



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. HCrO_4^- and 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⁻¹.

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⁻¹ 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 HNO₃. 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⁻¹, 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⁻¹ 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 HNO₃ before a fixed concentration of 5 μg L⁻¹ 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⁻¹ of ¹¹⁵In and ¹⁹³Ir 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

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