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Trace elements in fragments of fishing net and other filamentous plastic litter from two beaches in SW England

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Abstract

Filamentous plastic litter collected from two beaches in south west England has been characterized by FTIR and XRF. The majority of samples were constructed of polyethylene and consisted of twisted or braided strands of a variety of colours that appeared to be derived from commercial fishing nets. A number of different elements were detected among the samples but, from an environmental perspective, the regular occurrence of Cr and Pb and the occasional or isolated occurrence of Br, Cd and Se were of greatest concern. The highest total concentrations of Br (2420 μg g^{-1}), Cd (1460 μg g^{-1}), Cr (909 μg g^{-1}), Pb (3770 μg g^{-1}) and Se (240 μg g^{-1}) were always encountered among orange samples and are attributed to the presence of lead chromates and cadmium sulphoselenide as colourants and to brominated compounds as flame retardants. Element bioaccessibility was evaluated by ICP-MS following an acidic extraction test that mimics the digestive tract of seabirds, with maximum values after a seven-day incubation period and relative to respective total concentrations of 0.2 to 0.4% for Cd, Cr and Pb and about 7% for Br. In addition to the well-documented impacts on wildlife through entrapment, filamentous plastic waste may act as a significant source of hazardous chemicals into the marine foodchain through ingestion.

Keywords: filamentous plastic litter; fishing gear; FP-XRF; heavy metals; bromine; seabirds

Capsule: Many fragments of beached filamentous plastic litter contain elevated concentrations of hazardous elements and pose a chemical threat to wildlife

1. Introduction

Marine plastic litter is a global problem that has a variety of environmental, social, aesthetic and economic impacts. Amongst the risks of floating, deposited or beached plastics to marine wildlife, the most serious result from entanglement and ingestion. Entanglement may cause suffocation, impair swimming or mobility, disrupt feeding, and result in maiming-amputation and infection (Votier et al., 2011; Lawson et al., 2015), while ingestion may obstruct or damage the linings of digestive tracts, reduce feeding drive and lower fat deposition (Verlis et al., 2013; Welden and Cowie, 2016). Filamentous plastic material, including twine, netting, rope, cord, line and fibres, and ranging in length from a few hundred microns to several metres, is particularly significant in these respects, being responsible for the majority of entanglements of many animals (Gilardi et al., 2010; McIntosh et al., 2015) and frequently representing the dominant type of synthetic material retrieved from the digestive tracts of dissected organisms (Devriese et al., 2015; Nadal et al., 2016).

Despite the well-documented physical impacts incurred by synthetic filamentous products and fragments, there is little understanding of the chemical makeup of such material, and in particular the presence and mobility of potentially hazardous additives within the polymeric matrix. Inorganic and organic compounds are added to plastics to improve or modify processing, performance, safety, cost, strength, flexibility, appearance, colour, stability and durability, and, aside from reactive

organics, such as some flame retardants, are not chemically bound to the polymeric matrix (Hansen et al., 2010).

The present study, therefore, seeks to determine the presence, abundance and bioaccessibility of trace metals, metalloids and other elements that are either intrinsically harmful or that are indicative of harmful substances in samples of filamentous plastic litter collected from sections of two beaches in south west England. A technique based on x-ray fluorescence (XRF) configured in a low-density, 'plastics' mode is employed as a direct, non-destructive means of determining elemental content, while bioaccessibility is evaluated using a physiologically-based extraction test (PBET) that is based on the digestive environment of plastic-ingesting seabirds.

2. Materials and methods

2.1. Sampling and sample processing

Samples were collected from two high-energy, macrotidal, sandy beaches in Cornwall (Figure 1). Whitsand Bay, on the south (English Channel) coast of the county, is located about 10 km to the west of Plymouth; its expansive, south west-facing beach is backed by steep cliffs that fragment the region at high tide into a series of rocky coves. Constantine Bay is located on the north (Atlantic) coast of the county and about 60 km to the north west of Plymouth; its arcing, north west-facing beach is backed by shallow, grassy dunes.

The two beaches were sampled on single occasions and about an hour after high water during the autumn of 2015. Pieces of rope, netting, cord and fishing line that were

visible to the naked eye were collected by hand from a ~ 50 m transect of the high water line, evident from the recent accumulation of macroalgae and debris. Samples were transported in polyethylene zip-lock bags to the laboratory at Plymouth University where they were cleared of sand and algae under running tap water and with the aid of a Nylon brush before being dried at 40 ^{o}C in an oven for about 12 h. Samples were then weighed on a five-figure balance before being stored individually in labelled polyethylene specimen bags and in the dark pending analysis.

2.2. FTIR analysis

The component polymers of the filamentous plastic samples were determined by Fourier transform infra-red (FTIR) spectroscopy using a Bruker ALPHA Platinum attenuated total reflection QuickSnap A220/D-01 spectrometer. Samples were cut to a suitable size using a stainless steel scalpel or scissors 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, and 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 (As, Ba, Bi, Br, Cd, Cl, Cr, Cu, Hg, Ni, Pb, Se, Sb, Sn and Zn) by energy dispersive field portable-XRF using a battery-powered Niton XRF analyser (model XL3t 950 He GOLDD+) according to protocols described in detail elsewhere (Turner and Solman, 2016) and summarised below. Thus, the instrument was used in the laboratory in a bench-top accessory test stand and was connected to a laptop computer via USB and a remote trigger. The XRF was

operated in a plastics mode that employs a compensation for mass absorption coefficient based on Compton scatter and corrects for sample thickness down to 0.05 mm. Whole samples, offcuts or sections of monofilamentous material that had been manually intertwined were measured for thickness using digital callipers before being placed on 3.6 μm polyester film and positioned centrally and with the measurement surface face downwards over the XRF detector window. On closing the steel shield of the stand, measurements, with appropriate thickness correction, were activated through the laptop for a total period of 120 seconds (60 seconds each at 50 kV/40 μA and 20 kV/100 μA). Spectra were quantified by fundamental parameters to yield elemental concentrations on a dry weight basis (in $\mu g\ g^{-1}$) and a counting error of 2σ (95% confidence) that were downloaded to the laptop using Niton data transfer (NDT) PC software.

Limits of detection, calculated by fundamental parameters, varied according to the precise density, shape and thickness of sample, but median concentrations ranged from $< 10\ \mu g\ g^{-1}$ for As, Br and Pb to $> 300\ \mu g\ g^{-1}$ for Ba and Cl. Multiple analyses ($n = 5$) of two Niton reference plastics that had been impregnated with Br, Cd, Cr, Hg and Pb (PN 180-554, batch SN PE-071-N) and As, Ba, Cd, Cr, Hg, Pb, Sb and Se (PN 180-619, LOT#T-18) revealed measured concentrations that were within 10% of certified values.

2.4. PBET

In order to evaluate element bioaccessibility, nine 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).

149 The extraction was modelled on the digestive characteristics of the proventriculus-
150 gizzard (but not the intestine) of the northern fulmar, *Fulmarus glacialis*, a
151 procellariform known to ingest substantial quantities of plastics, including
152 filamentous waste.
153
154 Briefly, digestive fluid was prepared by dissolving 10 g of pepsin (lyophilised powder
155 from porcine gastric mucosa; Sigma-Aldrich) into one litre of 0.1 M NaCl solution
156 and adjusting the pH by addition of 1 M HCl to 2.5. Between 50 and 100 mg of 5 to
157 10 mm strands of each selected sample, cut with stainless steel scissors, were weighed
158 into individual 60 ml screw-capped polypropylene centrifuge tubes. After the addition
159 of 40 ml of extraction fluid, all tubes, including a control containing no solid material,
160 were capped and incubated in a shaking water bath set at 100 rpm and at 40 ^{o}C for a
161 period of about seven days (168 h). At pre-determined time-intervals, 1 ml aliquots of
162 extract were pipetted into individual Sterilin tubes where they were diluted to 5 ml
163 with 2% HNO_3 and stored at 4 ^{o}C and in the dark pending analysis.
164
165 *2.5. Analysis of extracts*
166 Elements detected directly in the rope samples by XRF (with the exception of Cl)
167 were determined in the PBET extracts by collision cell-inductively coupled plasma-
168 mass spectrometry (ICP-MS) using a Thermo X-series II (Thermoelemental,
169 Winsford UK) with a concentric glass nebuliser and conical spray chamber. The ICP
170 was calibrated externally using five mixed standards and five blanks prepared in 2%
171 HNO_3 and operated under conditions described elsewhere (Turner and Holmes, 2015).
172 Limits of detection, based on three standard deviations arising from blank
173 measurements, ranged from about 0.05 μg L^{-1} for Pb to about 10 μg L^{-1} for Br and Fe.

3. Results

3.1. Sample characteristics

In total, 153 samples of filamentous plastic litter were collected (100 from Whitsand and 53 from Constantine), a selection of which is illustrated in Figure 2. Sample length ranged from about 2 to 15 cm and sample thickness from about 0.1 to 20 mm. Dry sample mass ranged from about 90 mg to 6 g, and the total mass of material collected was 167 g (126 g from Whitsand and 41 g from Constantine).

The majority of samples (n = 149) consisted of twisted or braided strands that exhibited various degrees of fraying at the ends and disintegration throughout but with little evidence of fouling. Braided samples were usually flat but occasionally rounded and lacked a distinct or hollow core; many of these samples were kinked, hockled and/or knotted. Other samples consisted of monofilament line that was entangled and, in one case, bundled and knotted. FTIR analysis revealed that the majority (> 90%) of twisted and braided samples and two of the monofilament lines were polyethylene; remaining twisted and braided samples were polypropylene or a combination of polyethylene and polypropylene while remaining monofilament lines were polyamide.

Table 1 provides a classification of filamentous plastic litter by colour for both beaches. (Note that where braided samples were constructed of strands of two or more colours, the dominant colour was used for categorisation purposes.) Overall, green and blue were the principal colours on both a number and mass basis, with orange and yellow samples encountered on both beaches but black and white samples restricted to Whitsand and a single red sample encountered at Constantine. Monofilament line was

either green or orange, while all other green samples and the single red sample were braided; remaining colours were distributed between both braided and twisted types of filamentous litter.

3.2. Elemental concentrations

Also shown in Table 1 are summary statistics for each trace element on both beaches. Among the elements analysed, Hg was never detected and As, Ba, Bi, Cd, Ni, Sb, Se and Sn were detected in six cases or less; regarding the latter group, Ni was detected only in samples from Constantine while remaining elements were detected only in samples from Whitsand. Bromine, Cr and Cu were detected in more than half and Pb and Zn in just under half of all samples. These elements were distributed across all colour categories that contained multiple samples, but Cu was only detected in one orange sample and Br exhibited limited occurrence in yellow and orange samples. Median and maximum concentrations of Cr and Pb were considerably higher in the orange category than in the remaining colours, and the highest individual concentrations of Cr, Pb and Br and the only case in which Cd and Se were detected also occurred among the orange samples.

3.3. PBET results

There were only four cases in which extractable trace elements were detectable throughout the PBETs; namely, Br in an orange polyethylene braided fragment containing the highest total Br content, Cd in a bundle of orange, polyethylene strands knotted together and representing the only sample in which the metal was detectable by XRF (see below and Figure 3), and Cr and Pb in an orange polyethylene twisted fragment containing the highest contents of both elements. Extracted concentrations,

shown in Figure 4, exhibit a biphasic distribution consisting of a period of relatively rapid increase over the first few hours followed by a more protracted period of slower release. With no evidence of equilibrium being approached, data were fitted empirically with an equation of the following form (Turner and Lau, 2016):

$$[X(t)] = kt^{1/b} \qquad (1)$$

where t and $[X(t)]$ represent time and w/v time-dependent extractable elemental concentration, respectively, and k and b are constants. Concentrations and constants defining the kinetics of elemental mobilisation and derived from best-fit power equations to the timed data are given in Table 2. Here, $[X_T]$ is the total, w/w concentration as returned by the XRF, $[X_{max}]$ is the maximum w/w concentration at the termination of the PBET, and X_{max} relative to X_T represents the avian bioaccessibility after a period of seven days, with percentages ranging from < 0.5 for Cd, Cr and Pb to about 7 for Br.

4. Discussion

Although a few samples exhibited an appearance consistent with packaging or bale twine, it is suspected that the majority of filamentous plastic debris sampled in the present study originated from commercial fishing. Specifically, pieces of line or braided or twisted rope are generated during the damage, repair and abandonment of netting, and protective threads of dolly rope (chafer) are fractured as trawl nets are dragged along the seabed (Murray and Cowan, 2011). With samples being mostly constructed of polyethylene and polypropylene, whose densities (0.92 to 0.96 g cm^{-3}) are less than that of sea water (1.02 to 1.03 g cm^{-3}), and devoid of significant fouling,

this material is readily washed up on beaches. By the same reasoning, lack of samples retrieved that were composed of polyester, another common polymer used in fishing nets, can be explained by its higher density (about 1.4 g cm^{-3}) and propensity to sink when lost or discarded at sea.

The presence of trace elements in the samples is the result of additives or polymerisation catalyst residues in the plastic matrix. Depending on the application of the plastic, organic and inorganic additives may serve as fillers, pigments for colour, thermal stabilisers, UV-light stabilisers, flame retardants or antimicrobials (Ranta-Korpi et al., 2014). Regarding fishing rope and line, UV resistance is a particular requirement and specific colours may be needed for visibility, contrast and visual stimulus. Of concern from an environmental perspective is the addition of trace elements that are intrinsically hazardous (e.g. Cd, Cr and Pb) or that are a component of hazardous substances (e.g. Br) to achieve these requirements. Hazardous elements were most abundant in or restricted to filamentous material that was orange, a colour that is often employed to minimise horizontal contrast between netting and a grey-green water background (Wardle, 1986).

Where both Cr and Pb were detected in orange and yellow samples (that were all polyethylene), concentrations of the metals were significantly correlated (Figure 5), with all data points lying close to or below the slope defining the mass ratio of Pb to Cr in the pigment, lead chromate ($PbCrO_4$). Lead chromate itself is bright yellow but mixing with lead molybdate and lead sulphate produces a more light- and acid-resistant orange pigment (Maier and Calafut, 1998). While chromates have been used in many polymers and in a variety of applications for colour, brightness, opacity and

fastness, concerns about the toxicities and health impacts of Pb and hexavalent Cr have resulted in these compounds being restricted or phased out by the paint and plastic industries. Under the EU's REACH Regulation (EC 1907/2006 on the Registration, Evaluation, Authorisation and Restriction of Chemicals), for example, lead chromate has recently been banned following its identification as a substance of very high concern (SVHC) (ECHA, 2009). This classification requires suppliers of products containing more than 1000 $\mu g\ g^{-1}$ of the substance to provide guidance on the safe use and disposal of the material. Because lead chromate appears to be, or to have been, commonly employed in fishing nets and line, and at concentrations often well in excess of 1000 $\mu g\ g^{-1}$, such guidance would also be applicable to the fishing industry.

Cadmium was detected in one sample that, visually, was distinctly different to all other samples collected. Specifically, it consisted of about 15 bright orange polyethylene threads, of about 7 cm in length and 1 mm in diameter, that had not been intertwined but tied together as a bundle (Figure 3). It is suspected that this sample is a fragment of protective dolly rope that had been torn off on the sea bed or cast overboard during cutting or repair. The presence of Se in this sample suggests that the pigment employed for colour is cadmium sulphoselenide, a brilliant orange solid solution of CdS and CdSe. Although no hazards have been classified by the European Chemicals Agency for the pigment itself, compounds of both Cd and Se are highly toxic. According to the REACH Regulation, Cd is only permitted for use in plastics at concentrations below 100 $\mu g\ g^{-1}$ with the exception of articles constructed for safety reasons and where environmental or operating conditions are extreme or colour fastness and lifespan are critical (ECHA, 2012).

There are very few Br-containing colour pigments used in plastics, the principal one being based on halogenated copper phthalocynanine. Here, the ratio of Cl to Br is varied to effect different shades of green (Lewis, 2000), with the maximum Br content of the pigment being about 60% by weight and typical Br residue concentrations in plastics ranging from 60 to 3000 $\mu g\ g^{-1}$ (Ranta-Korpi et al., 2014). Consistent with these characteristics, Br was most frequently encountered in green ropes at concentrations up to about 80 $\mu g\ g^{-1}$, and in all but two of these samples Cu was detectable and at concentrations up to about 700 $\mu g\ g^{-1}$. A more important use of Br in polymers, however, is as a component of various aromatic and aliphatic brominated flame retardants, such as polybrominated diphenyl ethers, polybrominated biphenyl, tetrabromobisphenol A and hexabromocyclododecane. Flame retardants may be additive or reactive and occur in plastics at concentrations of up to a few per cent by weight (Leslie et al., 2016). Many of the more toxic retardants have been classified as SVHC under the REACH classification and as such have been restricted, phased out or banned. Neither FP-XRF nor FTIR are able to directly identify or discriminate brominated species in plastics unless molecular concentrations exceed a few percent. However, the three rope samples (one orange and two white) containing Br in excess of 500 $\mu g\ g^{-1}$ but with no detectable Cu and, in one case, the highest measured concentration of Sb (a component of the flame retardant synergist, antimony trioxide), are suspected to have been impregnated with brominated retardants.

Clearly, the impacts of toxic elements in filamentous plastic litter on wildlife depend on the scope for material to be ingested and the propensity of compounds to migrate from the polymeric matrix. Ingestion of synthetic fibres arising from the deterioration, degradation or abrasion of debris is known to occur in birds (Tanaka et al., 2013),

turtles (De Carvalho-Souza et al., 2016), invertebrates (Mathalon and Hill, 2014), crustaceans (Watts et al., 2015) and fish (Dantas et al., 2012), and there is evidence that orange material is preferentially ingested over other colours. For example, De Witte et al. (2014) observed a high proportion of orange fibres in the bodies of mussels from quayside mussels, while photographs of plastics retrieved from the stomachs of the short-tailed shearwater presented in Tanaka et al. (2013) illustrate filamentous debris that is orange. Although not empirically tested, it has been suggested that such colours could be popular due to food/prey resemblance (as, for example, fish eggs, larvae and zooplankton) (Kawamura et al., 2010; De Witte et al., 2014). Once ingested, filamentous material tends to remain in the digestive tract for longer periods than other plastic debris, and in particular in the less acidic gastric environments of small invertebrates, crustaceans and fish. This is because of both the requirement of individual strands having to orientate 'end-on' to pass through the gut and an increase in the effective size of strands through filament 'balling' (Murray and Cowie, 2011).

Regarding elemental mobilisation, lead chromate is sparingly soluble (Ksp = 1.8 x 10^{-14} at 25 ^{o}C) but dissolution is facilitated in saline solutions, with Pb appearing to leach more rapidly than Cr (White et al., 2014). Differential leaching under saline conditions may explain why many weathered, orange and yellow filamentous fragments retrieved from beaches have Pb to Cr ratios below the value defining pure lead chromate (Figure 5). With respect to mobilisation under the simulated acidic avian gastric conditions, we estimate seven-day bioaccessibilities of about 0.4% and 0.2% for Cr and Pb, respectively (Table 2).

Although both cadmium selenide and cadmium sulphide are negligibly soluble (*K*sp = 6.3×10^{-36} and 8.0×10^{-28} at 25 ^{o}C, respectively), Cd, but not Se, was detected throughout the time-course of the PBET, with a bioaccessibility relative to total Cd of about 0.3% at the end of the experiment (Table 2). In contrast, the bioaccessibility of Br at the end of the corresponding time-course was about 7%, from which we may infer that brominated flame retardants in this particular polyethylene were physically added to the polymer rather than being chemically bonded to it.

While the physical hazards to marine life arising from filamentous plastic, ranging from microscopic fibres to large fragments of fishing nets, are well-documented (Jacobsen et al., 2010; Denuncio et al., 2011; Benemann et al., 2016; Watts et al., 2014), this study has highlighted the potentially hazardous nature of such waste from a chemical perspective. Of particular concern is the occurrence of substances that have been restricted or banned in orange-yellow fragments derived from fishing activities. That these substances have been employed in (an albeit) decreasing range of plastic products over the past few decades (Hansen et al., 2010) suggests material for netting and rope is sourced from a variety of suppliers that are not necessarily tailored to the fishing industry. Among the most hazardous elements considered, Pb exhibited the highest abundance overall but Br exhibited the greatest avian bioaccessibility. This observation is consistent with the propensity of sea birds to accumulate congeners of brominated flame retardants that are not present in natural prey (pelagic fish) but in plastic fragments that have been ingested (Tanaka et al., 2013). Although the avian bioaccessibilities of Cd, Cr and Pb are relatively low, it must be borne in mind that kinetic profiles indicate continuous release from filamentous plastic and that synthetic material may be trapped in the digestive system

of some seabirds for periods of months or even years (Laist, 1987; Avery-Gomm et al., 2012).

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521 Table 1: Summary statistics for the concentrations of trace elements (μg g^{-1}) among the different

522 colours of beached filamentous plastic litter sampled from Whitsand and Constantine.

beach		As	Ba	Bi	Br	Cd	Cr	Cu	Fe	Ni	Pb	Sb	Se	Sn	Zn
Whitsand															
black (*n* = 9)	median				19.2		89.9	128	998		83.5	61.4			76.6
	min.				5.5		36.1	11.6	267		11.9				29.5
	max.				365		314	195	15,400		1010				163
	n				5		5	4	9		7	1			6
blue (*n* = 25)	median			11.3	20.1		122	119	1620		90.8	245			37.7
	min.			10.4	3.8		23.1	35.4	338		7.6				10.9
	max.			12.2	72.1		591	367	7790		834				588
	n			2	13		18	18	25		8	1			5
green (*n* = 39)	median	4.4	149	6.5	18.9		44.4	67.8	1360		17.5	99.0		20.0	40.2
	min.				5.0		23.2	22.0	242		2.8				16.6
	max.				63.7		219	671	8090		376				341
	n	1	1	1	28		19	32	39		17	1		1	16
orange (*n* = 8)	median			23.2	21.4	1460	420		713		806	75.4	240	23.9	33.8
	min.				11.2		160		92.5		336				18.4
	max.				2420		786		4900		2570				57.1
	n			1	3	1	7		8		7	1	1	1	5
white (*n* = 17)	median		1340		74.5		73.4	51.7	4080		35.1	795		183	52.2
	min.				5.3		24.9	37.9	789		8.0	276			28.5
	max.				681		431	60.9	18,900		348	1310			69.5
	n		1		12		12	3	17		8	2		1	7
yellow (*n* = 2)	median						157	235	658		653				24.7
	min.						31.9		607						
	max.						282		709						
	n						2	1	2		1				1
all (*n* = 100)	median	4.4	744	7.1	21.4	1460	79.1	76.7	1521		62.6	172	240	23.9	46.0
	min.		149	6.5	3.9		23.1	11.6	92.5		2.8	61.4		20.0	10.9
	max.		1340	23.2	2420		786	671	18,900		2570	1310		183	588
	n	1	2	4	61	1	63	58	100		48	6	1	3	40
Constantine															
blue (*n* = 7)	median				30.2		69.5	85.6	2630		123				34.2
	min.				17.4		27.8	30.7	513						29.7
	max.				90.9		109	808	3820						74.5
	n				3		4	7	7		1				3
green (*n* = 26)	median	16.9			18.4		35.9	58.7	1190	735	34.0				21.6
	min.				8.7		25.3	26.8	155		26.9				14.6
	max.				82.3		69.8	538	29,200		314				35.2
	n				12		8	24	26	1	7				10
orange (*n* = 8)	median				14.8		530	91	939	37.2	1570				36.4
	min.						71.8		465		216				22.9
	max.						909		1560		3770				47.5
	n				1		5	1	8	1	5				4
red (*n* = 1)	median				22.8		56.3		3690						145
	n				1		1		1						1
yellow (*n* = 11)	median				21.1		318	67.7	925		203				20.1
	min.				15.2		25.7	43.5	278		72.9				19.0
	max.				27.1		391	362	2110		838				66.2
	n				2		5	6	11		8				3
all (*n* = 53)	median	16.9			19.6		56.3	71.2	1160	386	182				26.0
	min.				8.7		25.3	26.8	155	37.2	26.9				14.6
	max.				90.9		909	808	29,200	735	3770				145
	n	1			19		23	38	53	2	21				21

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Table 2: Constants and concentrations defining the mobilisation of Br, Cd, Cr and Pb from three samples of orange, filamentous polyethylene (W = Whitsand; C = Constantine) whose kinetic profiles are illustrated in Figure 4. Note that an explanation of terms is given in the text.

sample	X	$[X_T]$, μg g^{-1}	$[X_{max}]$, μg g^{-1}	$[X_{max}]/[X_T]$, %	k, μg L^{-1} $h^{-1/b}$	b	r^2
W100	Br	2420	168	6.94	18.2	2.04	0.804
W86	Cd	1460	3.94	0.27	0.899	3.69	0.948
C51	Cr	909	3.28	0.36	9.17	14.6	0.276
C51	Pb	3770	8.40	0.22	13.7	6.17	0.813

532 Figure 1: Sampling locations for the filamentous plastic litter analysed in the present

533 study.

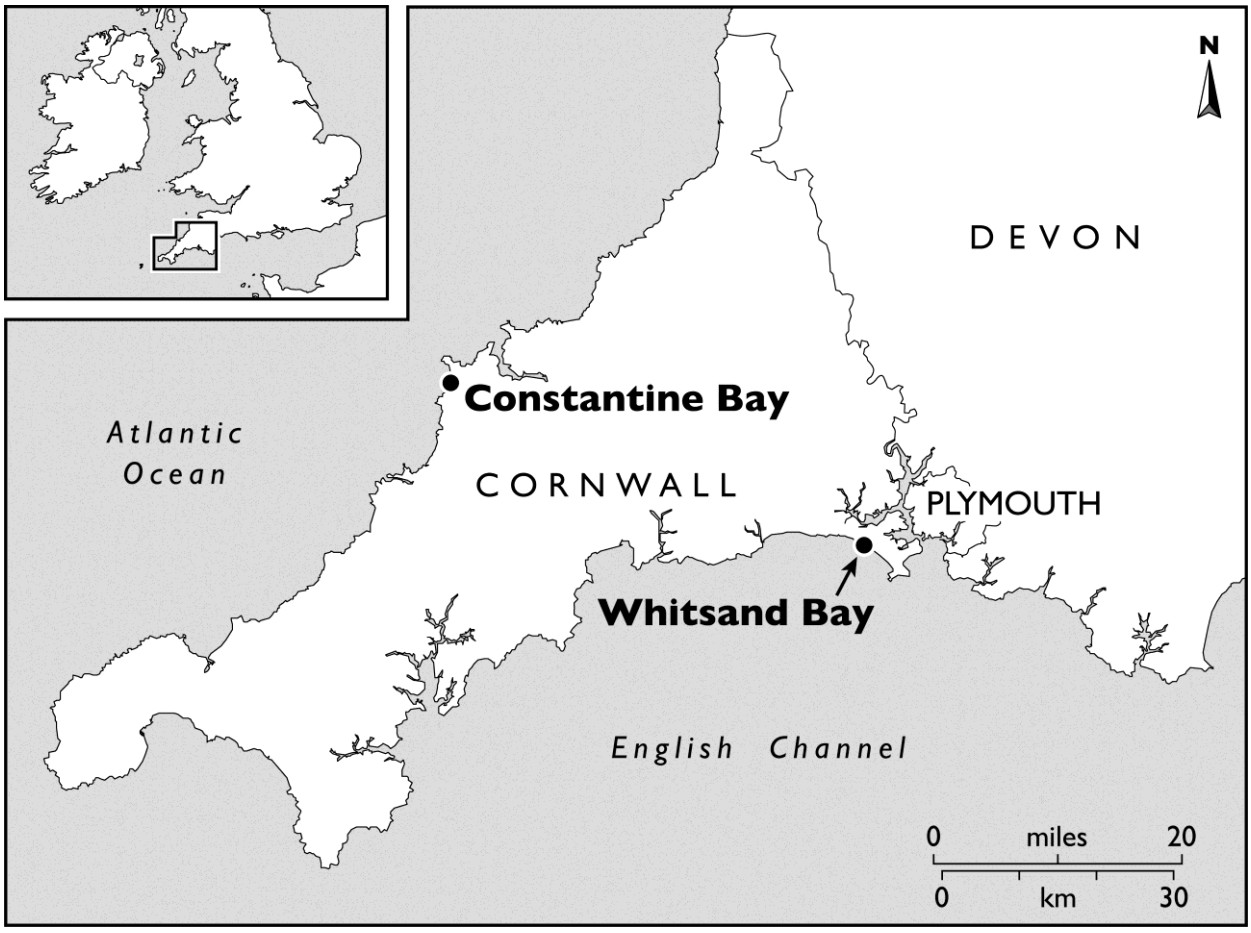

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Figure 2: A selection of filamentous plastic samples collected in the present study.

Figure 3: Orange polyethylene strands of approximately 7 cm in length that had been knotted together and in which Cd and Se were detected (sample W86).

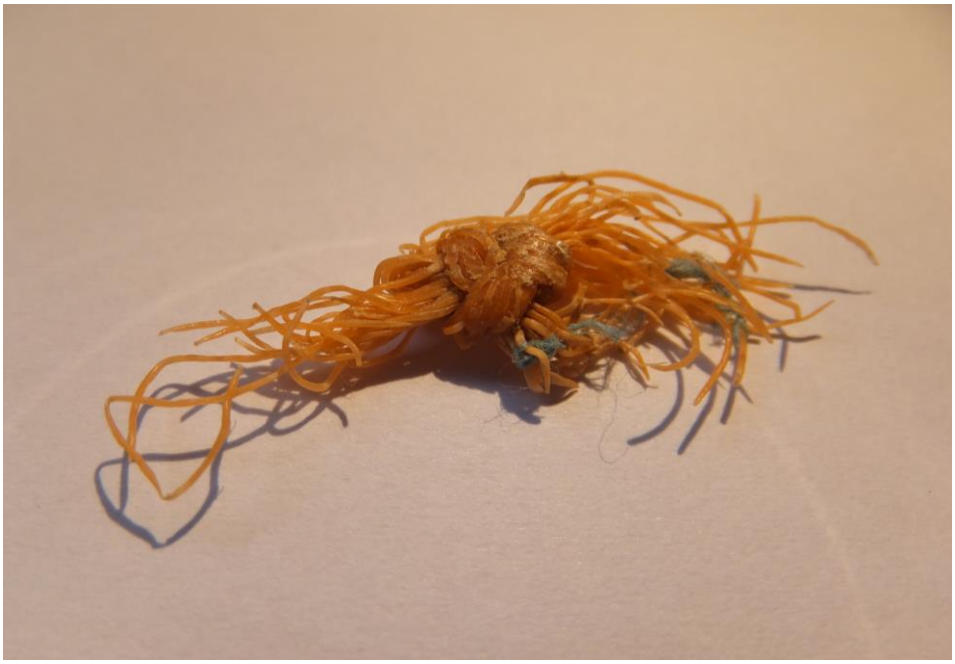
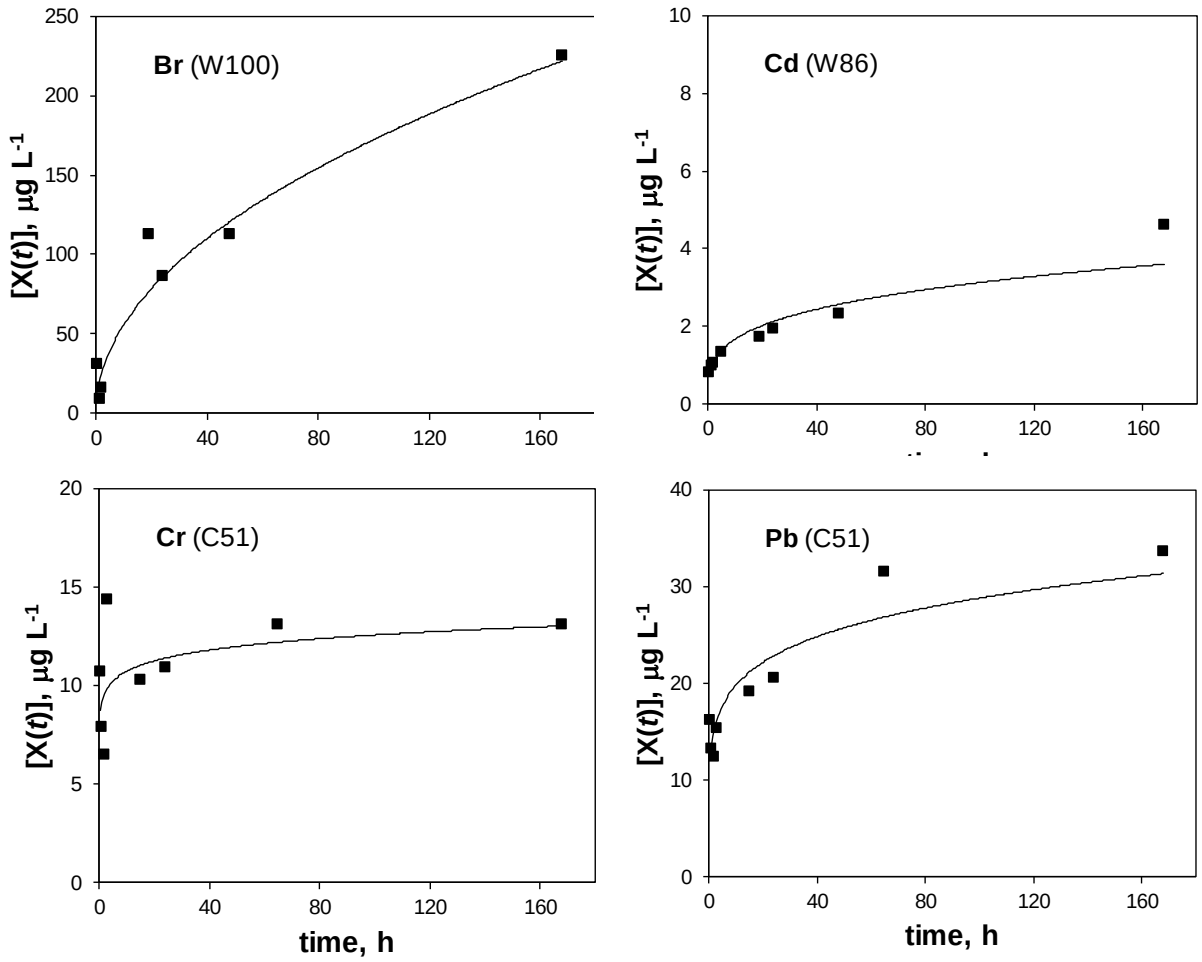


Figure 4: Kinetic profiles for the mobilisation of Br, Cd, Cr and Pb from three samples of orange, filamentous polyethylene (W = Whitsand; C = Constantine) by the avian PBET. Annotated are best-fits to the data according to equation 1. Constants and concentrations (in μg g^{-1}) defining the samples and profiles are given in Table 2.



572 Figure 5: Concentration of Pb versus concentration of Cr in the orange (filled) and
573 yellow (open) samples from Whitsand (triangles) and Constantine (squares). The solid
574 line represents the ratio of Pb to Cr in lead chromate (3.98).
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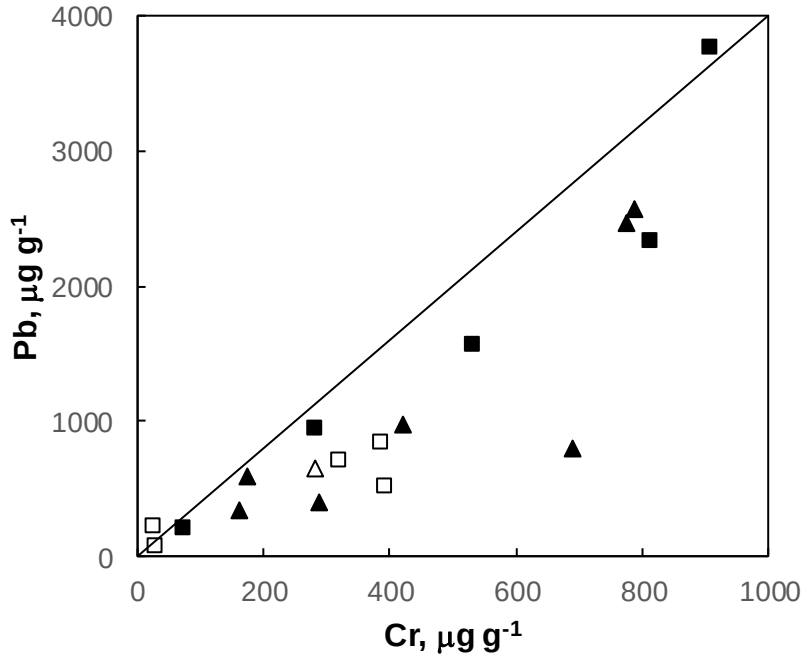

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