



Adsorption of trace metals to plastic resin pellets in the marine environment

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ABSTRACT

Plastic production pellets collected from beaches of south west England contain variable concentrations of trace metals (Cr, Co, Ni, Cu, Zn, Cd and Pb) that, in some cases, exceed concentrations reported for local estuarine sediments. The rates and mechanisms by which metals associate with virgin and beached polyethylene pellets were studied by adding a cocktail of $5 \mu\text{g L}^{-1}$ of trace metals to 10 g L^{-1} pellet suspensions in filtered seawater. Kinetic profiles were modelled using a pseudo-first-order equation and yielded response times of less than about 100 h and equilibrium partition coefficients of up to about 225 ml g^{-1} that were consistently higher for beached pellets than virgin pellets. Adsorption isotherms conformed to both the Langmuir and Freundlich equations and adsorption capacities were greater for beached pellets than for virgin pellets. Results suggest that plastics may represent an important vehicle for the transport of metals in the marine environment.

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1. Introduction

Since becoming widely available in the 1940s and 1950s, plastics have grown in popularity to their current annual levels of consumption of 245 million tonnes (Andrady and Neal, 2009). The benefits of plastics are vast and range from waste minimisation in the food packaging industry to weight reduction and improvement of energy efficiency of vehicles. The very properties that make plastics so useful (e.g. low density, durability), however, also ensure that they are persistent pollutants of the aquatic and terrestrial environments. The marine environment is of particular concern because of the abundance and diversity of products reported in regions remote from any urbanisation (Shiber and Barralesrienda, 1991; Khordagui and Abuhilal, 1994; Derraik, 2002). In addition to their aesthetic impacts, plastics in the marine environment pose a direct threat to animals by accumulation, entrapment, entanglement, choking and suffocation (Ryan, 1987; Boren et al., 2006; Browne et al., 2008; Gregory, 2009). Indirectly, plastics can act as a source of organic contaminants to animals through the ingestion of material that is mistaken for food (Teuten et al., 2007). Contaminants include components of the plastics themselves, including plasticisers, and hydrophobic organic compounds, such as polychlorinated biphenyls and polycyclic aromatic hydrocarbons, that

are adsorbed onto the material from seawater (Mato et al., 2001; Endo et al., 2005; Rios et al., 2007).

Empirical studies of the interactions between organic contaminants and plastics in the marine environment have largely focussed on resin pellets, the raw material used in the plastics industry for moulding or extruding into consumer items (Takada, 2006; Karapanagioti and Klontza, 2008). Plastic resin pellets are typically cylindrical, spherical or oval shaped pieces of unprocessed polymer of 1–5 mm diameter. When new they are commonly white, off-white or translucent, but on exposure to the natural environment they gradually become discoloured by the action of sunlight and through fouling by hydrogenous, biogenic and anthropogenic (e.g. tar) accumulations (Endo et al., 2005). Until recently, interactions between metals and plastic resin pellets and other polymeric debris had not been considered, presumably because polymers are generally considered to be relatively inert towards aqueous metal ions. However, loss of metal to plastic containers is a commonly reported problem during sample storage or in experiments involving spiking of metal standards (Giusti et al., 1994; Li et al., 2001; Cobelo-Garcia et al., 2007; Fischer et al., 2007). Analysis of composite samples of resin pellets collected from a variety of beaches in south west England revealed measurable trace metal concentrations and, in some cases, metal enrichment relative to local sand after normalisation with respect to Al (Ashton et al., 2010). The precise mechanisms by which metals associate with pellets are unclear but likely involve adsorption of ions to the polymer and coatings thereon and adherence of small, metal-bearing mineral particles to the pellet surface. Moreover, the

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buoyancy of pellets ensures they are exposed to relatively high concentrations of metals and other contaminants in the sea surface microlayer (Wurl and Obbard, 2004). Trace metals associated with plastic pellets in the marine environment have the propensity to be transported considerable distances and are potentially available to animals and birds that mistake plastics for food (Robards et al., 1997; Tourinho et al., 2010).

In the present study, we examine the mechanisms and kinetics of trace metal uptake by plastic resin pellets suspended in metal-amended seawater under controlled laboratory conditions. We use both new (virgin) pellets sourced from a plastics moulding facility and aged pellets collected from a local beach and whose chemical characteristics (e.g. polymer type, pre-existent metal content) had been previously established. Results of the study are discussed in terms of the implications of plastic–metal interactions on trace metal behaviour and cycling in the marine environment.

2. Materials and methods

2.1. Materials and reagents

Unless otherwise stated, reagents were supplied by Fisher Scientific (Loughborough, UK) or Romil (Cambridge, UK) and were of analytical grade or better. All plasticware used for sampling, sample processing and experimental work was soaked successively in a detergent with both ionic and non-ionic surfactant components (>24 h) and 10% HCl (>48 h) before being rinsed in Millipore Milli-Q water (MQW). After drying under laminar flow for 72 h in an ISO 9001:2000 accredited Bassaire S6 laminar flow hood, clean plasticware was stored in re-sealable polyethylene bags until use. Surface seawater of salinity 34 and pH 7.8 was collected in a 10 L high density polyethylene (HDPE) carboy from Station L4 in the English Channel (50.250°N 4.217°W) by staff at Plymouth Marine Laboratory aboard RV Plymouth Quest. In the laboratory, seawater was filtered through a 0.45 µm cellulose nitrate filter housed in a polypropylene vacuum filtration unit and stored at 4 °C and in the dark until required in the experiments.

2.2. Pellet sampling

Virgin polyethylene resin pellets were obtained from a local plastic processing facility (Algram Group Ltd., Plymouth) and beached pellets were collected from three coastal beaches (Ninney Rock, 50.339°N 4.239°W; Sharrow Point, 50.348°N 4.260°W; Watergate Bay, 50.445°N 5.042°W) and one estuarine silt-flat (Saltram, 50.378°N 4.099°W) in south west England (Fig. 1). About 100 beached pellets were collected from the strandline at each location using plastic tweezers and the pooled samples were stored in a series of 50 ml polypropylene centrifuge tubes. In the laboratory, adherent material was removed from the beached pellets by

ultrasonication for 5 min in filtered seawater before pellets were dried under laminar flow.

2.3. Pellet characterisation

To ascertain the metal content of individuals, 30 randomly selected pellets from each location were weighed into individual 8 ml screw-capped high density polyethylene vials containing 2 ml of 20% aqua regia. The contents were shaken on a Labortechnik KS125 orbital shaker at 150 rpm for 48 h before digests were transferred to clean vials. Earlier experiments revealed that dilute aqua regia recovered >85% of metals extracted by the full strength reagent. Pellets retrieved from the digests were dried under laminar flow and analysed by Fourier transform infra-red spectroscopy using a Bruker IFS 66 coupled with an MTEC 300 photo-acoustic cell to identify the component polymer. Spectra were recorded as an average of 64 scans in the range 4000–400 cm⁻¹ at a resolution of 8 cm⁻¹ and were compared with a library of synthetic polymer spectra.

2.4. Adsorption experiments

Because of the relatively low metal concentrations in pellets from Watergate Bay (see below), a greater quantity of samples ($n \sim 2000$) was subsequently collected from this location and used in the adsorption experiments along with virgin pellets obtained from the processing facility. For the kinetic experiments, undertaken in triplicate and including a metal-free control, 300 pellets were weighed and added to 750 ml of filtered seawater (pellet mass:seawater volume = 10 g L⁻¹) in 1 L Teflon (PTFE) bottles. After 24 h, 5 µg L⁻¹ of Cr, Co, Ni, Cu, Zn, Cd and Pb, prepared by serial dilution of 1000 mg L⁻¹ plasma emission standards in MQW, was added. Concentrations greatly exceed aqueous metal concentrations in open seawater but are closer to values encountered in contaminated inshore waters (Jonas and Millward, 2010) and in the sea surface microlayer where pellets reside during transport (Wurl and Obbard, 2004). The contents were then orbitally agitated at 150 rpm for a period of 7 d at room temperature (20 ± 1 °C), and subsamples of 50 ml and 20 pellets were abstracted using a plastic bulb pipette and 1 mm mesh, respectively, at different time intervals. Water samples were transferred to polypropylene centrifuge tubes and acidified to pH < 2 with 50 µl of HNO₃. Pellets were transferred to 8 ml HDPE vials and 2.5 ml of 10% HCl added in order to extract adsorbed trace metals and minimise digestion of pre-existent metal. Adsorption isotherms were undertaken in triplicate for a period of 48 h in a series of 60 ml PTFE bottles, each containing 20 pre-weighed pellets, 50 ml of filtered seawater and different concentrations of metals ranging from 0 to 20 µg L⁻¹, under otherwise identical conditions. On completion of the experiments, metal loss to the PTFE container surfaces was evaluated by rinsing empty bottles with 50 ml of 10% HCl for 48 h under orbital agitation.

2.5. Metal analysis

Aqua regia digests of individual pellets were analysed for Al, Fe and Mn (hereafter referred to as hydrogenous metals) by optical emission spectrometry (ICP-OES) using a Varian 725 ES (Mulgrave, Australia), and for Cr, Co, Ni, Cu, Zn, Cd and Pb (trace metals) by inductively coupled plasma-mass spectrometry (ICP-MS) using

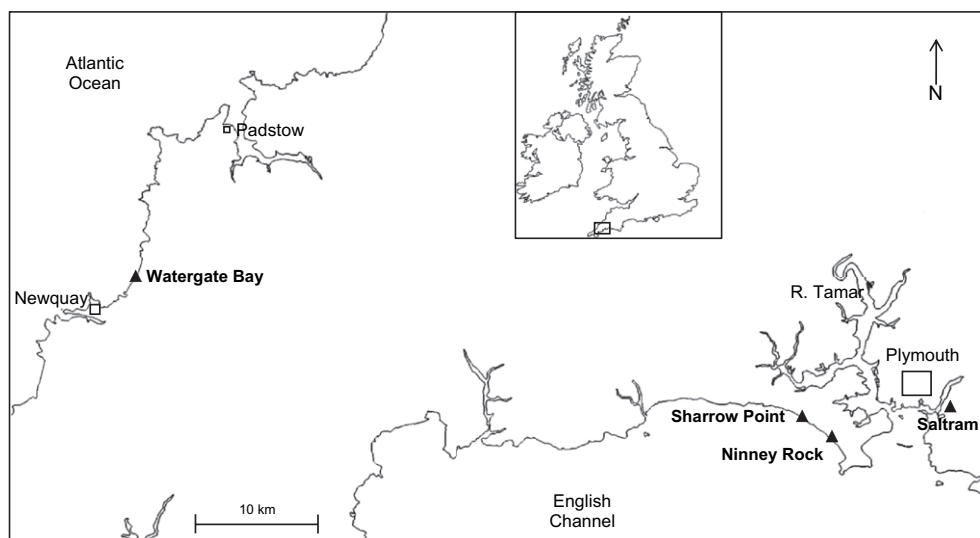


Fig. 1. Sampling locations for the beached pellets (▲) and their proximity to urban centres (□).

a Thermo X-series 2 (ThermoElemental, Winsford UK). Instruments were calibrated using five matrix-matched, mixed standards and a blank, and internal standardisation during ICP-MS analysis was achieved by the addition of $50 \mu\text{g L}^{-1}$ of ^{115}In and ^{193}Ir to all standards and samples. Seawater samples resulting from the adsorption experiments were diluted tenfold in MQW and, with acid digests of the corresponding pellets and acid rinses of the empty containers, analysed for trace metals by ICP-MS.

3. Results and discussion

3.1. Pellet characteristics

The average mass of the beached pellets from the four sites ranged from 26.4 mg (Sharrow Point) to 32.5 mg (Saltram) and the relative standard deviation (rsd) varied between about 20 and 35%. The average mass of the virgin pellets was 26.2 mg with an rsd of about 7%. These observations presumably reflect a relatively homogeneous source material supplied from the processing facility, and a multitude of beached pellet types that have undergone heterogeneous erosion, abrasion, and attrition of hydrogenous and biogenic matter during transport in seawater and after deposition. Most pellets were white or off-white and ovoidal, but a variety of other colours (e.g. black, grey, yellow) and shapes (e.g. cylinders, rods, discs) were also present. Despite differences in colour and shape, all pellets analysed by FTIR were polyethylene. (Scanning electron microscopy images of virgin and beached pellets are exemplified in Ashton et al. (2010).)

Table 1 summarises the dry weight normalised concentrations of pre-existent trace metals and hydrogenous metals (i.e. those largely arising from chemical precipitation; Al, Fe, Mn) extracted by dilute aqua regia on individual pellets collected from each location. Concentrations of a given metal are variable both within samples from the same site and between sample sites and no relationship between metal concentration and pellet colour or shape was evident. In some cases (e.g. Zn at Saltram, Sharrow and Ninney), we note that maximum concentrations on individual pellets are close to or exceed concentrations reported for contaminated estuarine sediment from south west England (between about 100 and $400 \mu\text{g g}^{-1}$; Kalman and Turner, 2007). In general, concentrations of

trace metals (but not hydrogenous metals) are lowest for samples collected from Watergate Bay, and it is for this reason that pellets used in the adsorption experiments were sourced from this location.

3.2. Trace metal adsorption

Since we employed polymer (PTFE) bottles during our examination of the uptake of trace metals by plastic resin pellets, it was important to quantify the loss of analyte to the container surfaces during the incubations. Analysis of the acid rinsings of empty bottles at the end of the experiments showed that, on average, about 5% of Cr had adsorbed to the PTFE surfaces, and that <1% of other metals had been lost by this process.

Although trace metal loss to containers was small relative to percentages remaining in seawater or adsorbed to pellets, results below have been computed from direct measurements of the aqueous and pellet phases and do not rely on mass balance. Thus, kinetic results are expressed as percentage aqueous metal, calculated from aqueous concentration relative to aqueous plus pellet concentration (both on a w/v basis), while isothermic results are shown as pellet metal concentration on a w/w basis versus aqueous metal concentration.

3.3. Adsorption kinetics

Examples of the time-dependencies of metal uptake by virgin and beached pellets are shown in Fig. 2. In most cases, profiles consisted of a period of rapid metal adsorption and subsequent approach to equilibrium or, in some cases, a more protracted period of slower adsorption, and the extent of metal uptake was greater on beached pellets than on virgin pellets, presumably because of the changes to surface properties incurred while pellets are in the marine environment (described below). Rates of interaction between metal, Me, and pellet surface, X, were modelled with a pseudo-first-order reversible reaction (Turner et al., 2006):

Table 1

Summary of concentrations of hydrogenous metals and trace metals in pellets sampled from four locations in south west England ($n = 30$ in each case).

	Al $\mu\text{g g}^{-1}$	Fe $\mu\text{g g}^{-1}$	Mn $\mu\text{g g}^{-1}$	Cu $\mu\text{g g}^{-1}$	Zn $\mu\text{g g}^{-1}$	Pb $\mu\text{g g}^{-1}$	Cr ng g^{-1}	Co ng g^{-1}	Ni ng g^{-1}	Cd ng g^{-1}
<i>Saltram</i>										
Mean	55.8	97.8	20.5	0.441	2.68	1.02	237	107	131	1.65
SD	42.7	79.1	56.8	0.470	2.40	1.24	159	177	117	1.19
Median	41.0	67.5	5.01	0.283	1.63	0.544	212	44.9	91.1	1.17
Minimum	8.33	11.7	0.35	0.012	0.051	0.052	nd	nd	14.9	0.208
Maximum	171	314	308	2.38	10.0	5.85	821	787	562	4.33
<i>Ninney Rock</i>										
Mean	22.3	41.9	1.51	1.11	21.0	1.34	751	17.7	69.8	76.7
SD	15.7	30.5	2.68	1.90	58.5	2.39	142	15.8	40.5	134
Median	20.8	38.3	0.760	0.265	0.818	0.269	413	14.7	62.8	14.9
Minimum	nd	6.21	0.075	nd	nd	0.0232	nd	nd	nd	nd
Maximum	64.8	124.6	14.4	7.73	288	10.3	7970	71.8	157	492
<i>Sharrow Point</i>										
Mean	23.0	64.6	1.51	1.32	23.3	1.64	430	20.7	95.1	74.4
SD	18.2	38.9	2.39	1.80	56.7	2.40	210	19.8	59.3	143
Median	18.4	55.8	0.669	0.652	1.99	0.74	408	13.9	81.3	9.61
Minimum	3.77	nd	0.193	nd	0.065	0.016	nd	4.43	15.5	nd
Maximum	71.8	159	13.0	5.76	207	8.82	935	103	242	493
<i>Watergate Bay</i>										
Mean	16.9	48.5	1.16	0.064	0.299	0.149	44.0	22.5	40.0	1.09
SD	18.4	48.2	1.62	0.0618	0.292	0.181	39.5	47.7	40.4	1.39
Median	7.43	34.4	0.712	0.047	0.196	0.109	42.5	13.8	29.3	0.523
Minimum	nd	nd	0.079	nd	nd	nd	nd	nd	nd	nd
Maximum	81.8	239	8.66	0.239	1.04	0.885	88.0	262	164	5.36

SD: standard deviation; nd: not detected.

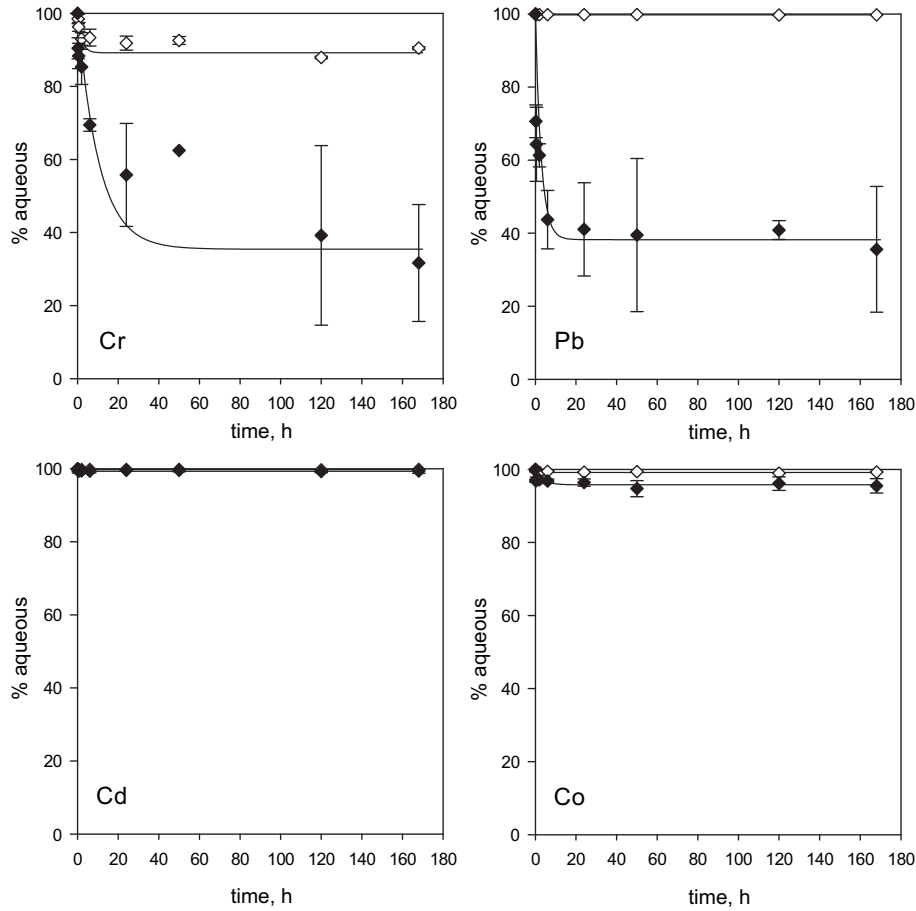


Fig. 2. Time-dependent adsorption of Cr, Pb, Cd and Co from seawater to virgin (\diamond) and beached (\blacklozenge) polyethylene resin pellets. Error bars represent one standard deviation about the mean of three determinations and lines are fits to the data based on a pseudo-first-order model (Eqs. (1) and (2)) and whose constants are given in Table 2.



$$\frac{d[\text{Me}]}{dt} = -k_1[\text{Me}]_t + k_{-1}[\text{MeX}]_t \quad (2)$$

where MeX (w/v) represents metal adsorbed to the pellet surface and k_1 and k_{-1} are forward and reverse rate constants, respectively. In each case, rate constants and an equilibrium constant ($k = k_1/k_{-1}$) were derived from the integrated form of Eq. (2) by assuming equilibrium concentrations were represented by the mean of the final two measurements in the time-course. An equilibrium partition coefficient, $(K_D)_e$ (ml g^{-1}), was calculated from the ratio of w/w pellet metal concentration at equilibrium, $[\text{MeX}]_e^*$, to aqueous metal concentration at equilibrium, $[\text{Me}]_e$, and a system response time, defined as the time required for the reaction to reach 63% of the new equilibrium (Turner et al., 2006), was derived from the reciprocal of the sum of the forward and reverse rate constants:

$$T_{\text{resp}} = \frac{1}{(k_1 + k_{-1})} \quad (3)$$

Constants defining all model fits with the exception of Zn, which was a contaminant of the control and whose pre-existent concentrations in beached pellets were relatively high and variable, are given in Table 2. Goodness of fit, represented by the regression coefficient defining the relationship between the integrated form of Eq. (2) and time, is better for trace metal uptake by the virgin pellets than by the beached pellets. This is because

interactions between metal and the beached pellet surface did not always appear to attain equilibrium, an effect attributed to the greater heterogeneity and porosity of the coated and fouled surface of aged plastics. Assuming that equilibrium is attained, system response times for both pellet types are within about 100 h and, in many cases, are less than 1 h. With the exception of Cu, which may have been affected by interferences from pre-existent metal, equilibrium partition coefficients are considerably higher for beached pellets than for virgin pellets; with respect to Pb, the difference in partitioning between pellet types is almost three orders of magnitude.

3.4. Adsorption isotherms

Isotherms defining the adsorption of trace metals to virgin and beached pellets are shown in Fig. 3 for the metals whose kinetic profiles were illustrated in Fig. 2. Variations among replicates were greater for the beached pellets, presumably due to the greater heterogeneity of the plastic surface incurred by aging. Both Langmuir and Freundlich models were fitted to the isothermic data. The former assumes monolayer adsorption to a homogeneous surface and is given as follows:

$$[\text{MeX}]_e^* = \frac{K_L[\text{MeX}]_{\text{max}}[\text{Me}]_e}{1 + K_L[\text{Me}]_e} \quad (4)$$

where, $[\text{MeX}]_e^*$ is the w/w concentration of metal adsorbed to the pellet surface, $[\text{Me}]_e$ is the equilibrium concentration of metal in

Table 2
 Constants defining time-dependent profiles of trace metal adsorption to virgin and beached polyethylene pellets as fitted using a pseudo-first-order model (Eqs. (1) and (2)).

	Virgin					Beached				
	k_1, h^{-1}	k_{-1}, h^{-1}	r^2	$T_{\text{resp}}, \text{h}$	$(K_D)_e, \text{ml g}^{-1}$	k_1, h^{-1}	k_{-1}, h^{-1}	r^2	$T_{\text{resp}}, \text{h}$	$(K_D)_e, \text{ml g}^{-1}$
Cr	0.055	0.45	0.974	1.97	11.6	0.061	0.025	0.598	11.6	221
Co	0.010	1.18	0.974	0.84	0.834	0.089	2.04	0.552	0.47	4.03
Ni	0.014	0.83	0.931	1.18	1.60	0.464	4.82	0.914	0.19	8.87
Cu	0.033	0.07	0.514	9.59	45.0	0.660	1.35	0.606	0.50	45.2
Cd	0.0002	0.01	0.649	105	1.24	0.002	0.265	0.126	3.75	7.94
Pb	0.002	0.67	0.986	1.49	0.245	0.210	0.130	0.912	2.94	149

solution, $[\text{MeX}]_{\text{max}}^*$ is the adsorption capacity of the metal and K_L (ml g^{-1}) is the Langmuir isotherm constant. The Freundlich equation assumes multilayer given as follows:

$$[\text{MeX}]_e^* = K_F [\text{Me}]_e^{1/n} \quad (5)$$

where K_F ($\mu\text{g}^{1-1/n} \text{g}^{-1}$) is the Freundlich constant and n is a measure of linearity. Values for the Langmuir and Freundlich constants, derived from linear regression analysis of $1/[\text{MeX}]_e^*$ versus $1/[\text{Me}]_e$, and non-linear regression of $[\text{MeX}]_e^*$ versus $[\text{Me}]_e$, respectively, are shown in Table 3 for trace metals that were unaffected by interferences from pre-existent metal or by experimental contamination. Despite the different assumptions of the two models and the different characteristics of the virgin and aged pellets, there are no clear or systematic differences in the goodness of fit (as r^2) to the datasets, either between the two models or between pellet type. (Note that Langmuir fits have been annotated for illustrative

purposes in Fig. 3.) Regardless of the model fits, and consistent with the kinetic results reported above, adsorption to beached pellets is greater than adsorption to virgin pellets, and adsorption capacities for beached pellets are greatest for Cr and Pb and lowest for Cd and Co.

3.5. General discussion

Analysis of individual polyethylene resin pellets collected from beaches and sediment flats of south west England has revealed variable concentrations of trace metals that, in some cases, exceed concentrations in local estuarine sediment. This is, perhaps, a surprising observation given that the geometric surface area of polythene pellets is a few $\text{cm}^2 \text{g}^{-1}$ (Mato et al., 2001) compared with BET specific surface areas of estuarine sediment on the order of several $\text{m}^2 \text{g}^{-1}$ (Millward, 1995).

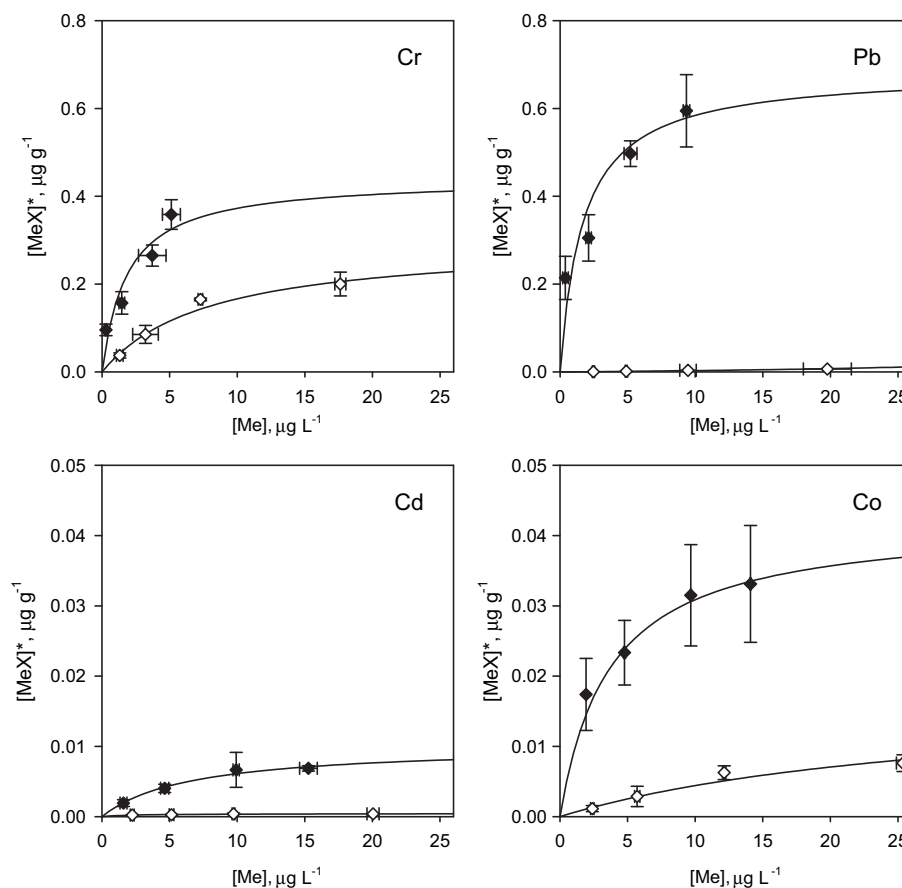


Fig. 3. Isotherms defining the adsorption of Cr, Pb, Cd and Co from seawater to virgin (\diamond) and beached (\blacklozenge) polyethylene resin pellets. Error bars represent one standard deviation about the mean of three determinations and lines represent Langmuir fits to the data according to Eq. (4) and whose constants are defined in Table 3.

Table 3

Constants defining trace metal adsorption to virgin and beached polyethylene pellets according to the Langmuir and Freundlich models (Eqs. (4) and (5), respectively). Note that interferences from pre-existent metal precluded fitting of beached Cu data and that Pb adsorption to virgin pellets was best defined by linear fitting ($r^2 = 0.988$; $(K_D)_e = 0.3 \text{ ml g}^{-1}$).

	Langmuir constants						Freundlich constants					
	Virgin			Beached			Virgin			Beached		
	$[\text{MeX}]_{\text{max}}^*$ $\mu\text{g g}^{-1}$	$k_L \text{ ml g}^{-1}$	r^2	$[\text{MeX}]_{\text{max}}^*$ $\mu\text{g g}^{-1}$	$k_L \text{ ml g}^{-1}$	r^2	$1/n$	$K_F \mu\text{g}^{1-1/n} \text{ g}^{-1}$	r^2	$1/n$	$K_F \mu\text{g}^{1-1/n} \text{ g}^{-1}$	r^2
Cr	0.297	0.127	0.96	0.441	0.503	0.78	0.624	0.038	0.83	0.570	0.131	0.79
Co	0.018	0.033	0.76	0.038	0.351	0.81	0.858	0.0006	0.84	0.344	0.014	0.61
Ni	0.008	0.047	0.80	0.070	2.67	0.82	0.671	0.0005	0.88	0.085	0.057	0.10
Cu	0.261	0.125	0.96	–	–	–	0.579	0.036	0.81	0.999	0.069	0.54
Cd	0.0004	0.413	0.98	0.010	0.140	0.77	0.287	0.0002	0.46	0.576	0.002	0.83
Pb	–	–	–	0.716	0.439	0.91	–	–	–	0.047	0.214	0.90

Despite the general assumption that plastics are relatively inert towards aqueous metals, virgin polyethylene pellets suspended in trace metal-amended seawater adsorb trace metals rapidly and in a Langmuir or Freundlich fashion with equilibrium partition coefficients (at $[\text{Me}] = 5 \mu\text{g L}^{-1}$) of up to about 50 ml g^{-1} . Presumably, metal adsorption proceeds through interactions between bivalent cations (e.g. Cu^{2+} , Cd^{2+} , Pb^{2+}) and oxyanions (e.g. $\text{Cr}_2\text{O}_4^{2-}$) with charged or polar regions of the plastic surface (effected by imperfections and the presence of charged contaminants and additives, for example), and via non-specific interactions between neutral metal-organic complexes and the hydrophobic surface of the bulk plastic medium. Aged, beached pellets accumulate trace metals to a significantly greater extent, with equilibrium partition coefficients ranging from about 4 ml g^{-1} (Co) to 220 ml g^{-1} (Cr). The reactivity of the surface of aged pellets is enhanced by both changes to the polymer itself and the presence of biofilms and chemical precipitates. With respect to the former, photo-oxidative weathering generates oxygen containing groups that increase the polarity of the polymer (Mato et al., 2001). Regarding the latter, accumulations of biofilms and hydrogenous precipitates increase the charge, roughness, porosity and hydrophilicity of the surface (Artham et al., 2009).

Although our enclosed, batch experiments have revealed that interactions between trace metals and the surface of virgin or beached pellets are both considerable and relatively rapid, the equilibrium constants that we have derived are likely underestimates of environmental values. Thus, metal adsorption in situ is predicted to be a longer term process as chemical precipitates and biofilms continuously accrue at the plastic surface; trace metal accumulation is also likely to be enhanced by co-precipitation, a slow process not replicated in short-term experiments conducted without the addition of hydrogenous metals. Overall, therefore, the relatively high concentrations of trace metals that we observe on beached pellets may be attributed to these sorptive mechanisms acting on pellets that are exposed to aqueous metals in the sea surface microlayer for up to decadal timescales.

The association of trace metals with plastics is likely to be a more general phenomenon, both in terms of other aquatic environments and with respect to different types and sizes of plastic. Accordingly, plastics may be considered as a vehicle for transport of metals in aquatic systems that has not, thus far, been acknowledged. Metal transport with plastics is particulate by definition but, at least with regard to small pieces of litter, is quasi-conservative, enabling metals to be transported considerable distances while buoyant. The association of trace metals with plastics also has implications for the transfer of these contaminants into the foodchain. Thus, invertebrates, fish, birds and mammals that mistake plastics for food (Teuten et al., 2009) have the potential to mobilise metals in their acidic, enzyme-rich digestive systems. Consequently, metals may be

either bioaccumulated or released back into seawater in a more soluble and biologically available form. Clearly, these and other potential impacts of plastic–metal interactions in the aquatic environment merit further study.

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