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Mobilization and bioaccessibility of cadmium in coastal sediment contaminated by microplastics

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Abstract

Cadmium has had a number of historical applications in plastics but is now highly regulated. Here, plastics containing pigmented or recycled Cd at concentrations up to $16300 \mu\text{g g}^{-1}$ were processed into microplastic-sized fragments and added to clean estuarine sediment. Plastic-sediment mixtures (mass ratio = 1:100) were subsequently exposed to fluids simulating the digestive conditions encountered in marine deposit-feeding invertebrates prepared from a protein and a bile acid surfactant in seawater and the mobilization of Cd measured as a function of time. Kinetic profiles over a six-hour period were complex, with some fitted using a diffusion model and others exhibiting evidence of Cd interactions between the plastic and sediment surface. The maximum concentration of Cd released from plastic-sediment mixtures was about $0.8 \mu\text{g g}^{-1}$ and orders of magnitude greater than Cd mobilization from sediment alone. It is predicted that large communities of deposit-feeders could mobilize significant quantities of Cd from historical microplastics.

1. Introduction

Cadmium is a highly toxic heavy metal which was used in plastics and paints as a sulphide or sulphoselenide pigment to effect a range of yellows and reds and in polyvinyl chloride (PVC) as a component of heat stabilising compounds (ECHA, 2012). In the European Union, Cd is now highly regulated, being limited to a concentration of $100 \mu\text{g g}^{-1}$ in new plastic consumer goods (European Union, 2011) and, in combination with various other heavy metals, to a concentration of $100 \mu\text{g g}^{-1}$ in packaging and packaging waste (European Parliament and Council of the EU, 1994). In electrical and electronic equipment, Cd is limited in all components, including plastics, to a concentration of $100 \mu\text{g g}^{-1}$ (European Parliament and Council, 2003) and in toys migratable Cd is limited to a concentration of $17 \mu\text{g g}^{-1}$ (European Parliament and Council of the EU, 2009). In consumer paints, Cd concentration is limited to $100 \mu\text{g g}^{-1}$ or, where the Zn content exceeds 10%, to $1000 \mu\text{g g}^{-1}$ (European Union, 2016).

Despite these regulations, Cd can still be encountered at relatively high concentrations in old or extant plastics, including children's toys, as a component of pigments or heat stabilisers (Turner, 2018a), and in a range of newer plastics at lower concentrations through the improper disposal, sorting and recycling of used goods, and in particular old electronic plastics (Turner, 2018b). Studies of beached waste plastics by x-ray fluorescence (XRF) spectrometry also reveal a range of Cd concentrations that reflects its historical use in plastics and its current inadvertent incorporation into newer items (Massos and Turner, 2017).

While it has generally been assumed that Cd and other heavy metals are tightly bound in the plastic or paint matrix, empirical studies have shown that, under certain conditions (for example, low pH, small particle size and the presence of sunlight), small but significant quantities can be released and are, therefore, potentially available in the environment or bioaccessible to humans and wildlife (Fowles, 1977; Liu et al., 2017). For example, a recent investigation into the release of metals in a simulated marine avian digestive fluid based on the acidic proventriculus-gizzard of the northern fulmar, *Fulmarus glacialis* showed that up to 2.6% of total Cd in processed (< 3 mm)

beached plastic fragments of polyethylene and polypropylene was mobilized (Turner, 2018c).

While many sea birds are known to inadvertently, or even deliberately, ingest marine plastics (Furtado et al., 2016; Lavers et al., 2018), little attention has been paid to sediment-dwelling and sediment-ingesting marine invertebrates in this respect (Coffin et al., 2019). Benthic deposit-feeding animals, like polychaetes, holothurians and bivalves, may non-selectively process large quantities of material, including any contaminant particulates, in a near-neutral tubular gut in which a range of enzymes and surfactants are secreted (Chen et al., 2000), resulting in the release and potential bioaccumulation of high concentrations of metals (Mayer et al., 1996; Zhong and Wang, 2006). Specifically, mobilization is believed to be largely a function of the ratio of gut ligand concentration to sediment (or particulate) metal loading and gut passage time (Chen and Mayer, 1999).

In the present study, the release of Cd is examined from clean estuarine sediment and from sediment amended with different plastics containing Cd by seawater and by different solutions designed to mimic the digestive fluids of coastal deposit-feeding invertebrates. Namely, we use solutions of the commercial protein, bovine serum albumin (BSA; molecular mass = 66,400 g mol⁻¹) to approximate concentrations of the complexing capacities of amino acids in the digestive tract (Chen and Mayer, 1998), and the vertebrate bile acid surfactant, sodium taurocholate (C₂₆H₄₄NO₇SNa; molecular mass = 537.7 g mol⁻¹), to simulate anionic surfactancy of the digestive environment (Smoot et al., 2003).

2. Materials and methods

2.1. Sample collection and processing

Approximately 1.5 L of surficial (< 5 cm) sandy-silty sediment was collected using a plastic trowel from the coastal, intertidal reaches of the Erme, a protected and relatively unpolluted estuary in south west England. The sample was sieved through a 1 mm Nylon mesh with the aid of a Nylon brush into a plastic bucket. In the laboratory, subsamples of about 250 g were transferred to a series of clear zip-locked polyethylene bags and stored frozen until required. Analysis of freeze-dried sediment

(~ 250 mg) by XRF spectrometry and inductively coupled plasma-optical emission spectrometry following aqua regia digestion revealed the following elemental concentrations: Fe = 17,500 $\mu\text{g g}^{-1}$, Mn = 303 $\mu\text{g g}^{-1}$, Ca = 175,000 $\mu\text{g g}^{-1}$ and Cd = 0.31 $\mu\text{g g}^{-1}$; while combustion of 5 g of sediment at 550 °C for 8 h resulted in a mass loss, approximating the organic content, of 1.45%.

Plastics containing Cd were sourced from archived samples that had been chemically characterised by XRF as part of independent projects and as indicated in Table 1. Specifically, one sample (a black crevice nozzle attachment for a Hoover) consisted of recycled electronic plastic where Cd was present as residues of electronic components and polyvinyl chloride; four brightly coloured samples of polyethylene (PE), polypropylene (PP) or acrylonitrile butadiene styrene (ABS) were plastic articles (mainly components of toys) manufactured in the 1970s where the metal was used as a sulphide (and often with ZnS) or sulphoselenide pigment; one sample (a red bottle top) was a weathered piece of beached plastic litter that also contained Hg as a constituent of the Cd-based pigment and that was estimated to be over sixty years old (Filella and Turner, 2018). Plastics were formulated to a particle size of < 1 mm in at least two dimensions using a stainless steel grater and about 1 g of each was stored in an individual polypropylene centrifuge tube.

2.2. *Experimental*

Solutions used in the experiment were designed to mimic the chemical conditions (specifically, the amino acid composition and surfactancy) in the digestive environment of marine deposit-feeding invertebrates (Mayer et al., 1997; Voparil and Mayer, 2004) and were prepared according to a similar protocol outlined in Jones and Turner (2010). Solutions of 4 g L⁻¹ of the protein, BSA (> 96% fraction V; Sigma Aldrich), 4 g L⁻¹ of the bile acid surfactant, sodium taurocholate (taurocholic acid sodium salt hydrate, 97%+; VWR International), and 4 g L⁻¹ of BSA plus 4 g L⁻¹ taurocholic acid were prepared by dissolving appropriate quantities of reagents in 500 mL of filtered (< 0.45 μm) English Channel seawater ($S = 33$; pH 7.8) in a series of 1 L borosilicate bottles.

As required, frozen sediment was defrosted and aliquots of 25 g (or 17.65 g on a dry weight basis) were weighed into a series of seven screw-capped 200 mL polyethylene bottles. To six bottles, 250 mg of the different microplastics were added, with the remaining bottle serving as a control without plastic. One hundred ml of seawater was pipetted into each bottle before the contents were wrapped in aluminium foil and agitated on a Stuart SSL1 benchtop orbital shaker set at 150 rpm at room temperature. At different time intervals up to 6 h (encompassing the gut passage time of most deposit-feeders; Mayer et al., 1995), subsamples of 5 mL were abstracted, transferred to polypropylene tubes and centrifuged at 1600 x g for 7 min. Two-mL supernatants were transferred to Sterilin tubes and diluted to 10 ml with 2% HNO₃ and stored under refrigeration pending analysis. This approach was repeated using BSA in seawater, taurocholic acid in seawater, and BSA plus taurocholic acid in seawater.

2.3. Analysis of digests

Cadmium (as ¹¹¹Cd) was analysed in triplicate in the diluted supernatants arising from the experiment in an ISO 9001-accredited laboratory by inductively coupled plasma-mass spectrometry using a Thermo Scientific iCAP RQ with a Glass Expansion micromist nebuliser and cyclonic spray chamber. The instrument was calibrated with a blank and three standards (up to 100 µg L⁻¹) prepared in 2% HNO₃, and RF power was set at 1.5 KW with coolant, nebuliser and auxiliary flows of 1.4, 1.07 and 0.8 L Ar min⁻¹ and a replicate read time of 10 ms. Detection limits, derived from three standard deviations of blank measurements, ranged from about 0.003 to 0.005 µg L⁻¹ and precision among replicate readings was generally better than 10%.

3. Results and Discussion

3.1. Cadmium release kinetics

Total concentrations of Cd in the plastics, determined non-destructively by XRF, range from around 1000 µg g⁻¹ in the beached bottle top (sample 6) and material recycled from electronic waste (sample 1) to over 15,000 µg g⁻¹ in the ABS-based toys (samples 4 and 5) (Table 1). As a result, dry weight Cd concentrations in the plastic-amended sediment samples used in the experiment, computed from the mass

fractions and Cd contents of plastic and dry sediment in each case, range from about 16 to 230 $\mu\text{g g}^{-1}$.

The dry weight concentrations of Cd released during the time-courses, [Cd], are shown for clean estuarine sediment in Figure 1 and for estuarine sediment amended with the different plastics in Figure 2. Profile shapes are variable amongst the different samples and reagents, with some cases exhibiting a rapid (< 30 min) attainment of quasi-equilibrium and others displaying rapid initial release followed by a slower approach to steady-state; in many cases in the presence of plastics, initial release of Cd is followed by a reduction in concentration or a succession of reductions and increases in concentration as metal mobilized from the plastic interacts with the surface of fine, silty sediment. For all samples, however, solutions of the protein, BSA, in seawater, both with and without the bile acid surfactant, taurocholic acid, mobilizes the greatest amount of Cd, and either the bile acid surfactant in seawater or seawater alone releases the lowest concentrations of the metal.

Due to the complex and varied distributions exhibited in Figures 1 and 2, it was not possible to apply a single, generic kinetic model to the data, and in particular to data derived in the presence of plastics. Nevertheless, in four cases time-dependent release of Cd by solutions of BSA, with and without taurocholic acid, could be best modelled with statistical confidence ($p < 0.05$) using a second-order diffusion model of the form outlined in Ruby et al. (1992) and that involves some surface reaction control:

$$1/([\text{Cd}]_e - [\text{Cd}]) = 1/[\text{Cd}]_e + kt \quad (1)$$

Here, $[\text{Cd}]_e$ is the “equilibrium” concentration of Cd measured at the termination of the time-course and k is a second-order rate constant of units $(\mu\text{g g}^{-1})^{-1} \text{min}^{-1}$. Values of k , derived from the slope of $(1/([\text{Cd}]_e - [\text{Cd}]) - 1/[\text{Cd}]_e)$ versus t , are annotated on Figure 2 along with regression coefficients defining the goodness of fit in each case; model fits to the data are also shown in Figure 2, as computed using equation 1 with the corresponding rate constants and $[\text{Cd}]_e$ values.

In Table 2, maximum concentrations, $[Cd]_{max}$, and equilibrium concentrations, $[Cd]_e$, are shown for all data sets, along with corresponding accessibilities or concentrations released relative to total concentrations and expressed as a percentage. The lowest maximum and equilibrium concentrations of Cd ($< 0.01 \mu\text{g g}^{-1}$) are released by all solutions from sediment alone and from sediment amended with plastic samples 1 and 3; for a given reagent, the highest maximum and equilibrium concentrations are released from sediment amended with ABS plastics 4 and 5, with an overall maximum concentration of $> 0.8 \mu\text{g g}^{-1}$ released from sediment amended with plastic 5 by the protein and bile acid surfactant in combined solution. The greatest percentages of maximum and equilibrium Cd release (> 0.3), however, are from sediment without plastic and from sediment amended with plastic 4 and the beach litter (plastic 6) by BSA solution, and both with and without taurocholic acid.

3.2. Cadmium release mechanisms

Regarding estuarine sediment without plastic, mobilization of Cd in seawater occurs through desorption from and ion exchange at the particle surface, with Cd stabilised in bulk solution through the formation of chloro-complexes (Dabrin et al., 2009). Regarding the plastic matrix, kinetics are limited by Cd^{2+} diffusion within the plastic particle, and the rate of mobilization is dependent on the inverse of particle diameter and is some function of porosity or degree of weathering (Town, 2018); when present in pigmented particulate form, Cd release may also be constrained by the rate of dissociation of the compound.

Unlike recent studies reporting the mobilization of metals from plastics subject to a marine avian physiologically-based extraction test (pepsin in HCl at pH 2.5 and 40°C) (Turner and Kwan, 2016; Turner, 2018c), however, a simple first-order diffusion model was not widely applicable to the data in Figure 2, suggesting that diffusion-desorption alone cannot account for Cd mobilization. In the present study, mobilization is offset and confounded by the presence of an additional phase which can act as an adsorbent for released Cd ions. That is, Cd migrating through and released from the plastic matrix via diffusion and desorption, respectively, may be subsequently sequestered by the high surface area of silty estuarine sediment in the suspension.

BSA solution accentuates Cd mobilization from sediment compared with seawater alone because the protein contains various complexants and its hydrophobic components are able to denude sedimentary organic host phases (Jones and Turner, 2010). BSA also assists in releasing Cd from the plastic matrix, presumably by accelerating the dissociation of pigmented compounds. With anionic surfactants being weak complexants and less able to interact with sediment organic matter (Doong et al., 1998), taurocholic acid solution itself does not appear to facilitate the release of Cd from sediment or plastic as effectively as BSA. However, in three cases (sediment amended with plastics 4, 5 and 6), the addition of both reagents to seawater results in an increase in Cd mobilization compared with BSA solution alone throughout the experimental time-course. Moreover, in two cases (plastics 5 and 6) the summed concentrations of Cd released by solutions of the individual reagents exceed the concentration mobilized by solutions of the reagents in tandem, while in the remaining case (plastic 4) the summed concentrations are lower than the concentration arising from reagent combination. Thus, taurocholic acid appears to exert a variable and complex role on the mobilization of Cd from plastics in the presence of BSA, with either little impact overall or non-additive effects that can be synergistic or antagonistic. Although this role is unclear, with all other experimental factors consistent in the time-courses the discrepancies above presumably arise from differences in the characteristics of the plastics, such as age, polymer type and pigment chemistry, and variations among these characteristics in their ability to interact with the protein and bile acid surfactant.

3.3. Environmental implications

Although the mechanisms of Cd mobilization from sediment amended with plastic are varied and complex, it is clear that significant quantities of the metal may be released from contaminated sediment under chemical conditions similar to those encountered in the digestive environments of deposit-feeding invertebrates. Given that the percentage mobilization of Cd in clean estuarine sediment and aged beached PE are similar (about 0.4%), plastic of $1000 \mu\text{g g}^{-1}$ of total Cd contains about 3200 times more available metal than sediment; put another way, 1 kg of clean sediment need

only be contaminated by about 300 mg of Cd-bearing microplastic in order to double its accessible Cd content.

The bioaccessible fraction of Cd in plastic-contaminated sediment, operationally defined as Cd mobilized after 6-h exposure to a solution of BSA plus taurocholic acid relative to total Cd (Table 2), represents an upper-bound limit of the amount of Cd that is bioavailable to a sediment-ingesting invertebrate and able to enter its systemic circulation. The relationship between the two measures is not known but results of experiments using the intestinal fluid of the sea cucumber, *Sclerodactyla birareus*, suggest that Cd mobilized from sediment under digestive conditions exhibits rather low bioaccumulation (McAloon and Mason, 2003). Nevertheless, given the density of deposit-feeders in shallow coastal environments and their propensity to process large quantities of material (Granberg et al., 2008), communities may be capable of not only redistributing microplastics through the sediment column (Nakki et al., 2017) but mobilizing significant amounts of Cd from historical microplastics into the interstitial and overlying waters where the metal may be more available to other wildlife.

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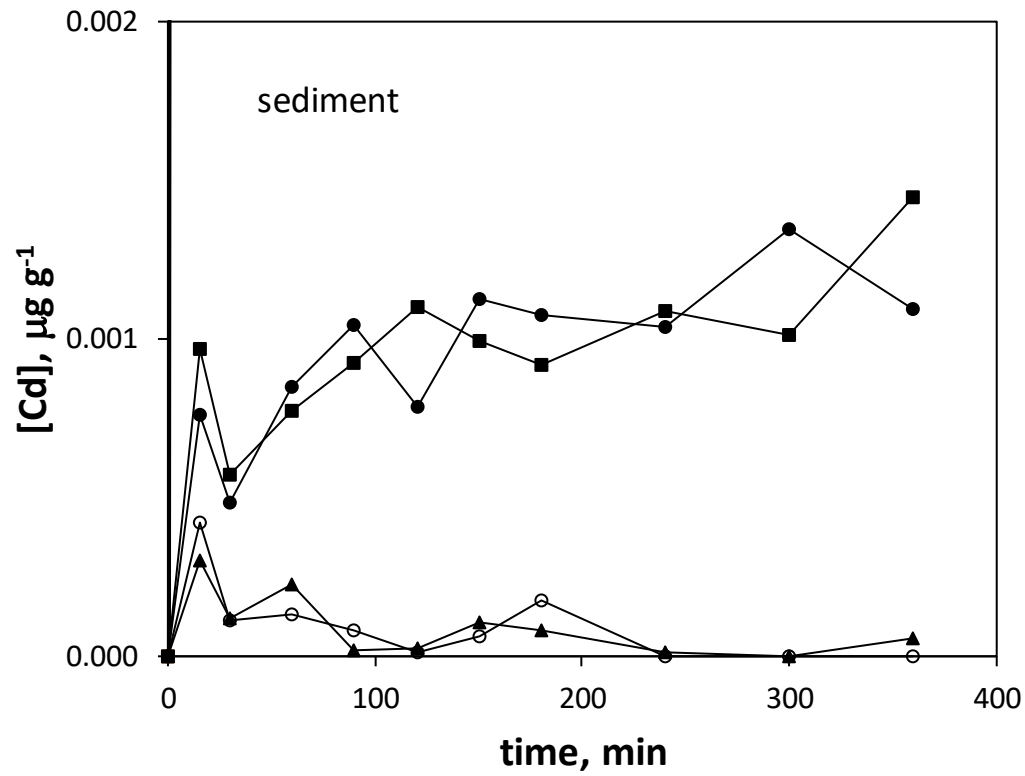
Table 1: Characteristics of the plastic samples used in the study. Total elemental concentrations were determined by XRF (in $\mu\text{g g}^{-1}$) and Cd-sediment refers to the computed concentration of Cd (in $\mu\text{g g}^{-1}$) in sediment amended with each plastic. PE = polyethylene; PP = polypropylene; ABS = acrylonitrile butadiene styrene; nd = not detected.

sample no.	polymer	colour	origin	Cd	Se	Zn	Hg	Cd-sediment
1	PE	black	recycled electronic plastic	1240	nd	18.9	nd	17.6
2	PE	yellow	toy	8950	nd	1460	nd	125
3	PP	orange	bowl	2470	335	132	nd	34.8
4	ABS	red	toy	10,900	1660	nd	nd	153
5	ABS	yellow	toy	16,300	nd	362	nd	228
6	PE	red	beach litter (bottle top)	1150	nd	13.2	241	16.3

1 Table 2: The maximum and “equilibrium” (6-h) concentrations and, in parentheses, percentages of Cd released from the different sediment-plastic preparations by
 2 combinations of seawater (SW), BSA and taurocholic acid (TA).
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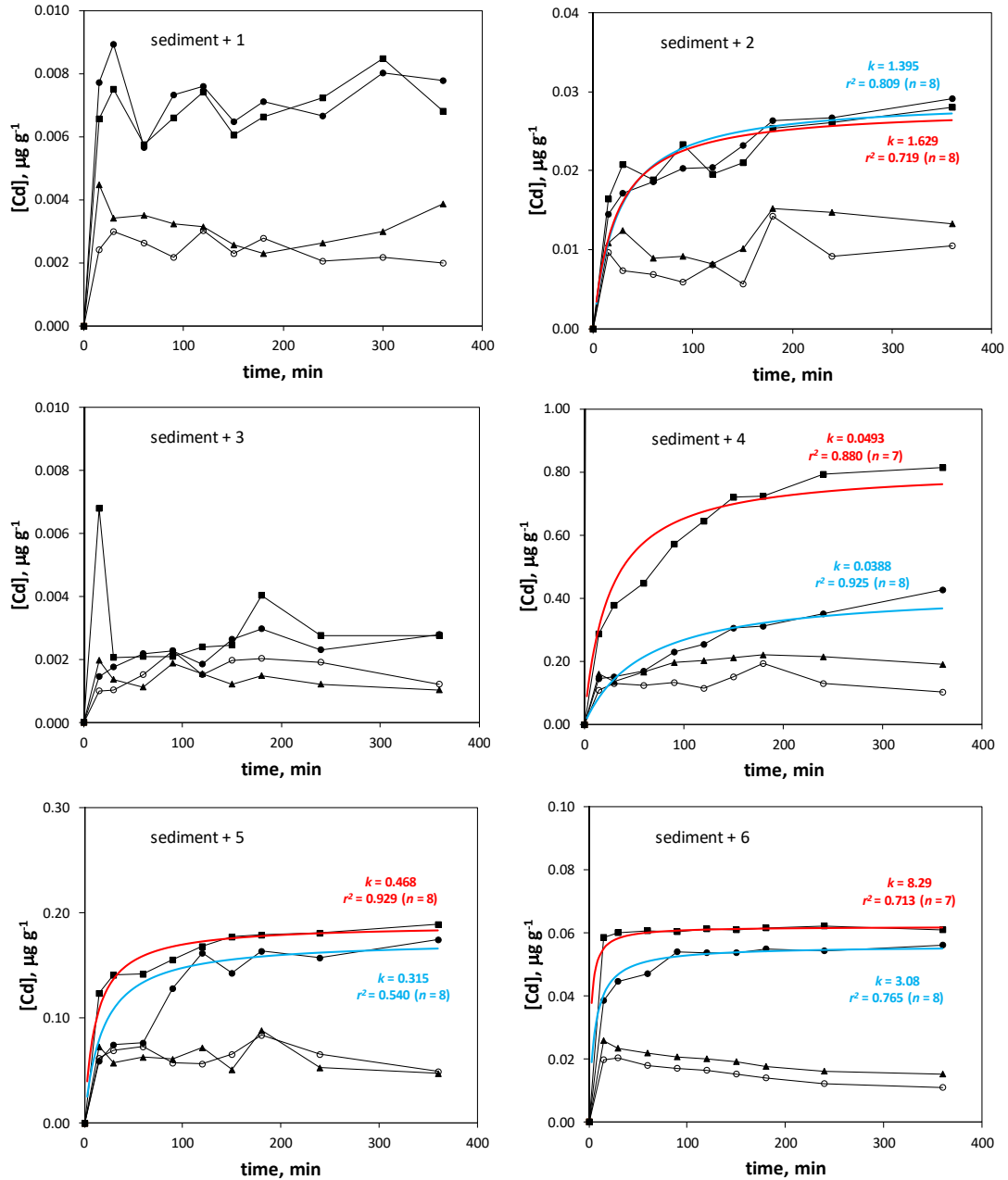
sample	SW		BSA+SW		TA+SW		BSA+TA+SW	
	[Cd] _{max} , µg g ⁻¹ (%)	[Cd] _e , µg g ⁻¹ (%)	[Cd] _{max} , µg g ⁻¹ (%)	[Cd] _e , µg g ⁻¹ (%)	[Cd] _{max} , µg g ⁻¹ (%)	[Cd] _e , µg g ⁻¹ (%)	[Cd] _{max} , µg g ⁻¹ (%)	[Cd] _e , µg g ⁻¹ (%)
sediment only	0.0004 (0.135)	< 0.0001 (< 0.03)	0.0013 (0.435)	0.0011 (0.353)	0.0003 (0.096)	0.0001 (0.033)	0.0014 (0.467)	0.0014 (0.467)
sediment + 1	0.0030 (0.017)	0.002 (0.011)	0.0089 (0.051)	0.0078 (0.044)	0.0045 (0.025)	0.0039 (0.022)	0.0085 (0.048)	0.0068 (0.039)
sediment + 2	0.0143 (0.011)	0.0105 (0.008)	0.0291 (0.023)	0.0291 (0.023)	0.0152 (0.012)	0.0133 (0.011)	0.0280 (0.022)	0.0280 (0.0212)
sediment + 3	0.0023 (0.007)	0.0012 (0.004)	0.0030 (0.009)	0.0028 (0.008)	0.0020 (0.006)	0.0010 (0.003)	0.0068 (0.019)	0.0028 (0.008)
sediment + 4	0.192 (0.126)	0.102 (0.067)	0.428 (0.279)	0.428 (0.279)	0.220 (0.144)	0.190 (0.124)	0.815 (0.533)	0.815 (0.533)
sediment + 5	0.0837 (0.037)	0.0489 (0.021)	0.174 (0.076)	0.174 (0.076)	0.0882 (0.039)	0.0472 (0.021)	0.189 (0.083)	0.189 (0.083)
4 sediment + 6	0.0203 (0.124)	0.0109 (0.067)	0.0561 (0.344)	0.0561 (0.344)	0.0259 (0.159)	0.0154 (0.094)	0.0622 (0.381)	0.0610 (0.374)

5 Figure 1: Concentrations of Cd released from 25 g of clean, wet estuarine sediment by seawater (○) and by seawater in the presence of BSA (●), taurocholic acid (▲) and
6 BSA plus taurocholic acid (■) as a function of time.



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11 Figure 2: Concentrations of Cd released from 25 g of wet estuarine sediment amended with 250 mg of
 12 different plastics by seawater (○) and by seawater in the presence of BSA (●), taurocholic acid (▲) and
 13 BSA plus taurocholic acid (■) as a function of time. Model fits according to equation 1 are shown for
 14 solutions of BSA (blue) and BSA plus taurocholic acid (red) using the rate constants annotated (in $(\mu\text{g}$
 15 $\text{g}^{-1})^{-1} \text{min}^{-1}$ and given along with regression coefficients defining their derivation).



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