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

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ABSTRACT

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

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1. Introduction

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

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

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

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

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

2. Materials and methods

2.1. Sampling and sample locations

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

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

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

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

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

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

2.2. XRF analysis

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

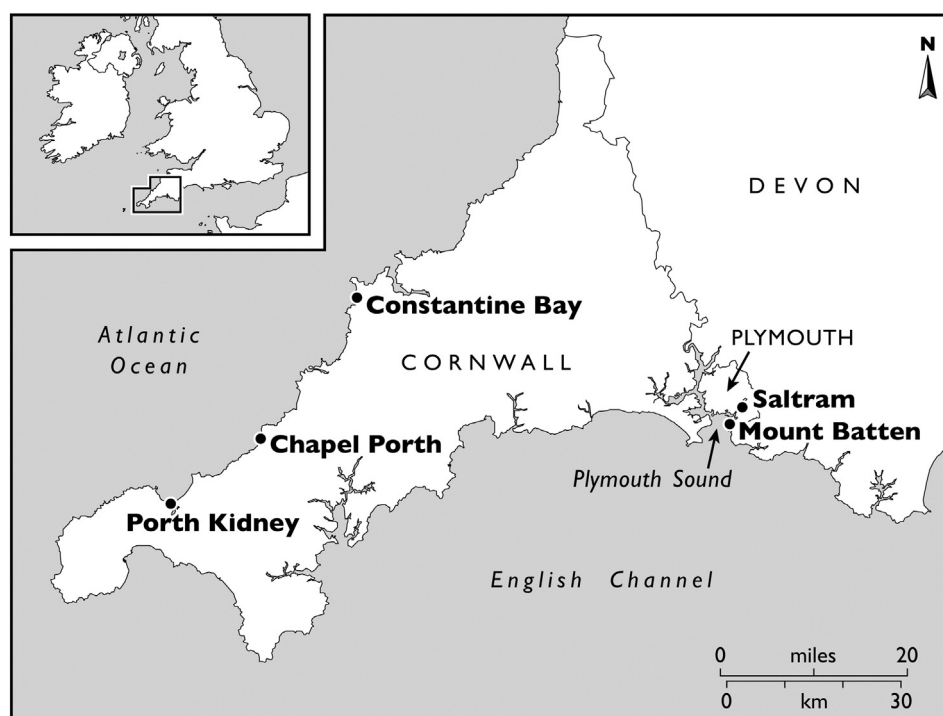


Fig. 1. Locations of the five beaches in SW England sampled in the present study.

Table 1

A comparison of measured and reference concentrations (in $\mu\text{g g}^{-1}$) in two impregnated Niton polyethylene disks. Errors denote either the 95% confidence level (reference) or one standard deviation (measured).

Material	As	Ba	Br	Cd	Cr	Hg	Pb	Sb	Se
PN 180-554									
Reference			495 \pm 20	150 \pm 6	995 \pm 40	1000 \pm 40	1002 \pm 40		
Measured ($n = 5$)			497 \pm 3	135 \pm 5	1063 \pm 7	912 \pm 5	964 \pm 21		
PN 180-619									
Reference	51 \pm 7	704 \pm 45		292 \pm 20	106 \pm 10	101 \pm 10	155 \pm 12	94 \pm 10	207 \pm 15
Measured ($n = 5$)	46 \pm 2	761 \pm 25		295 \pm 5	116 \pm 8	93 \pm 3	136 \pm 2	98 \pm 3	228 \pm 4

For the analysis of samples in the plastics mode, the instrument has a thickness correction algorithm down to 0.05 mm that employs a compensation for mass absorption coefficient based on Compton scatter so that variations in material density are factored in. Thickness correction was applied to all plastics whose depth was <10 mm and to all foams and ropes regardless of sample depth. Sample thickness was measured through the flattest ('measurement') surface using 300 mm Allendale digital callipers, and to increase the effective depth and flatness of the thinnest samples of plastic or rope, items were often cut (with scissors, pliers or a blade), folded or layered and, where necessary, held in place using crocodile clips.

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 μm polyester film and positioned centrally and with the measurement surface face downwards over the XRF measurement 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 μA and 20 kV/100 μA). Spectra were quantified by fundamental parameter coefficients to yield elemental concentrations on a dry weight basis (in $\mu\text{g g}^{-1}$) and with a counting error of 2σ (95% confidence). At the end of each 2–6 h session, spectra and elemental concentrations were downloaded to the laptop using Niton data transfer (NDT) PC software.

Element-specific limits of detection of the Niton XL3t are dependent on a number of factors, including mode of instrument application, counting time, and sample density, composition and thickness. In the plastics mode and for a counting time of 120 s, detection limits are generally lowest and below 40 $\mu\text{g g}^{-1}$ for each sample category (plastics, foams and ropes) for As, Br, Cr and Pb and highest and above 70 $\mu\text{g g}^{-1}$ for each category for Ba, Sb and Sn (Turner and Solman, 2016). Note that in the case of As, overlap of its K_{α} fluorescence peak with the L_{α} peak of Pb coupled with the relatively low intensity of the As- K_{β} line means that concentrations cannot be effectively calculated for samples with Pb:As ratios in excess of about 10 (Environmental Protection Agency, 2007). Arsenic concentrations reported herein are, therefore, restricted to those returned by the XRF where Pb was not detectable.

Table 1 shows the results of multiple analyses ($n = 5$) of two Niton reference plastics (PN 180-554, batch SN PE-071-N, and PN 180-619, LOT#T-18); these are polyethylene disks of thickness 13 mm and diameter 31 mm that have been impregnated with various elements. Where certified concentrations are reported, measured concentrations are

within 10% of reference concentrations in most cases and within 15% in all cases.

2.3. FTIR analysis

In order to identify the component polymers in the plastics, foams and ropes, a range of samples from each beach ($n = 100$ in total) were analysed by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) using a Bruker ALPHA Platinum ATR QuickSnap A220/D-01 spectrometer. Samples were cut to a suitable size, where necessary, using a stainless steel scalpel, before being firmly clamped down on to the ATR diamond crystal. 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, with subsequent identification involving comparisons of transmittance spectra with libraries of reference spectra.

3. Results

3.1. Sample characteristics

Table 2 presents a summary of the different categories of samples collected, in terms of both number and mass. The total number of samples was 573, with at least 70 samples being collected from each beach. Plastics comprised about a half of the number of samples in total, and on individual beaches percentage contributions of plastics to the total sample number ranged from 34% (MB) to 78% (SA). Foams comprised about a third of all samples on this basis with the percentage contribution ranging from 18 (SA) to 57 (MB), while values for ropes were 16% overall and relative contributions that ranged from about 4% (SA) to 36% (CB).

The total mass of material retrieved was about 1 kg, and the mass of individual items ranged from about 2 mg to 50 g. Overall, and on three individual beaches, plastics were the dominant material on a mass basis. The mass contribution of foams to the total loading was about a half of that of plastics, but on two beaches (MB and PK) foams represented the dominant material category. Overall, the mass contribution of ropes was the lowest of the three categories considered but on a location basis relative contributions were highly variable and ranged from about 1% to 36% of total mass (SA and CP, respectively). Sample thickness ranged from about 0.3 mm for a number of plastic films to >40 mm for several foams, and primary diameter or length ranged

Table 2

The numbers and masses of the items in different categories of marine litter retrieved from each beach.

Beach	Plastics			Foams			Ropes			Total	
	<i>n</i>	Total, g	Median (min-max), g	<i>n</i>	Total, g	Median (min-max), g	<i>n</i>	Total, g	Median (min-max), g	<i>n</i>	Combined mass, g
Chapel Porth	50	173.09	2.32 (0.17–27.92)	38	43.18	0.34 (0.01–15.02)	13	119.64	1.55 (0.20–40.10)	101	335.91
Constantine Bay	61	76.24	0.45 (0.02–13.49)	34	22.79	0.36 (0.01–5.43)	54	47.61	0.50 (0.13–6.81)	149	146.64
Mount Batten	41	98.30	0.95 (0.03–17.40)	70	100.90	0.23 (0.002–22.15)	11	7.95	0.69 (0.11–2.28)	122	207.15
Porth Kidney	67	38.61	0.19 (0.01–11.8)	47	42.43	0.07 (0.004–11.48)	10	3.22	0.26 (0.02–1.09)	124	84.26
Saltram	60	129.75	0.55 (0.009–20.19)	14	63.24	0.61 (0.09–49.80)	3	2.22	0.53 (0.13–1.56)	77	195.21
Total	279	515.99	0.54 (0.009–27.92)	203	272.54	0.26 (0.002–49.80)	91	180.64	0.56 (0.02–40.10)	573	969.17

Table 3
Distributions and summary statistics for the elemental concentrations in beached plastics ($n = 279$). All concentrations are in $\mu\text{g g}^{-1}$ and elements are ordered according to descending number detected.

	No. detected	$10^0\text{--}10^1$	$10^1\text{--}10^2$	$10^2\text{--}10^3$	$10^3\text{--}10^4$	$10^4\text{--}10^5$	$>10^5$	Min.	Max.	Median
Cl	225		23	117	68	4	13	22	532,000	672
Zn	139	1	83	43	8	4		5.1	26,700	58
Cr	127		113	13	1			21	1240	37
Cu	71	1	49	21				9.9	718	52
Br	53	16	29	6	1	1		4.7	17,900	20
Pb	43	8	15	7	10	3		6.3	17,500	87
Ba	39			11	24	3	1	236	143,000	1690
Sb	18			15	2	1		154	12,600	262
Sn	16		3	9	4			34	2090	211
Cd	11			5	6			117	4640	1270
As	8	6	2					4	21	8
Ni	7		6	1				17	555	29
Se	5			5				214	563	334
Hg	3		1	2				54	273	156

from about 3 mm for various plastic fragments and pellets to >10 cm for a number of plastic objects and pieces of foam and rope.

More than half of the samples in the plastics category were unidentifiable fragments of varying size. Many samples that were recognisable from either fragments or as whole objects could be classified according to the OSPAR marine litter monitoring guidelines (OSPAR Commission, 2010), and in descending order of abundance, as bottle caps and lids, production pellets, injection gun caps, lolly sticks, cutlery and straws, toys, shotgun cartridges, cigarette lighters, pens and strapping bands. Other recognisable fragments not categorised by OSPAR appeared to be derived from garden furniture and fencing, adhesive taping, piping, plant pots, vials and a traffic safety barrier. Likewise, and regarding foams, most items were unidentifiable fragments of varying size, but fast food containers, polystyrene cups, foam sponge and miscellaneous polystyrene pieces were consistent with OSPAR classifications; note that polyurethane and expanded rubber, which were abundant on some beaches, do not appear to have equivalent or distinct classifications. According to OSPAR, rope samples could be classified, in decreasing order of abundance, as rope per se (and by definition of diameter >1 cm), netting, tangled nets-cord-rope, string and cord (diameter <1 cm), fishing line and 'other' textiles.

3.2. Elemental content of litter

Tables 3 to 5 show the concentrations of the different elements in the three categories of litter. Here, data are pooled for the five locations in order to evaluate elemental differences among the different types of

material, and elements are shown in order of descending number of cases detected and in terms of both concentration distributions and summary statistics. Regarding plastics (Table 3), Cl was the most abundant element, being detected in 225 out of 279 samples and at concentrations up to about 50% by weight. Zinc was the most abundant heavy metal detected and at concentrations up to about $25,000 \mu\text{g g}^{-1}$. Among the remaining elements that were detected in more than ten cases, maximum concentrations were at least $1000 \mu\text{g g}^{-1}$ with the exception of Cu. Median detectable concentrations were greatest and above $500 \mu\text{g g}^{-1}$ for Cd, Cl and Ba and lowest and below 50 for Cr, Br, As and Ni. With respect to the foams (Table 4), and as above, the most abundant element was Cl, being detected in 195 out of 203 cases and up to concentrations of 63% by weight; compared with plastics, however, the median concentration was two orders of magnitude higher. The second most abundant element in the foams was Br, with maximum and median concentrations of about $18,000 \mu\text{g g}^{-1}$ and $250 \mu\text{g g}^{-1}$, respectively. Chromium, Cu, Pb, Sn and Zn were all detected in $>10\%$ of samples analysed with median concentrations above $100 \mu\text{g g}^{-1}$ and maxima ranging from about $1000 \mu\text{g g}^{-1}$ (Cr) to $>25,000 \mu\text{g g}^{-1}$ (Zn). Likewise, in the ropes category (Table 5) Cl was the most abundant element, being detected in 85 out of 91 samples, but median and maximum concentrations (about $1500 \mu\text{g g}^{-1}$ and $50,000 \mu\text{g g}^{-1}$, respectively) were lower than in both plastics and foams. Bromine, Cr, Cu, Pb and Zn were detected in $>40\%$ of rope samples, with median concentrations ranging from $26 \mu\text{g g}^{-1}$ for Br to $139 \mu\text{g g}^{-1}$ for Pb and maxima that were about an order of magnitude higher than corresponding medians.

Table 4
Distributions and summary statistics for the elemental concentrations in beached foams ($n = 203$). All concentrations are in $\mu\text{g g}^{-1}$ and elements are ordered according to descending number detected.

	No. detected	$10^0\text{--}10^1$	$10^1\text{--}10^2$	$10^2\text{--}10^3$	$10^3\text{--}10^4$	$10^4\text{--}10^5$	$>10^5$	Min.	Max.	Median
Cl	195			3	20	96	76	743	633,000	65,700
Br	155		38	86	28	3		12	17,600	244
Cr	148		23	125				23	940	252
Zn	120		19	68	31	2		26	25,300	248
Cu	39		4	32	3			71	1910	219
Pb	34	1	15	11	6	1		6.7	17,000	111
Sn	26		3	20	3			53	2280	209
As	12		9	3				25	210	62
Ba	12			6	6			298	4620	1000
Sb	4		1	2	1			67	5820	259
Ni	2			2				224	410	317
Cd	0									
Hg	0									
Se	0									

Table 5

Distributions and summary statistics for the elemental concentrations in beached ropes ($n = 91$). All concentrations are in $\mu\text{g g}^{-1}$ and elements are ordered according to descending number detected.

	No. detected	10^0 – 10^1	10^1 – 10^2	10^2 – 10^3	10^3 – 10^4	10^4 – 10^5	$>10^5$	Min.	Max.	Median
Cl	85			35	30	20		189	49,900	1510
Cu	63		42	20	1			26	1230	76
Br	51	3	46	2				6.3	247	26
Zn	40	1	32	7				9.1	535	35
Cr	39		27	12				25	908	72
Pb	36	1	14	18	3			9.5	3770	139
Sn	8		4	4				49	467	121
As	3	1	2					6.6	17	15
Ba	2			2				196	356	278
Ni	2		1	1				37	735	386
Sb	1			1				122	122	122
Cd	0									
Hg	0									
Se	0									

Overall, and across all litter categories, Cl was detected in the most cases (505 out of 573), with Br, Pb, Zn, Cu and Cr detected in >100 samples each and Hg and Se detected in the fewest cases (3 and 5 samples, respectively); overall median concentrations were $>1000 \mu\text{g g}^{-1}$ for Ba, Cd and Cl and $<50 \mu\text{g g}^{-1}$ for As.

4. Discussion

Only a limited number of previous studies have addressed associations of heavy metals and other hazardous elements with marine litter. Specifically, Ashton et al. (2010) determined the concentrations of metals that could be extracted by acid from beached plastic production pellets in south west England and found aluminium-normalised enrichment factors, relative to extraneous material (e.g. silt), that exceeded unit value in a few cases. Holmes et al. (2012) studied the kinetics of uptake of heavy metals from sea water by production pellets and found that aged pellets were more effective accumulators than virgin pellets, while Rochman et al. (2014) conducted a 12-month study in San Diego Bay and demonstrated that many metals could be accumulated by different types of plastic in the long-term.

Although plastics clearly have the ability to accumulate or adsorb heavy metals, resultant, absolute concentrations are typically on the order of a few ng g^{-1} to a few $\mu\text{g g}^{-1}$ (Ashton et al., 2010). In the plastic matrix itself, however, the results of the present study and the limited data reported by Nakashima et al. (2012) for metals (and mainly Pb) in a variety of plastics retrieved from a number of Japanese beaches reveal elemental concentrations that are highly variable but that may exceed a few percent by weight in many cases. The present study also reveals that metals and other elements are not just restricted to moulded plastic products and fragments, but are also encountered in foams and ropes.

Plastics with high concentrations of Cl (typically above 20%) were classified as polyvinyl chloride (PVC) by the XRF, an identification that was used to correct for mass absorption and density in the fundamental parameters calculations and that was subsequently confirmed by selected FTIR analyses. Many foams, with the exception of those that appeared to have been used for food packaging, were also classified as PVC by the XRF, and while FTIR confirmed that some of these samples were PVC-based, the majority analysed by this technique were identified as elasticated rubbers or expanded-extruded polystyrene and polyurethane. Elasticated rubber likely includes neoprene, or polychloroprene, a polymer resistant to burning which is used for cushioning, padding and thermal insulation (e.g. wet suits and waders). Regarding polystyrene and polyurethane foams, while Cl is not an inherent component of the respective polymers, it is a constituent of various flame retardants, such as Dechlorane Plus and chlorinated organophosphates, that have been added to products used for insulation or in soft furnishings (Katz and Milewski, 1987; King et al., 2009).

Bromine is also a component of many flame retardants, including those added to expanded-extruded polymers employed for thermal insulation and furnishings in both buildings and in transportation, and in plastics used for construction and electronic equipment. Hexabromocyclododecane (HBCD) was the principal flame retardant added to both expanded and extruded polystyrenes used for building insulation but was recently banned in the European Union under the EU Reach programme (Koch-Jugl et al., 2015) and in the US safer alternatives are currently being sought (US EPA, 2014). Depending on their use, flexible and rigid polyurethanes are often impregnated with a variety of brominated flame retardants. Polybrominated diphenyl ethers (PBDEs) were the main type used in flexible furnishings until health concerns at the beginning of the century led to the phase-out of certain congeners (Keimowitz et al., 2016), while bromine-containing polyols have been commonly added to rigid polyurethanes used for construction and insulation within the EU (Weil and Levchik, 2004).

Fig. 2 shows a scatter plot of the concentration of Br versus the concentration of Cl, where both elements were detected, for the plastics, foams and ropes categories of marine litter. While there was no significant correlation in the data, either overall or within a specific sample category, the distribution clearly shows a greater degree of both chlorination and bromination among the foams compared with the plastics and ropes. The latter two categories exhibit similar distributions because the dominant component materials, as identified by FTIR, were the same (polyethylene and polypropylene), while greater concentrations of Cl and Br associated with the expanded-extruded samples is

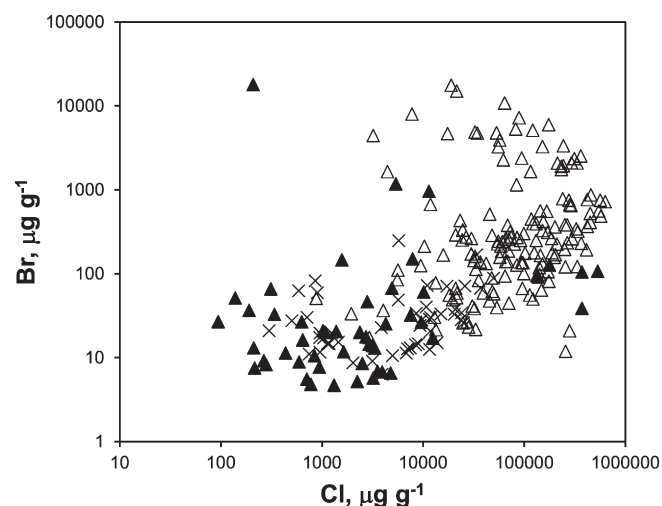


Fig. 2. Concentration of Br versus concentration of Cl in the beached plastics (▲), foams (Δ) and ropes (x).

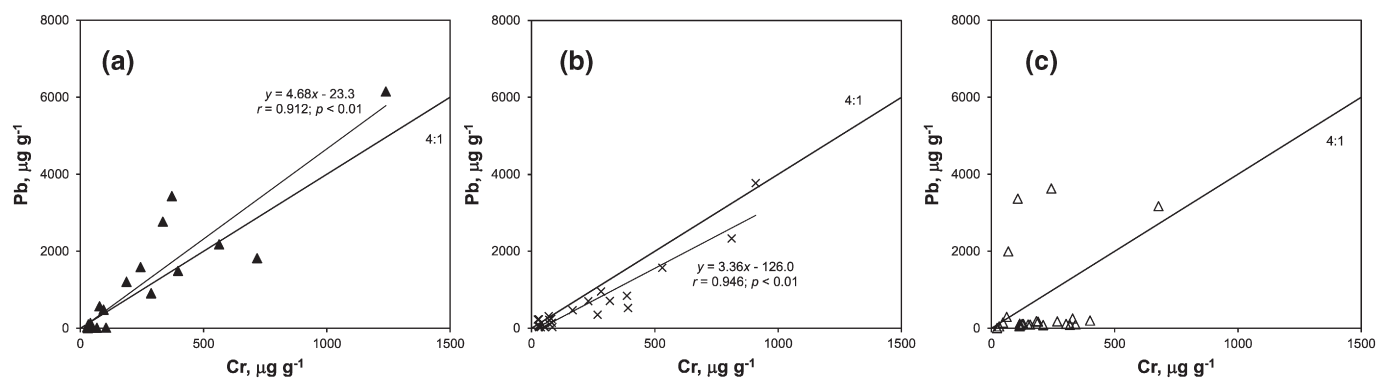


Fig. 3. Concentration of Pb versus concentration of Cr in beached litter: (a) plastics; (b) ropes; (c) foams. Also shown are the lines defining the mass ratio of Pb to Cr in lead chromate (4:1) and, for plastics and ropes, best fit regression lines.

due to the incorporation of flame retardants in the matrix. Presumably, therefore, the relative abundance of Cl and Br in polymeric foams reflects the type of flame retardant in the material, while low concentrations of both elements (including no detection) indicate the absence of such additives. Lack of flame retardants suggests use of the foams other than in construction, insulation or furnishing, or application in certain (marine) settings where fire would not be a concern (e.g. pontoons, buoys, boat hulls, life jackets).

Compounds of heavy metals and metalloids are added to plastics as fillers, heat and UV stabilisers, pigments for colour, release agents, activators, biostabilisers, antimicrobial agents, catalysts and intermediates. In expanded and extruded materials, and in particular in rigid polyurethane, some compounds of Sb and Zn also serve as flame retardants and/or smoke suppressants (Zatorski et al., 2008) (note that Zn was frequently measured at concentrations exceeding $1000 \mu\text{g g}^{-1}$ in the polyurethane foams in the present study; Table 4). Antifouling agents containing Cu(I), Zn, Sn, Pb or Hg are (or have been) added to marine paints to prevent biofouling, and such formulations may have also been applied to netting and ropes if used for aquaculture (Guardiola et al., 2012).

Among the heavy metals studied, Cd and Pb are of greatest concern because of their risks to health and the environment and their widespread occurrence and elevated concentrations in a variety of litter samples. Cadmium was detected at concentrations above $100 \mu\text{g g}^{-1}$ in 11 samples of beached plastics, of which only one was clearly classifiable (a shot gun cartridge). Although Cd has been used as a heat and UV stabiliser in some PVC products at concentrations up to about $30,000 \mu\text{g g}^{-1}$ by weight (Tamaddon and Hogland, 1993), it has been more widely employed in a variety of plastics for colour and at concentrations up to about $10,000 \mu\text{g g}^{-1}$ (Hansen et al., 2013). Cadmium sulphide and Cd selenosulphide pigments provide a range of colours that can be adjusted by partial replacement of Cd^{2+} by Zn^{2+} (yellow to green) or replacement of sulphur by selenium (forming oranges and reds) (Pritchard, 1998). In the samples of plastic where Cd was detected, Se was reported in 5 cases, with the mass ratio of Cd to Se ranging from about 3 to 8 and colours that were mainly orange or green. Although Cd in plastic has been restricted or banned under various Directives, it is likely to be encountered in certain products still in use in the domestic and urban settings (Hansen et al., 2013), thereby explaining its widespread occurrence in beached marine litter.

Lead was detected in a range of plastics, ropes and foams in the present study. Among the plastics, the highest concentrations were encountered in various fragments that were mainly red or yellow but occasionally green, white or grey. Ropes and netting that contained Pb in excess of a few hundred $\mu\text{g g}^{-1}$ were always orange, while foams containing Pb in excess of $1000 \mu\text{g g}^{-1}$ were usually rigid polyurethane. Lead was commonly employed as a heat and UV stabiliser in PVC, and

in a number of pigments (but largely lead chromates) provided a wide range of colours in a variety of plastics. Concentrations of Pb added to plastics were variable but generally $<50,000 \mu\text{g g}^{-1}$ by weight (Hansen et al., 2013) until various Directives resulted in the discontinuation or phase-out of lead compounds by the plastics industry.

Among the 43 plastics in which Pb was detected, only three were PVC (according to the XRF classification based on Cl content); however, where both Pb and Cr were both measurable ($n = 22$) there was a significant relationship between the two metals with a slope that was close to the mass ratio of Pb to Cr in lead chromate (about 4; Fig. 3a). No rope samples containing Pb were classified as PVC by the XRF but, as above, a significant relationship between Pb and Cr with a slope close to the Pb to Cr mass ratio in lead chromate was observed among the 24 samples in which both metals were detected (Fig. 3b). Regarding the foams, there was no significant relationship between Pb and Cr where both metals were present ($n = 26$) and the concentration of Cr exceeded that of Pb in most cases (Fig. 3c). Overall, however, the highest concentrations of Pb among the foams were encountered where Cr was not detected.

The observations above suggest that lead chromates are the most abundant form of Pb among the plastics and ropes but that expanded-extruded polymers, and in particular rigid polyurethanes, contain Pb derived from a different source. Although it is unclear why Pb is so abundant among the polyurethane samples, Szycher (2013) makes reference to a few heavy metals, including Pb, as possible leachable toxins in such polymers, while Carraher (2005) notes the catalytic properties of monomeric, organolead compounds in the formation of some foams produced in the 1960s.

The presence of plastic litter containing hazardous elements represents a potential source of localised contamination in the marine environment. For example, the highest concentrations of Cd and Pb in the plastics category are three to four orders of magnitude higher than the respective median concentrations in sandy sediment from the south west coast of the UK (0.5 and $12.6 \mu\text{g g}^{-1}$; Schuwerack et al., 2007); consequently, the presence of just 0.1% of plastic fragments among the sediment may result in an order of magnitude elevation in the net content of Cd and Pb. Clearly, the risks and impacts associated with these elements will depend on their mobilities and bioaccessibilities in the polymeric matrix. Most metallic compounds are added to plastics as finely-divided solids that are incorporated into the polymer while in a liquid phase, meaning that dispersed particles are retained physically within the matrix and have little tendency to migrate, at least from new or undamaged products (Pritchard, 1998). With wear and tear, abrasion and degradation, however, or the very effects that plastics are subjected to while suspended or beached in the marine environment, particles may be released (Hansen et al., 2013). Of particular concern in this respect are PVC-based materials, where the release of Cl appears to facilitate the migration of other components (Piorek 2004). The nature and

kinetics of hazardous element mobilisation from a variety of plastics, foams and ropes are currently under investigation.

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