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# Mobilisation of antimony from microplastics added to coastal sediment

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3	Mobilisation of antimony from microplastics added to
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#### 29 Abstract

30 Antimony (Sb) widely occurs in plastics as a pigment and reaction residue and 31 through the use and recycling of electronic material enriched in Sb as a flame 32 retardant synergist. In this study, clean estuarine sediment has been contaminated by 33 different microplastics prepared from pre-characterised samples of different types of 34 plastic (including a rubber) containing a range of Sb concentrations (256 to 47,600 µg 35 g<sup>-1</sup>). Sediment-plastic mixtures in a mass ratio of 100:1 were subject to 6-hour extractions in seawater and in seawater solutions of a protein (bovine serum albumin; 36 BSA) and a surfactant (taurocholic acid; TA) that mimic the digestive conditions of 37 38 coastal deposit-feeding invertebrates. Most time-courses for Sb mobilisation could be 39 defined by a second-order diffusion equation, with rate constants ranging from 44.6 to  $0.0216 (\mu g g^{-1})^{-1} min^{-1}$ . Bioaccessibilities, defined as maximum extractable 40 concentrations throughout each time course relative to total Sb content, ranged from < 41 42 0.01 % for a polycarbonate impregnated with Sb as a synergist exposed to all 43 solutions, to > 1 % for acrylonitrile butadiene styrene containing a Sb-based colour 44 pigment exposed to solutions of BSA and TA and recycled industrial polyethylene 45 exposed to BSA solution. The potential for Sb to bioaccumulate or elicit a toxic effect 46 is unknown but it is predicted that communities of deposit-feeders could mobilise 47 significant quantities of Sb in sediment contaminated by microplastics through 48 bioturbation and digestion. 49 50 Keywords: antimony; plastics; sediment; mobilisation; bioaccessibility 51 52 Capsule: Antimony is mobilised from plastics added to sediment by seawater and

- 53 solutions of a protein and a surfactant via a diffusion model
- 54

#### 55 **1. Introduction**

56 Antimony and many of its compounds display both acute and chronic toxicity to a 57 range of organisms (Tschan et al., 2010; Paoli et al., 2013; Yang, 2014; Yang et al., 58 2018). In humans, exposure to Sb has been related to respiratory, cardiovascular and 59 gastrointestinal symptoms and antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>) is classified as possibly 60 carcinogenic (Sundar and Chakravarty, 2010; Tamás, 2016). Antimony is also a 61 technology-critical element in that is has economic importance to emerging 62 technologies but is subject to a high supply risk (Nuss and Blengini, 2018). Current 63 applications of Sb include pigments for colour or colour protection, decolouring and 64 refining agents in glass, catalysts for polycondensation, synergists for flame 65 retardants, and alloys in batteries in ammunition, antifriction bearings, cable sheaths

- 66 and roofing (Yellishetty et al., 2017).
- 67

68 Antimony is particularly pervasive in synthetic polymers (including textiles, plastics 69 and rubbers) (Filella et al., 2020). Here it is used in various pigments, but its principal 70 application that results in the highest concentrations is as a synergist for halogenated 71 flame retardants (as Sb<sub>2</sub>O<sub>3</sub>, the pentoxide, Sb<sub>2</sub>O<sub>5</sub>, or sodium antimonite, Na<sub>3</sub>SbO<sub>4</sub>; 72 Papazoglou, 2004). The trioxide is also used as a catalyst for the production of 73 polyethylene terephthalate (PET), including fibrous polyester, and residues of the 74 compound and other reaction products (including organic-complexes of Sb) remain in 75 the material after manufacture (Welle and Franz, 2010). Antimony is more widely 76 dispersed amongst consumer and commercial plastics through the recycling of end-of-77 life products. In this respect a particular problem arises when flame-retarded 78 electronic plastics are recycled into consumer goods in which halogenated compounds 79 and Sb are neither expected nor desired (Turner and Filella, 2017). 80

Concerns over the presence and possible migration of Sb in consumer products, and in particular plastics, has resulted in guidelines or regulations for the metalloid. In PET food-contact and storage items, where Sb concentrations are typically a few hundred µg g<sup>-1</sup> (Westerhoff et al., 2008), migration into liquids is effectively limited to 5 µg L<sup>-</sup> <sup>1</sup> according to EC Directive 2003/40 on natural mineral waters (European Commission, 2003). Migration into foods is limited to 40 µg per kg of food according to EU Regulation 10/2011 European Commission, 2011) and based on the tolerable

88 daily intake of 6 µg kg<sup>-1</sup> body weight (World Health Organization, 2003). In plastic, 89 rubber or painted toys, migration of Sb is limited by the amended EC Toy Safety Directive to between 11.3 and 560  $\mu$ g g<sup>-1</sup> depending on the characteristics of the 90 91 material (based on pliability, size, thickness, brittleness) (European Parliament and 92 Council of the EU, 2009). Despite concentrations of Sb in flame-retarded electronic 93 plastics that can exceed several percent by weight (Papazoglou, 2004), the metalloid 94 is currently not included in the list of substances defined by the original or recast 95 Restriction on Hazardous Substances (RoHS) Directives (European Parliament and 96 Council, 2003; 2011). However, the EU regards Sb as a "heavy metal" and defines 97 waste as "ecotoxic" if heavy metal concentrations exceed certain thresholds 98 (European Commission, 2018).

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99

100 As a result of its widespread use in and contamination of polymers, Sb is predicted to 101 be commonly encountered in marine litter. X-ray fluorescence (XRF) analysis of 102 consumer, maritime and industrial plastics collected by hand from the strandlines of 103 various beaches in south west England has revealed the presence of Sb in up to 50% 104 of a wide variety of samples of relatively low density (but mainly polyethylene and 105 polypropylene) (Shaw and Turner, 2019; Turner et al., 2019). However, given that 106 microplastics buried below the sediment surface, including microfibers, appear to 107 contain a higher proportion of denser materials like PET (Yu et al., 2018; Zheng et al., 108 2019), the overall abundance of Sb in marine litter may be significantly greater.

109

110 In coastal regions where the substrate is contaminated by synthetic polymers 111 (hereafter referred to as plastics), benthic and infaunal animals may be exposed to 112 elevated levels of Sb. Of particular significance in this respect are deposit-feeding 113 invertebrates that non-selectively process large quantities of material through 114 burrowing, ingestion and egestion. Exposure could increase should quantities of Sb be 115 mobilised from microplastics through bioturbating activities, and in particular during 116 digestion. Accordingly, the present study examines the potential for Sb to be released 117 from plastics via coastal deposit-feeders by incubating preparations of clean sediment 118 and a range of microplastics in fluids that simulate the invertebrate digestive 119 environment. Specifically, we use seawater solutions of the protein, bovine serum albumin (BSA; molecular mass =  $66,400 \text{ g mol}^{-1}$ ), to mimic the complexing capacity 120

- 121 of amino acids (Chen and Mayer, 1998), and the vertebrate bile acid surfactant,
- 122 taurocholic acid (TA;  $C_{26}H_{44}NO_7SNa$ ; molecular mass = 537.7 g mol<sup>-1</sup>), as a
- 123 surrogate for anionic surfactancy (Voparil and Mayer, 2004).
- 124

## 125 **2. Materials and methods**

- 126 2.1. Sourcing and characterisation of plastics
- About 50 plastics items sourced from archived litter samples and consumer products
  were analysed for total Sb and polymer type according to protocols outlined
  elsewhere (Turner et al., 2019). Briefly, Sb was determined on three regions of each
  sample by portable XRF spectrometry using a battery-operated Niton XL3t 950 He
  GOLDD+ portable XRF. The instrument was operated for a period of 60 seconds in
- 132 a "plastics" mode with thickness correction and performance was checked regularly
- by analysing a polyethylene reference disk reference (Niton PN 180-619) that
- 134 contained Sb at a concentration of  $96 \pm 10 \ \mu g \ g^{-1}$ . Polymer identification on small (<
- 135 5 mg) sample offcuts was performed by attenuated total reflectance Fourier-
- 136 transform-infrared (ATR-FTIR) spectrometry using a Bruker Vertex 70.
- 137

138 Based on the analyses above, seven plastics of varying Sb content and polymeric

- 139 composition, including one sample of rubber, were selected for use in the extraction
- 140 experiments (Table 1). The sample of PET likely contains Sb as catalytic residue
- 141 arising from the manufacture of the material, while acrylonitrile butadiene styrene
- 142 (ABS) contains Sb as a component of the pigment titanium yellow (CI Pigment
- 143 Yellow 53; NiO·Sb<sub>2</sub>O<sub>3</sub>·20TiO<sub>2</sub>, and confirmed by the presence of Ni and Ti in the
- 144 XRF spectrum). Polystyrene (PS), polycarbonate (PC) and polyethylene (PE) contain
- 145 Sb as a flame retardant synergist in the presence of brominated compounds, and
- 146 polyvinyl chloride (PVC) and rubber (R) appear to contain Sb as a synergist in the
- 147 presence of chlorinated compounds. Using a stainless steel grater, at least 1 g of each
- 148 sample was formulated into microplastic particles (< 1 mm in at least two
- 149 dimensions) that were stored in individual polyethylene specimen bags.
- 150
- 151 2.2. Sediment sampling and processing
- 152 Approximately 1.5 L of surficial, oxic sandy-silty sediment was collected using a
- 153 plastic trowel from the lower, intertidal reaches of a protected estuary that is

154 relatively unpolluted with regard to both metals and plastics (Erme, south west England; 50.3111, -3.9457). On site, the sample was sieved though a 1 mm Nylon 155 156 mesh into a plastic bucket. In the laboratory, subsamples of about 250 g were 157 transferred to a series of clear zip-locked polyethylene bags and stored frozen until 158 required. The chemical characteristics of the fractionated sediment sample, 159 determined on freeze-dried aliquots, are given in Table 2. Here, metal concentrations 160 were determined by inductively coupled plasma-optical emission spectrometry (ICP-161 OES) and Sb concentration by inductively coupled plasma-mass spectrometry (ICP-162 MS; see below) according to established protocols (Turner, 2019) and following 163 digestion of triplicate 250 mg aliquots in aqua regia heated to 80 °C for 2 h. Loss on 164 ignition (LOI) as a proxy for organic matter content was determined by mass loss on 165 ignition at 500°C for 8 h.

166

## 167 *2.3. Experimental*

168 One-litre solutions that mimic the chemical conditions (amino acid composition and 169 surfactancy) encountered in the digestive environment of temperate, coastal deposit-170 feeding invertebrates were prepared in 0.45  $\mu$ m-filtered English Channel seawater (*S* 171 = 33; pH 7.8) in a series of borosilicate bottles. Specifically, these consisted of 4 g L<sup>-1</sup> 172 <sup>1</sup> of the protein, BSA (> 96% fraction V; Sigma Aldrich), 4 g L<sup>-1</sup> of TA (taurocholic

- acid sodium salt hydrate, 97%+; VWR International), and 4 g  $L^{-1}$  of BSA plus 4 g  $L^{-1}$
- 174

TA.

175

176 Experiments were undertaken according to protocols outlined in Jones and Turner

- 177 (2010) and Martin and Turner (2019). Thus, bags of sediment were defrosted as
- 178 required and aliquots of 25 g (or 18.26 g on a dry weight basis) were weighed into a
- 179 series of eight screw-capped 200 mL polyethylene bottles. To seven of the bottles,
- 180 250 mg of the different microplastics were added, with the eighth bottle serving as a
- 181 plastic-free control. The concentration of plastic in the sediment on a dry weight
- 182 basis was, therefore, about 14 g kg<sup>-1</sup>. This is higher than microplastic abundance
- 183 reported in contaminated sediments (up to about 130 mg kg<sup>-1</sup>; He et al., 2020) but
- 184 was selected in order to allow the ready detection of mobilised Sb.

185

186 One hundred ml of seawater (SW) was pipetted into each bottle before the contents 187 were agitated on a Stuart SSL1 benchtop orbital shaker set at 150 rpm at room 188 temperature and in the dark. After 15 min, 30 min, 1 h, 2 h, 4 h, 5 h and 6 h, 189 subsamples of 5 mL were pipetted into 15 mL polypropylene centrifuge tubes and 190 centrifuged at 3000 rpm for 10 min before 2-mL supernatants were transferred to 191 Sterilin tubes, diluted to 10 ml with 2% HNO<sub>3</sub> and stored at 4°C and in the dark 192 pending analysis. This approach was repeated using seawater solutions of BSA (SW 193 + BSA), taurocholic acid (SW + TA) and BSA plus taurocholic acid (SW + BSA + 194 TA).

195

## 196 2.4. Analysis of extracts

197 A ThermoScientific iCAP RQ ICP-MS with a Glass Expansion micromist nebuliser 198 and cyclonic spray chamber was used to determine Sb concentrations in the diluted 199 extracts. The instrument was calibrated with a blank and four standards (up to 20 µg L<sup>-1</sup>) prepared by serial dilution of a LabKings 10000 mg L<sup>-1</sup> Sb standard in 2% HNO<sub>3</sub>. 200 201 Radio frequency power was set at 1.5 KW with coolant, nebuliser and auxiliary flows of 1.4, 1.07 and 0.8 L Ar min<sup>-1</sup> and a replicate (n = 3) read time of 10 ms. Detection 202 203 limits arising from three standard deviations of blank measurements were between 204 0.05 and 0.10  $\mu$ g L<sup>-1</sup> and precision among replicate readings was better than 15% for mean concentrations above 0.5  $\mu$ g L<sup>-1</sup> and up to 25% for lower mean concentrations . 205 206

#### 207 **3. Results and Discussion**

208 *3.1.* Antimony concentrations in the plastic-amended sediment samples

209 Table 3 presents the dry weight concentrations of total Sb in the estuarine sediment

and in sediment amended by the different microplastics defined in Table 1. Note that

- 211 in the sediment amendments concentrations are computed from the fractional
- 212 contributions of sediment and plastic to total dry mass and the total concentrations of
- 213 Sb in the different solids. Thus, mass contamination of coastal sediment by about
- 214 1.4% of these plastics results in total Sb concentrations that are orders of magnitude
- 215 greater than the Sb content of sediment itself.
- 216

217 *3.2. Antimony mobilisation kinetics* 

Figure 1 shows the dry weight normalised concentrations of Sb released from the sediment and sediment amendments, [Sb], for the different solutions as a function of time, *t*. In some cases, [Sb] increases throughout the incubation (e.g. sediment + R in SW + BSA) or there is a reduction in [Sb] following a period of rapid increase (e.g. sediment + PE in SW + BSA). In most cases, however, [Sb] increases over the experimental period and appears to approach equilibrium. Here, data were modelled

using a second-order diffusion model (Ruby et al., 1992; Martin and Turner, 2019):

224 225

226

26  $1/([Sb]_e - [Sb]) = 1/[Sb]_e + kt$  (1)

227

where  $[Sb]_e$  is the "equilibrium" concentration of the metalloid defined as the highest concentration reported among the last five data points (i.e. t > 120 min), and k is a second-order rate constant of units ( $\mu g g^{-1}$ )<sup>-1</sup> min<sup>-1</sup>. Rate constants were derived from the slopes of (1/( $[Sb]_e - [Sb]$ ) - 1/ $[Sb]_e$ ) versus t, provided that linear regressions were significant (p < 0.05), and are given in Table 4 along with values of  $[Sb]_e$ . Where timed data were more complex or equilibrium was not approached, maximum measured values of the metalloid,  $[Sb]_{max}$ , are given in the table.

235

For sediment alone, the greatest concentration of Sb mobilised (as  $[Sb]_e$  or  $[Sb]_{max}$ ) was in SW. Among the samples amended with plastics, however, there was no clear pattern of mobilisation among the different solutions, with each mobilising the greatest concentration of Sb from at least one sample. Overall, second-order rate constants ranged from 44.6 ( $\mu$ g g<sup>-1</sup>)<sup>-1</sup> min<sup>-1</sup> for sediment amended with PS in the presence of SW + BSA + TA to 0.0216 ( $\mu$ g g<sup>-1</sup>)<sup>-1</sup> min<sup>-1</sup> for sediment amended with PE in the presence of SW alone.

243

244 3.3. Antimony bioaccessibility

Bioaccessibility may be defined as the fraction of a contaminant that is available for dissolution in the digestive tract of an organism, and provides an upper-estimate of bioavailability, or the amount that is able to enter the systemic circulation (Weston and Mayer, 1998). Upper estimates of the percentage bioaccessibility of Sb in sediment and sediment amended with plastic to a range of deposit-feeding invertebrates (i.e. with varying proteins and degrees of surfactancy in their digestive

- environments) were calculated from [Sb]<sub>e</sub> or [Sb]<sub>max</sub> relative to total Sb and are shown
- in Table 5. Overall, BA is greatest for sediment alone, where the metalloid is likely
- adsorbed to the particles surface and bound in different mineral phases of varying
- solubility, with estimates ranging from 0.67 for SW + TA to 2.67 % for SW itself.
- 255 Where plastic is present, the highest values of bioaccessibility were observed for
- amendments with ABS, PE and R. For ABS, similar values of bioaccessibility were
- 257 exhibited for each solution. However, sediment amended with PE exhibits a value that
- 258 is greatest by two orders of magnitude when BSA is present without TA, and
- sediment amended with R exhibits values that are an order of magnitude greater for
- 260 SW and SW + BSA than when TA is present. Among the remaining plastics,
- 261 bioaccessibility is lowest overall for PC and greatest for PET.
- 262

# 263 3.4. Mechanisms of antimony mobilisation from plastics

The release of ions and molecules from polymers normally proceeds by diffusion (Nakashami et al., 2016; Town et al., 2018) but very little has been studied in respect of Sb release from marine plastics. Specifically, as part of a study into metal and

267 metalloid bioaccessibility in various plastics subject to simulated, acidic avian

- 268 digestion, Turner (2018) established that Sb mobilisation from two samples of
- 269 micronized polypropylene under simulated avian digestive conditions proceeded via a
- 270 pseudo-first-order diffusion process with rate constants of about  $0.05 \text{ h}^{-1}$ .
- 271

272 Because of human health concerns, a greater body of literature exists regarding the 273 migration of Sb from polyethylene terephthalate (PET) food-contact plastics that 274 contain the metalloid as catalytic residue (Haldimann et al., 2007; Rungchang et al., 275 2013; Chapa-Martínez et al., 2016). It appears that Sb diffusion is dependent on the 276 physical and chemical nature of migrating species or compounds, the properties of the 277 plastic, including crystallinity, polarity and molecular weight, plastic surface area to 278 solution volume ratio, and the presence of any other additives in the plastic that may 279 retard or facilitate the diffusion process through, for example, adsorption (Westerhoff 280 et al., 2008; Haldimann et al., 2013).

281

In this study, Sb is likely present as  $Sb_2O_3$  where the metalloid is employed directly (or introduced through recycling) as a flame retardant synergist (Papazoglou, 2004), and, additionally, as a series of glycolate complexes in PET as products of the

285 polymerisation process (El-Toufaili et al., 2006); in ABS, however, Sb is present as 286 part of the complex pigment, titanium yellow. Accordingly, the comparatively rapid 287 release of Sb from PET can be attributed to the relatively high diffusivity of rather 288 small organic-complexes of Sb (Welle and Franz, 2010), while for ABS enhanced 289 mobilisation could be due to the presence of Ti, which, despite its sorptive properties, 290 has been observed to promote diffusion of Sb in plastic (Haldimann et al., 2013). 291 Differences between the mobilisation of Sb from other materials can be related to 292 polymer permeability; for example, published permeation coefficients (for oxygen) are around 10<sup>3</sup> cm<sup>3</sup> mm m<sup>-2</sup> d<sup>-1</sup> atm<sup>-1</sup> for various rubbers but are an order of magnitude 293 294 lower for PVC, PS and PC (Keller, 2017).

295

Despite these qualitative explanations, however, it is important to bear in mind that net mobilisation of Sb is also dependent on largely unknown interactions of migrating species with the sediment surface (e.g. through adsorption) and substances present in the aqueous medium (e.g. through complexation), and interactions among aqueous constituents and between these constituents and the sediment surface.

301

# 302 *3.5. Bioaccessibility and mobilisation of Sb in the coastal zone*

303 Antimony is commonly encountered in a wide range of plastics as a flame retardant 304 synergist (often through the recycling of electronic waste), a pigment and a catalyst, 305 and is one of the main inorganic residues in polyester fibres (Turner, 2019). Given the 306 abundance of microplastics in many coastal sediments (up to several thousand kg<sup>-1</sup> 307 have been recorded; Lots et al., 2017; Lo et al., 2018; Wang et al., 2019) these 308 particles could represent a significant anthropogenic source of Sb in the littoral zone. 309 For example, 1 kg of the estuarine sediment used in the present study would double its 310 Sb concentration (to 0.36  $\mu$ g g<sup>-1</sup>) if contaminated by just 3.6 mg of flame-retarded 311 rubber particles.

312

313 Many invertebrates inhabiting the littoral zone incidentally and non-selectively ingest

314 microplastics as part of their sedimentary diet (Van Cauwenberghe et al., 2015; Setala

et al., 2016) and are thereby exposed to quantities of additives and residues that, in

- 316 some cases, could be considerable. For example, colonies of the deposit-feeding
- 317 lugworm, Arenicola marina, may actively process up to 80 cm<sup>3</sup> of sediment per m<sup>2</sup>

318 per day (Kesy et al., 2016) while individual holothurians may ingest-defecate up to 82

- 319 kg per year (Renzi et al., 2018). Whether sufficient Sb is bioaccessible and
- 320 accumulated to elicit some adverse effect is unknown because the toxicity of the
- 321 metalloid in the marine environment is poorly documented. However, the processing
- 322 and bioturbation of plastic-contaminated sediment is likely to be critical to the
- 323 mobilisation and redistribution of more bioavailable forms of the element (and to
- polymer-bound contaminants more generally) in the local interstitial environment andoverlying water column.
- 326

# 327 **4. Conclusions**

328 Antimony is a technology-critical element that is commonly present in plastics as an 329 additive, residue or contaminant. This study has shown that Sb can be partially 330 mobilised from micronized plastics added to sediment by seawater and solutions 331 mimicking the digestive chemistry of deposit-feeding invertebrates. Mobilisation 332 often proceeds via a second-order diffusion model and over a six-hour period can 333 range from between about 0.01% and 3.5% of total Sb depending on the type of 334 solution and nature of the plastic. Large communities of deposit-feeders could be 335 instrumental to the dissolution and mobilisation of the element from sediment

- 336 contaminated by microplastic.
- 337

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341

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- 524 case study in Jiaozhou Bay, China. Science of the Total Environment 674, 27-35.

525 Table 1: Characteristics of the plastic samples employed in the experiments. Total Sb concentrations are reported as the mean and one standard

526 deviation arising from three XRF measurements.

sample description	polymer	Sb, µg g⁻¹	Sb origin
clear water bottle	polyethylene terephthalate (PET)	365 <u>+</u> 66.6	catalytic residue
black Xmas bauble	polystyrene (PS)	890 <u>+</u> 29.6	flame-retardant synergist (recycled)
white beached litter fragment	polyvinyl chloride (PVC)	6260 <u>+</u> 14.7	flame-retardant synergist
white electrical casing	polycarbonate (PC)	27800 <u>+</u> 100	flame-retardant synergist
yellow-green Lego brick	acrylonitrile butadiene styrene (ABS)	256 <u>+</u> 23.9	colour pigment
black beached industrial biobead	polyethylene (PE)	2170 <u>+</u> 30.1	flame-retardant synergist (recycled)
black rubber	rubber (R)*	47600 <u>+</u> 321	flame-retardant synergist

529 \*FTIR failed to determine the precise nature of the rubber because of the high absorbance of the material.

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- 536 Table 2: Concentrations of geochemically important metals, total Sb and organic
- 537 matter (as loss on ignition, LOI) in the sieved estuarine sediment sample.
- 538 Concentrations of metals and Sb are totals recovered by aqua regia and are shown as
- the mean and one standard deviation arising from three independent determinations.

Al, mg g⁻¹	6.75 <u>+</u> 0.36
Ca, mg g⁻¹	82.2 <u>+</u> 8.9
Fe, mg g⁻¹	14.4 <u>+</u> 0.7
Mn, μg g⁻¹	290 <u>+</u> 11
Sb, µg g⁻¹	0.18 <u>+</u> 0.04
LOI. %	1.44

- 542 Table 3: Total concentrations of Sb in the sediment amended by the different
- 543 micronized plastics (as defined in Table 1).
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plastic-amended sediment	Sb, µg g⁻¹
sediment	0.18
sediment + PET	5.1
sediment + PS	12.2
sediment + PVC	84.8
sediment + PC	376
sediment + ABS	3.6
sediment + PE	36.8
sediment + R	643

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- 548 Table 4: Equilibrium or maximum concentrations of Sb in the time-courses shown in
- 549 Figure 1. Rate constants were derived from equilibrium concentrations by linear
- regression analysis according to equation 1, and values are not shown where

551 regressions were non-significant (p > 0.05).

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sample	constant	SW	SW+BSA	SW+TA	SW+BSA+TA
sediment	[Sb] <sub>e</sub> (or [Sb] <sub>max</sub> ), μg g <sup>-1</sup> k, (μg g <sup>-1</sup> ) <sup>-1</sup> min <sup>-1</sup> r <sup>2</sup>	(0.0048)	0.0016 8.88 0.655	(0.0012)	(0.0044)
sediment + PET	[Sb] <sub>e</sub> (or [Sb] <sub>max</sub> ), μg g <sup>-1</sup> k, (μg g <sup>-1</sup> ) <sup>-1</sup> min <sup>-1</sup> r <sup>2</sup>	0.0029 4.36 0.504	(0.0013)	(0.0013)	(0.0037)
sediment + PS	[Sb] <sub>e</sub> (or [Sb] <sub>max</sub> ), μg g <sup>-1</sup> k, (μg g <sup>-1</sup> ) <sup>-1</sup> min <sup>-1</sup> r <sup>2</sup>	0.0043 6.58 0.688	0.0024 2.78 0.634	(0.0013)	0.0040 44.6 0.857
sediment + PVC	[Sb] <sub>e</sub> , μg g <sup>-1</sup> k, (μg g <sup>-1</sup> ) <sup>-1</sup> min <sup>-1</sup> r <sup>2</sup>	0.013 1.18 0.846	0.0095 7.99 0.774	0.014 10.8 0.807	0.022 9.25 0.777
sediment + PC	[Sb] <sub>e</sub> , μg g <sup>-1</sup> k, (μg g <sup>-1</sup> ) <sup>-1</sup> min <sup>-1</sup> r <sup>2</sup>	0.020 0.240 0.731	0.011 2.43 0.814	0.035 0.908 0.840	0.025 0.917 0.827
sediment + ABS	[Sb] <sub>e</sub> (or [Sb] <sub>max</sub> ), μg g <sup>-1</sup> k, (μg g <sup>-1</sup> ) <sup>-1</sup> min <sup>-1</sup> r <sup>2</sup>	0.026 1.54 0.379	0.036 0.74 0.692	0.036 3.19 0.887	(0.055)
sediment + PE	[Sb] <sub>e</sub> (or [Sb] <sub>max</sub> ), μg g <sup>-1</sup> k, (μg g <sup>-1</sup> ) <sup>-1</sup> min <sup>-1</sup> r <sup>2</sup>	0.0019 2.87 0.760	(1.30)	(0.015)	0.012 4.25 0.791
sediment + R	[Sb] <sub>e</sub> (or [Sb] <sub>max</sub> ), μg g <sup>-1</sup> k, (μg g <sup>-1</sup> ) <sup>-1</sup> min <sup>-1</sup> r <sup>2</sup>	1.65 0.0216 0.933	(2.11)	0.13 0.132 0.882	(0.17)

- 560 Table 5: Percentage bioaccessibilities of Sb in sediment amended by different
- 561 microplastics derived from equilibrium or maximum concentrations reported in Table
- 562 4 relative to total concentrations given in Table 3.

	SW	SW+BSA	SW+TA	SW+BSA+TA
sediment	2.67	0.89	0.67	2.44
sediment + PET	0.057	0.025	0.025	0.073
sediment + PS	0.035	0.020	0.011	0.033
sediment + PVC	0.015	0.011	0.017	0.026
sediment + PC	0.005	0.003	0.009	0.007
sediment + ABS	0.72	1.00	1.00	1.53
sediment + PE	0.005	3.53	0.041	0.033
sediment + R	0.26	0.33	0.020	0.026

- 567 Figure 1: Concentrations of Sb released from 25 g of wet estuarine sediment (or 18.26 g on a dry
- 568 weight basis) and 25 g of wet sediment amended with 250 mg of different plastics by seawater ( $\circ$ ) and
- by seawater in the presence of BSA ( $\bullet$ ), taurocholic acid ( $\blacktriangle$ ) and BSA plus taurocholic acid ( $\blacksquare$ ) as a
- 570 function of time.



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