



# Interactions between trace metals and plastic production pellets under estuarine conditions



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## ABSTRACT

Pre-production pellets are an abundant form of plastic waste in the marine environment whose principal impacts arise from inadvertent ingestion by various organisms when mistaken for food. Pellets also represent a carrier for both organic and metallic contaminants through their adsorption to the modified plastic surface. In the present study, we examine the adsorption of trace metals (Cd, Co, Cr, Cu, Ni, Pb) to both virgin and beached (aged) pellets under estuarine conditions in order to better understand the role of plastic materials on the transport and behaviour of metals from river to ocean. Metals added to river water and sea water adsorbed to both pellet types with isotherms defined by either the Langmuir or Freundlich model. With increasing pH in river water, adsorption of Cd, Co, Ni and Pb increased, adsorption of Cr decreased and adsorption of Cu was relatively invariant. Along a salinity gradient, created by mixing river and sea waters in different proportions, adsorption of Cd, Co and Ni decreased, adsorption of Cr increased and adsorption of Cu and Pb exhibited a minimum towards the fresh water end-member. In all experiments and for all metals, adsorption was considerably greater to beached pellets than to virgin pellets, presumably because of the weathering of and adsorption and attrition of charged minerals by the former. Speciation considerations suggest that adsorption to the pellet surface largely involves metal cations or oxyanions (e.g.  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ ), although additional forms of Cu and Pb (e.g. organic complexes) may also be involved. Despite mass-normalised adsorption constants being lower than equivalent values defining the adsorption of metals to sediments, microplastics should be regarded as a component of the suspended load of estuaries whose precise role on contaminant transport requires further study.

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## 1. Introduction

The ubiquitous, global problem of marine pollution from plastic materials has received considerable attention in the scientific and managerial literature over the past two decades (Debrot et al., 1999; Santos et al., 2005; Eriksson et al., 2013). The sources of plastic to the oceans are diverse and complex but, ultimately, arise from the irresponsible handling of materials during their production, usage and disposal. As well as the aesthetics associated with plastic debris floating in sea water or deposited on shorelines, plastic poses a threat to wildlife through inadvertent or deliberate ingestion, entanglement and habitat smothering (Goldberg, 1997; Gregory, 2009; Mrosovsky et al., 2009). Plastics in the marine environment are also able to sequester contaminants from sea water. Significant in this respect are the adsorption of hydrophobic organic micropollutants, such as polychlorinated biphenyls and polycyclic aromatic hydrocarbons, to the plastic surface (Fries

and Zarfl, 2012; Koelmans et al., 2013), affording a means by which such contaminants may be ingested by invertebrates, fish, birds and turtles and subsequently enter the food chain. Recent attention has also focussed on the adsorption of trace metals to plastics suspended in sea water (Holmes et al., 2012; Rochman et al., 2014). Thus, although plastic has no inherent charge or significant porosity, the weathering and modification of the surface through the attrition or precipitation of minerals and organic matter appears to provide a suitable, charged surface for the adsorption of various metal ions.

Compared with the marine environment, very little information exists on the occurrence and effects of plastics in rivers and in estuaries (Williams and Simmons, 1997; Browne et al., 2010; Bakir et al., 2014). This is, perhaps, surprising because many catchments are direct and significant recipients of stormwater runoff and municipal and industrial effluents. In a recent monitoring programme, Moore et al. (2011) measured two size classifications of plastic debris (1–5 mm and >5 mm) in urbanised rivers of the Los Angeles basin and estimated a flux of more than 2 billion pieces of plastic, weighing 30 tonnes, over a three day period encompassing different hydrological regimes. The majority of plastic on a number basis was foam fragments but on a mass basis

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was “whole” items. Overall, estimates of the concentrations of plastic encountered during a number of sampling periods ranged from about 1.6 to 41 mg L<sup>-1</sup>.

Clearly, rivers represent an important source of a diversity of plastics to the oceans; moreover, since flow in non-tidal reaches is unidirectional, plastic debris in rivers is likely to be less weathered and chemically modified than marine-derived material that has, generally, been suspended or beached for considerable periods of time. Estuaries may, therefore, be regarded as zones of mixing of relatively “new” riverine plastic, which has a local source(s), with “older” (or “aged”) and more modified marine plastic, which likely has a multitude of geographically diverse sources.

In the present study, and as an extension to an earlier publication and using selected data contained therein (Holmes et al., 2012), we examine the role of estuaries in modifying the adsorptive properties of new and aged plastics towards trace metals. As our model plastic particle, and in line with previous studies examining plastic–contaminant interactions (Karapanagioti and Klontza, 2008; Fries and Zarfl, 2012), we use pre-production, resin pellets. These pellets are the raw material used in the plastic industry for moulding or extruding into consumer items and, as litter, are abundantly observed on and readily collected from the coastal strandline. We study the adsorption of metals to both new (virgin) polyethylene pellets, sourced from a local moulding plant, and aged (beached) pellets, collected from a local sandy beach, as a function of environmental variables that are carefully controlled in the laboratory.

## 2. Methods

### 2.1. Materials

Reagents used throughout were of analytical grade or better and were purchased from Fisher Scientific (Loughborough, UK) or Sigma Aldrich (Cambridge, UK), and all solutions used were prepared in high purity (18.2 MΩ cm at 25 °C) Millipore Milli-Q water (MQW). Plasticware used for sampling, storage and reagent preparation was either purchased new or was pre-cleaned by successive washes in 2% Decon (24 h), 1.2 M HCl (48 h) and MQW (double rinse).

River water was collected, as required, in a 10 L high density polyethylene (HDPE) carboy from the Plym (50.410°N, 4.079°W). The catchment above the sampling location consists largely of agricultural land, protected granitic moorland and forest, and is not significantly impacted by metal inputs. Surface sea water of salinity ~33.5 was collected, as required, in a 10 L high density polyethylene carboy from Station L4 in the English Channel (50.250°N 4.217°W) by staff at Plymouth Marine Laboratory aboard RV Plymouth Quest. Water samples were filtered immediately upon return to the laboratory through 0.45 μm Whatman cellulose nitrate filters using a Nalgene polysulfone vacuum filter unit. Filtrates were stored for no longer than a week in 1 L HDPE bottles at 4 °C and in the dark before being used in the experiments.

Virgin polyethylene pellets were obtained from a local injection moulding and assembly plant (Algram Ltd, Plymouth). Beached pellets were collected by hand from Watergate Bay, a beach 70 km to the north east of Plymouth and facing the North Atlantic Ocean. Previous studies had shown that pellets from this location were predominantly polyethylene and, compared with other locations in south west England, contained relatively low concentrations of trace metals (Holmes et al., 2012). (Specifically, median concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn in individual pellets and as extracted by dilute aqua regia were 0.005 nM, 0.23 nM, 0.82 nM, 0.74 nM, 0.50 nM, 0.53 nM and 3.00 nM, respectively.) Beached pellets were collected from the strandline using plastic tweezers and were stored in a series of 60 mL polycarbonate centrifuge tubes. In the laboratory, samples were sieved through a 1 mm Nylon mesh and subsequently ultrasonicated for five minutes in filtered sea water in order to remove loosely adherent material. Pellets were then dried under laminar flow at room temperature (~20 ± 2 °C) and stored in clean centrifuge tubes.

### 2.2. Experimental

Adsorption experiments were performed at room temperature in 60 mL Teflon (PTFE) bottles, each containing 20 pellets (whose combined weight had been recorded) and 50 mL of water, according to a protocol outlined in Holmes et al. (2012). After a conditioning period of 24 h, a spike containing the same mass–volume concentration of Cd, Cr(VI), Co, Cu, Ni, Pb and Zn was added to each bottle. Spikes had been prepared by serial dilution of 1000 mg L<sup>-1</sup> plasma emission standards in MQW and their addition did not significantly alter the pH of the aqueous medium. After the contents of each bottle had been orbitally agitated at 150 rpm for a further 48 h, water samples of 2.5 mL were pipetted from each bottle into individual 8 mL HDPE vials and acidified to pH < 2 with 1 M HNO<sub>3</sub>. All pellets from each bottle were retrieved using a custom-built Nylon strainer before being rinsed with MQW and transferred to HDPE vials. Aliquots of 2.5 mL of 1.2 M HCl were added to each vial for a period of 24 h in order to extract adsorbed trace metals before solutions were syphoned off into new vials pending analysis (Holmes et al., 2012).

Adsorption isotherms were conducted in triplicate in both river water and sea water and in the presence of virgin and beached pellets. For a given type of water and pellet, different concentrations of trace metals (0 to 20 μg L<sup>-1</sup>, or up to 178 nM of Cd, 340 nM of Co, 385 nM of Cr, 315 nM of Cu, 341 nM of Ni, 97 nM of Pb and 306 nM of Zn) were added to different bottles under otherwise identical conditions. (Note that four different concentrations were added to sea water while five were added to river water.) Adsorption to virgin and beached pellets was studied in triplicate along a simulated estuarine gradient created by mixing river water and sea water end-members in different proportions in a series of bottles. In this experiment, a fixed concentration of 5 μg L<sup>-1</sup> of each trace metal (or 44 nM of Cd, 85 nM of Co, 96 nM of Cr, 79 nM of Cu, 85 nM of Ni, 24 nM of Pb and 76 nM of Zn) was employed. The dependence of adsorption on pH was studied in river water in the presence of virgin and beached pellets. Here, the pH of a series of 50 mL samples, monitored using a Mettler Delta 340 pH meter, was adjusted to between about 4 and 10.5 and at intervals of about 0.5 by dropwise addition of either 0.1 M NaOH or 0.1 M HNO<sub>3</sub> before a fixed concentration of 5 μg L<sup>-1</sup> of each trace metal was added. The pH of each reactor was re-recorded at the end of the experiment and these values were used for data presentation purposes.

### 2.3. Metal analysis

Water samples containing more than 0.3% salt (or more than about 10% sea water) were diluted five- or tenfold in MQW prior to analysis. Cadmium, Cr, Co, Cu, Ni, Pb and Zn were determined in acidified water samples and HCl pellet extracts by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-Series II ICP mass spectrometer with collision cell (ThermoElemental, Winsford, UK). Samples were introduced via a concentric glass nebuliser coupled with a conical spray chamber with acquisition parameters and gas flow rates as described elsewhere (Vyas et al., 2014). Optimisation was carried out using a multi-element tune-up solution at the beginning of each data acquisition period and external calibration was achieved using 5 matrix-matched, multi-element standards and three blanks. Fifty μg L<sup>-1</sup> of <sup>115</sup>In and <sup>193</sup>Ir were added to all standards, blanks and samples for internal standardisation to compensate for instrumental drift and variations in plasma conditions. Limits of detection were calculated from 3 standard deviations of blank concentrations (Cd: 0.089 nM, Co: 0.170 nM, Cr: 3.27 nM, Cu: 9.44 nM, Ni: 0.511 nM, Pb: 0.820 nM, Zn: 7.80 nM).

## 3. Results

Results presented below are shown for or have been derived from both adsorbed metal (and as extracted by 1.2 M HCl), with or without normalisation for pellet mass, and aqueous metal; thus, we have not

relied on mass balance to derive concentrations in one phase. Metal recovery (that is, the sum of adsorbed and aqueous metal concentrations relative to the concentration added) was generally between 90 and 100%. Recoveries above 100% were attributed to interferences arising from the presence of pre-existent metal in the aqueous phase and/or on beached pellets. In cases where recoveries exceeded 105% (Zn in most cases and Cu in a few cases in sea water), data have been excluded from further consideration.

### 3.1. Adsorption isotherms

Fig. 1 shows the w/w concentrations of Cd, Co, Cr, Cu, Ni and Pb adsorbed to virgin and beached pellets,  $[\text{MeX}]^*$  ( $\text{nmol g}^{-1}$ ), as a function of corresponding concentrations remaining in the aqueous phase,  $[\text{Me}]$  (nM), for both river water (pH = 6.3) and sea water (pH 7.8). In many cases isotherms could be defined significantly ( $p < 0.05$ ) using a linear model. More generally, however, isotherms were better fitted using non-linear Langmuir or Freundlich equations. The Langmuir isotherm assumes monolayer adsorption to a homogeneous surface and is given as follows:

$$[\text{MeX}]^* = \frac{K_L [\text{MeX}]_{\text{max}}^* [\text{Me}]}{1 + K_L [\text{Me}]} \quad (1)$$

where  $[\text{MeX}]_{\text{max}}^*$  ( $\text{nmol g}^{-1}$ ) is the adsorption capacity of the metal on the surface and  $K_L$  ( $\text{in nM}^{-1}$ ) is the Langmuir constant. The Freundlich equation assumes multilayer adsorption to a heterogeneous surface and is given as follows:

$$[\text{MeX}]^* = K_F [\text{Me}]^{1/n} \quad (2)$$

where  $K_F$  ( $\text{in nmol}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$ ) is the Freundlich constant and  $n$  a measure of non-linearity. Values for the Langmuir and Freundlich constants, derived from linear regression analysis of  $1/[\text{MeX}]^*$  versus  $1/[\text{Me}]$  and non-linear regression of  $[\text{MeX}]^*$  versus  $[\text{Me}]$ , respectively, and using

mean values derived from replicate measurements, are shown in Tables 1 and 2. Fits to the data according to the Langmuir model, where significant, are annotated on Fig. 1.

It is clear from the plotted data that the adsorption of all trace metals is greater to beached pellets than to virgin polyethylene pellets in both river water and sea water and, with the exception of Cr and Cu, adsorption to beached pellets is greater in river water than in sea water. Examination of the Langmuir constants, where significant, reveals that values of  $[\text{MeX}]_{\text{max}}^*$  are greater for beached pellets than for virgin pellets in both river water and sea water and, with the exception of Cu and Cr,  $[\text{MeX}]_{\text{max}}^*$  decreases from river water to sea water for both virgin and beached pellets. The value of  $K_L$  is greater for beached pellets than for virgin pellets in river water and, with the exception of Cd, in sea water. However, for a given pellet type, differences in  $K_L$  between river water and sea water are highly variable among the different trace metals. Examination of the Freundlich constants reveals that values of  $K_F$  are one or two orders of magnitude greater for beached pellets than for virgin pellets suspended in the same medium; values of  $K_F$  decrease from river water to sea water for Cd, Ni and Pb on virgin pellets and Cd and Co on beached pellets, while values increase from river water to sea water for Co, Cr and Cu on virgin pellets and Cr and Pb on beached pellets. In most cases, isotherms are convex ( $1/n < 1$ ); for Cr adsorption to virgin pellets in river water and Pb adsorption to virgin pellets in sea water, however, isotherms are concave ( $1/n > 1$ ), and for Co adsorption to virgin pellets in river water and Cu adsorption to beached pellets in river water, isotherms are approximately linear ( $1/n \sim 1$ ). In most cases, isotherms are more convex (or the magnitude of  $1/n$  smaller) for beached pellets than for virgin pellets suspended in the same medium.

### 3.2. Adsorption along the estuarine gradient

The adsorption of Cd, Co, Cr, Cu, Ni and Pb to virgin and beached pellets along the simulated estuarine gradient, attained by mixing river water (pH = 6.3) and sea water (pH 8.1) end-members in different

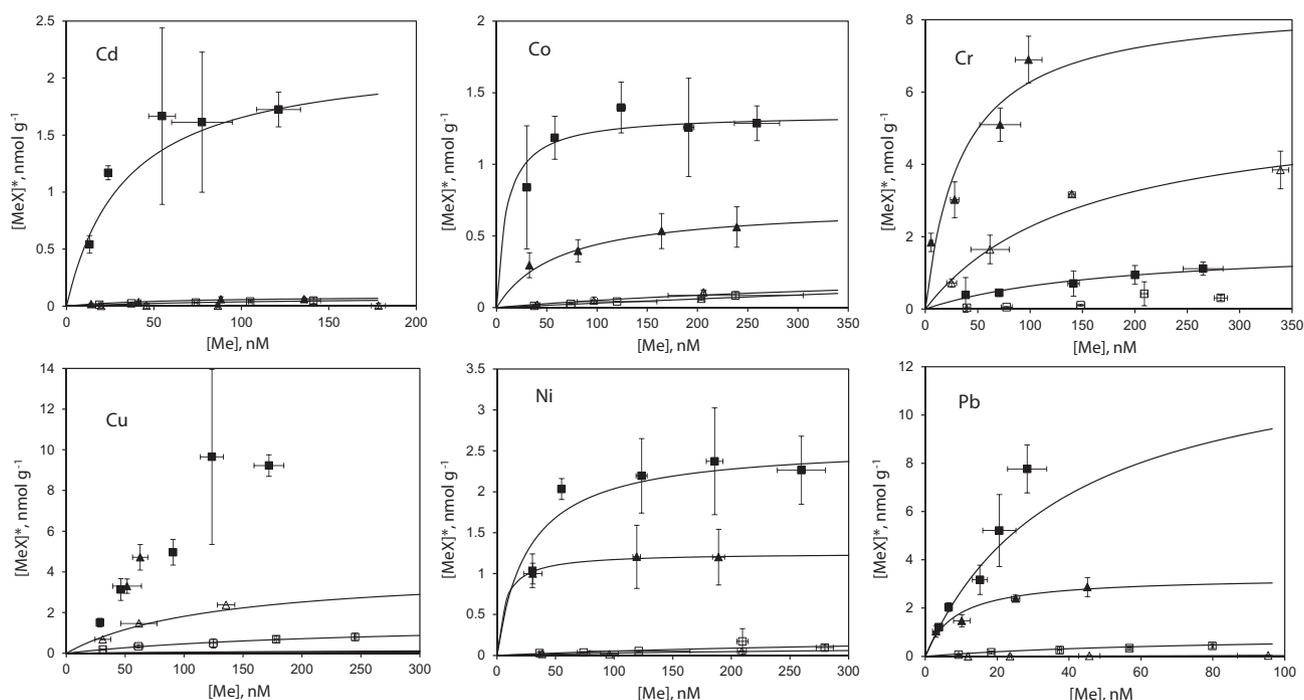


Fig. 1. Isotherms defining the adsorption of Cd, Co, Cr, Cu, Ni and Pb to virgin pellets suspended in river water ( $\square$ ) and sea water ( $\triangle$ ) and to beached pellets suspended in river water ( $\blacksquare$ ) and sea water ( $\blacktriangle$ ). Errors denote the standard deviation about the mean of three independent measurements and solid lines represent best fits to each data set according to the Langmuir model (Eq. 1).

**Table 1**

Constants defining trace metal adsorption to virgin and beached pellets according to the Langmuir model (Eq. (1) and Fig. 1). Note that Cr adsorption to virgin pellets suspended in river water, Cu adsorption to beached pellets in river water and sea water and Pb adsorption to virgin pellets suspended in sea water could not be defined significantly by the Langmuir equation.

	River water						Sea water					
	Virgin			Beached			Virgin			Beached		
	[MeX] <sup>*</sup> <sub>max</sub> , nmol g <sup>-1</sup>	K <sub>L</sub> , L nmol <sup>-1</sup>	r <sup>2</sup>	[MeX] <sup>*</sup> <sub>max</sub> , nmol g <sup>-1</sup>	K <sub>L</sub> , L nmol <sup>-1</sup>	r <sup>2</sup>	[MeX] <sup>*</sup> <sub>max</sub> , nmol g <sup>-1</sup>	K <sub>L</sub> , L nmol <sup>-1</sup>	r <sup>2</sup>	[MeX] <sup>*</sup> <sub>max</sub> , nmol g <sup>-1</sup>	K <sub>L</sub> , L nmol <sup>-1</sup>	r <sup>2</sup>
Cd	0.0894	0.00717	0.907	2.21	0.0297	0.958	0.00383	0.0464	0.984	0.0904	0.0170	0.976
Co	1.17	0.000270	0.186	1.35	0.101	0.992	0.299	0.00200	0.758	0.717	0.0159	0.994
Cr	–	–	–	1.79	0.00550	0.880	5.72	0.00660	0.963	8.48	0.0285	0.871
Cu	1.58	0.00412	0.944	–	–	–	4.11	0.0079	0.960	–	–	–
Ni	0.282	0.00228	0.197	2.58	0.0375	0.977	0.129	0.0028	0.803	1.25	0.148	0.999
Pb	0.922	0.0103	0.841	13.2	0.0257	0.783	–	–	–	3.30	0.121	0.965

**Table 2**

Constants defining trace metal adsorption to virgin and beached pellets according to the Freundlich model (Eq. 1). Note Cu and Ni adsorption to beached pellets suspended in sea water could not be defined significantly by the Freundlich equation.

	River water						Sea water					
	Virgin			Beached			Virgin			Beached		
	K <sub>F</sub> , nmol <sup>1-1/n</sup> g <sup>-1</sup> L <sup>1/n</sup>	1/n	r <sup>2</sup>	K <sub>F</sub> , nmol <sup>1-1/n</sup> g <sup>-1</sup> L <sup>1/n</sup>	1/n	r <sup>2</sup>	K <sub>F</sub> , nmol <sup>1-1/n</sup> g <sup>-1</sup> L <sup>1/n</sup>	1/n	r <sup>2</sup>	K <sub>F</sub> , nmol <sup>1-1/n</sup> g <sup>-1</sup> L <sup>1/n</sup>	1/n	r <sup>2</sup>
Cd	0.000173	0.677	0.968	0.193	0.492	0.812	0.000816	0.287	0.862	0.00379	0.589	0.972
Co	0.000293	1.03	0.993	0.507	0.182	0.661	0.000982	0.836	0.951	0.0905	0.339	0.988
Cr	0.000243	1.29	0.870	0.0452	0.567	0.967	0.0987	0.659	0.939	0.812	0.440	0.957
Cu	0.0162	0.715	0.988	0.0508	1.04	0.952	0.0992	0.613	0.910	–	–	–
Ni	0.00124	0.821	0.800	0.421	0.327	0.703	0.000959	0.701	0.812	–	–	–
Pb	0.0130	0.812	0.977	0.373	0.869	0.967	0.000140	1.22	0.986	0.650	0.390	0.983

proportions, is shown as a function of salinity in Fig. 2. Here, results are given in terms of the distribution coefficient,  $K_D$  ( $\text{mL g}^{-1}$ ), defining the concentration ratio of adsorbed to aqueous metal:

$$K_D = \frac{[\text{MeX}]^*}{[\text{Me}]} \quad (3)$$

It is important to appreciate that the distribution coefficient is conditional inasmuch as it defines the partitioning for a given concentration of added metal (which, in our case, is  $5 \mu\text{g L}^{-1}$ ). Thus, because adsorption isotherms are mainly convex in nature (Fig. 1),  $K_D$  exhibits an inverse dependency on added metal concentration. Nevertheless, the coefficient provides a useful means of examining the sensitivity of adsorption to variations in environmental conditions, and in the current context, to variations encountered along the estuarine gradient.

Results of the experiment are qualitatively consistent with the isothermic results reported in Fig. 1. Specifically, adsorption of all metals is greater to beached pellets than to virgin pellets, and while the adsorption of Cd, Co, Ni and Pb is greater in river water than in sea water, the converse is observed for Cr and the adsorption of Cu is similar in the two end-members. In the case of Cd, Co and Pb along the estuarine gradient, there was a significant ( $p < 0.05$ ) correlation between distribution coefficients for the beached pellets and distribution coefficients for the virgin pellets.

### 3.3. Dependence of adsorption on pH of river water

Results of the experiment in which metal adsorption was studied in river water whose pH was varied between about 4 and 10 are shown in Fig. 3. Here, data are shown in terms of the percentage of metal adsorbed to the pellets:

$$\% \text{ adsorbed} = \frac{[\text{MeX}]}{[\text{Me}] + [\text{MeX}]} \cdot 100\% \quad (4)$$

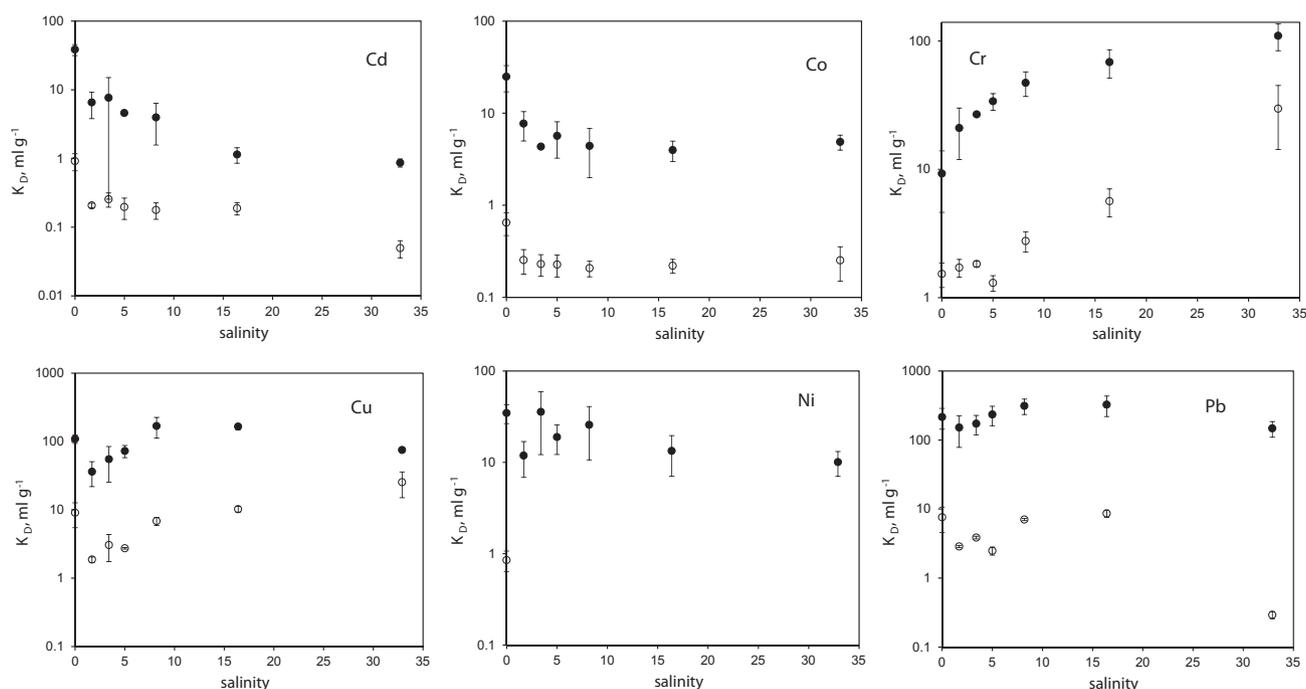
where  $[\text{MeX}]$  denotes the concentration of metal adsorbed to the pellets on a w/v (nmol) basis. For all metals, adsorption is greater to beached

pellets than to virgin pellets throughout the pH range studied. For Cd, Co and Ni, adsorption to both pellet types increases progressively with increasing pH, while for Pb adsorption increases to about pH 6 (beached pellets) or 7 (virgin pellets) and is, thereafter, relatively constant. For the beached pellets, the pH at which 50% adsorption occurs was in the following order: Ni (~10) > Co (~9) > Cd (7.8) > Pb (~5). In contrast, Cu adsorption exhibits no clear dependence on pH for either pellet type while Cr exhibits a reduction in adsorption with increasing pH for both pellet types. The latter effect is largely confined to the pH region below 6, and is more pronounced for the adsorption of the metal to beached pellets than to virgin pellets.

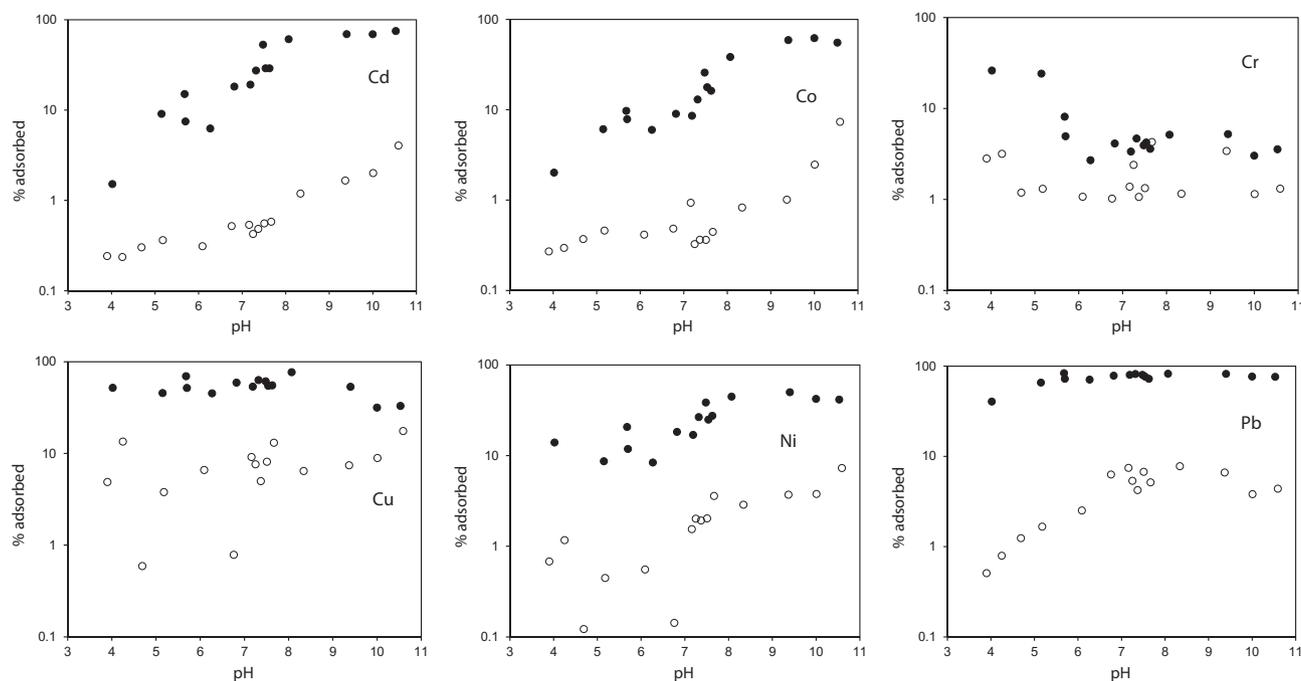
## 4. Discussion

### 4.1. Mechanisms of metal–pellet interactions

This is one of only a limited number of studies to examine the interactions of metals with plastics in the aquatic environment (Ashton et al., 2010; Holmes et al., 2012) and, to our knowledge, the first to examine the interactions of metals with plastics in estuaries and in fresh water. Given that virgin polyethylene pellets exhibit no inherent charge or acid–base behaviour (Fotopoulou and Karapanagio, 2012) it is perhaps surprising that metals are able to interact appreciably with these solids under a variety of environmental conditions. However, once suspended in natural waters virgin pellets acquire a charged surface, which is net negative at the pH of river water and sea water, through the rapid adsorption of organic matter and that is able to effect the adsorption of metal ions. The increase in adsorption of Cd, Co, Ni and Pb with increasing pH shown in Fig. 3 is consistent with the interactions of divalent cations with functional groups of natural organic matter and the acid–base properties of the latter (Jones and Bryan, 1998). In contrast, since Cr exhibits a reduction in adsorption to virgin pellets with increasing pH, we surmise that this metal remains as Cr(VI) in the experiments and, therefore, exists in oxyanionic form (and, specifically, as  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ ); adsorption involves relatively weak coulombic interactions between these species and positive regions of charge on the organically-modified pellets whose abundance diminishes with increasing pH.



**Fig. 2.** Distribution coefficients defining the adsorption of metals to virgin pellets (o) and beached pellets (●) along the simulated estuarine gradient. Errors denote the standard deviation about the mean of three independent measurements. Note that, with the exception of the river water end-member,  $K_D$ s defining Ni adsorption to virgin pellets were below 0.1 or the metal was not detected in the pellet phase.



**Fig. 3.** The percentage of metals adsorbed to virgin pellets (o) and beached pellets (●) suspended in Plym river water as a function of pH (and as measured at the termination of the experiment).

With regard to Cu, lack of a clear dependence of adsorption on pH suggests that additional, non-ionic forms (e.g. neutral organic complexes) are also able to interact with the polymeric surface.

In most cases, adsorption, measured in terms of % adsorbed metal,  $K_D$ ,  $K_L$ ,  $K_F$  or  $[MeX]_{max}$ , is at least an order of magnitude greater on beached pellets than on virgin pellets. Clearly, ageing of pellets, while suspended in water or when beached, confers a more heterogeneous and reactive surface. Specifically, these characteristics are engendered through both the erosion of the plastic itself, including the formation of various surface functional groups, and the attrition and adsorption-precipitation of different charged minerals and organic matter. In many respects, therefore, the physico-chemical characteristics of the beached pellet surface are similar to those of suspended particles, containing appreciable concentrations of oxidic Fe and Mn (Ashton et al., 2010) and a measurable specific surface area (Fotopoulou and Karapanagio, 2012). These properties, coupled with the potential of pellets for sustained and long-range transport within the surface microlayer where contaminants are often concentrated (Hardy et al., 1990), are favourable for the adsorption and accumulation of metals from the aqueous phase.

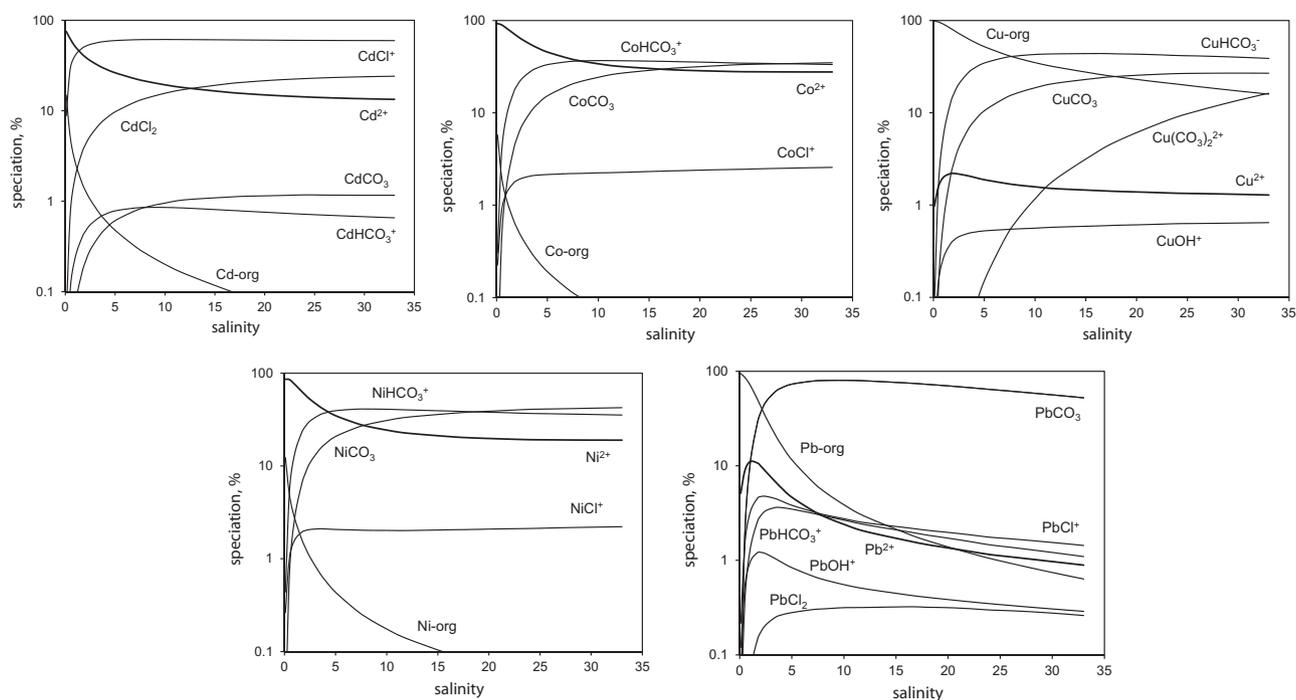
#### 4.2. Metal speciation along the estuarine gradient

In order to ascertain the forms of Cd, Co, Cr, Cu, Ni and Pb interacting with the pellets along the simulated estuarine gradient, the aqueous equilibrium speciation of the metals was computed or evaluated using available constants and data. For Cd, Co, Cu, Ni and Pb, speciation was computed using the Windermere Humic Aqueous Model (WHAM, v7) at a temperature of 293 K and assuming equilibrium with the atmosphere ( $pCO_2 = 3.5 \times 10^{-4}$  atm). The chemical compositions of average sea water and of Plym river water (Turner et al., 2006) were used to calculate the ionic properties along the gradient while measured values of pH and interpolations thereof were used to define the pH profile. Dissolved organic matter (DOM) was not measured in the present end-members but concentrations of dissolved organic carbon (DOC) along the estuarine gradient were based on the conservative mixing of  $2 \text{ mg L}^{-1}$  in Plym river water and  $1.5 \text{ mg L}^{-1}$  in English Channel sea water (Turner et al., 2004). For inorganic species, the default formation

constants in the WHAM database were employed (Tipping, 1998) and the Davies equation was used to correct for ion activity coefficients. For organic complexation, we assumed that polyelectrolytes existed in a 4:1 ratio of fulvic acid (FA) to humic acid (HA) throughout the estuarine gradient, and that the combined, absolute concentrations of FA and HA were equal to the concentrations of DOC (or roughly half of the concentrations of DOM; Tipping et al., 1998). Default complexation constants for both FA and HA were then employed.

The results of the equilibrium speciation calculations for Cd, Co, Cu, Ni and Pb are shown in Fig. 4 in terms of the percentage concentration of each species modelled as a function of salinity. Qualitatively consistent with the experimental adsorption results along the estuarine gradient and the assertion that the free ion is the principal or only species interacting with the pellet surface, a salinity-dependent reduction in the percentage of  $Cd^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  is predicted. For Cd, quantitative agreement was also apparent since a significant ( $p < 0.05$ ) correlation was observed between  $K_D$  for both virgin and beached pellets and either the percentage or activity of computed  $Cd^{2+}$ . Presumably, where agreement was not quantitative other effects are important, such as increasing competition for adsorption sites on the pellet surface from divalent sea water cations with increasing salinity (Du Laing et al., 2009). Regarding Cu and Pb, although the relative abundances of the free ion in the river water and sea water end-members are in agreement with the relative magnitudes of  $K_D$  in the corresponding samples, discrepancies exist between the precise distributions of the free ion and  $K_D$  between the end-members. Specifically, a minimum in  $K_D$  observed at low salinity is approximately coincident with a maximum in the abundance of the free ion. As discussed above for Cu, additional organic complexes that are not factored into the default settings of the WHAM software may either interact with the pellet surface (in addition to or rather than  $Cu^{2+}$  and  $Pb^{2+}$ ) or compromise the accuracy of the computed abundance and distribution of the free ion.

The speciation of Cr(VI) along the estuarine gradient is predicted to be dominated by a series of negatively charged, tetra-oxyanionic species that have little tendency to interact with organic matter and surfaces that bear a net negative charge (Mayer and Schick, 1981). Specifically, Turner et al. (1981) computed Cr(VI) in freshwater at pH 6 to be comprised of  $HCrO_4^-$  (74%) and  $CrO_4^{2-}$  (26%), and in seawater of pH 8.2,



**Fig. 4.** The equilibrium speciation of Cd, Co, Cu, Ni and Pb along the estuarine gradient, calculated using WHAM v7 and the default constants in its database. Note that Me-org denotes complexation by humic and fulvic acids.

$\text{CrO}_4^{2-}$  (71%) and  $\text{NaCrO}_4^-$  (28%). Such speciation is consistent with the inverse dependence of Cr(VI) adsorption on pH reported above (Fig. 3). However, both the magnitude and salinity-dependence of Cr adsorption along the estuarine gradient are, perhaps, surprising. For example, Mayer and Schick (1981) found that chromate adsorption to estuarine sediment was rather low and declined with increasing salinity. The latter effect was attributed to increasing competition from sea water anions for positively charged adsorption sites and a reduction in the activity of the chromate ion (including complexation and ion pair formation with sea water cations) along the salinity gradient, although the possibility that some metal was reduced by sediment organic matter to Cr(III) could not be ruled out. In our case, the inverse dependency of adsorption on pH and the relatively low content of available or reactive particulate organic matter suggest that reductive adsorption is unlikely. Rather, given that the pH throughout the estuarine gradient was above the point of zero charge for the beached pellet surface (about 6.1 for polyethylene pellets; Fotopoulou and Karapanagiotou, 2012), a more plausible explanation is an increase in the compression of the electrical double layer with increasing ionic strength, resulting in a progressive reduction in the negative–negative (surface–chromate) repulsion with increasing salinity.

#### 4.3. General implications

Although estuaries have long been recognised as filters and accumulators of sediment and contaminants (Olsen et al., 1993; Bell et al., 1997), a more recent realisation is that they represent a direct receptor for plastic waste (Acha et al., 2003; Browne et al., 2010; Costa et al., 2011) and an important conduit for the transport of plastics from land to ocean (Moore et al., 2011; Morrill et al., 2014). The findings of this study also suggest that an abundant form of discarded plastic (in the form of pre-production pellets) is able to interact with trace metal contaminants in a qualitatively similar way to suspended sediment particles. Thus, Cd, Co, Ni and Pb undergo a net reduction in adsorption with increasing salinity and decreasing pH, while Cr(VI) exhibits an increase in adsorption with increasing salinity and decreasing pH and Cu adsorption displays relatively little dependence on these variables

(Mayer and Schick, 1981; Li et al., 1984; Turner and Millward, 2002). The reactivity of plastic pellets towards trace metals is attributed to both the short-term adsorption of organic matter and the long-term ageing and modification of the plastic pellet surface. Quantitatively, adsorption constants on a mass basis are lower than respective constants defining adsorption to suspended sediments; however, it must be appreciated that the specific surface area of weathered or modified plastic is orders of magnitude lower than that of fine sediment (Holmes et al., 2012).

While our observations are also likely to be applicable to a broader range of plastic materials and products and to a wider range of metallic and organic contaminants, the significance to which plastics affect the overall transport, availability and reactivity of contaminants in estuaries is difficult to ascertain. Data from Moore et al. (2011) indicate that, in urban estuaries at least, the loading of plastic captured by various nets can be as high as  $40 \text{ mg L}^{-1}$ . However, this estimate neglects microscopic ( $< 1 \text{ mm}$ ) particles and fragments of plastic whose contribution to the net mass may be small but whose adsorptive capacity is likely to be disproportionately high. Clearly, plastics should be regarded as a component of the suspended load in estuaries which has at least some impact on the behaviour, transport and fate of contaminants, but whose precise role and contribution in these respects merits further study.

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#### References

- Acha, E.M., Mianzan, H.W., Iribarne, O., Gagliardini, D.A., Lasta, C., Daleo, P., 2003. The role of the Rio de la Plata bottom salinity front in accumulating debris. *Mar. Pollut. Bull.* 46, 197–202.

- Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic production pellets in the marine environment. *Mar. Pollut. Bull.* 60, 2050–2055.
- Bakir, A., Rowland, S.J., Thompson, R.C., 2014. Transport of persistent organic pollutants by microplastics in estuarine conditions. *Estuar. Coast. Shelf Sci.* 140, 14–21.
- Bell, F.G., Lindsay, P., Hytiris, N., 1997. Contaminated ground and contaminated estuary sediment illustrated by two case histories. *Environ. Geol.* 32, 191–202.
- Browne, M.A., Galloway, T.S., Thompson, R.C., 2010. Spatial patterns of plastic debris along estuarine shorelines. *Environ. Sci. Technol.* 44, 3404–3409.
- Costa, M.F., Silva-Cavalcanti, J.S., Barbosa, C.C., Portugal, J.L., Barletta, M., 2011. Plastics buried in the inter-tidal plain of a tropical estuarine ecosystem. *J. Coast. Res.* 64, 339–343.
- Debrot, A.O., Tiel, A.B., Bradshaw, J.E., 1999. Beach debris in Curacao. *Mar. Pollut. Bull.* 38, 795–801.
- Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., Tack, F.M.G., 2009. Trace metal behaviour in estuarine and riverine floodplain soils and sediments: a review. *Sci. Total Environ.* 407, 3972–3985.
- Eriksson, C., Burton, H., Fitch, S., Schulz, M., van den Hoff, J., 2013. Daily accumulation rates of marine debris on sub-Antarctic island beaches. *Mar. Pollut. Bull.* 66, 199–208.
- Fotopoulou, K.N., Karapanagiotou, H.K., 2012. Surface properties of beached plastic pellets. *Mar. Environ. Res.* 81, 70–77.
- Fries, E., Zarfl, C., 2012. Sorption of polycyclic aromatic hydrocarbons (PAHs) to low and high density polyethylene (PE). *Environ. Sci. Pollut. Res.* 19, 1296–1304.
- Goldberg, E.D., 1997. Plasticizing the seafloor: an overview. *Environ. Technol.* 18, 195–201.
- Gregory, M.R., 2009. Environmental implications of plastic debris in marine settings – entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philos. Trans. R. Soc. B Biol. Sci.* 364, 2013–2025.
- Hardy, J.T., Crecelius, E.A., Antrim, L.D., Kiessler, S.L., Broadhurst, V.L., Boehm, P.D., Steinhauer, W.G., Coogan, T.H., 1990. Aquatic surface microlayer contamination in Chesapeake Bay, USA. *Mar. Chem.* 28, 333–352.
- Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. *Environ. Pollut.* 160, 42–48.
- Jones, M.N., Bryan, N.D., 1998. Colloidal properties of humic substances. *Adv. Colloid Interf. Sci.* 78, 1–48.
- Karapanagiotou, H.K., Klontza, I., 2008. Testing phenanthrene distribution properties of virgin plastic pellets and plastic eroded pellets found on Lesbos island beaches (Greece). *Mar. Environ. Res.* 65, 283–290.
- Koelmans, A.A., Besseling, E., Wegner, A., Foekema, E.M., 2013. Plastic as a carrier of POPs to aquatic organisms: a model analysis. *Environ. Sci. Technol.* 47, 7812–7820.
- Li, Y.-H., Burkhardt, L., Teraoka, H., 1984. Desorption and coagulation of trace elements during estuarine mixing. *Geochim. Cosmochim. Acta* 48, 1879–1884.
- Mayer, L.M., Schick, L.L., 1981. Removal of hexavalent chromium from estuarine waters by model substrates and natural sediments. *Environ. Sci. Technol.* 15, 1482–1484.
- Moore, C.J., Lattin, G.L., Zellers, A.F., 2011. Quantity and type of plastic debris flowing from two urban rivers to coastal waters and beaches of southern California. *J. Integr. Coast. Zone Manag.* 11, 65–73.
- Morritt, D., Stefanoudis, P.V., Pearce, D., Crimmen, O.A., Clark, P.F., 2014. Plastic in the Thames: a river runs through it. *Mar. Pollut. Bull.* 78, 196–200.
- Mrosovsky, N., Ryan, G.D., James, M.C., 2009. Leatherback turtles: the menace of plastic. *Mar. Pollut. Bull.* 58, 287–289.
- Olsen, C.R., Larsen, I.L., Mulholland, P.J., Vondamm, K.L., Grebmeier, J.M., Schaffner, L.C., Diaz, R.J., Nichols, M.M., 1993. The concept of an equilibrium surface-applied to particle sources and contaminant distributions in estuarine sediments. *Estuaries* 16, 683–696.
- Rochman, C.M., Hentschel, B.T., The, S.J., 2014. Long-term sorption of metals is similar among plastic types: implications for plastic debris in aquatic environments. *PLoS One*. <http://dx.doi.org/10.1371/journal.pone.0085433>.
- Santos, I.R., Friedrich, A.C., Wallner-Kersanach, M., Fillmann, G., 2005. Influence of socio-economic characteristics of beach users on litter generation. *Ocean Coast. Manag.* 48, 742–752.
- Tipping, E., 1998. Humic ion-binding model VI: an improved description of the interactions of protons and metal ions with humic substances. *Aquat. Geochem.* 4, 3–48.
- Tipping, E., Lofts, S., Lawlor, A.J., 1998. Modelling the chemical speciation of trace metals in the surface waters of the Humber system. *Sci. Total Environ.* 210/211, 63–77.
- Turner, A., Millward, G.E., 2002. Suspended particles: their role in estuarine biogeochemical cycles. *Estuar. Coast. Shelf Sci.* 55, 857–883.
- Turner, A., Le Roux, S.M., Millward, G.E., 2004. Speciation and partitioning of cadmium and zinc in two contrasting estuaries: the role of hydrophobic organic matter. *Limnol. Oceanogr.* 49, 11–19.
- Turner, A., Crussell, M., Millward, G.E., Cobelo-Garcia, A., Fisher, A.S., 2006. Adsorption kinetics of platinum group elements in river water. *Environ. Sci. Technol.* 40, 1524–1531.
- Turner, D.R., Whitfield, M., Dickson, A.G., 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25 °C and 1 atm pressure. *Geochim. Cosmochim. Acta* 45, 855–881.
- Vyas, N., Turner, A., Sewell, G., 2014. Platinum-based anticancer drugs in waste waters of a major UK hospital and predicted concentrations in recipient surface waters. *Sci. Total Environ.* 493, 324–329.
- Williams, A.T., Simmons, S.L., 1997. Estuarine litter at the river/beach interface in the Bristol Channel, United Kingdom. *J. Coast. Res.* 13, 1159–1165.