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Identification, origin and characteristics of bio-bead microplastics from beaches in western Europe

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Abstract

Primary microplastics have been collected from 17 beaches along the Atlantic, English Channel and southern North Sea coasts of western Europe. Based on visual characteristics, these plastics were differentiated as either relatively smooth, lentil- or disc-shaped pre-production pellets (or nurdles), which were usually a few mm in diameter and were mainly white to off-white, or rougher and more irregular pellets that were slightly larger and usually black. The latter appeared to be bio-beads, or plastics that are specifically manufactured for use as biomedia in certain sewage water treatment (SWT) plants, and possibly in other industrial wastewater treatment applications. Identification of bio-beads was confirmed following the acquisition of identical samples from a SWT plant in southwest England and a French supplier of bio-beads. Infrared and x-ray fluorescence analysis revealed that bio-beads have, at least historically, been constructed of plasticised polyethylene and, unlike pre-production pellets, contained variable quantities of potentially toxic elements: Br, Cd, Cr, Hg, Pb and Sb; with a distinctive Br to Sb ratio indicative of brominated flame retardants and antimony-based retardant synergists. It is asserted that bio-beads have been manufactured from a heterogeneous mix of recycled polyethylene and end-of-life electrical and electronic plastic, with concentrations of Br, Cd, Cr or Pb in about 50 bio-beads (out of 500 analysed) non-compliant or potentially non-compliant with respect to current regulations on hazardous plastic waste. Concentrations of Br, Cd, Cr, Pb and Sb extracted from individual bio-beads by a simulated avian digestive fluid were variable, with maximum values of about 14, 0.8, 1.3, 20 and 1.4 $\mu g\ g^{-1}$, respectively. The presence and, in many cases, dominance of bio-beads among beached primary microplastics is discussed with regard to the classification of microplastics and potential impacts on wildlife.

1. Introduction

Plastic pre-production pellets, or nurdles, are the industrial raw material used by the thermoplastics industry for melting and injection moulding-extrusion (Redford et al., 1997). Typically, pre-production pellets are a few mm in diameter and several tens of mg in weight and are manufactured in a range of colours. The volume of plastic shipped globally, coupled with spillages and losses during transportation, handling and processing, has ensured that these pellets are one of the most abundant and pervasive forms of primary marine microplastic in aquatic systems, and in particular in environments favourable for the deposition of low density material (Takada, 2006; Moreira et al., 2016). On some coastal beaches, for example, the number of pre-production pellets can exceed several thousand per m^3 and may be encountered at depths of up to 2 m (Kusui and Noda, 2003;

Turra et al., 2014), while on lake beaches, pellets may comprise more than 90% of plastic debris on a number basis (Zbyszewski and Corcoran, 2011).

Because of their buoyancy, colour and size, pre-production pellets are often consumed by birds and fish that mistake them for food or prey, resulting in potential obstruction of the gastrointestinal tract, suffocation, starvation and internal injuries (Pierce et al., 2004; Colabuono et al., 2009). Ingestion may also enable chemicals and contaminants that are associated with the plastic, either as additives or that have adsorbed to the surface during suspension, to bioaccumulate (Endo et al., 2005; Turner, 2018a).

Recently, the Cornish Plastic Pollution Coalition, a grouping of over 30 voluntary organisations based in south-west England, suggested that many of the primary microplastics retrieved from local beaches, and in some cases the majority of such plastics, are not in fact conventional pre-production pellets (CPPC, 2018). Thus, although many microplastics are of similar dimensions to these pellets, they are not smooth or regular in form but are amorphous, wrinkled and/or ridged. The intricacy of some of these designs suggests that they have been deliberately engineered for a specific purpose rather than being manufactured by simple extrusion for pre-production use. Thus, the authors asserted that these microplastics were bio-beads, used in a number of local sewage water treatment (SWT) plants as part of the filtration process. Specifically, biological aerated flooded filter (BAFF) plants employ pellets as a buoyant, high surface area substrate for the attachment of a biofilm of bacteria used to digest compounds such as ammonia (Gray, 2004). Wastewater is passed in a flooded condition, a process that requires a smaller area of land than an equivalent activated sludge process and that is able to treat high salinity sewage.

A visit by the Cornish Plastic Pollution Coalition to a SWT works in Plympton (Plymouth) serving 85,000 people revealed that approximately 43 billion bio-beads were in operation in a series of reactors. An abundance of bio-beads in storage and on the ground was noted that were consistent in form and colour distribution to those collected on beaches from the region. It was also established how readily spillages and losses could occur during reactor top-ups, leaks and accidents. Nationally, at least 55 plants serving 2 million people appear to employ this technology, with available information suggesting that bio-beads have been purchased from FLI Water (Kempston, Bedford) who source them from a French company (Plasti-Negoce, Lormaison, Picardie). The majority of bio-beads used are black which, presumably, is one of the cheaper colours to source. Thus, although SWT plants are designed to remove suspended solids and deliver clean effluent water (Murphy et al., 2016), some facilities appear to act as a direct source of microplastic pollution to the environment.

In the present study, primary microplastics collected from beaches of south-west England and throughout the English Channel and parts of the southern North Sea are examined in order to explore the wider distribution and occurrence of bio-beads. Both bio-beads and pre-production pellets are analysed non-destructively by Fourier transform infrared (FTIR) spectroscopy and x-ray fluorescence (XRF) spectrometry in order to attempt to chemically discriminate the two types of microplastic and ascertain the nature and sources of plastics employed. The wider implications of bio-beads for plastic identification and classification and for impacts on wildlife are also addressed.

2. Methods

2.1. Sampling campaigns

Several thousand microplastics were collected by hand, either by the authors or by colleagues, through inspections of visible accumulations of litter along the sand or silt strandlines of beaches, harbours and estuaries at locations shown in Figure 1 that are encompassed by OSPAR regions II (Greater North Sea, including the English Channel) and III (Celtic Seas, extending into the Atlantic Ocean) and where plastic pollution is of greatest concern (QSR, 2010). In most cases (Cornwall, Scilly Islands, Jersey, southern England, Wales) unsorted beached microplastics were retrieved during 2017 or early 2018; in other cases, however, French and Dutch colleagues supplied suspected bio-beads isolated from archived plastics that dated back to 2011 and that had been stored dry in darkened air-tight containers. Samples were foil-wrapped and returned or posted to the laboratory at Plymouth University where, as necessary, they were visually sorted by colour and type (pre-production pellets, bio-beads and any secondary fragments that were generally angular, film-like or fibrous). In addition, bio-beads were collected by hand from spillages around the reactors at Plympton SWT works, Plymouth, in January 2017, and new bio-beads were sourced directly from the manufacturer, Plasti-Negoce, in March 2018 (Figure 1). A selection of individual primary microplastics of each type (pre-production pellets and bio-beads) and from each location or source was weighed on a five-figure balance (Sartorius Genius) and measured for diameter through the widest axis and for height through the thickest part using digital callipers.

2.2. XRF analysis

All or a selection of at least 20 primary microplastics from each location or source, as indicated in Figure 1 and totalling 616 (537 bio-beads and 79 pre-production pellets), were analysed for twelve elements that are proxies for important additives in plastics and/or are potentially toxic contaminants (Ba, Br, Cd, Cl, Cr, Cu, Fe, Hg, Pb, Sb, Ti, Zn) using an energy-dispersive Niton XL3t He GOLDD+ portable XRF. The instrument was configured nose upwards in a shielded laboratory test-

stand and activated remotely by a laptop via USB connection. Samples were measured for thickness through the measurement surface (usually the smoothest or flattest face) using digital callipers before being suspended above the detector window on 3.6 μm Mylar film with the aid of a pair of tweezers and real-time video footage projected on the laptop through a CCD camera located next to the x-ray source. Samples were counted in a standardless plastics mode with thickness correction for 20 seconds at 40 μA and 50 kVp and 10 seconds at 100 μA and 20 kVp. Spectra arising from sample counting were quantified by fundamental parameter coefficients to yield elemental concentrations in $\mu g\ g^{-1}$ and a measurement error of 2σ (95% confidence) that were downloaded to the laptop via Niton data transfer software.

For quality assurance and instrument performance purposes, two 13 mm-thick Niton reference plastics that had been impregnated with various elements (PN 180-554 batch SN PE-071-N and PN 180-619 LOT#T-18) were analysed at regular intervals throughout each measurement session. To evaluate measurement precision and the importance of the thickness correction algorithm, selected samples were analysed in quintuplicate after varying thickness correction had been applied between 1 and 6 mm (approximating the range of sample thicknesses determined using the callipers). Median precisions were found to range from < 5% for Br, Cr and Ti to about 15% for Cd and Cl, and errors in thickness estimation of at least 50% were required to produce significant errors in reported concentration (relative to the concentration returned for true thickness and according to a series of paired *t*-tests; $\alpha = 0.05$) for elements whose fluorescent energies are less than 10 keV (Cl, Cr, Cu, Fe, Ti, Zn).

Limits of detection under the operating conditions of the XRF are dependent on sample thickness, density and chemical composition. Median values, based on the analysis of 50 pellets and 50 bio-beads from various locations and derived from counting errors multiplied by 1.5 (i.e. 3σ), were similar for the two types of microplastic for a given element and ranged from < 10 $\mu g\ g^{-1}$ for Br and Pb to several hundred $\mu g\ g^{-1}$ for Ba and Cl.

2.3. FTIR analysis

A selection of primary microplastics of varying size, form, colour and, according to XRF analysis, composition, and sampled from different environments, including those supplied by the manufacturer and totalling 30, was analysed by attenuated total reflectance FTIR (ATR-FTIR) spectrometry using a Bruker Vertex 70. The ATR diamond crystal was cleaned with isopropanol before whole samples or offcuts thereof were clamped against the crystal and spectra recorded with 16 scans in the region 4000 to 600 cm^{-1} and at a resolution of 4 cm^{-1}. After being smoothed, baseline-corrected and normalised via Bruker OPUS 7 software, spectra were compared with

libraries of reference spectra for the identification of component polymers and were visually inspected for signs of polymer modification.

2.4. Extraction tests and analysis

In order to evaluate the mobility of potentially toxic contaminants from bio-beads, 11 samples from various locations (and including the STW plant) were extracted under conditions approximating those encountered in the digestive tract of a seabird (Turner, 2018a). Thus, whole bio-beads were weighed into individual 10-ml polypropylene centrifuge tubes before the addition of 5-ml aliquots of 0.07 M HCl (Fisher Scientific Trace Analysis Grade in Elga ultrapure water). The contents were then placed in a Fisher Scientific Isotemp SW27 water bath for 24 h at 40 ^{o}C and under lateral shaking at 100 rpm before extracts were pipetted into clean centrifuge tubes and stored for up to two weeks under refrigeration pending analysis.

Concentrations of Br, Cd, Cr, Cu, Fe, Hg, Pb, Sb and Zn in the HCl-extracts were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Scientific iCAP RQ analyser with a Glass Expansion micromist nebuliser and cyclonic spray chamber. The instrument was calibrated with a blank and three mixed and matrix-matched standards in the range 10 to 100 μg L^{-1}, and RF power was set at 1.5 KW with coolant, nebuliser and auxiliary flows of 1.4, 1.07 and 0.8 L Ar min^{-1} and a replicate (n = 3) read time of 10 ms.

3. Results

3.1. Appearance and physical characteristics of new and SWT bio-beads

A total of 25 bio-beads were returned from Plympton SWT works, where BAFF media have been employed for over 20 years. Here, 16 bio-beads were black (including charcoal or dark grey), while the remainder were white to off-white or blue-green (Figure 2). The majority of these used bio-beads had a distorted and irregular cylindrical form and were amorphous-looking, with poorly-defined faces which, in some cases, appeared to be pitted, bumpy or concertinaed. Occasional bio-beads, however, were more defined in shape with at least one distinctive face that was usually circular.

The physical characteristics of a selection of SWT bio-beads are summarised in Table 1. Briefly, bio-bead mass ranges from around 28 to 53 mg and averages about 38 mg, while the diameter measured across the widest axis of the bio-bead, d_1, ranges from about 3.2 to 4.5 mm, and height

183 measured through the thickest part, d_2, ranges from about 3.1 to 5.7 mm. The aspect ratio of the
184 bio-beads (d_1:d_2) ranges from around 0.6 to 1.3, with an average that is close to unit value.

185 All new bio-beads supplied by Plasti-Negoce (n = 15) were black, irregular cylinders with a rough
186 texture throughout and no smooth faces evident (Figure 2). These were less variable in size and
187 aspect than the bio-beads retrieved from the SWT plant, with an average mass of about 41 mg, an
188 average diameter and height of about 3.6 and 4.8 mm, respectively, and an average aspect ratio of
189 0.76.

190 Microscopic images, exemplified in Figure 3, revealed that new bio-bead surfaces were uneven
191 throughout and edges were jagged. Used bio-beads, however, were generally smoother and more
192 eroded on surfaces and edges where concertinaing was absent, and were characterised by deposits
193 of brown, white or black particulates on their surfaces.

194 ***3.2. Appearance and physical characteristics of beached primary microplastics***

195 Nearly all of the primary microplastics collected from various estuarine and coastal beaches
196 throughout the region under study could be categorised either as bio-beads, based on the
197 description above, or pre-production pellets (nurdles); occasional, distinctive components of fishing
198 equipment or children's toys-jewellery were the only other type of primary microplastic evident.
199 Pre-production pellets were generally smooth and disc- or lentil-shaped with a distinctive depression
200 often visible on one side (Figure 2), although some were well-defined cylinders that reflect simple
201 extrusion of the polymer, and the majority were white to off-white or translucent, with the latter
202 often accompanied by yellowing resulting from photo-oxidative weathering. Based on
203 measurements of 40 random samples from various beaches, and as summarised in Table 1, pre-
204 production pellet mass averaged 23 mg and ranged from about 15 to 38 mg. Average dimensions
205 were 4.1 mm and 2.2 mm for d_1 and d_2, respectively, with a mean aspect ratio of around 2. In
206 contrast, beached bio-beads were mainly black and less frequently grey, green-blue, or white to off-
207 white. Measurements of 67 random samples from different beaches, and summarised in Table 1,
208 revealed that bio-beads were more variable in mass and size than pre-production pellets but were,
209 overall, larger. Thus, bio-bead mass averaged over 40 mg and ranged from about 13 to 74 mg, and
210 both d_1 and d_2 average about 4 mm, but with a relatively large range of values that resulted in a
211 mean aspect ratio close to unit value.

212 The microscopic images shown in Figure 3 highlight the differences between beached bio-beads and
213 pre-production pellets. Specifically, the latter generally have a better-defined, regular shape and
214 exhibit a relatively smooth surface while the former are mostly irregular with a rougher surface that

allows extraneous material to be more readily accumulated during suspension or beaching. Accumulation appears to be particularly favourable where the surface is concertinaed, an effect most evident on blue-green bio-beads, or where there were cracks and bumps. Note also that some bio-beads that were usually black, grey or dark green were distinctly smoother and more regular than most of the other bio-beads. Although it was originally suspected that these samples may have been pre-production pellets, similar characteristics to some of the smoother used bio-beads from the SWT plant and a form that precludes ready extrusion for pre-production pelletisation, including distortion and doming, suggested otherwise.

3.3. Polymeric composition of bio-beads and pre-production pellets

Results of FTIR analysis, exemplified in Figure S1, revealed that all bio-beads tested (n = 22), including those supplied by Plasti-Negoce, were constructed of polyethylene and, based on a carbonyl peak of varying intensity at around 1730 cm^{-1}, contained variable quantities of ester-based plasticiser. For the SWT and beached bio-bead spectra, a broad peak between 3700 and 3000 cm^{-1} that was considerably reduced when the internal structure of the plastic was exposed after dissection suggests the presence of absorbed water and/or hydrolysis of the surface. Although methyl bending deformation evident in many black samples at 1377 cm^{-1} was initially attributed to chain length reduction through weathering and aging, the presence of this absorption peak in new bio-beads suggests that low density polyethylene may also be an inherent component of the plastic matrix (Jung et al., 2018).

FTIR spectra for the pre-production pellets analysed (n = 8) revealed plastics composed of either polyethylene or polypropylene with variable quantities of plasticiser. There was less evidence of water absorption and/or hydrolysis at the surface and absorption peaks were less evident at 1377 cm^{-1}.

3.4. Elemental composition of bio-beads and pre-production pellets

Table 2 reports summary statistics for the concentrations of the twelve elements analysed by portable XRF in the different primary microplastics. All new bio-beads sourced from the manufacturer contained measurable quantities of Fe, Ti and Zn, while some bio-beads contained detectable Ba, Cu and Cl. Likewise, all bio-beads that had been employed in SWT reactors contained measurable Fe, Ti and Zn and some bio-beads contained detectable Ba, Cu and Cl. However, concentrations of a given element were more variable than in the new bio-beads, with standard deviations close to the mean and a concentration range that spanned more than an order of magnitude in some cases. In addition, many used bio-beads contained measurable quantities of the

more toxic elements: Br, Cr, Pb and Sb; concentrations of which spanned up to two orders of magnitude.

For the bio-beads collected from various beaches, the frequency of detection of each element overall was similar to that of the used bio-beads but with Cd and Hg present in a number of cases. Concentrations of each element were highly variable, with a range spanning two or more orders of magnitude for Br, Fe and Ti. The correlation matrix shown in Figure 4 reveals associations with a Pearson's moment correlation coefficient (*r*) above 0.75 occur in eight cases that are limited to combinations between six elements (Br, Cd, Cu, Hg, Pb, Sb) and a coefficient above 0.9 for Br-Sb and Cd-Hg; in contrast, no associations with a coefficient above 0.5 are evident among the elements Cl, Fe and Ti.

Regarding the beached pre-production pellets, Cd, Cu and Sb were never detected and concentrations of Br, Hg and Pb were only returned in one case each. Overall, detection frequency (as a percentage of samples analysed) in pre-production pellets was lower than in new bio-beads for Ba, Cl, Fe, Ti and Zn and lower than or equal to used bio-beads for all elements with the exception of Cr. Compared with beached bio-beads, detection frequency, mean concentration and median concentration were lower for all elements considered with the exception of Cl (a higher mean) and Cr (a higher detection frequency and median). The results of correlation analysis shown in Figure 4 reveal only one association (Ba-Cr) with a coefficient exceeding 0.5.

The heterogeneity in bio-bead composition overall was also reflected by high elemental variability at each location where bio-beads were reported and provided, with evidence of geographical patterns limited to differences in detection frequencies between regions. Specifically, Ba appeared to be more commonly detected towards the east-southeast (for example, 65% in Texel compared with < 40% at Perranporth and Freshwater West) while Cl appeared to be more commonly detected towards the west (less than a third in the Netherlands and northern France compared with up to 80% in Jersey and Cornwall).

3.5. Elemental extraction from bio-beads

Table 3 presents a summary of the concentrations of various elements extracted from 11 bio-beads by the simulated avian digestive solution. Iron and Zn were detected in all extracts and at the highest concentrations, with respective maximum values of 1120 and 161 $\mu g\ g^{-1}$ encountered in a bio-bead from the SWT. Relative to the total concentrations returned by the XRF, percentage extraction for both metals ranged from about 10 to over 100. Mercury was never detected in the extracts and remaining elements were detected in between 1 (Cr) and 11 (Br, Pb) cases with average

concentrations always below 10 μg g^{-1} and, with the exception of Cu, percentage extractions less than 1%.

4. Discussion

4.1. Sources and distributions of bio-beads

Bio-beads are primary microplastics that are used as filtering media in many biological aerated flooded filter SWT works. The results of the present study indicate that bio-beads are polyethylene-based, irregularly-shaped and usually black, and are, on average, larger and heavier than plastic production pellets (nurdles). Bio-beads are distributed throughout a wide region of western Europe with a range of about 900 km from the Scilly Islands in the west to Texel in the east evident in the present study. Because of the nature of the sampling, including subsampling from archived and previously manipulated stocks, it was not possible to precisely quantify the relative abundance of beached bio-beads and other visible primary microplastics. Nevertheless, observations indicated that the occurrence of bio-beads varied considerably throughout the region, being relatively uncommon in the Scilly Islands, for example, but the dominant form of primary microplastic at Camber Sands. A previous, more quantitative distributional approach undertaken by the Cornish Plastic Pollution Coalition (CPPC, 2018) also indicated a widely varying abundance of bio-beads relative to other primary microplastics but one that had no clear geographical patterns, with relative abundances of about 20% reported on one beach on the Atlantic coast of Cornwall to 90% on an English Channel beach near to the border of France and Belgium.

The incidence of bio-beads beyond the region under study is not clear because a variety of different types and sizes of plastic biomedia are used in SWT globally (Bailly et al., 2018). However, we note that they have recently been reported along the Atlantic coast of south west France and the western coast of Denmark (CPPC, 2018), while XRF analysis of archived black microplastics collected from the Mediterranean island of Malta (Turner and Holmes, 2011) and performed as part of the present study revealed similar chemical characteristics to those of bio-beads reported herein. An examination of internet images of beached microplastics also suggests that the presence of bio-beads may extend beyond Europe.

Bio-beads may enter the environment during handling at SWT plants and during their processing and transportation by the manufacturers or suppliers. However, the principal environmental source appears to be related to loss from SWT reactors, an assertion confirmed by the presence of polycyclic aromatic hydrocarbons, characteristic of urban runoff, adsorbed to the surfaces of bio-beads but not to other primary microplastics (i.e. pre-production pellets) collected from Cornish

beaches (Hideshige Takada, pers. comm). Large-scale loss of bio-beads to the environment may occur when the retaining mesh of the reactors fails. As an example, the utility company, South West Water, was alerted to a spillage of over 5 billion bio-beads into the Truro River, south west England, in 2010, when the 3-mm steel mesh of a reactor split (CPPC, 2018). Although the company subsequently attempted to clear bio-beads from the environment, this incident exemplifies the lack of any fail-safe containment mechanism to trap lost bio-beads to any meaningful degree.

The requirement to occasionally top-up reactors with bio-beads suggests that spillages may also take place during maintenance, or that continuous loss occurs through partial damage to the mesh or through encapsulation by sludge. Abrasion of bio-beads with the interior reactor walls may also facilitate escapement should the primary or secondary diameter be denuded to a value that is less than the 3-mm pore size of the steel mesh. Table 1 shows that the minimum values of both d_1 and d_2 for the new and used bio-beads exceeds this value but that d_2 for beached bio-beads may be less than 2 mm.

Within the UK, the Cornish Plastic Pollution Coalition report that eight out of the twelve national water companies use bio-beads at more than 55 SWT plants that serve about two million people, and that a further two companies use, or have used, a type of plastic bead medium but could not provide specific details (CPPC, 2018). However, given the rather vague, ambivalent and contradictory responses to requests for information from some companies we contend that this figure may represent a significant underestimate. Available information suggests, but cannot confirm, that bio-beads are not used for treating sewage in neighbouring countries, despite their abundance on sandy beaches outside the UK and the parent company of FLI Water being based in Ireland. Their exclusive use by British utility companies would require bio-beads to be readily transported throughout the region, and to both the west and east, by ocean currents, or that additional industries employ bio-beads for water treatment.

4.2. Chemical characteristics and signature of bio-beads

Bio-beads are chemically complex and many are associated with relatively high concentrations of potentially toxic elements (and in particular, Cd, Pb and Sb) and/or brominated compounds. This observation, coupled with the use of combinations of brominated compounds, Cd, Pb and Sb in electronic plastic as contaminants or in order to engender flame retardancy to heat-generating articles (Turner and Filella, 2018), suggests that many bio-beads are, or have been, manufactured, directly or indirectly, from end-of-life waste electrical and electronic equipment (WEEE). Potentially harmful chemicals are supposed to be removed from the WEEE stream but poor or inefficient practices have resulted in contamination of recycled consumer goods (Turner, 2018b). This is a

particular problem for black products because domestic waste plastic coloured in this way is difficult to identify and recycle at municipal sorting facilities (Rozenstein et al., 2017) and, being inherently black, most electrical equipment casings afford a convenient and cheap alternative recyclate. Consistent with this problem, Br, Cd, Pb and Sb were most frequently encountered in bio-beads that were black or that appeared to have been blended from black plastic (e.g. dark green).

In addition to the widespread, heterogeneous contamination of bio-beads from (likely) WEEE plastic, many samples contain one or more toxic or potentially toxic chemical additives that exceed the respective limits defined by the Restriction of the use of certain Hazardous Substances in electrical and electronic equipment (RoHS) Directive (European Parliament and Council, 2003) (Table 4). Strictly, therefore, these bio-beads should be classified as 'hazardous' themselves. Specifically, and with respect to electrical goods placed on the market in Europe after 2006, the metals Cd, Cr (as Cr VI) and Pb are restricted to concentrations of 100 $\mu g\ g^{-1}$, 1000 $\mu g\ g^{-1}$ and 1000 $\mu g\ g^{-1}$, respectively, in homogenous materials or components of EEE, while concentrations of the polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants are restricted to concentrations of 1000 $\mu g\ g^{-1}$. (Note that, despite compounds of Sb commonly used as halogenated flame retardant synergists (Papazoglou, 2004), the potentially toxic metalloid itself has not been considered in the directive.) Accordingly, 20 samples from a variety of locations but with a relatively high proportion on the East Looe river estuary are RoHS-non-compliant (or derived from non-compliant products) with respect to Cd and four samples are non-compliant with respect to Pb. One sample from the Scilly Islands is potentially non-compliant with respect to Cr (XRF cannot discriminate Cr III and Cr VI) and 26 samples from throughout the region are potentially non-compliant with respect to Br in that concentrations exceed 700 $\mu g\ g^{-1}$ Br (the approximate concentration of Br in 1000 $\mu g\ g^{-1}$ of penta-PBDE, one of the more commonly used lower brominated congeners). Potential Br non-compliance occurs in a sample from Plympton STW and in a relatively high proportion of samples collected from Texel and Marazion but was not observed in the Scillies or at East Looe, where Pb and either Cd or Cr non-compliance (or potential non-compliance) was observed. Overall, there were 51 cases of potential RoHS-exceedance among 49 samples that were all black and that had been retrieved from all locations studied with the exception of Cayeux-sur-mer, Freshwater West Bay and Kimmeridge Bay.

The heterogeneous distribution of restricted chemicals among the bio-beads, both within and between locations and at concentrations both above and below their respective RoHS limits, suggests that the bio-beads have been derived from a variety of multiple sources or a single (or limited number of) source(s) whose supply is either chemically heterogeneous or is variable in make-up over time. The lack of restricted chemicals detected in the new bio-beads obtained from Plasti-

Negoce, the only apparent supplier of bio-beads within the UK, is consistent with the latter explanation and sourcing raw material that is linked with the availability, historical processing and degree of contamination of black plastic. Thus, it is possible that better practices in sorting non-compliant materials from the WEEE stream or the phasing out of restricted chemicals has resulted in a reduction in contamination of the raw material. On this basis, we may assert that bio-beads from Texel, for example, where restricted chemicals are abundant and, in the case of Br, frequently exceed RoHS limits, are older than ones from the Scillies or the northern coast of France. That said, however, recent studies into contemporary consumer goods suggests that contamination of black plastic is a long-term but highly variable problem and that once contaminants are introduced and blended into the recyclate are difficult to eliminate (Turner, 2018b).

Further evidence for the use of recycled WEEE to manufacture bio-beads is the correlations between the concentrations of restricted elements (Figure 4), and in particular that between Br, indicative of the quantity of brominated flame retardants, and Sb, representative of the amount of antimony-based compounds (and mainly Sb_2O_3) used as flame retardant synergists. The association of Br and Sb for bio-beads where both elements were detected is illustrated in Figure 5. Here, data are discriminated by location but most data-points, including those from the SWT plant, lie within 20% of the best-fit regression line forced through the origin. Significantly, the gradient of the best-fit line (Br-Sb = 1.45) is lower than that defining pre- and post-RoHS EEE plastics (Br-Sb = 2.92) and as determined by portable XRF and reported by Turner (2018b). Given that different types of polymer may require different kinds and quantities of halogenated flame retardant and synergist for protection (Papazoglou, 2004), the discrepancy in gradients may be partly attributed to the apparent use of recycled polyethylene in bio-beads compared with the use of a multitude of polymers in EEE (including polystyrene, polypropylene and acrylonitrile butadiene styrene). However, it is also possible that differential release of flame retardants and synergist occurs while bio-beads are suspended in sewage water or seawater; specifically, a greater gradient defining EEE than bio-beads requires a higher propensity for the mobilisation of brominated compounds from the polymeric matrix than compounds of Sb. The mobilisation of either or both Br and Sb also has implications for the chemical quality of effluent water discharged from SWT plants that employ plastic biomedia.

4.3. Elemental mobility from bio-beads

Results of the extraction tests reveal relatively high but variable mobilities of Fe and Zn from the bio-beads, consistent with the adherence, entrapment, adsorption or (co-)precipitation of material at the polymer surface. That extractable concentrations were greatest in a bio-bead from the SWT plant suggests phases derived from sewage water are more labile than those derived from the

411 coastal environment or that the phases derived from sewage water plants desorb readily when
412 beads are released to the environment. The restricted elements, Br, Cd, Cr, Pb and Sb, are less
413 available to extraction, both in terms of absolute concentration and percentage relative to total
414 concentration, presumably because high proportions are associated with the plastic matrix rather
415 than material physically or chemically attached to the polymer surface. This assumption was
416 subsequently confirmed by analysis of the interiors of a selection of bio-beads (after slicing with
417 pliers) returning concentrations that were almost identical to those derived from whole bio-bead
418 analyses performed through the plastic surface. Nevertheless, given the potential or known toxicities
419 of these elements to marine wildlife, including potential impacts on physiology, reproduction,
420 survival, growth, neurobehaviour and endocrine systems (Burger and Gochfeld, 2000; De Andres et
421 al., 2016; Sebastiano et al., 2016), their mobilities are of concern for organisms that inadvertently
422 ingest bio-beads into an acidic digestive system. The ingestion of bio-beads by the herring gull, *Larus*
423 *argentatus*, has recently been reported to the authors by a fisherman working on the Truro River,
424 downstream of a major spill at a sewage water treatment plant in early 2010. The regurgitated
425 contents from one individual are illustrated in Figure 6, with plastic contributing more than 40% to
426 the total matter on a dry mass basis (about 3.2 g) and bio-beads dominating the microplastic pool.

427 ***4.4. Concluding remarks***

428 Bio-beads are small, irregularly shaped plastics derived from waste water treatment processes that
429 constitute a significant fraction of microplastic pollution on beaches of western Europe. Bio-beads
430 are often black and associated with Br, Cd, Pb and Sb in quantities that are characteristic of plastic
431 recycled from WEEE. Their distinctive physical and chemical characteristics warrant classification
432 that is both separate from pre-production pellets (nurdles) and is based on colour for monitoring,
433 scientific and risk assessment purposes. With respect to BAFF treatment plants that employ bio-
434 beads, it is recommended that more stringent prevention and remediation plans are adopted in
435 order to minimise the occurrence and potential impacts of spillages and leakages in the
436 environment.

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Table 1: Summary statistics for the mass and dimensions (d_1 = diameter, d_2 = height) of a selection of new bio-beads sourced from Plasti-Negoce, used beads collected from Plympton SWT plant, beached bio-beads and beached pre-production pellets.

		new bio-beads	SWT bio-beads	beached bio-beads	beached pre-production pellets
mass, mg	*n*	10	16	67	40
	mean±sd	41.14±7.00	37.66±7.01	42.25±13.11	23.06±4.95
	min	23.98	27.90	12.9	14.98
	max	49.59	53.45	73.94	37.62
d_1, mm	*n*	10	16	67	40
	mean±sd	3.58±0.30	3.88±0.37	3.96±0.57	4.08±0.36
	min	3.08	3.17	2.87	2.83
	max	4.09	4.47	5.67	4.58
d_2, mm	*n*	10	16	67	40
	mean±sd	4.79±0.73	4.03±0.70	3.90±0.84	2.20+0.41
	min	3.52	3.10	1.87	1.59
	max	6.09	5.66	7.14	3.10
d_1:d_2	*n*	10	16	67	40
	mean±sd	0.76±0.10	1.00±0.21	1.06±0.27	1.92±0.44
	min	0.59	0.61	0.58	1.06
	max	0.88	1.27	1.74	2.52

Table 2: Summary statistics for the elemental composition of new, used (SWT) and beached bio-beads and beached pre-production production pellets. All concentrations are in μg g^{-1}.

		Ba	Br	Cd	Cl	Cr	Cu	Fe	Hg	Pb	Sb	Ti	Zn
new bio-beads (*n* = 15)	no. detected (%)	10 (66.7)	0	0	5 (33.3)	0	2 (13.3)	15 (100)	0	0	0	15 (100)	15 (100)
	mean±sd	409±89.7			1130±677		21.2	160±22.9				9830±1560	495±46.8
	median	386			855		21.2	160				10,200	496
	min	300			786		20.2	122				6850	420
	max	606			2340		22.2	201				12,276	588
SWT bio-beads (*n* = 25)	no. detected (%)	17 (68.0)	17 (68.0)	0	16 (64.0)	7 (28.0)	7 (28.0)	25 (100)	0	11 (44.0)	11 (44.0)	25 (100)	25 (100)
	mean±sd	1410±1840	204±235		659±360	42.0±14.4	34.1±23.6	1130±1020		38.6±18.8	192±135	2970±1550	320±244
	median	548	85.3		685	37.3	31.1	768		38.9	131	3270	262
	min	318	7.8		215	24.9	14.3	116		9.4	58.9	809	58.6
	max	5500	739		1210	62.4	83.5	3670		69.9	420	5240	854
beached bio-beads (*n* = 497)	no. detected (%)	280 (56.5)	247 (49.7)	73 (14.7)	269 (54.2)	169 (34.0)	145 (29.2)	490 (98.5)	14 (2.8)	231 (46.4)	71 (14.3)	487 (97.9)	428 (86.1)
	mean±sd	869±604	283±892	93.9±60.8	1250±1200	77.2±137	56.7±53.6	509±670	19.5±4.3	105±379	621±1010	5200±4310	236±223
	median	768	35.5	73.9	827	37.0	41.8	323	19.4	38.6	307	4460	222
	min	342	5.40	35.1	180	17.4	13.5	50.4	12.0	8.1	77.8	59.0	16.3
	max	8020	6730	312	8140	1400	363	10,900	26.1	5380	4730	35,100	1590
beached pre-production pellets (*n* = 79)	no. detected (%)	9 (11.4)	1 (1.3)	0	25 (31.6)	35 (44.3)	0	72 (91.1)	1 (1.3)	1 (1.3)	0	21 (26.6)	4 (5.1)
	mean±sd	610±115	12.0		1380±1330	40.9±9.7		197±271	20.4	22.2		4600±5900	83.9±41.6
	median	635	12.0		940	41.9		101	20.4	22.2		87.1	89.7
	min	417	12.0		212	18.5		35.9	20.4	22.2		14.7	30.2
	max	781	12.0		6280	62.7		1700	20.4	22.2		13,900	126

543 Table 3: Summary statistics for the concentrations of elements (in μg g^{-1}) extracted from bio-beads under simulated avian digestive conditions.

	Br	Cd	Cr	Cu	Fe	Hg	Pb	Sb	Zn
no. detected	11	8	1	10	11	0	11	2	11
mean±sd	7.6±2.6	0.34±0.24	1.3	3.0±1.9	366±421		6.0±6.2	1.3	53.2±53.0
median	7.2	0.28		2.2	111		3.3	1.3	44.6
min	3.1	0.08		1.0	34.1		0.6	1.1	8.8
max	13.5	0.77		5.6	1120		20.0	1.4	161

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559 Table 4: Number of cases in which bio-beads were non-compliant (Cd, Pb) or potentially non-compliant (Br, Cr) with respect to corresponding RoHS limits
560 (and as indicated).

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Location	Br > 700 μg g^{-1}	Cd > 100 μg g^{-1}	Cr > 1000 μg g^{-1}	Pb > 1000 μg g^{-1}
Plasti-Negoce				
Plympton STW	1			
Freshwater West				
Burnham on Sea	2			
Perranporth	1	1		
St Mary's			1	1
Marazion	4			
Truro-Tresillian	1			
East Looe		11		2
Tregantle	2	2		1
Kimmeridge Bay				
Camber Sands	2			
Texel	8	1		
Wimereux	2	2		
Cayeux-sur-mer				
Le Havre		1		
Bel Royal	1	2		
Greve d'Azette	2			
total	26	20	1	4

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Figure 1: Location of the sampling sites in the present study, including the French manufacturer of bio-beads. Numbers in parentheses denote the number of bio-beads analysed by XRF from each site.

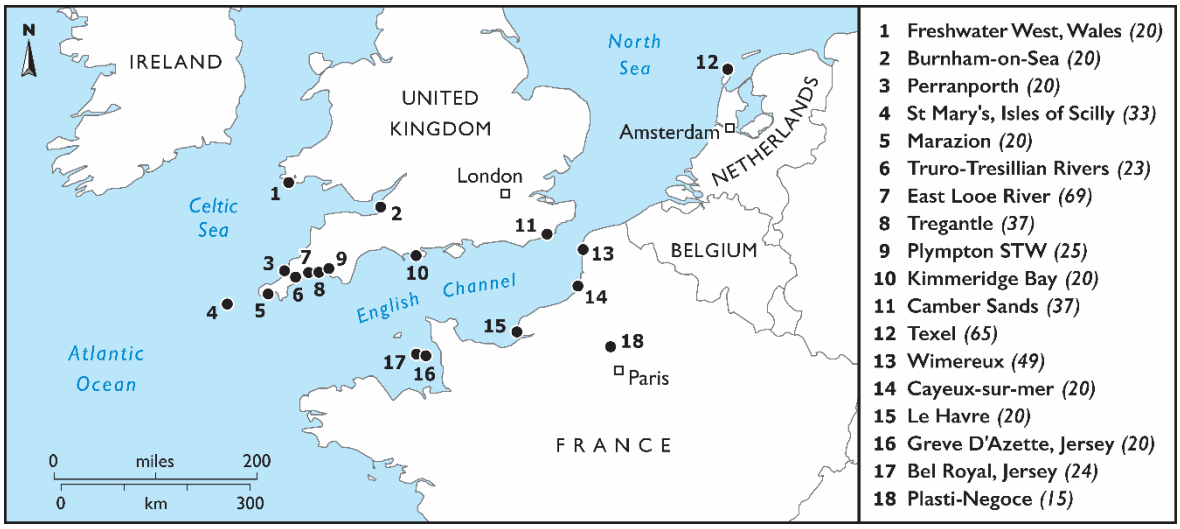

Figure 2: Photographs of a selected of samples on cm-scaled graph paper. (a) Bio-beads supplied by Plasti-Negoce, (b) bio-beads retrieved from Plympton SWT works, (c) bio-beads collected from Camber Sands and East Looe, and (d) pre-production pellets collected from Tregantle, Perranporth and Camber Sands.

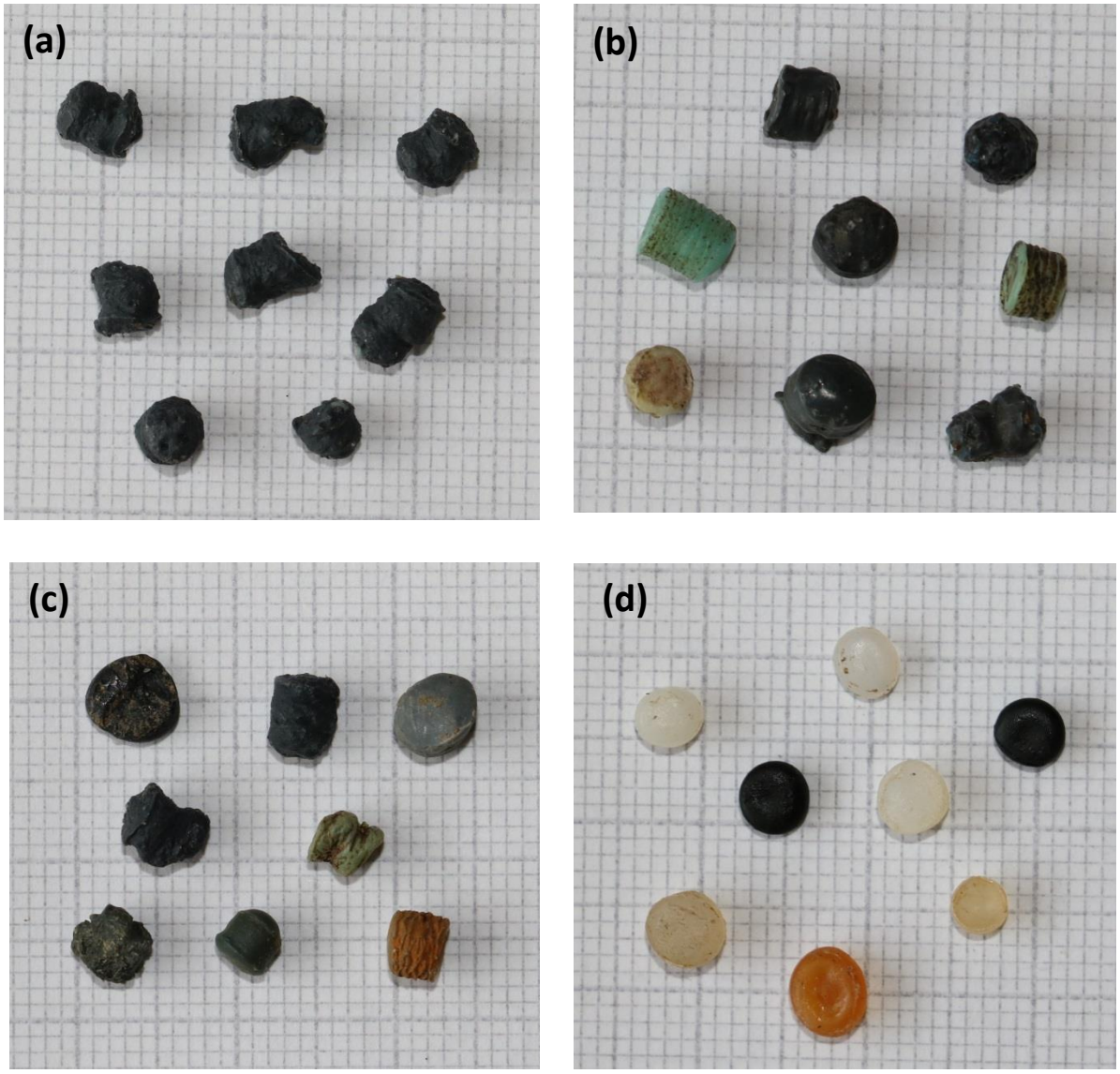

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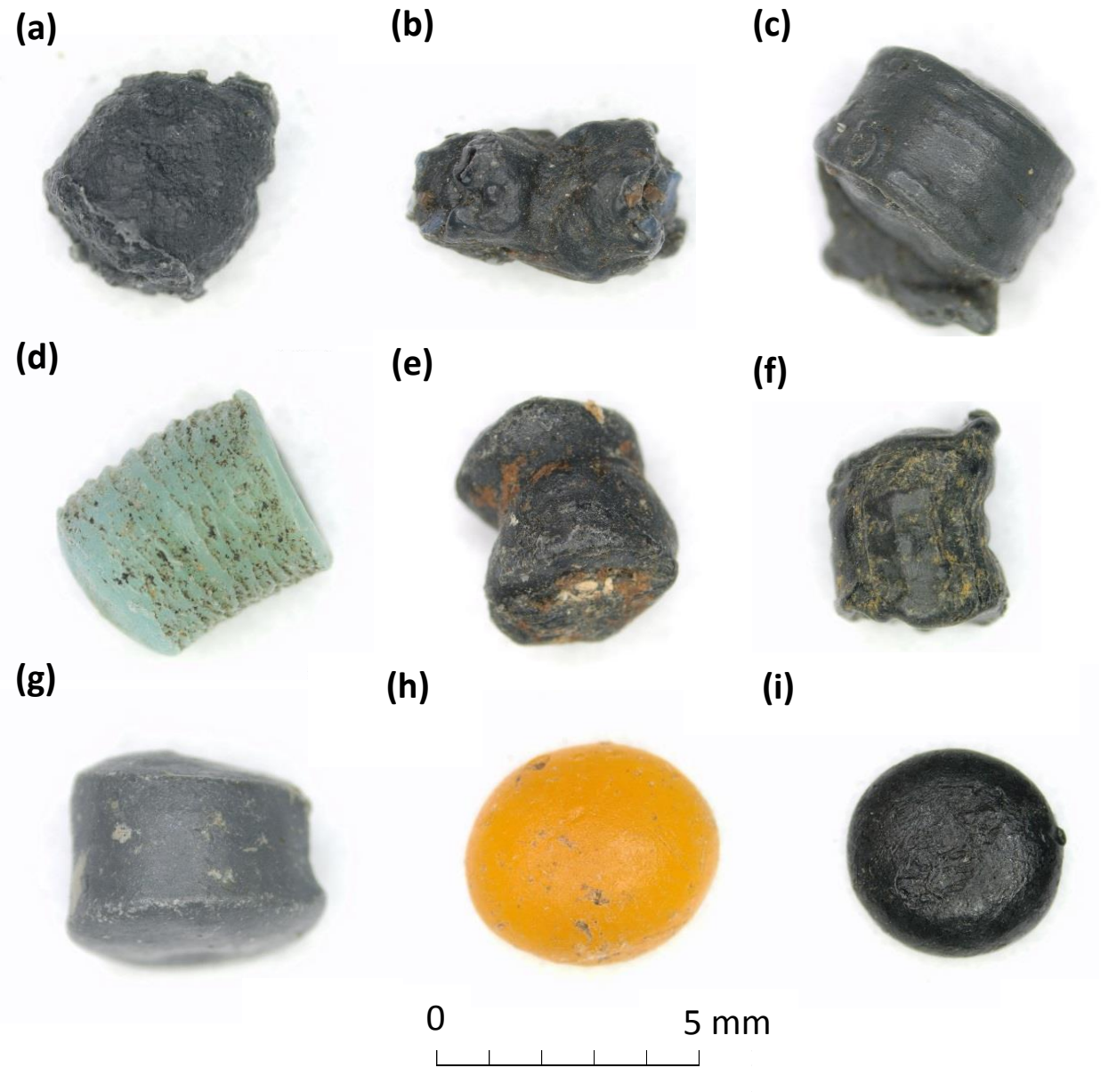
Figure 3. Microscopic images of selected bio-beads and pre-production pellets. (a) A bio-bead supplied by Plasti-Negoce, exhibiting a rough surface and jagged edges; (b) an irregular black bead from Plympton SWT works showing evidence of erosion and material accumulation; (c) a smoother, more cylindrical black bead from the STW; (d) a blue-green bead from the STW revealing material accumulation along the concertinaed edges; (e) an irregular black bio-bead from Cayeux-sur-Mer with visible accumulation of brown and white material; (f) an irregular black bead from Camber Sands with evidence of yellow-brown material accumulation; (g) a smoother and more regular black bead from the Scilly Islands; (h) a translucent pre-production pellet from East Looe that had undergone yellowing; (i) a black pre-production pellet from the Scilly Islands.



579 Figure 4: Correlation matrix showing associations between different elements for the beached bio-
580 beads (▲, $r > 0.5$; ▲▲, $r > 0.75$; ▲▲▲, $r > 0.9$) and pre-production pellets (◊, $r > 0.5$).

	Ba	Br	Cd	Cl	Cr	Cu	Fe	Hg	Pb	Sb	Ti
Br											
Cd											
Cl											
Cr	◊		▲▲								
Cu	▲				▲▲						
Fe											
Hg	▲		▲▲▲								
Pb			▲▲		▲▲	▲▲					
Sb	▲	▲▲▲	▲▲								
Ti											
Zn	▲							▲			

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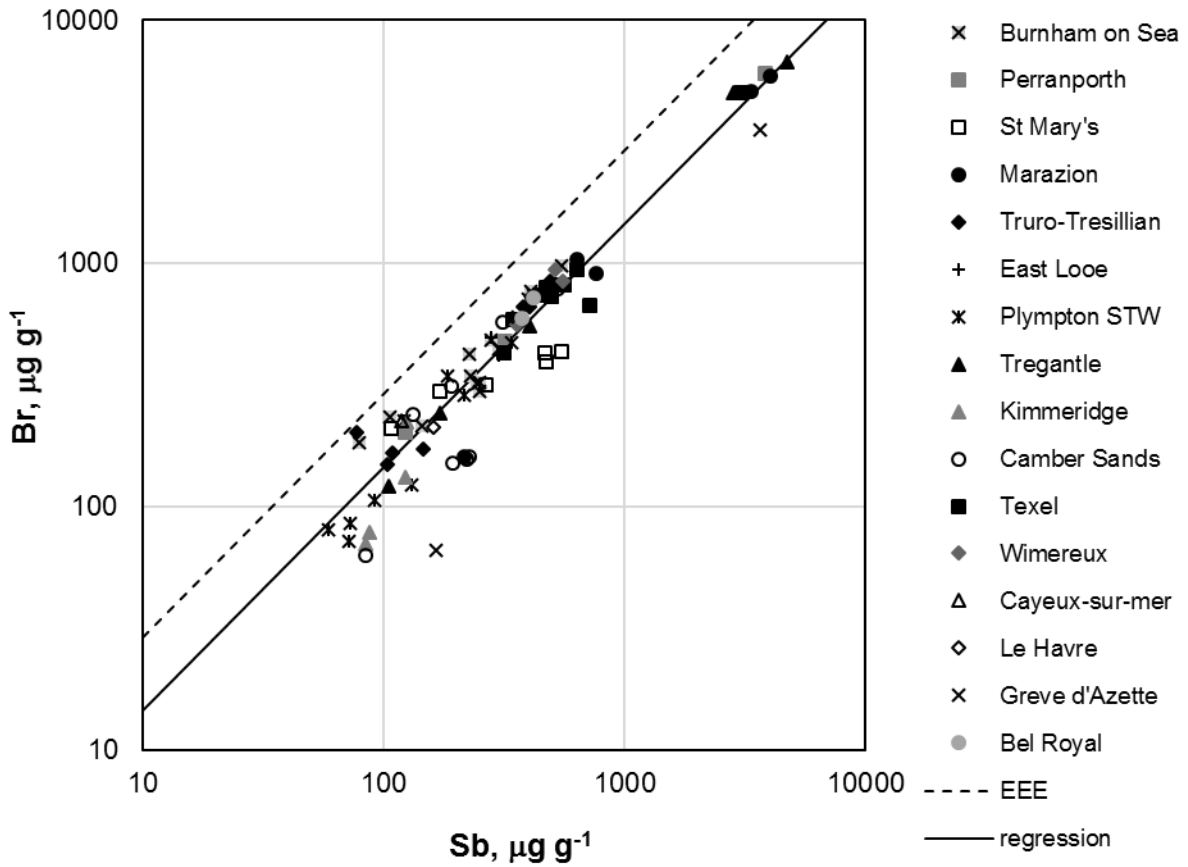
583 Figure 5: Relationship between Br and Sb in SWT bio-beads and beached bio-beads ($n = 89$, $r = 0.983$,
584 $m = 1.45$, $p < 0.01$). Note that Sb was not detected in samples form Freshwater West.



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589 Figure 6: Material regurgitated by *L. argentatus* illustrating the presence of pre-production pellets,
590 bio-beads and various secondary microplastics amongst food and other material (seaweed,
591 crabshell, barnacle fragments).

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