellets from each tube were
128 subsequently retrieved, rinsed in Millipore Milli-Q water (MQW) and dried under laminar flow
129 before being extracted in 2.5 mL of 20% aqua regia for 16 h at room temperature. Lead removed
130 here is defined as being residually adsorbed, or adsorbed to the plastic surface or hydrogenous and
131 biogenic coatings thereon but resistant to the PBET. Extracts were diluted to 10 mL in volumetric
132 flasks using MQW pending analysis.

133 PBET digests and aqua regia extracts were analysed in triplicate for ²⁰⁸Pb by inductively coupled
134 plasma-mass spectrometry (ICP-MS) using a Thermo X-Series II (Thermo Elemental, Winsford UK)
135 operated in an ISO 9001-accredited laboratory. The instrument was calibrated externally using five
136 mixed standards and five blanks prepared in 2% HNO₃ and internally through the addition of 100 µg
137 L⁻¹ of ¹¹⁵In and ¹⁹³Ir to all samples, standards and blanks. The limit of detection for ²⁰⁸Pb in extracts
138 and diluted digests, based on three standard deviations arising from blank measurements, was
139 about 0.02 µg L⁻¹, and precision, based on relative standard deviations of triplicate measurements,
140 was usually better than 10%.

141 2.4. FTIR analysis

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

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

149

150 **3. Results and Discussion**

151 *3.1. Sample characteristics*

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

168 *3.2. PBET results*

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

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

$$184 \text{ BA, \%} = [\text{Pb}]_{\text{des}}^{\text{e}} * 100\% / ([\text{Pb}]_{\text{des}}^{\text{e}} + [\text{Pb}]_{\text{res}}^{\text{e}})$$

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

189

190 Figure 3 shows the time-dependent concentrations of weight-normalised Pb released by diffusion
191 from the micronized plastics subject to the avian PBET ($[\text{Pb}]_{\text{dif}}$). In this case, release encompasses
192 additives and reaction residues that are sufficiently small to diffuse through the matrix, as well as Pb
193 ions and small complexes that have dissociated from additives and residues under the acidic
194 conditions of the PBET (Figure 1; Town et al., 2018), and concentrations are orders of magnitude
195 higher than those shown in Figure 2. Significantly, since (i) Pb release was not detected from the
196 control sample prepared from plastic with no XRF-detectable Pb, and (ii) micronization exposes a
197 greater proportion of the internal structure of the plastic relative to its original surface, the
198 magnitude of desorption of the metal from the surface that had been acquired from the
199 environment appears to be of minor importance here. The time courses of Pb release from the
200 matrix are less complex than those defining release of Pb adsorbed to the plastic pellets but, as
201 above, data did not conform to a simple diffusion model; specifically, there is evidence for secondary
202 maxima in some cases (samples 1 and 2) suggesting that adsorption of mobilised Pb is possible at the
203 micronized plastic surface or that there is some physical or chemical interaction between species
204 diffusing through the plastic matrix. The concentrations of Pb released at the end of the time course,
205 $[\text{Pb}]_{\text{dif}}^{\text{e}}$, are shown in Table 2, along with measures of bioaccessible Pb and where BA is now
206 computed as follows:

$$207 \text{ BA, \%} = [\text{Pb}]_{\text{dif}}^{\text{e}} * 100\% / [\text{Pb}]_{\text{matrix}}$$

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

211 *3.3. Adsorbed versus added Pb*

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

226 *3.4. Wider implications*

227 Clearly, not all plastics contain leaded additives, but using the wider observations of samples made
228 by XRF as part of the study may afford some indication of the quantity of added Pb that is
229 bioaccessible more generally. Thus, despite Pb being restricted or phased out in consumer plastics,
230 28 beached samples out of 180 analysed by XRF were positive for Pb, presumably because of the
231 presence of legacy plastics and the dilution of Pb through the recycling of older plastics (Nakashima
232 et al., 2016; Rambabu et al., 2018), with a median concentration of $[\text{Pb}_{\text{matrix}}]$ of about $100 \mu\text{g g}^{-1}$.
233 Assuming that there is a similar abundance and concentration distribution of Pb among the (non-
234 pellet) microplastic population that is amenable to ingestion and that 3% is a representative
235 (median) bioaccessibility of added Pb (Table 2), an average concentration of bioaccessible Pb in
236 microplastics would be about $0.5 \mu\text{g g}^{-1}$, or an order of magnitude greater than adsorbed Pb that is
237 bioaccessible on a similar size of microplastics. It would appear, therefore, that potential impacts on
238 wildlife from exposure to Pb through ingestion is greater overall for metals present as additives or
239 residues from manufacturing. Moreover, based on general reaction considerations and for a given
240 plastic, risk is predicted to increase with decreasing particle size, gut acidity and length of digestion.

241 Although the focus of the present study has been on Pb, data garnered simultaneously or
242 independently on Cd (albeit more limited owing to constraints on detection by both ICP-MS and XRF)
243 reveal similar findings. Thus, compared with Pb, there were fewer Cd-positive plastics among the
244 180 beached samples analysed by XRF ($n = 9$) but a higher median concentration ($[Cd]_{\text{matrix}} \sim 900 \mu\text{g}$
245 g^{-1}), and greater bioaccessible concentrations as additive metal ($[Cd]_{\text{dif}}^{\text{e}}$ up to $30 \mu\text{g g}^{-1}$) relative to
246 bioaccessible concentrations when adsorbed to the surface of plastic pellets ($[Cd]_{\text{des}} < 0.001 \mu\text{g g}^{-1}$
247 throughout the time courses of the PBET).

248 **4. Conclusions**

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

258

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262

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356 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 ($[Pb]_{ads}$)
 357 and from XRF analysis for the micronized plastics ($[Pb]_{matrix}$).

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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

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

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sample		$[Pb]_{des}^e$ or $[Pb]_{dif}^e, \mu\text{g g}^{-1}$	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

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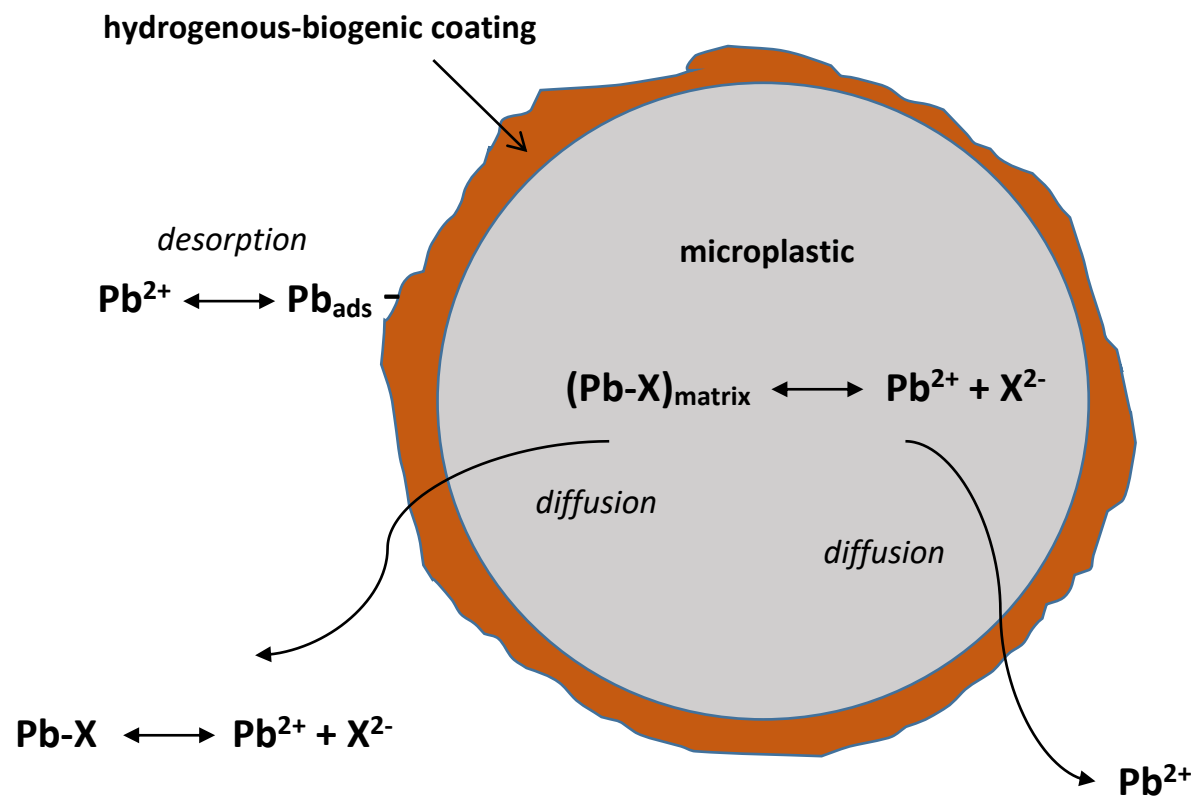
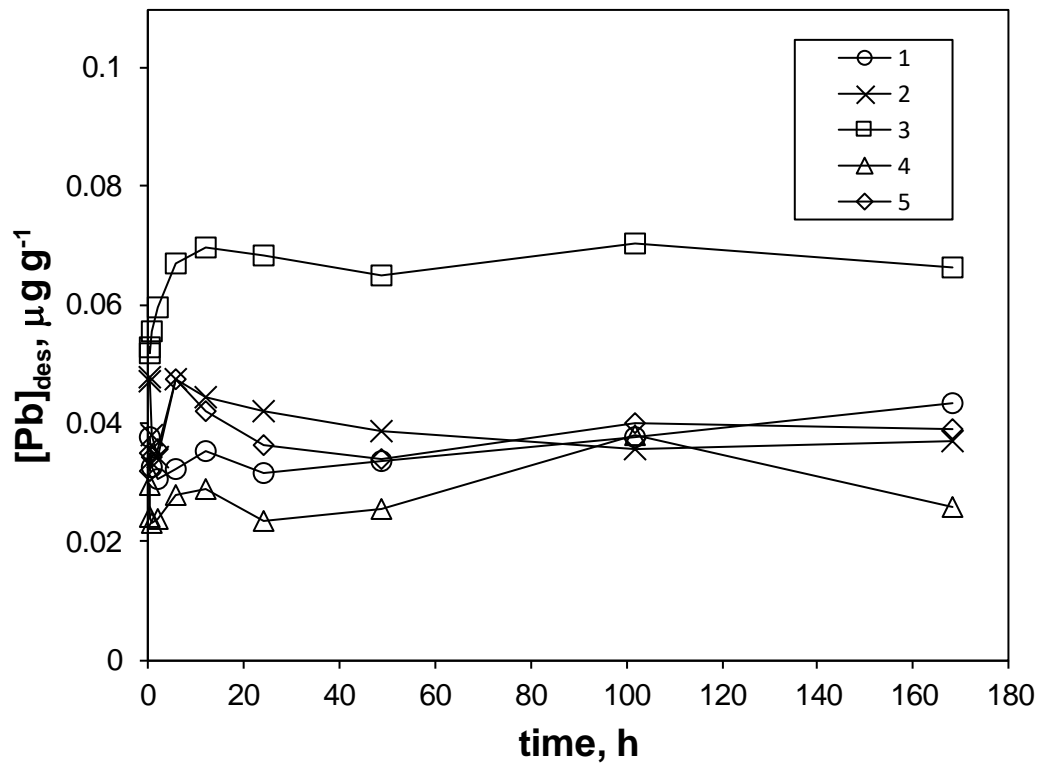
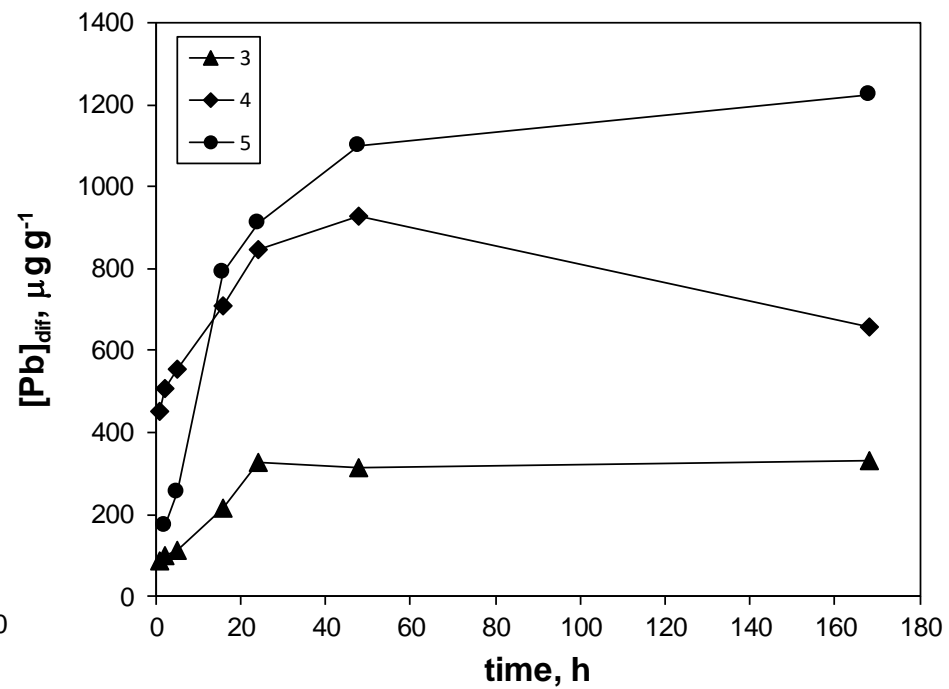
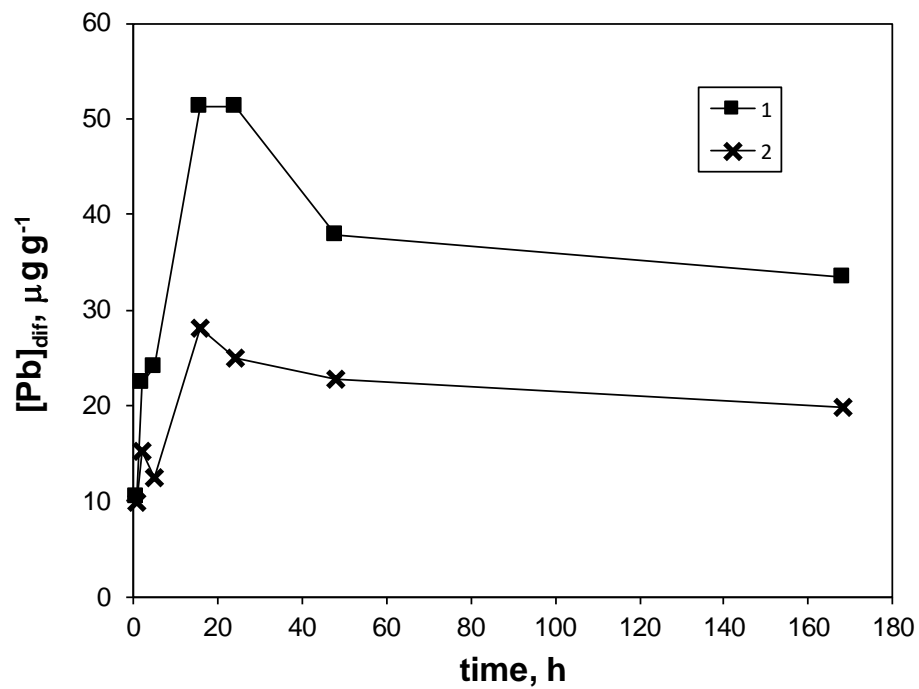


Figure 1: Associations of Pb (and other metals) with microplastics in the marine environment and mechanisms by which they are released. Note that Pb-X represents an additive or residue in the polymeric matrix.



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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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.