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Association of metals with expanded polystyrene in the marine environment

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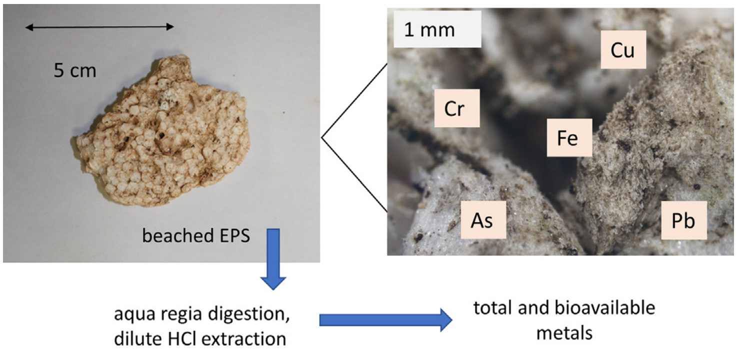
HIGHLIGHTS

- Fragments of expanded polystyrene (EPS) from coastal beaches analysed for metals
- Total metal concentrations similar at surface (<0.5 cm) and subsurface (>0.5 cm)
- All metals except Cu and Pb greater in EPS from an open beach than EPS from a harbour
- Metal availability to 0.7 M HCl ranged from <20 % for Al and Fe to >60 % for Mn and Pb
- Al-normalised enrichment factors suggest significant metal-EPS interactions in seawater

GRAPHICAL ABSTRACT



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ABSTRACT

Expanded polystyrene (EPS) has characteristics distinctively different to many thermoplastics that strongly influence its behaviour in the marine environment. However, the extent and nature of its interactions with metals are poorly understood. In the present study, fragments of beached EPS have been retrieved from an urban harbour and an open sandy beach in southwest England and the concentrations, locations and availabilities of various metals (and metalloids) of geochemical importance and anthropogenic significance determined. Total (aqua regia-digestible) metal concentrations at the surface (normalised to a depth of 0.5 cm) were considerably greater than surface concentrations reported for polyolefins retrieved from the same region and, with the exception of Cd, Sb and Zn, were significantly greater than those in unweathered EPS packaging material. Median surface concentrations of Al, As, Co, Fe, Mn, Ni and Sb were significantly greater at the open beach than the harbour, but concentrations of Cu and Pb were significantly greater at the latter. Where measured, concentrations of all metals were similar at the surface and subsurface (0.5 to 1 cm), and availability to 0.7 M HCl ranged from <20 % for Al and Fe to >60 % for Mn and Pb. These results, coupled with visible characteristics, suggest that aqueous and particulate metals are able to interact with the EPS surface via a number of mechanisms (adsorption, precipitation, entrapment) and migrate through the weathered, porous structure to within the polymer matrix. Enrichment factors normalised to Al as a granulometric proxy and relative to a regional baseline indicate "moderately severe" contamination with respect to Cd, Cu, Pb, Sb and Zn in at least one of the environments studied, suggesting that EPS might be a significant carrier and means of exposure for these metals in the marine environment.

1. Introduction

Over the past decade there has been considerable interest in the association of contaminants, like metals and persistent organic compounds, with marine plastics (including microplastics). This interest usually relates to the significance of plastics as carriers of contaminants in the marine environment (Ashton et al., 2010; Hirai et al., 2011; Mai et al., 2018; Maršić-Lučić et al., 2018) or as vectors of contaminant exposure to animals that inadvertently or incidentally ingest plastic (Rochman et al., 2014; Tanaka et al., 2015; Provencher et al., 2018; Turner, 2018). In these respects, the majority of such studies have focussed on low density plastics that are

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suspended in seawater or readily beached along strandlines, and in particular polyolefins like polyethylene and polypropylene.

Despite expanded polystyrene (EPS) being reported extensively, and often dominantly, among plastics retrieved from beach surveys and ocean trawls (Davis and Murphy, 2015; Lo et al., 2018; Kwon et al., 2020; Esiukova et al., 2021), relatively little attention has been paid to the association of potentially toxic contaminants with this polymer. The presence and effects of hexabromocyclododecane (HBCD), a brominated flame retardants added to EPS for the construction industry, have been reported in the Asia-Pacific region (Jang et al., 2016, 2017), and the presence of a limited number of metals added to EPS during manufacture or acquired from the environment has been documented where detection was achieved using X-ray fluorescence (XRF) spectrometry (Turner, 2021). Recent research employing more sensitive techniques (inductively coupled plasma spectrometry) following acid digestion suggest that metal concentrations in beached EPS are higher than in other plastics (Xie et al., 2021; Fred-Ahmadu et al., 2022). However, the precise reasons for this enrichment have not been fully explored or related to the distinctive features of aged EPS (highly porous surface and propensity to physically and chemically break down) and geochemical mechanisms that regulate metal-metal and metal-polymer interactions in the environment (including the sea surface microlayer).

In order to better understand the interactions between EPS and metals in the marine environment, beached EPS fragments have been retrieved from two different types of location in southwest England: a semi-enclosed, urban harbour and a sandy beach facing the open ocean. Sample surfaces have been investigated by conventional techniques (microscopy and Fourier Transform Infrared, FTIR, spectroscopy), and a broad range of metals of geochemical interest (e.g., Fe, Mn) and metals (and metalloids) with distinctive anthropogenic signatures (e.g., As, Cd, Cr, Pb) have been determined by inductively coupled plasma-mass spectrometry (ICP-MS) following total digestion. For a general evaluation of availability or bioaccessibility, metals have also been determined following extraction in dilute HCl, and for an assessment of the location of metals in the polymer, additional measurements have been made in sections taken from below the surface.

2. Methods

2.1. Sampling and sample processing

Sampling took place from two locations in the Plymouth district of southwest England during October 2021. Namely, Coxside, an urbanised, west-facing, pebble-gravel beach within 1 km of the city centre and in a relatively sheltered, semi-enclosed harbour setting (50.366; −4.130), and Wembury, a protected, sandy beach facing south and directly towards the English Channel and 7 km to the southeast of the city centre (50.318; −4.085).

Pieces of EPS of at least 2 cm in length were retrieved manually from the strandline or intertidal zone and were stored in individual polyethylene specimen bags. In total, 33 samples of sufficient size were obtained: 24 from Coxside and numbered C1 to C24, and 9 from Wembury and numbered W1 to W9. In the laboratory, samples were photographed with a scaled rule before being cleaned with a nylon brush under distilled water to remove any adherent sand and algae. Samples were then dried overnight at 40 °C in a drying cabinet and stored individually in clean bags. Additional, unweathered pieces of EPS ($n = 3$) were cut from polystyrene packaging using a stainless-steel blade and stored likewise.

2.2. Sample characterisation

Dried samples were inspected and photographed under a Nikon SMZ800 microscope fitted with an Olympus SC30 camera and coupled to Olympus Stream Motion software. Confirmation of the polymer and evidence of any aging were established by attenuated total reflectance FTIR spectrometry using a Bruker Vertex 70. A stainless-steel scalpel was used to scrape a piece of a few mm^2 and a thickness of <1 mm from sample surfaces. Scrapings were clamped with the outer face against the diamond crystal before spectra were acquired with 16 scans in the region 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1}.

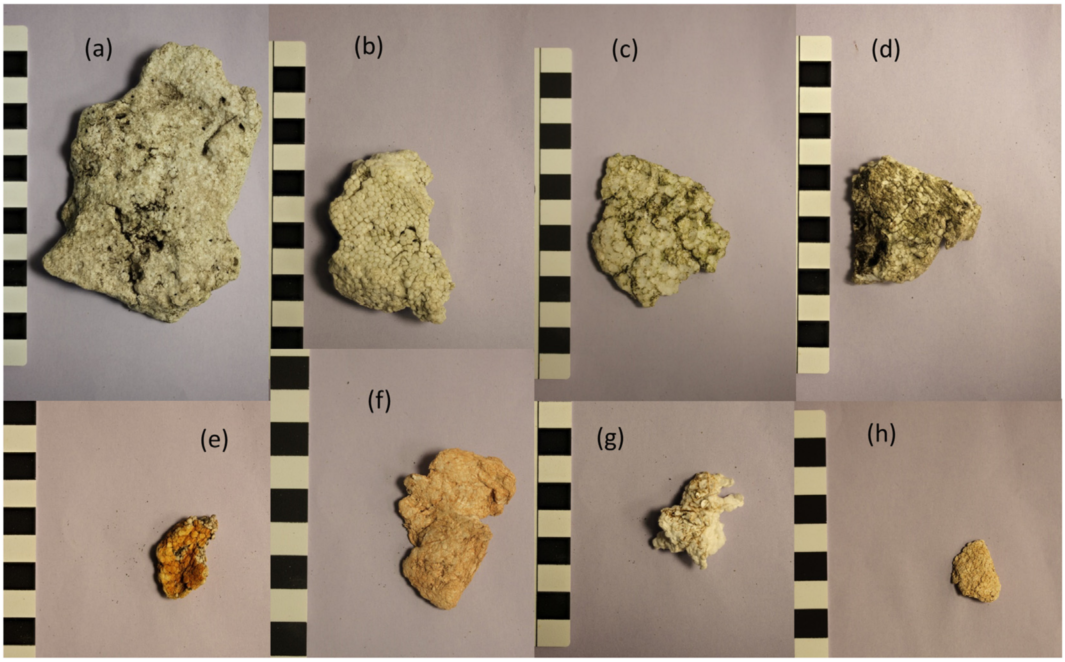

Fig. 1. A selection of EPS samples photographed against a cm-scaled rule: (a) to (d) off-white-greenish fragments of various sizes from Coxside (sample #s C2, C6, C7, C10), with black staining evident within pits and cracks and 2–5 mm-sized beads of varying form and distinctiveness; (e) a bright orange, 3-cm fragment from Coxside (sample # C24) with black staining within pits and cracks and distinctive 2–3 mm-sized quasi-circular beads; (f) a brown, 5-cm fragment from Wembury (sample # W1) with limited staining within cracks and barely perceptible beads; (g) an off-white-brown, 4-cm fragment from Wembury (sample # W6) with brown staining within cracks and grooves and moderately perceptible 2–3 mm irregular beads that in parts appear layered; (h) a 2.5-cm brown fragment from Wembury (sample # W9) with moderately perceptible 2-mm irregular beads that in parts appear layered.

2.3. Sample digestion, extraction and analysis

The surfaces of each piece of EPS were sampled over areas of 1 cm^2 and, operationally, to a depth of 0.5 cm (or as close as possible) using a stainless-steel scalpel and with the aid of digital callipers. One surface offcut was digested in aqua regia to determine total metal (and metalloid) concentration while a second, adjacent surface offcut (sample size and shape permitting) was extracted in dilute HCl to gain a general measure of metal bioavailability (Bryan and Langston, 1992; Smith and Turner, 2020). In addition, and where sufficient material was available and sample thickness exceeded 1.5 cm ($n = 21$; Coxside only), a subsurface area of 1 cm^2 from 0.5 to 1 cm depth was obtained for aqua regia digestion in order to investigate the depth distribution of metals.

For aqua regia digestion, surface and subsurface offcuts were weighed into individual, acid-cleaned 25 mL Pyrex beakers to which 6 mL aliquots of a 3:1 mixture of concentrated hydrochloric acid to concentrated nitric acid (both Fisher Scientific TraceMetal grade) were added. Controls ($n = 3$) consisted of beakers plus aqua regia but without EPS. The contents of each beaker were covered with watch glasses and left at room temperature overnight before being heated to about 90 °C on a hot plate for 90 min. Cooled digests were subsequently vacuum-filtered through 22 μm using Whatman 541 hardened ashless filter papers and filtrates were washed into a series of 25 mL Pyrex volumetric flasks and diluted to mark with Milli-Q distilled deionised water.

For HCl extraction, surface samples were weighed into individual 50 mL polypropylene centrifuge tubes and 5 mL aliquots of 0.7 M HCl added. The contents were left at room temperature for 2 h before 3 mL extracts were pipetted into a series of clean 10 mL tubes. Three controls were processed likewise but in the absence of polystyrene.

Digests and extracts were analysed for metals (Al, Cd, Co, Cr, Fe, Mn, Ni, Pb, Zn) and metalloids (As, Sb) by collision cell ICP-MS using an iCAP RQ with a concentric glass nebuliser and conical spray chamber that was operated with Qtegra software (Thermo Fisher Scientific). The instrument was calibrated externally using mixed, matrix-matched standards and blanks prepared by serial dilution of Labkings quality control solutions, and internally by the addition of 115-indium and 193-iridium to all samples, standards and blanks, and was operated under conditions described elsewhere (Smith and Turner, 2020).

2.4. Quality control and assurance and data processing

Sample processing and analysis was performed in an ISO 9001-accredited laboratory. No reference material exists for metal concentrations in expanded polystyrene but aqua regia digestion of sediment using the same protocol has been validated with in-house and independent reference sediments and soils (Braungardt et al., 2020; Turner, 2022). All digests and extracts were analysed by ICP-MS in triplicate, with relative standard deviations below 20 % in all cases and below 10 % in most cases. As a performance and calibration check of the ICP-MS, dilutions of a reference drinking water (EP-L, SCP Science) certified for concentrations of all elements considered were analysed after every ten samples. Where measured concentrations deviated from certified values by >5 %, the instrument was re-calibrated and the preceding batch of ten samples was re-analysed.

Limits of detection, defined as three standard deviations of five blank readings, ranged from 0.11 μg L^{-1} for Co in the HCl extracts and aqua regia digests to 22.2 μg L^{-1} for Fe in the aqua regia digests. Concentrations in digests and extracts were corrected for mean concentrations in the respective controls and converted to concentrations in dry weight of offcut of polystyrene. On this basis, metals were detected in all cases with the exception of Cd in extracts and digests where concentrations were below about 0.03 mg kg^{-1} and Sb in digests where concentrations were below about 0.04 mg kg^{-1}.

All descriptive statistics and inferential statistics (with significance defined as $p < 0.05$ or, for correlations, $r > 0.75$) were performed in Minitab v19.

3. Results

3.1. Sample characteristics

A selection of EPS samples is illustrated in Fig. 1. All samples were fragmented but were smoothed and with rounded edges, reflecting significant weathering in the environment. Surfaces were heterogeneous in terms of discolouration, staining-soiling, contamination, pitting and cracking, but most samples from Coxside tended to be off-white to green whereas those from Wembury were usually orange or brown. Among the samples, individual beads ranged from barely perceptible to distinctive, from circular or hexagonal to irregular, and from about 2 to 5 mm in diameter.

Microscopic images of three EPS samples are shown in Fig. 2. The beaded structure and surface morphology of EPS are clearly illustrated in Fig. 2a, with accumulation of particulate matter, including microplastic fibres, evident on the surface and within the crevices between beads. A more ragged morphology, with staining and occlusion of fine particulate matter, is evident in Fig. 2b, along with the development of inter-bead spaces as cracks and pits. In Fig. 2c there is more extensive and intense discolouration and dark staining, with beads more loosely held together and irregular in form.

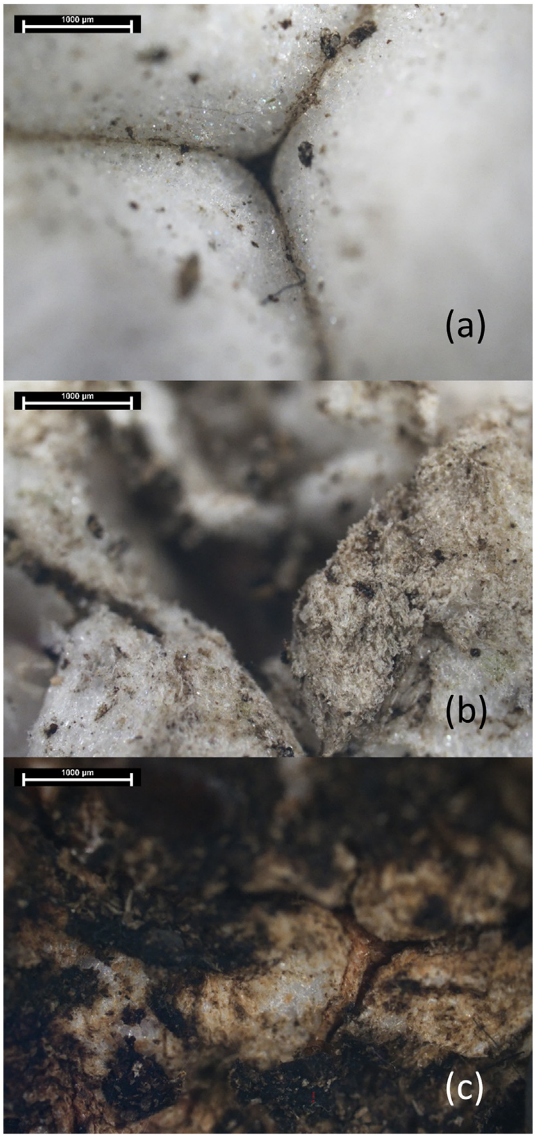

Fig. 2. Microscopic images of two EPS samples from Coxside (# C8 (a) and # C14 (b)) and an EPS fragment from Wembury (# W1 (c)). Note the scale bar of 1 mm.

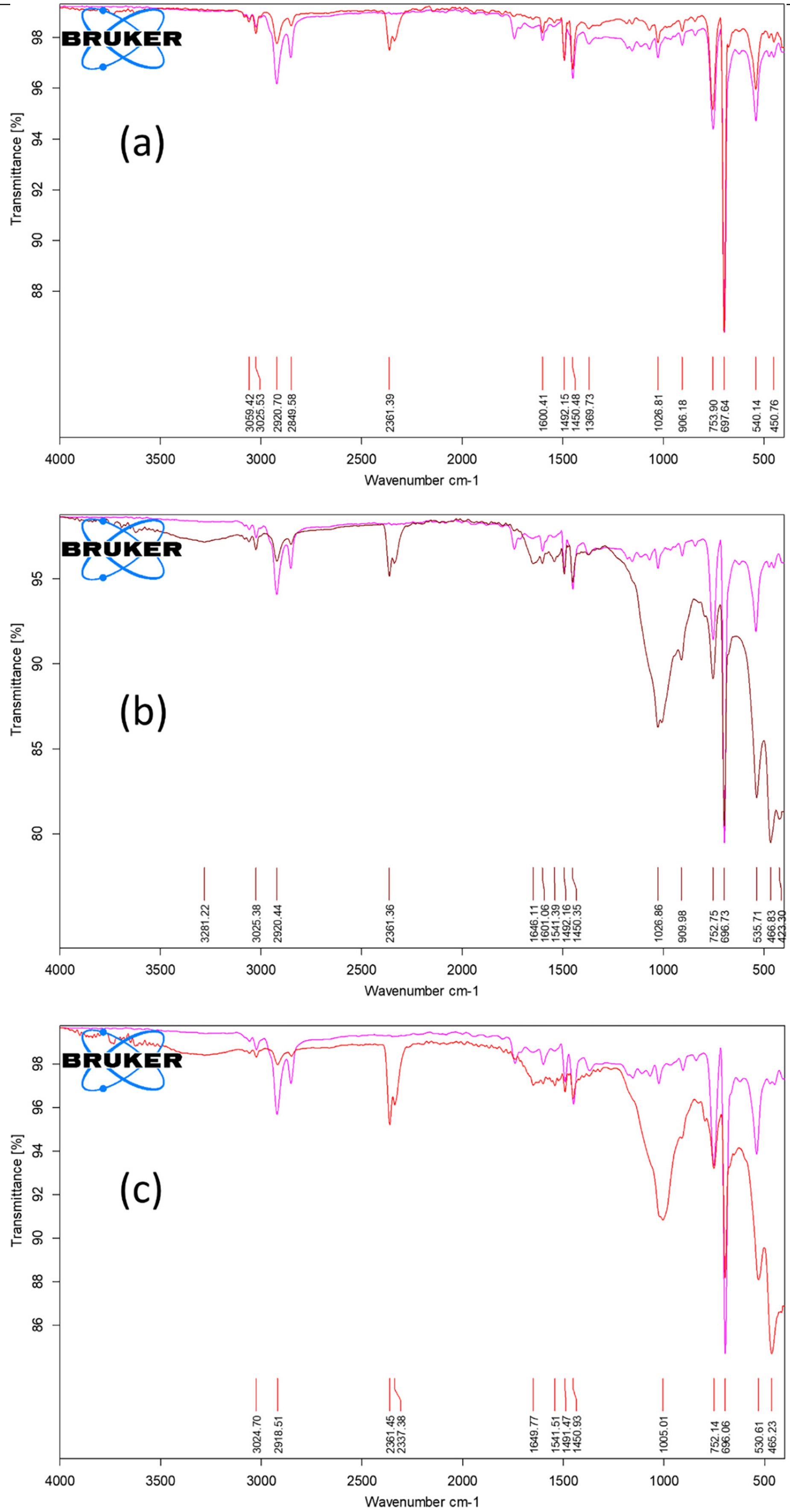

Fig. 3. FTIR spectra for EPS samples (a) # C6 (illustrated in Fig. 1b), (b) # C10 (Fig. 1d) and (c) # W9 (Fig. 1h) relative to unweathered EPS (shown in pink). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3 shows FTIR spectra for three of the samples illustrated in Fig. 1, along with the spectrum for unweathered EPS as a reference. Sample # C6, an off-white-greenish fragment with little staining or soiling (Fig. 3a), returned a spectrum that was very similar to the reference EPS if the CO_2 peak at 2360 cm^{-1} is neglected. By contrast, sample #s C10 and W9, an off-white-greenish fragment with extensive staining and contamination and a brown fragment (Fig. 3b and c, respectively) returned additional broad peaks centred around 3500 cm^{-1} and 1000 cm^{-1}.

The masses of the surface and subsurface offcuts (1 $cm^2 \times 0.5$ cm) used for digestion or extraction allowed the density of the EPS fragments to be estimated. Thus, surface offcuts ($n = 33$) yielded a mean (and one standard deviation) of 0.061 ± 0.009 g cm^{-3} and with a range from 0.046 to 0.083 g cm^{-3} that were not statistically different to subsurface offcuts ($n = 21$; mean = 0.058 ± 0.011 g cm^{-3}; range = 0.038 to 0.078 g cm^{-3}). By comparison, the estimated densities of the unweathered EPS samples ($n = 3$) were 0.070 ± 0.007 g cm^{-3}.

3.2. Total metal concentrations in EPS samples

The concentrations of total metals (including the metalloids, As and Sb) in the surface and subsurface offcuts of the EPS samples are summarised in Table 1. Here, concentrations represent both the quantity of metal per mass of material to depth of 0.5 cm and the amount of metal per cm^2 of surface or cross-section that was digested in aqua regia. Because of the different dimensions, surface areas and thicknesses of EPS fragments, the former measure at the surface is useful in, effectively, normalising the concentration to the mass of an EPS sphere of diameter 1 cm.

For each set of samples or surfaces from Coxside or Wembury, concentrations of all metals were non-normally distributed and highly variable, with ranges that spanned more than an order of magnitude in most cases. According to a series of Mann-Whitney *U* tests, there were significant differences in median surface concentrations between Coxside and Wembury but not between median surface and subsurface values at Coxside. Specifically, surface concentrations of Al, As, Co, Fe, Mn, Ni and Sb values were greater at Wembury while surface concentrations of Cu and Pb were greater at Coxside. With the exception of Cd, Sb and Zn, median concentrations or all concentrations at Coxside or Wembury exceeded corresponding concentrations in the unweathered EPS.

Table 2
Correlation matrix identifying the strongest ($r > 0.75$) inter-metal relationships for Coxside surface (C), Coxside subsurface (C*) and Wembury (W) EPS fragments. The total number of associations involving each metal (*n*) is shown in the bottom row.

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Zn
Al												
As	C,C*											
Cd												
Co	C,W	C,C*										
Cr												
Cu	C	C		C								
Fe	C,C*,W	C,C*		C,W		C						
Mn	C	C,W		C,C*								
Ni	C,C*,W	C,C*		C,W		C	C,C*,W	C				
Pb		C*			W		C*					
Sb				C*				C*				
Zn	C	C,C*		C			C		C		W	
n	13	14	0	13	1	5	13	7	13	3	3	7

A correlation matrix identifying the strongest linear inter-metal associations for each total metal data set (Coxside surface and subsurface EPS and Wembury surface EPS) is shown in Table 2. Note that, in the absence of significant outliers (maxima or minima), Pearson's moment correlations have been performed with an acceptance criterion of $r > 0.75$. Strong linear associations occur for all data sets among Al, Fe and Ni, and for both surface and subsurface data at Coxside between As-Co, As-Fe, As-Ni, As-Zn and Co-Mn and for surface data at Coxside and Wembury between As-Mn, Co-Fe and Co-Ni. Regarding each metal, associations are most abundant for Al, As, Co, Fe and Ni ($n \geq 13$) and least abundant for Cd, Cr, Pb and Sb ($n \leq 3$).

3.3. Available metal concentrations in EPS samples

Concentrations of metals available to 0.7 M HCl in the surface offcuts of EPS from Coxside and Wembury are summarised in Table 3. As above, concentrations were highly variable and non-normally distributed and a series of Mann-Whitney *U* tests revealed that median concentrations of Cu, Pb and

Table 1
Frequency of detection (*n*) and summary statistics for total concentrations of metals in surface and subsurface offcuts of EPS samples from Coxside and surface offcuts of EPS from Wembury and unweathered material. Units are mg kg^{-1} dry weight to a depth of 0.5 cm or mg cm^{-2} of surface. Significant differences between Coxside and Wembury surface medians are superscripted with "a", significant differences between Coxside or Wembury surface medians and unweathered medians are superscripted with "b", and, instances where all Coxside or Wembury values exceed a single unweathered concentration are superscripted with a "c".

		Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Zn
Coxside, surface	*n*	24	24	17	24	24	24	24	24	24	24	21	24
($n = 24$)	Mean	1015	2.81	0.15	1.03	6.04	42.4	2478	74.5	4.56	29.6	0.51	76.4
	Min	155	0.27	0.03	0.27	1.55	13.4	325	7.0	0.56	5.7	0.04	32.7
	Q1	312	0.92	0.07	0.41	3.63	21.8	777	17.9	1.38	14.1	0.17	45.0
	Median	$622^{a,b}$	$1.20^{a,b}$	0.10	$0.56^{a,c}$	4.70^{b}	$31.1^{a,b}$	$1740^{a,b}$	$26.5^{a,c}$	$2.08^{a,b}$	$20.4^{a,b}$	0.41^{a}	66.9
	Q3	1237	2.38	0.15	1.00	7.06	44.6	3040	48.5	3.54	37.4	0.72	101
	Max	5917	20.7	0.61	5.50	28.5	211	12,065	528	53.7	92.4	1.72	216
Coxside, subsurface	*n*	21	21	16	21	21	21	21	21	21	21	16	21
($n = 21$)	Mean	810	1.60	0.13	0.84	5.02	35.6	1768	54	2.49	30.4	0.79	71.8
	Min	12.0	0.04	0.04	0.09	2.07	7.4	117	1.1	0.49	0.82	0.13	15.2
	Q1	168	0.35	0.07	0.23	2.89	17.8	321	10.9	1.31	7.7	0.30	52.7
	Median	476	1.19	0.10	0.67	4.18	35.7	995	20.0	1.92	19.7	0.52	66.9
	Q3	956	2.44	0.20	0.89	5.92	47.7	2398	42.4	3.03	47.7	0.80	85.7
	Max	5693	5.95	0.28	4.59	13.3	72.0	10,155	498.3	11.7	91.3	4.21	134
Wembury, surface	*n*	9	9	8	9	9	9	9	9	9	9	9	9
($n = 9$)	Mean	2086	10.3	1.36	1.94	7.03	12.7	4649	117	5.71	13.4	1.72	64.9
	Min	566	1.31	0.03	0.58	1.81	3.9	1131	35.5	2.35	2.2	0.17	14.6
	Q1	863	2.07	0.10	1.02	2.10	9.4	2115	52.7	3.41	3.7	0.34	42.0
	Median	$1938^{a,b}$	$7.66^{a,b}$	0.24	$1.60^{a,c}$	4.51^{b}	$10.7^{a,b}$	$4845^{a,b}$	$73.8^{a,c}$	$5.34^{a,b}$	$10.5^{a,b}$	1.07^{a}	68.4
	Q3	2913	12.1	1.00	2.66	9.98	17.4	6861	141	8.23	21.9	2.07	83.9
	Max	5143	40.8	8.54	3.92	22.9	25.2	9092	370	11.1	36.7	7.33	110
Unweathered, surface	*n*	3	3	3	1	3	3	3	1	3	3	3	3
($n = 3$)	Min	17.6	0.07	0.06		0.96	2.8	31.9		0.20	1.1	1.09	44.2
	Median	63.7	0.13	0.13	0.04	1.31	4.1	36.1	0.78	0.24	1.1	1.12	46.9
	Max	110	0.18	0.18		1.66	5.4	40.4		0.29	1.1	1.14	49.6

Table 3

Frequency of detection (*n*) and summary statistics for concentrations of metals available to 0.7 M HCl in surface offcuts of EPS samples from Coxside and Wembury. Units are mg kg^{-1} dry weight to a depth of 0.5 cm or mg cm^{-2} of surface. Significant differences between surface medians are superscripted with “a”.

		Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Zn
Coxside, surface (*n* = 24)	*n*	24	24	19	24	24	24	24	24	24	24	24	24
	Mean	295	1.08	0.15	0.44	3.74	28	614	41.5	1.16	32.9	0.11	54.2
	Min	35.0	0.16	0.03	0.08	1.03	6.8	81.0	4.4	0.51	4.8	0.04	17.5
	Q1	83.0	0.31	0.05	0.17	1.88	11.0	116	17.5	0.74	11.4	0.05	27.9
	Median	135	0.42^{a}	0.10	0.32	3.18	22.2^{a}	178^{a}	27.5^{a}	0.86	24.2^{a}	0.07^{a}	39.8^{a}
	Q3	177	0.95	0.20	0.46	4.55	38.0	344	39.5	1.36	44.0	0.12	81.2
	Max	3949	7.67	0.73	2.53	11.0	96.7	5111	300	4.16	103	0.48	156
Wembury, surface (*n* = 8)	*n*	8	8	3	8	8	8	8	8	8	8	8	8
	Mean	177	5	0.12	0.51	2.86	3.36	1058	97.4	1.35	11.9	1.11	23.7
	Min	73.8	0.67	0.05	0.15	0.20	1.51	145	20.1	0.47	3.1	0.06	6.0
	Q1	97.7	1.15	0.05	0.24	0.40	2.37	264	47.3	0.61	3.9	0.13	8.0
	Median	159	2.17^{a}	0.16	0.38	1.13	2.64^{a}	506^{a}	54.8^{a}	0.88	6.2^{a}	0.30^{a}	13.5^{a}
	Q3	236	8.10	0.17	0.70	5.04	4.47	1774	90.5	2.16	22.5	1.30	44.0
	Max	355	18.7	0.17	1.40	10.1	6.54	3744	384.4	3.36	34.5	5.73	53.4

Zn were significantly greater at Coxside and median concentrations of As, Fe, Mn and Sb were significantly greater at Wembury. The median percentage of each metal available to 0.7 M HCl (and relative to the corresponding total metal content) is shown for Coxside and Wembury in Fig. 4. Individual metal data were variable, and in particular for Cd and Sb, but overall Pb and Mn exhibited the greatest availabilities and Al, Cu and Fe exhibited the lowest availabilities.

4. Discussion

It is not possible to determine the precise origins or ages of the EPS fragments retrieved from the coastal zone of SW England, but they have clearly undergone significant weathering relative to new packaging material. A qualitative assessment of weathering may be gained visually from the degree of rounding, discoloration, fouling, cracking and bead integrity. Significantly, the majority of fragments from the semi-enclosed harbour environment at Coxside and where wave action is diminished were largely off-white-greenish and usually considerably stained and contaminated, while all those from the beach at Wembury had a brown-orange hue and were generally less stained. It is possible that EPS that has resided in the more sheltered, nutrient-rich setting has had time and suitable conditions to acquire a more distinctive biofilm and capture other floating anthropogenic debris. In contrast, EPS washed up on an exposed, sandy beach has acquired more hydrogeneous (e.g., oxidic) fouling and less debris from its time spent in the open-ocean. (Note that the surface concentrations of Fe and Mn, presumably largely acquired through oxidation and precipitation in seawater (Usui et al., 2020), were significantly higher at Coxside than Wembury.) Exceptions to and hybrids of these two types of EPS are clearly evident (e.g., Fig. 1e) that may reflect the exchange of EPS between the two settings.

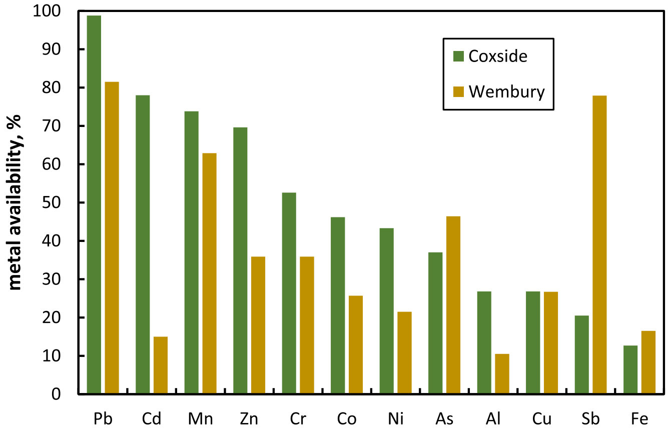

Fig. 4. Median percentages of metals extracted by 0.7 M HCl relative to total metal contents for EPS fragments from Coxside (*n* = 15 to 24) and Wembury (*n* = 3 to 8) and illustrated in descending order for Coxside.

FTIR spectra reveal additional chemical changes to the EPS surface that are not necessarily visible with or without a microscope. Thus, the distinctive C-H backbone and phenyl group stretching for polystyrene at 2800 to 3000 cm^{-1} were always present but O-H stretching at higher wavenumbers and absorption at about 1030 cm^{-1} were most evident in EPS samples exhibiting significant visible deterioration (e.g., Fig. 3b and c). The O-H stretching could represent a degradation product based on an organic acid or a compound with a hydroxyl group while absorption around 1030 cm^{-1} may indicate Si-O stretching vibrations (Cox et al., 2000; Parikh et al., 2014) and, therefore, chemical and/or biological fouling at the EPS surface.

A fraction of some metals, including Sb and Zn, appear to be associated with EPS as additives or contaminants from the manufacturing process. However, more significant is the acquisition of metals from the environment, and either while suspended or floating or when beached. Aside from the hydrogenous precipitation of Fe and Mn, there are a number of ways by which metals can interact with EPS. Thus, (i) metal ions and complexes may directly adsorb to the EPS surface from seawater, and in particular if the surface has become weathered, (ii) metal ions and compounds may bind to or precipitate with hydrogenous and biological phases acquired in situ, and (iii) particulate metals may adhere to the modified surface or become entrapped within the porous structure of the plastic (Holmes et al., 2012).

Total metal concentrations in EPS are broadly similar to those reported for EPS microplastics retrieved from island beaches in the Pearl River Estuary by Xie et al. (2021) (e.g., and as arithmetic mean ± 1 standard deviation in mg kg^{-1}, As = 5.50 ± 3.84; Cd = 0.27 ± 0.19; Cr = 14.9 ± 8.25; Cu = 15.0 ± 7.66; Fe = 8340 ± 4760; Pb = 24.8 ± 7.39). However, concentrations are significantly greater than those determined in dilute aqua regia digests of beached polyolefin pellets collected from beaches close to the locations studied here. For example, Ashton et al. (2010) report concentrations of Cr, Cu, Pb and Zn that are generally below 1 mg kg^{-1} and concentrations of Cd, Co and Sb that are at least an order of magnitude lower. There are several reasons why EPS is a more effective carrier of environmental metals than unexpanded (but low density) polymers on a mass basis. Firstly, the (beaded) surface area and porosity of EPS are greater, with clear evidence that regions well below the surface (and through cracks and fissures) can adsorb aqueous metals and entrap particulate metals. Secondly, the low density of EPS (mean value = 0.06 g cm^{-3}) compared with polyethylene and polypropylene (close to 1 g cm^{-3}) results in a considerably greater surface area to mass ratio for aqueous and particulate metal association than polyolefins. And thirdly, a density well below that of seawater ensures that EPS will reside (float) in the surface microlayer when at sea, a thin film known to be enriched in contaminants (Wurl and Obbard, 2004).

In some cases, metal concentration differences in EPS sampled from the harbour and open sea settings can be understood from sources or geochemistry. For instance, significantly greater concentrations of As and Co at Wembury may be attributed to the higher content of and co-association with hydrous Fe oxides and Mn oxides, which are known to be instrumental in the oxidation and scavenging of the respective metals (Sadiq, 1990; Murray et al., 2007). By contrast, the high affinity of Cu for marine organic matter (Turner, 2000; Burton et al., 2005) may partly explain its greater accumulation on EPS from Coxside. Higher concentrations of Cu and Pb on EPS sampled from Coxside may also be attributed to both urban and maritime (e.g., boating) sources of these metals (Singh and Turner, 2009; Hosono et al., 2010).

Although differences in metal concentrations between locations and comparisons with other plastics have been addressed, a more general means of evaluating the degree of metal contamination on the EPS fragments is to determine enrichment factors (EF). That is, normalise the concentration of a metal to some proxy for granulometry and divide this value by the proxy-normalised metal concentration in a suitable baseline (Rubio et al., 2000; Abrahim and Parker, 2008). Aluminium has been selected as a normaliser because it is usually little affected by anthropogenic activities and exhibits an inverse dependency of concentration on particle size (Birch, 2020), and for a baseline we have employed metal concentrations (in mg kg^{-1}) derived from the aqua regia digestion of sediments from the coastal zone 2 km to the east of Wembury and reported by Varma et al. (2011): Al = 10,980; As = 18.8; Cd = 0.19; Co = 7.9; Cr = 28.4; Cu = 143; Ni = 29.7; Pb = 41.1; Sb = 0.76; Zn = 125.

Median values of EF are shown for metals that are potentially toxic and that are subject to environmental contamination (rather than hydrogenous precipitation) in Fig. 5. According to a series of Mann-Whitney *U* tests, Cr, Cu, Pb and Zn were significantly greater at Coxside (surface and subsurface) than at Wembury, while As was significantly greater at Wembury than Coxside. According to the classification given by Birch and Olmos (2008), As, Co, Cr and Ni exhibit “minor”, enrichment, Cu exhibits “moderate” enrichment at Coxside, Cd and Sb exhibit “moderately severe” enrichment, and Pb and Zn exhibit “moderately severe” enrichment at Coxside.

In terms of weight normalised concentration or geochemically-normalised enrichment, and compared to other forms of suspended plastic, EPS is evidently a significant medium for transporting a number of potentially toxic metals in the marine environment. Moreover, these metals are also highly available compared with corresponding metals in other plastics. Specifically, the present study shows that >20 % of potentially toxic metals in EPS are available to HCl of a strength between that used to define avian bioaccessibility (Turner, 2018) and that used as a general indicator of bioavailability (Bryan and Langston, 1992). This compares with HCl-bioaccessibilities in polyolefins of up to a few percent (Smith and Turner, 2020). Presumably, results for EPS fragments considered here can be extrapolated to pieces and individual beads in the size range of material ingested by marine wildlife, including fish and birds, suggesting that EPS could exert a disproportionately high impact on metal exposure to some plastic-ingesting animals.

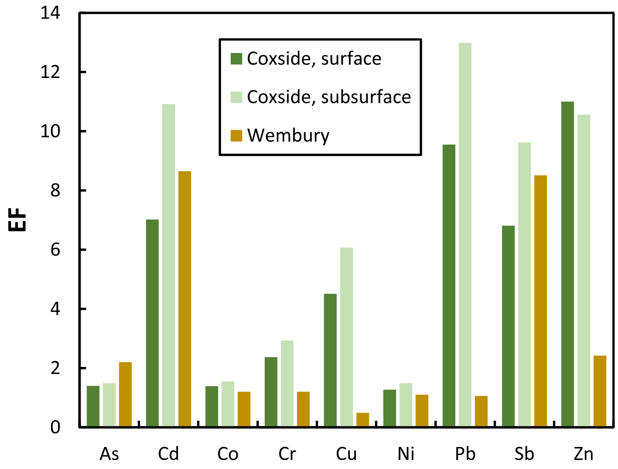

Fig. 5. Median enrichment factors (EF) for contaminant metals in EPS fragments from Coxside (surface, n = 17 to 24; subsurface, n = 16–21) and Wembury (n = 8 to 9).

5. Conclusions

This study has demonstrated that beached, marine EPS is associated with metals (and metalloids) of geochemical and anthropogenic significance, with concentrations on a weight or surface area basis exceeding those typical of other marine plastics and, in many cases, exhibiting considerable enrichment compared with baseline sediment. Metals appear to be acquired through adsorption, precipitation and particle capture and are encountered both on the surface of the EPS and within its porous structure. According to extraction in dilute HCl, metals exhibit bioavailabilities ranging from about 10 % (Fe) to 100 % (Pb), suggesting that the inadvertent ingestion of EPS by marine wildlife could result in relatively high exposure of some metals.

CRediT authorship contribution statement

AT: conceptualization; methodology; investigation; formal analysis; writing – original draft; writing – review and editing; project management.

ST: conceptualization; methodology; formal analysis; writing – review and editing;

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abrahim, G.M.S., Parker, R.J., 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ. Monit. Assess. 136, 227–238.

Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic production pellets in the marine environment. Mar. Pollut. Bull. 60, 2050–2055.

Birch, G.F., 2020. An assessment of aluminum and iron in normalisation and enrichment procedures for environmental assessment of marine sediment. Sci. Total Environ. 727, 138123.

Birch, G.F., Olmos, M.A., 2008. Sediment-bound heavy metals as indicators of human influence and biological risk in coastal water bodies. ICES J. Mar. Sci. 65, 1407–1413.

Braungardt, C., Chen, X., Chester-Sterne, D., Quin, J.G.A., Turner, A., 2020. Arsenic concentrations, distributions and bioaccessibilities at a UNESCO World Heritage Site (Devon Great Consols, Cornwall and West Devon Mining Landscape). Environ. Pollut. 264, 114590.

Bryan, G.W., Langston, W.J., 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environ. Pollut. 76, 89–131.

Burton, E.D., Phillips, I.R., Hawker, D.W., 2005. Geochemical partitioning of copper, lead, and zinc in benthic, estuarine sediment profiles. J. Environ. Qual. 34, 263–273.

Cox, R.J., Peterson, H.L., Young, J., Cusik, C., Espinoza, E.O., 2000. The forensic analysis of soil organic by FTIR. Forensic Sci. Int. 108, 107–116.

Davis, W., Murphy, A.G., 2015. Plastic in surface waters of the inside passage and beaches of the Salish Sea in Washington State. Mar. Pollut. Bull. 97, 169–177.

Esiukova, E., Lobchuk, O., Haseler, M., Chubarenko, I., 2021. Microplastic contamination of sandy beaches of national parks, protected and recreational areas in southern parts of the Baltic Sea. Mar. Pollut. Bull. 173, 113002.

Fred-Ahmadu, O.H., Ayejuyo, O.O., Tenebe, I.T., Benson, N.U., 2022. Occurrence and distribution of micro(meso)plastic-sorbed heavy metals and metalloids in sediments, Gulf of Guinea coast (SE Atlantic). Sci. Total Environ. 813, 152650.

Hirai, H., Takada, H., Ogata, Y., Yamashita, R., Mizukawa, K., Saha, M., Kwan, C., Moore, C., Gray, H., Laursen, D., Zettler, E.R., Farrington, J.W., Reddy, C.M., Peacock, E.E., Ward, M.W., 2011. Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. Mar. Pollut. Bull. 62, 1683–1692.

Holmes, L., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. Environ. Pollut. 160, 42–48.

Hosono, T., Su, C.C., Okamura, K., Taniguchi, M., 2010. Historical record of heavy metal pollution deduced by lead isotope ratios in core sediments from the Osaka Bay, Japan. J. Geochem. Explor. 107, 1–8.

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

Jang, M., Shim, W.J., Han, G.M., Rani, M., Song, Y.K., Hong, S.H., 2017. Widespread detection of a brominated flame retardant, hexabromocyclododecane, in expanded polystyrene marine debris and microplastics from South Korea and the Asia-Pacific coastal region. Environ. Pollut. 231, 785–794.

Kwon, O.Y., Kang, J.H., Hong, S.H., Shim, W.J., 2020. Spatial distribution of microplastic in the surface waters along the coast of Korea. Mar. Pollut. Bull. 155, 110729.

Lo, H.S., Xu, X.Y., Wong, C.Y., Cheung, S.G., 2018. Comparisons of microplastic pollution between mudflats and sandy beaches in Hong Kong. Environ. Pollut. 236, 208–217.

Mai, L., Bao, L.J., Shi, L., Liu, L.Y., Zeng, E.Y., 2018. Polycyclic aromatic hydrocarbons affiliated with microplastics in surface waters of Bohai and Huanghai Seas, China. Environ. Pollut. 241, 834–840.

Maršić-Lučić, J., Lušić, J., Tutman, P., Bojanić Varezić, D., Šiljić, J., Pribudić, J., 2018. Levels of trace metals on microplastic particles in beach sediments of the island of Vis, Adriatic Sea, Croatia. Mar. Pollut. Bull. 137, 231–236.

Murray, K.J., Webb, S.M., Bargar, J.R., Tebo, B.M., 2007. Indirect oxidation of Co(II) in the presence of the marine Mn(II)-oxidizing bacterium *Bacillus* sp. strain SG-1. Appl. Environ. Microbiol. 73, 6905–6909.

Parikh, S.J., Goyne, K.W., Margenot, A.J., Mukome, F.N.D., Calderón, F.J., 2014. Soil chemical insights provided through vibrational spectroscopy. In: Sparks, D.L. (Ed.), Advances in Agronomy. Elsevier, Amsterdam, pp. 1–148.

Provencher, J.F., Avery-Gomm, S., Liboiron, M., Braune, B.M., Macauley, J.B., Mallorty, M.L., Letcher, R.J., 2018. Are ingested plastics a vector of PCB contamination in northern fulmars from coastal Newfoundland and Labrador? Environ. Res. 167, 184–190.

Rochman, C.M., Kurobe, T., Flores, I., Teh, S.J., 2014. Early warning signs of endocrine disruption in adult fish from the ingestion of polyethylene with and without sorbed chemical pollutants from the marine environment. Sci. Total Environ. 493, 656–661.

Rubio, B., Nombela, M.A., Vilas, F., 2000. Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. Mar. Pollut. Bull. 40, 968–980.

Sadiq, M., 1990. Arsenic chemistry in marine environments: a comparison between theoretical and field observations. Mar. Chem. 31, 285–297.

Singh, N., Turner, A., 2009. Trace metals in antifouling paint particles and their heterogeneous contamination of coastal sediments. Mar. Pollut. Bull. 58, 559–564.

Smith, E.C., Turner, A., 2020. Mobilisation kinetics of Br, Cd, Cr, Hg, Pb and Sb in microplastics exposed to simulated, dietary-adapted digestive conditions of seabirds. Sci. Total Environ. 733, 138802.

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M.A., Watanuki, Y., 2015. Facilitated leaching of additive-derived PBDEs from plastic by seabirds'stomach oil and accumulation in tissues. Environ. Sci. Technol. 49, 11799–11807.

Turner, A., 2000. Trace metal contamination in sediments from UK estuaries: an empirical evaluation of the role of hydrous iron and manganese oxides. Estuar. Coast. Shelf Sci. 50, 355–371.

Turner, A., 2018. Mobilisation kinetics of hazardous elements in marine plastics subject to an avian physiologically-based extraction test. Environ. Pollut. 236, 1020–1026.

Turner, A., 2021. Polystyrene foam as a source and sink of chemicals in the marine environment: an XRF study. Chemosphere 263, 128087.

Turner, A., 2022. Metal contamination of intertidal sediment and macroalgae in an area impacted by paint from abandoned boats. Mar. Pollut. Bull. 182, 113958.

Usui, A., Hino, H., Suzushima, D., et al., 2020. Modern precipitation of hydrogenetic ferromanganese minerals during on-site 15-year exposure tests. Sci. Rep. 10, 3558.

Varma, R., Turner, A., Brown, M.T., 2011. Bioaccumulation of metals by *Fucus ceranoides* in estuaries of south west England. Mar. Pollut. Bull. 62, 2557–2562.

Wurl, O., Obbard, J.P., 2004. A review of pollutants in the sea-surface microlayer (SML): a unique habitat for marine organisms. Mar. Pollut. Bull. 48, 1016–1030.

Xie, Q., Li, H.X., Lin, L., Li, Z.L., Huang, J.S., Xu, X.R., 2021. Characteristics of expanded polystyrene microplastics on island beaches in the Pearl River Estuary: abundance, size, surface texture and their metals-carrying capacity. Ecotoxicology 30, 1632–1643.