Cadmium, lead and bromine in beached microplastics

Angelo Massos & Andrew Turner*

School of Geography, Earth and Environmental Sciences

Plymouth University

Drake Circus

Plymouth PL4 8AA

UK

*Corresponding author. Tel: +44 1752 584570; Fax: +44 1752 584710; e-mail: aturner@plymouth.ac.uk

http://dx.doi.org/10.1016/j.envpol.2017.04.034

Accepted 14/4/17.

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 μg 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 μg 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 μg g^{-1} and 8 μg g^{-1}, respectively. These concentrations exceed those estimated for the diet of local seabirds by factors of about 50 and 4, respectively.

Keywords: cadmium; lead; bromine; microplastics; pellets; flame retardants

Capsule: XRF analysis of beached microplastics reveals the common occurrence of the hazardous elements, Cd, Pb and Br

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 ex-foliating 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 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 and distributions 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 (Figure 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 items of foamed plastic were not considered because of their friability and difficulties in identification, while small pieces of filamentous waste were not sampled because strands were generally too thin to perform XRF analysis.) 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^{o}C for 24 hours. 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 16 scans in the range 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1}, were activated via Bruker OPUS spectroscopic software. Identification involved a comparison of sample transmittance spectra with libraries of reference spectra.

2.3. XRF analysis

Samples were analysed for a suite of elements, of which Cd, Pb and Br are the focus of the present study, by energy dispersive FP-XRF using a battery-powered Niton XRF analyser (model XL3t 950 He GOLDD+) configured in a 'plastics' mode. Although the general approach has been described and independently validated elsewhere (Turner and Solman, 2016), the current study makes use of the instrument's

149 ‘small-spot’ facility for probing samples smaller than the 10-mm diameter of the
150 detector window. Here, 3-mm collimation is applied to the beam by means of a
151 tapered, tungsten alloy tube of appropriate distal exit aperture diameter that is aligned
152 over the x-ray source via a geared shutter mechanism.
153
154 In the laboratory, the instrument was fixed, nose-upwards, into a Thermo Fisher
155 Scientific accessory test stand (PN 420-017) and connected to a laptop computer via
156 USB. Each sample was measured for thickness through the flattest (measurement)
157 surface using digital callipers before being placed on a 20 cm^2, 3.6 μm thick polyester
158 film that was suspended above the detector window. The sample was positioned
159 centrally over the window using plastic tweezers, a process aided by referring to real-
160 time video footage projected on the laptop through a CCD camera located next to the
161 x-ray source. On closing the shield of the stand, measurements, with appropriate
162 thickness correction, were activated through the laptop for 60 seconds, comprising
163 periods of counting of 40 seconds at 50 kV and 40 μA and 20 seconds at 20 kV and
164 100 μA. Spectra were quantified by fundamental parameters to yield elemental
165 concentrations on a dry weight basis (in $\mu g\ g^{-1}$) and a counting error of 2σ (95%
166 confidence) that were downloaded to the laptop using Niton data transfer (NDT) PC
167 software.
168
169 Limits of detection, defined as 3σ and calculated by fundamental parameters, varied
170 according to the precise density, shape, thickness and composition of sample, and
171 ranged from about 30 to 50 $\mu g\ g^{-1}$ for Cd, 5 to 20 $\mu g\ g^{-1}$ for Pb and 4 to 10 $\mu g\ g^{-1}$ for
172 Br. Multiple analyses (n = 20) of two Niton reference plastics that had been
173 impregnated with Cd, Pb and Br (PN 180-554, batch SN PE-071-N) and Cd and Pb

(PN 180-619, LOT#T-18) revealed measured concentrations that were within 5% of certified values.

2.4. PBET

In order to evaluate element bioaccessibility in the microplastics, ten samples of varying colour, appearance and elemental composition (based on XRF analysis) were subjected to a marine avian physiologically-based extraction test (PBET) (Turner and Lau, 2016). The extraction was modelled on the digestive characteristics of the proventriculus-gizzard of the northern fulmar, *Fulmarus glacialis*, a procellariform known to ingest substantial quantities of microplastics. Briefly, digestive fluid was prepared by dissolving 10 g of pepsin (lyophilised powder from porcine gastric mucosa; Sigma-Aldrich) into one litre of 0.1 M NaCl solution and adjusting the pH by addition of 1 M HCl to 2.5. Selected samples were weighed into individual 60 ml screw-capped polypropylene centrifuge tubes to which 40 ml of extraction fluid was added. All tubes, including a control containing no solid material, were then capped and incubated in a shaking water bath set at 100 rpm and at 40 ^{o}C. After a period of about seven days (168 h), 1 ml aliquots of extract from each tube were pipetted into individual Sterilin tubes where they were diluted to 5 ml with 2% HNO_3 and stored at 4 ^{o}C and in the dark pending analysis.

2.5. Analysis of extracts

Cadmium, Pb and Br were determined in the PBET extracts by collision cell-ICP-MS using a Thermo X-series II (Thermo Elemental, Winsford UK) with a concentric glass nebuliser and conical spray chamber. The ICP was calibrated externally using five mixed standards and five blanks prepared in 2% HNO_3 and operated under conditions

described elsewhere (Turner and Holmes, 2015). Limits of detection, based on three standard deviations arising from blank measurements, were about 0.5 μg L^{-1} for Cd and Pb and about 10 μg L^{-1} for Br, or, on a dry weight basis and for a representative mass of microplastic of 35 mg, about 0.6 μg g^{-1} and 11 μg g^{-1}, respectively.

3. Results and Discussion

3.1. Sample characteristics

In total, 924 samples of microplastic that satisfied the size criteria outlined above were analysed by FP-XRF, with a summary of their categorisation and colour coding given in Table 1. The total mass of material retrieved from Whitsand (n = 436) was 16.35 g, with an average individual mass of microplastic of 37.2 mg, while from Woolacombe (n = 488), the total mass was 16.50 g with an average individual mass of 33.8 mg. On both beaches, the only identifiable pieces of primary plastic were cylindrical and disk-shaped pre-production pellets, and these comprised about 90% and 75% of all samples from Whitsand and Woolacombe, respectively. Colour coding revealed that the majority of primary, pelletised plastics from both beaches were white-clear (including translucent and off-white), with the next most abundant colours being black and orange-brown; the latter category included a large number of aged, translucent pellets whose distinctive amber colouration is likely to have been caused by the photo-oxidative formation of by-products having quinonoidal structures (Endo et al., 2005). The most common colours encountered in secondary, fragmented and irregularly-shaped microplastics were white and red, while colour differences between the two beaches included a relatively high number of purple pellets from Whitsand, and the absence of red and grey primary plastics from Woolacombe.

FTIR analysis revealed that most samples considered were polyethylene or polypropylene, with the remainder being of polystyrene construction. Out of all samples analysed by XRF, and based on chlorine content measured at 2.62 and 2.82 keV, only three (white fragments from Woolacombe) were classified as polyvinyl chloride (PVC). Significantly, therefore, it would appear that nearly all samples have a density less than that of sea water across its normal temperature range.

3.2. Occurrence and concentrations of Cd, Pb and Br

Also shown in Table 1 are the numbers of microplastics in which Cd, Pb and Br were detected by XRF. Overall, Cd was detected in about 7% of all samples, and was more abundant on a number basis in pellets and on a percentage basis in fragments. Although the number of cases in which Cd was detected was greatest among white microplastics, the highest percentages of detectable Cd were encountered in purple and red samples. Within the purple category, Cd was detected exclusively in production pellets, while in red samples the metal was detected in both pellets and fragments.

Lead was detected in 7.5% of all samples analysed and, like Cd, was more abundant on a number basis in plastic pellets and on a percentage basis in plastic fragments. Regarding colour categories, the number of cases in which Pb was detected was greatest among black samples, while the highest percentages of detectable Pb were encountered in grey, purple and black plastics; Pb occurred least frequently in white-clear microplastics, with only one out of nearly 500 pellets of this colour containing measurable quantities of the metal.

249 Bromine was detected in more than 10% of all samples analysed, and in a greater
250 number of pellets than fragments but in similar percentages of the two types of
251 microplastic. Overall, and on both a number basis and percentage basis, Br was most
252 frequently detected amongst samples that were neutrally-coloured (black, grey and
253 white-clear).
254
255 Table 2 summarises the occurrences and co-associations (but not correlations) of the
256 three elements on both beaches and among the two types of microplastic. Thus, in
257 total, one or more of the elements was encountered in 182 samples, or about 20% of
258 all microplastics analysed. Cadmium and Pb were detectable in the same sample in
259 eight cases, Cd and Br in three cases and Pb and Br in 20 cases, while all three
260 elements co-existed in five, additional cases. Co-associations were more common at
261 Whitsand (n = 28) than at Woolacombe (n = 8) and, overall, were most frequent
262 among black pellets (n = 16).
263
264 The distribution of Cd, Pb and Br concentrations for both beaches and among the two
265 types of microplastic is shown in Table 3. For Cd, concentrations spanned two orders
266 of magnitude and from about 40 to 3400 μg g^{-1}, with mean and median concentrations
267 higher in plastic fragments than in production pellets. Although the highest Cd
268 concentration was recorded in a grey pellet, most samples containing concentrations
269 above 1000 μg g^{-1} were red in colour, with concentrations exceeding 100 μg g^{-1}, or
270 the RoHS (2006) maximum level for the metal, also encountered in green, black and
271 orange microplastics.
272

Regarding Pb, concentrations spanned more than three orders of magnitude and from about 3 to over 5000 μg g^{-1}. Mean and median concentrations were higher in fragments than in primary microplastics, with concentrations in excess of the RoHS (2006) maximum Pb level of 1000 μg g^{-1} encountered in a number of red, yellow and green fragments and in a single, yellow pellet.

Concentrations of Br spanned more than three orders of magnitude and from about 4 to over 13,000 μg g^{-1}. Median concentrations were similar among both fragments and pellets from the two beaches, with an elevated mean concentration in Whitsand fragments attributed to an exceptionally high concentration in a grey pellet. Concentrations exceeded the RoHS (2006) limit values for various brominated compounds (but not Br itself) of 1000 μg g^{-1} in six cases, and samples containing the halogen at concentrations above 100 μg g^{-1} were restricted to samples of neutral colour.

3.3. Relationships with other elements and composition of additives

Despite lack of inter-element correlations among Cd, Pb and Br, correlations were observed with additional elements analysed by XRF. Thus, concentrations of Pb in pellets and fragments from both beaches were highly correlated with concentrations of Cr, where detected, and with a slope derived from linear regression of about 2 (Figure 2). The majority of samples conforming to this relationship were red fragments and yellow fragments and pellets, qualitatively consistent with the presence of the pigments, lead chromate molybdate sulphate red ($Pb(Cr,S,Mo)O_4$) and lead chromate, ($PbCrO_4$), respectively. In addition to Pb, these pigments contain Cr in its hexavalent form (although XRF is not able to verify elemental speciation) which, because of its

298 carcinogenicity and toxicity to reproduction, is also both hazardous and restricted in
299 plastics (Hansen et al., 2010; European Chemicals Agency, 2016), with an RoHS
300 (2006) limit value of 1000 μg g^{-1}.
301
302 Concentrations of Cd in the microplastics were correlated with concentrations of Se,
303 where detected, and with a slope of about 5 (Figure 3). Here, samples were restricted
304 to both pellets and fragments that were red or orange in colour, consistent with the use
305 of the pigment, cadmium sulphoselenide, a solid solution of CdS and CdSe whose
306 colour can be bright orange or bright red depending on the ratio of Se to S. Although
307 no hazards have been classified for the pigment itself by the European Chemicals
308 Agency (2016), compounds of both Cd and Se are known to be highly toxic (Ayres
309 and Hellier, 1998).
310
311 Bromine concentrations were highly correlated with concentrations of Sb, where
312 detected, and with a slope of about 2 derived from linear regression analysis of the
313 data (Figure 4); moreover, microplastics exhibiting this relationship were restricted to
314 pellets that were neutrally-coloured, and mainly black. These observations are
315 consistent with microplastics impregnated with both a variety of brominated
316 compounds as halogenated flame retardants and oxides of antimony as fire
317 suppressant synergists (Dupont et al., 2016). However, although the mass ratio of Br
318 to Sb is similar to that employed in the plastic casings of heat-generating electronic
319 and electrical goods (Papazoglou, 2004), the concentrations of Br measured herein are
320 too low to provide adequate flame retardancy. This suggests that pellets are not the
321 feedstock for the electronics industry itself but have been derived from diluted,

322 recycled electrical waste and are destined for the more general manufacturing market
323 (Leslie et al., 2016).
324
325 *3.4. Implications for plastic-consuming seabirds*
326 Previous research has shown that trace metals are able to interact with microplastics
327 suspended in sea water through adsorption onto the aged and coated surface, with
328 resulting concentrations from this process that are typically below 1 μg g^{-1} (Rochman
329 et al., 2014; Turner and Holmes, 2015; Brennecke et al., 2016). More recently,
330 however, XRF analysis of marine litter has revealed considerably higher
331 concentrations of metals and other hazardous elements in many plastics that are an
332 inherent part of the polymeric matrix (Turner, 2016). The present study has confirmed
333 that this inherent load is also encountered in beached microplastics of both primary
334 and secondary origin. Since the densities of the majority of samples analysed herein
335 are less than the density of sea water they are positively buoyant and amenable to
336 seabirds and other organisms that mistake them for food while filtering, skimming,
337 hydroplaning or diving (Acampora et al., 2014).
338
339 The total quantity of Cd, Pb and Br per g of microplastic was estimated for Whitsand
340 and Woolacombe from the overall mean elemental concentration (for pellets and
341 fragments combined) multiplied by the fraction of total samples in which the
342 corresponding element was detected. For Cd and Pb, estimates of 30 μg were obtained
343 for both beaches, while for Br, estimates of 59 μg and 37 μg were obtained for
344 Whitsand and Woolacombe, respectively. The quantities of plastic-bound Cd and Pb
345 exceed the respective mean quantities in local beach sand (< 1 μg and about 10 μg)
346 and in local crab tissue (1 and 2 μg) (Schuwerack et al., 2007), the latter representing

347 an important dietary component of many seabirds (Schwemmer and Garthe, 2005).
348 Comparisons for Br are not as straightforward since its occurrence in microplastics is
349 attributed to the presence of a complex mixture of halogenated flame retardants.
350 However, that the concentration of Br as brominated flame retardants in marine
351 sediment and shellfish is generally a few tens of ng g^{-1} or lower (Munschy et al.,
352 2015; Suhring et al., 2015) suggests a quantity of equivalent Br in microplastic that is
353 orders of magnitude greater.
354
355 Critical to the uptake of Cd, Pb and Br from ingested microplastics is the accessibility
356 or mobility of the elements from the polymeric matrix. Results of the avian PBETs
357 were rather limited in that concentrations of the three elements in the digestive fluid
358 after a 168-h period of incubation were close to the corresponding detection limits of
359 the ICP-MS. Nevertheless, Pb was detected in the digests of two yellow fragments
360 (one polyethylene and one polypropylene) containing measurable Cr, with
361 concentrations of about 4 and 8 μg g^{-1} or bioaccessibilities (relative to the respective
362 total Pb concentrations returned by the XRF) of about 0.1% and 0.2%. Cadmium was
363 detected in the digest of one red polyethylene fragment containing measurable Se, and
364 at a concentration of 52 μg g^{-1} and with a bioaccessibility of about 2%. Thus,
365 accessible concentrations of Pb in the microplastics tested are greater than but a
366 similar order of magnitude to concentrations of dietary Pb (based on its presence in
367 local crab meat) while accessible concentrations of Cd are about fifty times greater
368 than dietary concentrations. These comparisons suggest that a seabird having 1 g of
369 coloured microplastics containing lead chromate or cadmium sulphoselenide trapped
370 in its gizzard-proventriculus for a period of seven days would be exposed to the same
371 quantity of Pb or Cd from the ingestion of about 4 g or 50 g of food.

4. Conclusions

This study has shown that the abundance and type of non-porous, moulded microplastics from two sandy beaches of different aspect on the south west peninsula of England are broadly similar. Specifically, the stock is composed of primary plastics in the form of production pellets and smaller quantities of secondary, unidentifiable fragments. Cadmium and Pb were detected in about 7% of over 900 samples analysed by XRF, with the highest concentrations usually encountered in red and yellow pellets or fragments and in association with Se and Cr, respectively (or as the coloured pigments, cadmium sulphoselenide and lead chromate, respectively). Bromine was detected in over 10% of samples analysed but was mainly encountered in neutrally-coloured pellets; a co-association with Sb is consistent with the occurrence of a variety of halogenated flame retardants in primary plastics that had been recycled from the casings of heat-generating electronic equipment. Although the avian bioaccessibilities of Cd, Pb and Br in microplastics are low, accessible concentrations of Cd and Pb in brightly coloured fragments may exceed corresponding concentrations in the seabird diet by factors of 50 and 4, respectively.

Acknowledgements

Dr Andrew Fisher (UoP) is thanked for technical assistance and advice during the study. This work was funded by a UoP Marine Institute HEIF V grant.

References

Acampora, H., Schuyler, Q.A., Townsend, K.A., Hardesty, B.D., 2014. Comparing plastic ingestion in juvenile and adult stranded short-tailed shearwaters (*Puffinus tenuirostris*) in eastern Australia. Marine Pollution Bulletin 78, 63-68.

Arthur, C., Baker, J., Bamford, H., (eds)., 2009. Proceedings of the international research workshop on the occurrence. Effects and fate of microplastic marine debris. National Oceanic and Atmospheric Administration Technical Memorandum NOS-OR&R-30.

Ayres D.C., Hellier, D.G., 1998. Dictionary of Environmentally Important Chemicals. Blackie, London, 332pp.

Brennecke, D., Duarte, B., Paiva, F., Caçador, I., Canning-Clode, J., 2016. Microplastics as vector for heavy metal contamination from the marine environment. Estuarine, Coastal and Shelf Science 178, 189-195.

Dupont, D., Arnout, S., Jones, P.T., Binnemans, K., 2016. Antimony recovery from end-of-life products and industrial process residues: a critical review. Journal of Sustainable Metallurgy 2, 79-103.

Endo, S., Takizawa, R., Okuda, K., Takada, H., Chiba, K., Kanehiro, H., Ogi, H., Yamashita, R., Date, T., 2005. Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: Variability among individual particles and regional differences. Marine Pollution Bulletin 50, 1103-1114.

European Chemicals Agency, 2016. ECHA info cards. https://echa.europa.eu/substance-information/-/substanceinfo/, accessed 12/16.

Hansen, E., Nilsson, N.H., Lithner, D., Lassen, C., 2010. Hazardous substances in plastic materials, COWI and the Danish Technological Institute on behalf of The Norwegian Climate and Pollution Agency, Oslo, 150 pp.

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: a review of the methods used for identification and quantification. Environmental Science & Technology 46, 3060-3075.

Jang, M., Shim, W.J., Han, G.M., Rani, M., Song, Y.K., Hong, S.H., 2016. Styrofoam debris as a source of hazardous additives for marine organisms. Environmental Science & Technology 50, 4951–4960.

Leslie, H.A., Leonards, P.E.G., Brandsma, S.H., de Boer, J., Jonkers, N., 2016. Propelling plastics into the circular economy - weeding out the toxics first. Environment International 94, 230-234.

Lusher, A.L., 2015. Microplastics in the marine environment: distribution, interactions and effects. In: Marine Anthropogenic Litter, ed. Bergmann, M., Gutow, L., Klages, M., Springer, pp. 245–307.

443 Munschy, C., Olivier, N., Veyrand, B., Marchand, P., 2015. Occurrence of legacy and
444 emerging halogenated organic contaminants in marine shellfish along French coasts.
445 Chemosphere 118, 329-335.
446
447 Narvaez Valderrama, J.F., Baek, K., Molina, F.J., Allan, I.J., 2016. Implications of
448 observed PBDE diffusion coefficients in low density polyethylene and silicone
449 rubber. Environmental Science-Processes & Impacts 18, 87-94.
450
451 Papazoglou, E.S., 2004. Flame retardants for plastics. In: Handboook of Building
452 Materials for Fire Protection, ed. C.A. Harper. McGraw-Hill, New York,
453
454 Rochman, C.M., Hentschel, B.T., Teh, S.J., 2014. Long-term sorption of metals is
455 similar among plastic types: Implications for plastic debris in aquatic environments.
456 PLOS ONE http://dx.doi.org/10.1371/journal.pone.0085433.
457
458 RoHS, 2006. Restriction of Hazardous Substances, EU Directive 2002/95/EC
459 http://www.rohsguide.com/rohs-substances.htm (accessed March 2017).
460
461 Schuwerack, P.-M.M., Neal, M., Neal, C., 2007. The Dart estuary, Devon, UK: a case
462 study of chemical dynamics and pollutant mobility. Hydrology and Earth System
463 Sciences 11, 382-398.
464
465 Schwemmer P., Garthe S., 2005 At-sea distribution and behaviour of a surface-
466 feeding seabird, the lesser black-backed gull *Larus fuscus*, and its association with
467 different prey. Marine Ecology Progress Series 285, 245–258.

Suhring, R., Barber, J.L., Wolschke, H., Kotke, D., Ebinghaus, R., 2015. Fingerprint analysis of brominated flame retardants and Dechloranes in North Sea sediments. Environmental Research 140, 569-578.

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., Watanuki, Y., 2013. Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics. Marine Pollution Bulletin 69, 219-222.

Turner, A., 2016. Hazardous metals, metalloids and other elements in marine litter. Marine Pollution Bulletin 111, 136-142.

Turner, A., Holmes, L., 2015. Adsorption of trace metals by microplastic pellets in fresh water. Environmental Chemistry 12, 600-610.

Turner, A., Lau, K., 2016. Elemental concentrations and bioaccessibilities in beached plastic foam litter, with particular reference to lead in polyurethane. Marine Pollution Bulletin 112, 265-270.

Turner, A., Solman, K.R., 2016. Analysis of the elemental composition of marine litter by field-portable-XRF. Talanta 159, 262-271.

Wesch, C., Bredimus, K., Paulus, M., Klein, R., 2016. Towards the suitable monitoring of ingestion of microplastics by marine biota: A review. Environmental Pollution 218, 1200–1208.

Table 1: The number of primary pellets and secondary fragments retrieved from 10 m sections of each beach, along with their colour distributions and the occurrence of Cd, Pb and Br.

	black	blue	green	grey	orange-brown	red	purple	white-clear	yellow	total
Whitsand pellets	55	16	15	13	34	4	15	213	22	387
Whitsand fragments	1	9	4	4	5	13	0	11	2	49
Woolacombe pellets	36	10	6	9	30	0	1	266	7	365
Woolacombe fragments	1	15	13	0	6	18	1	63	6	123
total	93	50	38	26	75	35	17	553	37	924
%	10.1	5.4	4.1	2.8	8.1	3.8	1.8	59.8	4.0	100
cadmium										
Whitsand pellets	5	2	1	1	1	4	12	6	0	32
Whitsand fragments	0	0	1	1	2	2	0	0	0	6
Woolacombe pellets	3	0	0	1	1	0	0	10	0	15
Woolacombe fragments	1	1	0	0	1	3	0	5	0	11
total	9	3	2	3	5	9	12	21	0	64
%	9.7	6.0	5.3	11.5	6.7	25.7	70.6	3.8	0.0	6.9
lead										
Whitsand pellets	14	2	0	5	1	0	5	0	1	28
Whitsand fragments	1	4	1	1	0	2	0	1	2	12
Woolacombe pellets	10	3	2	2	0	0	0	0	0	17
Woolacombe fragments	1	2	1	0	1	3	0	2	2	12
total	26	11	4	8	2	5	5	3	5	69
%	28.0	22.0	10.5	30.8	2.7	14.3	29.4	0.5	13.5	7.5
bromine										
Whitsand pellets	22	2	2	9	5	0	0	10	0	50
Whitsand fragments	1	3	0	1	1	1	0	2	0	9
Woolacombe pellets	13	0	1	3	1	0	0	10	0	28
Woolacombe fragments	1	1	4	0	1	0	0	2	0	9
total	37	6	7	13	8	1	0	24	0	96
%	39.8	12.0	18.4	50.0	10.7	2.9	0.0	4.3	0.0	10.4

Table 2: Number of cases in which Cd, Pb and Br co-existed, along with the total number of samples in which one or more of the elements was detected.

	Cd-Pb	Cd-Br	Pb-Br	Cd-Pb-Br	Cd, Pb, Br
Whitsand pellets	9	3	13	3	85
Whitsand fragments	2	1	3	0	18
Woolacombe pellets	1	3	5	1	49
Woolacombe fragments	1	1	1	1	30
total	13	8	22	5	182

505 Table 3: The distribution of Cd, Pb and Br concentrations among the samples (in μg g^{-1})
506 and the colour category in which the maximum elemental concentration was
507 recorded.
508

	< 10	10-10^2	10^2-10^3	10^3-10^4	> 10^4	mean	median	min	max	max colour
cadmium										
Whitsand pellets	0	23	6	3	0	232	64	38	1980	red
Whitsand fragments	0	1	2	3	0	895	974	66	1610	red
Woolacombe pellets	0	13	1	1	0	334	64	39	3390	grey
Woolacombe fragments	0	3	3	5	0	968	509	45	2622	red
lead										
Whitsand pellets	1	22	4	1	0	241	36	3.4	5330	yellow
Whitsand fragments	0	4	5	3	0	554	241	17	1660	red
Woolacombe pellets	0	14	3	0	0	108	36	12	941	black
Woolacombe fragments	0	4	4	4	0	1210	605	32	4820	yellow
bromine										
Whitsand pellets	18	21	8	3	0	241	18	4.0	4590	black
Whitsand fragments	0	8	0	0	1	1490	18	10	13,300	grey
Woolacombe pellets	5	17	5	1	0	283	25	6.6	4980	white
Woolacombe fragments	3	5	0	1	0	247	18	7.9	2050	white

509
510

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

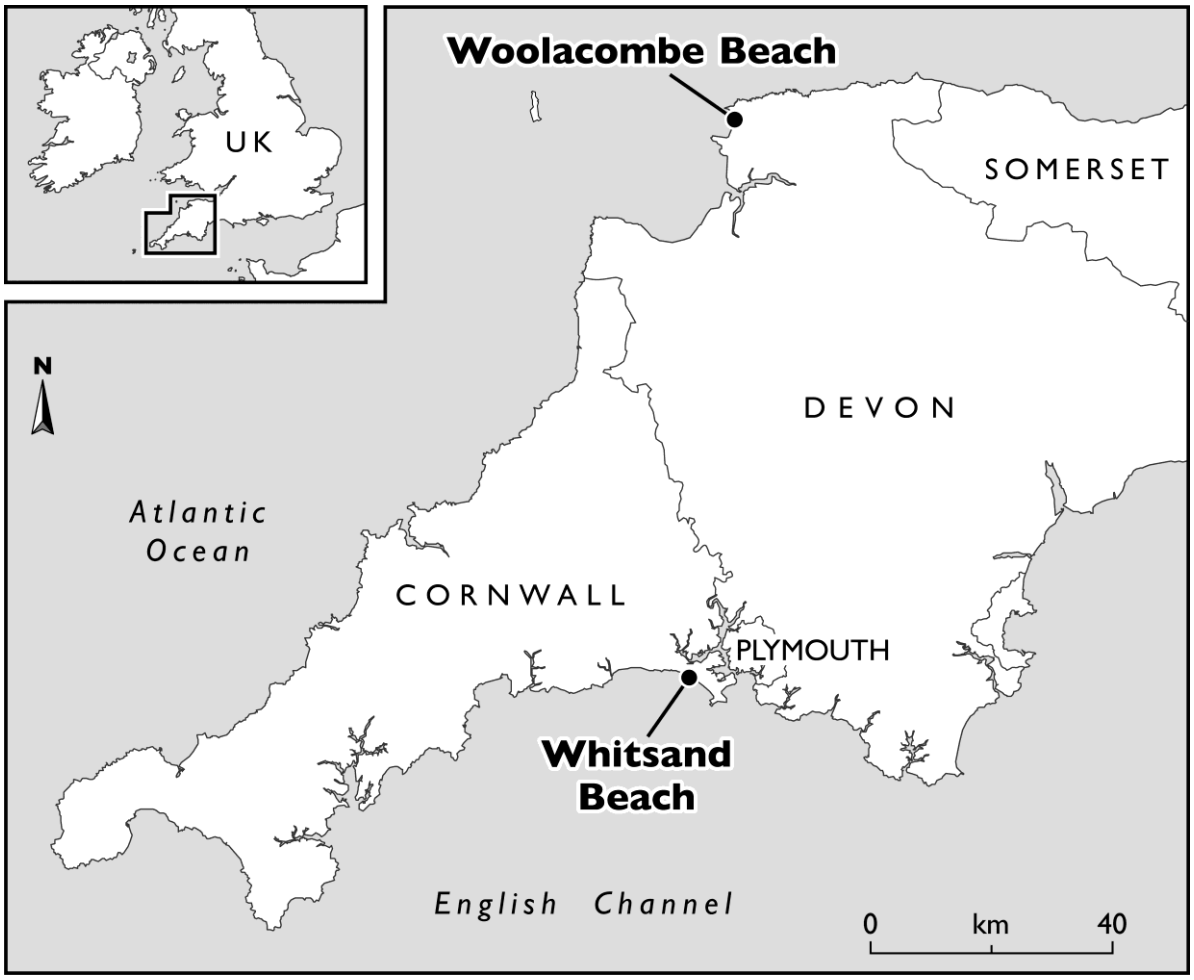


Figure 2: Concentration of Pb versus concentration of Cr in pellets (●) and fragments (▲) from Whitsand and in pellets (○) and fragments (Δ) from Woolacombe.

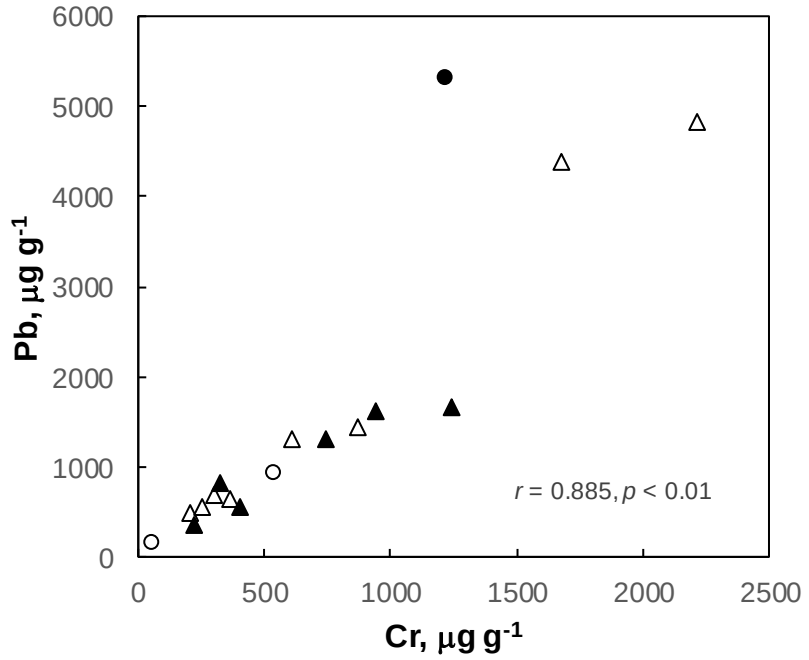
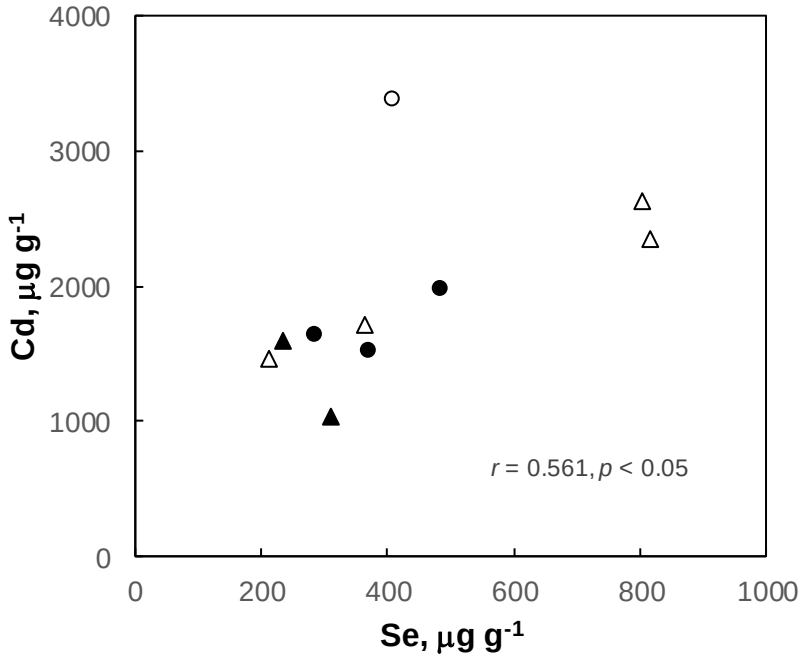


Figure 3: Concentration of Cd versus concentration of Se in pellets (●) and fragments (▲) from Whitsand and in pellets (○) and fragments (Δ) from Woolacombe.



539 Figure 4: Concentration of Br versus concentration of Sb in pellets from Whitsand (●)

540 and Woolacombe (○).

541

542

543