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# Elemental concentrations and bioaccessibilities in beached plastic foam litter, with particular reference to lead in polyurethane

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## ABSTRACT

Seventy samples of foamed plastic collected from a high-energy, sandy beach in SW England have been characterised by FTIR and XRF. Most samples were polyurethane (PU;  $n = 39$ ) or polystyrene (PS;  $n = 27$ ) that were associated with variable concentrations of Br-Cl, Fe and Zn, indicative of the presence of halogenated flame retardants, iron oxides and Zn-based additives, respectively. Many samples of rigid PU contained Pb, historically used as a catalyst, at concentrations of up to  $16,000 \mu\text{g g}^{-1}$ . A physiological extraction test that simulates the conditions in the gizzard of plastic-ingesting seabirds was applied to selected samples and results revealed that while Br and Zn were not measurably bioaccessible, Pb mobilisation progressed logarithmically over a period of time with maximum accessibilities after 220 h of  $\sim 10\%$  of total metal. Foamed PU is a source of bioaccessible Pb in the marine environment that has not previously been documented.

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## 1. Introduction

Because of their wide usage in society, coupled with a high durability, poor degradation and low density, plastics are widely distributed throughout the global ocean and littoral zone (Li et al., 2016). The impacts of plastic waste in the marine environment are many and varied and include a reduction in aesthetic and amenity value, damage to vessels and fishing gear, a threat to public safety and adverse effects on wildlife (Gregory, 2009). Regarding the latter, plastics can cause entanglement, strangulation and suffocation, alterations to benthic community structure, and starvation and choking via ingestion when material is mistaken for food (Baulch and Perry, 2014; Sigler, 2014; Wilcox et al., 2016). Through the association of chemicals with the polymeric matrix or the adsorption of aqueous species to the polymer surface, ingestion can also act as a vehicle for the transfer of contaminants into the foodchain (Ashton et al., 2010; Rochman et al., 2013; Tanaka et al., 2013).

Beached plastic items categorised by OSPAR include multi-pack yokes, bags, bottles, engine oil containers, injection gun containers, cigarette lighters, toys, crates, food packaging, lobster pots, rope, cord, netting and foams (OSPAR Commission, 2010). With respect to foams, different size categories of expanded or extruded polystyrene (PS) pieces are specified but polyurethane (PU) is not mentioned. This is perhaps surprising because beach surveys that we have recently conducted have revealed an abundance of foamed PU that, in some cases,

represents the dominant form of plastic litter on a number basis (Turner, 2016; Turner and Solman, 2016). The widespread occurrence of PU waste may be attributed to its extensive application in the domestic, industrial, transportation and maritime settings, with an annual demand among synthetic polymers that is exceeded only by polyethylene, polypropylene and polyvinyl chloride (Plastics Europe, 2015). PU foam may be classified as flexible or rigid, with the former being open-cell, porous and having a density typically between  $10$  and  $80 \text{ kg m}^{-3}$ , and the latter being closed-cell, semi-porous to non-porous and having a density ranging from  $30$  to  $400 \text{ kg m}^{-3}$ . Flexible PU foam is used for packaging and as cushioning in furniture and bedding, under carpets and in automobile and aircraft seating, while rigid PU foam is used principally as an insulator in buildings, refrigerators, pipelines, vehicles and storage facilities. Additional, maritime applications of rigid foam involve flotation, buoyancy, support and void filling in boats, pontoons, docks, baffles and barrels (Szycher, 1999).

PU is formed by reacting a diisocyanate or polyisocyanate with an oligomeric polyol (polyester or polyether) to produce a urethane linkage, with the precise properties of the product dependent on the nature (e.g. molecular weight) of the reactants and the preparation process. For the formation of PU foam, a blowing reaction is also required in which a gas is either added or created. Additives used in the production of PU include tertiary amine or metal salt catalysts for the polymerisation and blowing reactions, pigments for colour, fillers, halogenated flame retardants, smoke suppressants and plasticisers. Based on these characteristics and the carcinogenic and mutagenic properties of its component monomers, Lithner et al. (2011) ranked polyurethanes among the most hazardous polymers in current production. Accordingly, PU

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waste is a potential source of a variety of highly toxic contaminants to the environment whose concentrations, mobilities and fates are largely unknown.

In the present study, foamed plastic waste has been collected from a section of a high-energy, macrotidal sandy beach in south west England and classified by polymer type using Fourier transform infra-red (FTIR) spectrometry. The elemental composition of the foams is ascertained by field portable-x-ray fluorescence (FP-XRF) spectrometry configured in a 'plastics' mode for the analysis of low density samples, and the bioaccessibilities of the predominant elements in selected foams (and mainly PU) is determined by means of a physiological solution that simulates the digestive fluids encountered in the gizzard of a plastic-ingesting marine bird.

## 2. Materials and methods

### 2.1. Sampling and sample location

Whitsand Bay is a protected coastal region a few km to the west of Plymouth Sound that is characterised by an expansive, sandy beach. The beach faces south west and directly towards the western English Channel and is backed by steep cliffs that, at high tide, fragment the region into a series of rocky coves. During October 2015, pieces of foamed plastic that were visible to the naked eye were collected by hand from a 30 m-wide transect of the beach at Tregantle (50.3525, -4.2719) between the high water line and the backshore. Samples were stored in a series of clear polyethylene bags and transported to the laboratory where individual items were cleared of sand and other debris under running tap water and with the aid of a Nylon brush before being dried under vacuum desiccation at room temperature for 48 to 96 h. Samples were then weighed on a five-figure balance and measured for thickness through the flattest surface using 300 mm Allendale digital callipers before being stored individually in labelled polyethylene specimen bags and in the dark pending analysis.

### 2.2. FTIR analysis

In order to identify the polymeric composition of the foams, samples were analysed by FTIR spectroscopy. Initially, samples were analysed by attenuated total reflection- (ATR-) FTIR using a Bruker ALPHA Platinum ATR QuickSnap A220/D-01 spectrometer. Samples were cut to a suitable size using a stainless steel scalpel before being firmly clamped down on to the ATR diamond crystal in order to ensure good contact and sufficient penetration of the evanescent wave. Measurements, consisting of 16 scans in the range 4000 to 400  $\text{cm}^{-1}$  and at a resolution of 4  $\text{cm}^{-1}$ , were activated via Bruker OPUS spectroscopic software, and polymer identification involved a comparison of sample transmittance spectra with libraries of reference spectra. Where indetification was not definitive, sample offcuts were re-analysed by photoacoustic FTIR using a Bruker Vertex 70 spectrometer coupled with an MTEC 300 photoacoustic cell that was purged with He. Measurements were recorded as an average of 32 scans in the range 4000 to 400  $\text{cm}^{-1}$  and at a resolution of 8  $\text{cm}^{-1}$  with activation and identification undertaken as above.

### 2.3. XRF analysis

Sample surfaces were analysed for a suite of elements, of which Br, Cl, Fe, Pb and Zn are the focus of the present study, by energy dispersive field portable-XRF using a battery-powered Niton XRF analyser (model XL3t 950 He GOLDD+). The instrument was operated in a plastics mode that employs a compensation for mass absorption coefficient based on Compton scatter and corrects for sample thickness down to 0.05 mm. The XRF was used in the laboratory in a bench-top accessory stand and was connected to a laptop computer via USB and a remote trigger. Samples were placed on 3.6  $\mu\text{m}$  polyester film and positioned centrally and with the measurement surface face downwards over the XRF

detector window. On closing the steel shield of the stand, measurements, with appropriate thickness correction, were activated through the laptop for a total period of 120 s (60 s each at 50 kV/40  $\mu\text{A}$  and 20 kV/100  $\mu\text{A}$ ). Spectra were quantified by fundamental parameters to yield elemental concentrations on a dry weight basis (in  $\mu\text{g g}^{-1}$ ) with a counting error of  $2\sigma$  (95% confidence). At the end of each measurement session data were downloaded to the laptop using Niton data transfer (NDT) PC software.

Limits of detection, as  $1.5 \times 2\sigma$ , varied according to the precise density, shape and thickness of sample, but mean values were about 20  $\mu\text{g g}^{-1}$  for Br and Pb, 40  $\mu\text{g g}^{-1}$  for Zn and 300  $\mu\text{g g}^{-1}$  for Cl and Fe. Multiple analyses ( $n = 5$ ) of two Niton reference plastics (PN 180-554, batch SN PE-071-N, and PN 180-619, LOT#T-18) that had been impregnated with Br and Pb revealed measured concentrations that were within 10% of reference concentrations.

### 2.4. PBET

In order to evaluate the bioaccessibility of Pb and other elements (with the exception of Cl), selected foams ( $n = 8$ ) of varying appearance and polymeric and elemental composition (based on XRF and FTIR analyses) were subjected to an avian physiologically-based extraction test (PBET). The extraction was modelled on the digestive characteristics of the northern fulmar, *Fulmarus glacialis*, a procellariiform seabird known to ingest substantial quantities of plastic debris. Because dissected specimens have revealed ingested plastic within the proventriculus-gizzard but not within the duodenum (Furness, 1985; Robards et al., 1995), the PBET described below replicates conditions encountered in the former components of the digestive tract.

Briefly, the extraction fluid was prepared by dissolving 10 g of pepsin (lyophilised powder from porcine gastric mucosa; Sigma-Aldrich) in 1 L of 0.1 M NaCl solution and adjusting the pH by dropwise addition of 1 M HCl to 2.5. Shavings of about 0.1 g of each foam sample were weighed into individual 60 mL screw-capped polypropylene centrifuge tubes before 40 mL of extraction fluid was added. All tubes, including a control containing no solid, were then capped and incubated in a shaking water bath set at 100 rpm and at 40 °C, or the average body temperature of marine birds (Warham, 1996), for a period of about 220 h. Although this is longer than typical proventriculus-gizzard retention times for food in piscivorous birds, ingested plastic may remain trapped in this part of the digestive tract for periods of weeks or months (Avery-Gomm et al., 2012). At pre-determined time-intervals, 1 mL aliquots of extract, including triplicate aliquots at selected intervals, were pipetted in to individual Sterilin tubes where they were diluted to 5 mL with 2%  $\text{HNO}_3$  and stored at 4 °C and in the dark pending analysis.

### 2.5. Analysis of extracts

Extracts were analysed for  $^{79}\text{Br}$ ,  $^{56}\text{Fe}$ ,  $^{208}\text{Pb}$  and  $^{66}\text{Zn}$  by collision cell-inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-series II (ThermoElemental, Winsford UK) with a concentric glass nebuliser and conical spray chamber. The instrument was calibrated externally using five mixed standards and five blanks prepared in 2%  $\text{HNO}_3$  and operated under conditions described elsewhere (Turner and Holmes, 2015). Limits of detection, based on three standard deviations arising from blank measurements, ranged from about 0.03  $\mu\text{g L}^{-1}$  for Pb to about 10  $\mu\text{g L}^{-1}$  for Br and Fe.

## 3. Results

### 3.1. Sample characteristics

Overall, 70 samples were retrieved from Whitsand Bay, with a selection illustrated in Fig. 1. Sample mass ranged from a few mg to >10 g and thickness through the flattest (measurement) surface ranged from about 2 to 40 mm. FTIR spectra revealed that the majority of

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