



# Cadmium, lead and bromine in beached microplastics<sup>☆</sup>



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## ABSTRACT

Samples of microplastic ( $n = 924$ ) from two beaches in south west England have been analysed by field-portable-x-ray fluorescence (FP-XRF) spectrometry, configured in a low-density mode and with a small-spot facility, for the heavy metals, Cd and Pb, and the halogen, Br. Primary plastics in the form of pre-production pellets were the principal type of microplastic (>70%) on both beaches, with secondary, irregularly-shaped fragments representing the remainder of samples. Cadmium and Pb were detected in 6.9% and 7.5% of all microplastics, respectively, with concentrations of either metal that exceeded  $10^3 \mu\text{g g}^{-1}$  usually encountered in red and yellow pellets or fragments. Respective correlations of Cd and Pb with Se and Cr were attributed to the presence of the coloured, inorganic pigments, cadmium sulphoselenide and lead chromate. Bromine, detected in 10.4% of microplastics and up to concentrations of about  $13,000 \mu\text{g g}^{-1}$ , was mainly encountered in neutrally-coloured pellets. Its strong correlation with Sb, whose oxides are effective fire suppressant synergists, suggests the presence of a variety of brominated flame retardants arising from the recycling of plastics originally used in casings for heat-generating electrical equipment. The maximum bioaccessible concentrations of Cd and Pb, evaluated using a physiological extraction based on the chemical characteristics of the proventriculus-gizzard of the northern fulmar, were about  $50 \mu\text{g g}^{-1}$  and  $8 \mu\text{g g}^{-1}$ , respectively. These concentrations exceed those estimated for the diet of local seabirds by factors of about 50 and 4, respectively.

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## 1. Introduction

Plastic litter is a global problem that has a variety of environmental, social, aesthetic and economic impacts. In the marine environment, floating, deposited and beached plastics pose risks to marine wildlife, principally through entanglement and ingestion. Regarding the latter, the extent of the impacts bears some inverse relationship to particle size in that the smaller the plastic, the greater its potential to affect a wider range of organisms through, for example, blockages and internal abrasions (Wesch et al., 2016). Ingestion of microplastics, or plastics of diameter <5 mm (Arthur et al., 2009), may occur intentionally (e.g. when particles are mistaken for food), incidentally (e.g. during filter feeding), via consumption of contaminated prey, or, regarding cetaceans, through inhalation (Lusher, 2015).

Microplastics in the marine environment can be classified as primary or secondary according to their origin (Hidalgo-Ruz et al.,

2012). Thus, primary microplastics are those that have been manufactured for a specific purpose and usually enter the environment from spillages or via wastewater. Primary microplastics are frequently identifiable and include pre-production pellets used for the moulding of finished articles and microbeads employed as exfoliating agents in cosmetic and personal care products. Secondary microplastics are those derived from the gradual breakdown and fragmentation of larger objects or fragments (macroplastics) that have entered the environment from a variety of additional sources such as shipping, fishing activities and coastal littering.

Another concern regarding ingested microplastics is their propensity to release additives from the polymeric matrix while transiting or trapped in the gastro-intestinal tract. In this respect, most focus has been on organic compounds added to plastics to enhance their performance, durability and safety, like plasticisers, antioxidants and flame retardants (Tanaka et al., 2013; Jang et al., 2016; Narvaez Valderrama et al., 2016). However, recent research using field-portable-x-ray fluorescence (FP-XRF) spectrometry configured in a low density, 'plastics' mode has reported high concentrations of many hazardous elements in beached marine litter, and in particular the toxic heavy metals, cadmium and lead (Turner and Solman, 2016; Turner, 2016). Inorganic compounds of

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these metals were used as heat and UV stabilisers in polyvinyl chloride (PVC) and as coloured pigments in other plastics before being restricted or phased out (Hansen et al., 2010).

Based on these observations, it would be reasonable to hypothesise that hazardous elements are present in primary and secondary microplastics, and that particle ingestion affords a potential route of their exposure to a range of marine organisms. To this end, therefore, we examine the elemental concentrations in primary and secondary microplastics retrieved from two beaches in south west England using FP-XRF. Coupled with a 'small-spot' facility that collimates the x-ray beam to a width of 3 mm, this technique is able to provide rapid, quantitative information on the elemental content of plastics down to about 1 mm in diameter and 0.1 mm in thickness. The focus of the study is on elements that are both hazardous and restricted in plastics (RoHS, 2006; Hansen et al., 2010; European Chemicals Agency, 2016); namely, the halogen, Br, as an indicator of brominated compounds that are used as flame retardants, and the heavy metals, Cd and Pb. In order to evaluate the avian bioaccessibility of these elements, selected samples are digested in a physiological fluid that mimics the chemistry of a seabird proventriculus-gizzard and the digests analysed by inductively coupled plasma-mass spectrometry (ICP-MS).

## 2. Materials and methods

### 2.1. Sampling and sample processing

Samples were collected from two high-energy, macrotidal, sandy beaches in south west England that are popular with tourists, surfers and other recreational users (Fig. 1). Whitsand Bay, on the south (English Channel) coast of Cornwall comprises an expansive, 8-km, south west-facing beach that is backed by steep cliffs. Woolacombe, on the north (Atlantic Ocean) coast of Devon is a 3-

km, west-facing beach that is flanked by shallow, grassy sand dunes.

Selective sampling was undertaken on single occasions and about an hour after high water during December 2015 (Woolacombe) and January 2016 (Whitsand). Samples of non-porous, moulded plastics that were visible to the naked eye were retrieved from a 10 m transect of the strandline using plastic tweezers and stored in a clear, polyethylene box. (Note that small pieces of foamed plastic and filamentous waste were not considered in the present study.) Sample size was screened in situ with a clear plastic ruler and measured more accurately with callipers in the laboratory (see below). Our working definition of microplastics was <5 mm in at least two dimensions and no more than 10 mm in any one dimension, with visibility and analytical constraints resulting in a minimum primary particle diameter of about 1 mm. This size range is consistent with the diameters of plastics typically recovered from the digestive environments of different seabirds (Hidalgo-Ruz et al., 2012).

In the laboratory, samples from each beach were rinsed in Millipore Milli-Q water through a sieve and with the aid of a Nylon brush in order to remove debris and epiphytes before being dried at 40 °C for 24 h. After recording the total dry weights using a two figure balance, samples were divided according to appearance as primary plastics (identifiable objects) or secondary plastics (unidentifiable fragments derived from the breakdown of primary products) and coded according to colour.

### 2.2. FTIR analysis

The component polymers of selected samples ( $n = 30$ ) were determined by Fourier transform infra-red (FTIR) spectroscopy using a Bruker ALPHA Platinum attenuated total reflection QuickSnap A220/D-01 spectrometer. Samples were clamped down on to the ATR diamond crystal before measurements, consisting of

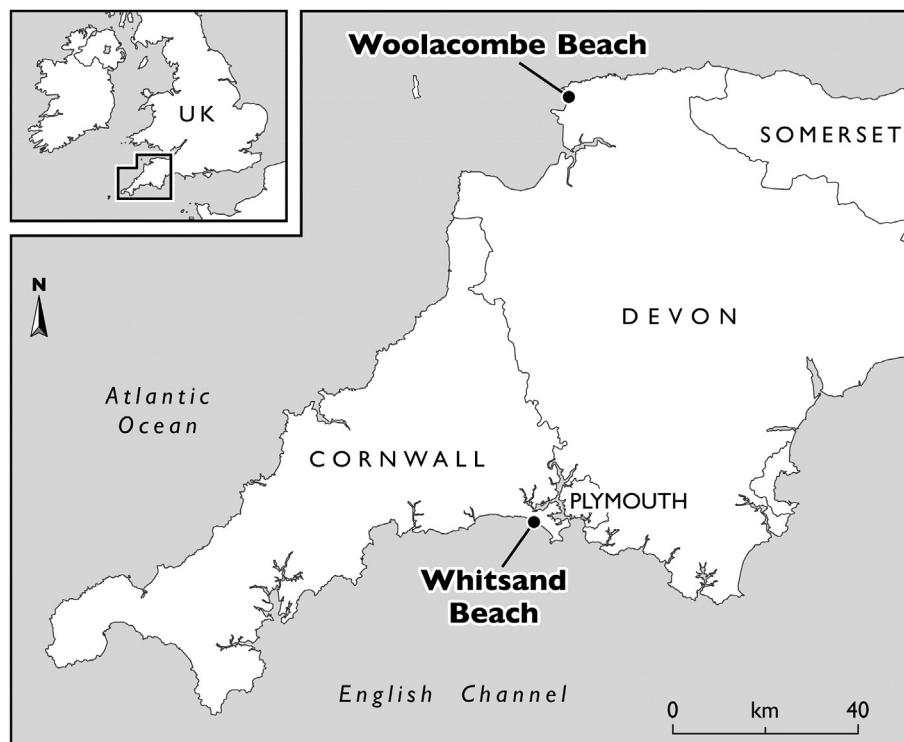


Fig. 1. Locations in south west England for the sampling of microplastics.

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