



Heavy metals, metalloids and other hazardous elements in marine plastic litter

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ABSTRACT

Plastics, foams and ropes collected from beaches in SW England have been analysed for As, Ba, Br, Cd, Cl, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn and Zn by field-portable-x-ray fluorescence spectrometry. High concentrations of Cl in foams that were not PVC-based were attributed to the presence of chlorinated flame retardants. Likewise, high concentrations of Br among both foams and plastics were attributed to the presence of brominated flame retardants. Regarding heavy metals and metalloids, Cd and Pb were of greatest concern from an environmental perspective. Lead was encountered in plastics, foams and ropes and up to concentrations of $17,500 \mu\text{g g}^{-1}$ due to its historical use in stabilisers, colourants and catalysts in the plastics industry. Detectable Cd was restricted to plastics, where its concentration often exceeded $1000 \mu\text{g g}^{-1}$; its occurrence is attributed to the use of both Cd-based stabilisers and colourants in a variety of products.

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1. Introduction

Marine litter is a global problem, with sources of waste related to a variety of human activities that are both marine-based and land-based. Accumulation of litter is found at the sea surface, on the seabed and washed up on beaches and, because of the persistence and buoyancy of many processed materials, often represents a transboundary issue and one that affects regions remote from urbanisation or shipping. Marine plastics in particular have received a great deal of attention over the past two decades because of their scale of production, poor rates of recycling and durability (Browne et al., 2010).

Aside from the aesthetic and economic impacts, plastic waste also poses a hazard to navigation and a threat to the health and safety of humans and wildlife. Regarding the latter, the potential of plastic products and fragments for entanglement, strangulation and ingestion are well-documented for fish, birds and mammals (Carson, 2013; Yorio et al., 2014; McIntosh et al., 2015). Less understood, however, is the role of plastics in providing a vector for exposure to and accumulation of chemicals that are adsorbed to or incorporated within the polymeric matrix. Moreover, the majority of studies in this respect have targeted persistent organic micropollutants, like polychlorinated biphenyls and polycyclic aromatic hydrocarbons (Frias et al., 2010; Rochman et al., 2013; Gauque et al., 2015).

Given the widespread contemporary and historical use of heavy metals and metalloids by the plastics industry, it is perhaps surprising that very little attention has been paid to the occurrence and impacts of these elements in marine litter (Ashton et al., 2010; Nakashima et al.,

2012). Compounds of many metals and metalloids are currently used as catalysts, biocides, pigments for colour and UV and heat stabilisers and, while many of the more hazardous compounds, including those of Cd, Cr, Hg and Pb, have been phased out or banned, they are still likely to be encountered at elevated concentrations in litter derived from or containing older plastic products. According to a recent report prepared on behalf of the Norwegian Environmental Protection Agency (Hansen et al., 2013), for instance, certain historical materials or products are expected to contain concentrations of Hg up to $3000 \mu\text{g g}^{-1}$ and concentrations of Cd, Cr and Pb up to $50,000 \mu\text{g g}^{-1}$. Such concentrations are orders of magnitude greater than corresponding values one would expect to find in even the most contaminated marine sediments.

In the present paper, a variety of heavy metals and metalloids (As, Ba, Br, Cd, Cl, Cr, Cu, Hg, Ni, Pb, Se, Sb, Sn and Zn) and other elements that are potentially indicative of hazardous chemicals (Br, Cl) are analysed in samples of marine plastic litter collected from five beaches across south west England. Specifically, the focus is on objects and/or fragments of plastic, foam and rope, and analysis is performed by a field-portable-x-ray fluorescence spectrometer in a mode that is configured for the analysis of low density materials according to protocols described in detail elsewhere (Turner and Solman, 2016).

2. Materials and methods

2.1. Sampling and sample locations

Five beaches of contrasting aspect, profile, size, sediment characteristics, fetch, wave climate and usage, and that were not subjected to routine litter collection and were free of buildings, were visited just after

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high water on single occasions between late August and late September 2015 (Fig. 1). Chapel Porth (CP) and Constantine Bay (CB) are west- (Atlantic-) facing sandy beaches that are popular destinations for both tourists and surfers. While the sweeping arc of Constantine Bay is backed by a network of sand dunes, Chapel Porth is set in a sheltered cove that is bound by high, steep cliffs. Porth Kidney (PK) is an expansive, north-facing and dune-backed beach in St Ives Bay that lies at the mouth of a small, protected estuary (Hayle), while Saltram (SA) is a small, silty-sandy intertidal region on the east bank of a shallow, urbanised estuary (Plym) that is close to a recently capped landfill site. Mount Batten (MB) is a south-facing pebble-sand beach in Plymouth Sound, a bay that receives freshwater inputs from the Plym and Tamar estuaries and, being protected to the south by a 1.6 km breakwater, is a natural harbour for naval and commercial ships and a popular location for yachting.

On each beach, pieces of plastic litter that were visible to the naked eye were collected by hand from a transect of the high (or highest) water line. This line was readily apparent from the accumulation of debris and macroalgae and was either located on the beach itself (SA, PK), along the seaward edge of the dune system (CB), or on boulders and rocks at the landward limit of the backshore (MB, CP). Depending on the abundance of material, the lengths of the transects varied between about 10 m and 200 m, ensuring that at least 50 samples were collected in each case.

For the purposes of the present study, plastic litter is defined as relatively mobile, low density, poorly-degradable, manufactured or processed material. Items falling within this description were categorised on collection as 'plastics' (non-porous, moulded objects or fragments, and including rubber), 'foams' (pieces of open- or closed-cell expanded and extruded polymer) or 'ropes' (fragments of rigging, cord, netting and fishing line). While, strictly, all samples are plastic-based, this categorisation is consistent with distinct groupings within the OSPAR classification of plastic litter based on visual appearance (OSPAR Commission, 2010). From a practical perspective, this classification also reflects the requirement for different approaches to sample

preparation and differences in absorption of x-rays that relate to density and the presence of air within the matrix (Turner and Solman, 2016). While components of these categories made up the majority of the litter pool (>90% on a number basis), items neglected included pieces of masonry, objects and fragments that were composed principally or wholly of metal, pieces of glass or ceramic, paper and cardboard waste, and machined wood. Also neglected were foils or films of food packaging that had evidently been recently discarded as earlier, independent analyses of a variety of contemporary packaging failed to detect any of the elements under study.

Categorised litter collected from each beach was stored in a series of clear polyethylene bags and transported to the laboratory. Here, individual items were cleared of sand and other debris under running tap water and with the aid of a Nylon brush before being dried at 40 °C in an oven for 12 h or, for foams, under desiccation at room temperature for 48 h. Samples were then weighed on a three- or five-figure balance, depending on their size, and stored individually in labelled polyethylene specimen bags at room temperature and in the dark until required for XRF analysis.

2.2. XRF analysis

All samples were analysed by energy dispersive FP-XRF using a battery-powered Niton XRF analyser (model XL3t 950 He GOLDD+) for elements of a hazardous nature (or elements indicative of hazardous compounds) and/or regarded as important marine contaminants (that is, As, Ba, Br, Cd, Cl, Cr, Cu, Hg, Ni, Pb, Se, Sb, Sn and Zn). The instrument was operated in a plastics mode that is capable of quantifying the concentrations of up to 18 elements, whose fluorescent peaks range from 2.62 keV (Cl-K α) to 32 keV (Ba-K α), in complex, low density materials through a fundamental parameters-based alpha coefficient correction model. Fundamental parameters eliminates the requirement for sample-specific standards, has a wide dynamic range and is independent of the size and shape of the surface (Bosco, 2013).

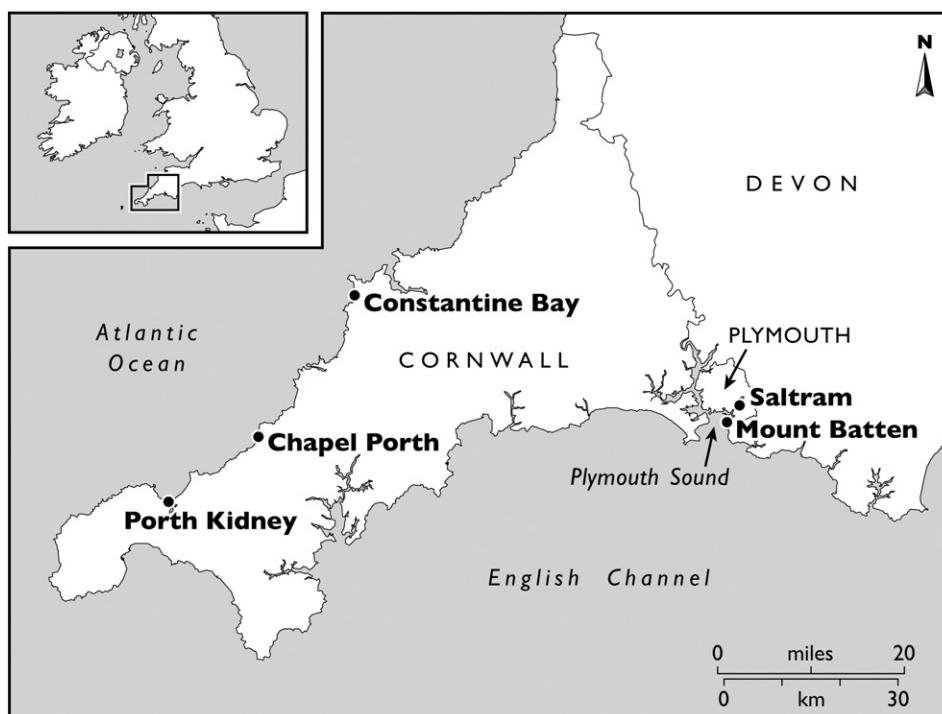


Fig. 1. Locations of the five beaches in SW England sampled in the present study.

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