



Marine pollution from pyroplastics

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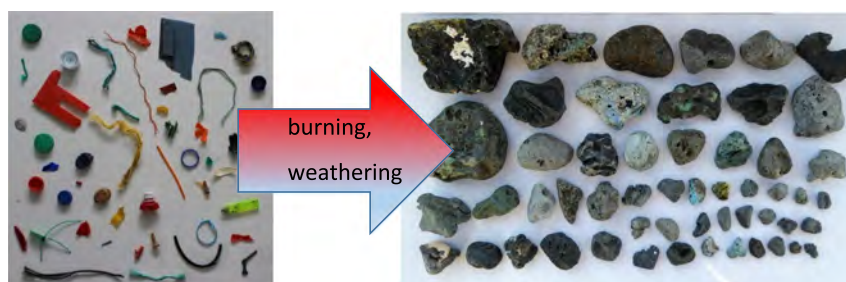
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HIGHLIGHTS

- Pyroplastics are a type of marine litter derived from the burning of manufactured plastics.
- They range from angular plastiglomerates to more weathered-rounded clasts.
- X-ray fluorescence analysis reveals the presence of restricted plastic additives like lead chromate.
- Analysis of fouling worm tubes exhibit evidence of lead accumulation from the plastic.
- With a distinctly geogenic appearance, pyroplastics evade ready detection.

GRAPHICAL ABSTRACT



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ABSTRACT

Items of marine plastic litter are conventionally classified as primary or secondary, depending on whether they are distinct objects or angular fragments, respectively. "Pyroplastic" is an additional type of plastic litter that is described here, based on observations made on beached samples from south west England. Pyroplastics are derived from the informal or more organised burning of manufactured plastics and may be angular "plastiglomerates", comprising pieces of plastic debris within a matrix, or rounded plastic "pebbles", where agglomerated material has been weathered and smoothed into more brittle and neutrally-coloured geogenic-looking clasts. Beached pyroplastics are usually positively buoyant because of a polyethylene or polypropylene matrix, and exhibit a bimodal mass distribution attributed to the breakage of larger clasts (>20 mm) into smaller fragments (<5 mm). XRF analysis reveals variable quantities of Pb in the matrix (up to 7500 $\mu\text{g g}^{-1}$), often in the presence of Cr, implying that material in many samples pre-dates restrictions on the use of lead chromate. Low concentrations of Br and Sb relative to pieces of manufactured plastics in the marine environment suggest that pyroplastics are not directly or indirectly derived from electronic plastic. Calcareous worm tubes on the surfaces of pyroplastics dense enough to be temporarily submerged in the circalittoral zone are enriched in Pb, suggesting that constituents within the matrix are partly bioavailable. Evading ready detection due to their striking visual similarity to geogenic material, pyroplastics may contribute to an underestimation of the stock of beached plastics in many cases.

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1. Introduction

Marine pollution from plastics is a growing global problem that results from a complex interplay between demand, consumption, disposal and

recycling of the material. Because of their persistence, hydrophobicity and low density, plastics in the marine environment have a variety of well-established economic, visual and ecological impacts (Wilcox et al., 2016; Krelling et al., 2017) in addition to emerging potential consequences on health and food security (Santillo et al., 2017; Barboza et al., 2018).

While suspended, deposited or beached, plastics undergo gradual and progressive mechanical, chemical and photo-oxidative breakdown

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(Song et al., 2017; Cai et al., 2018). Consequently, plastics may be classified as primary, bearing the recognisable integrity of the original plastic structure, or secondary, where objects have been broken down into smaller fragments or pieces whose primary source is often difficult to establish. Examples of primary plastics include shot-gun cartridges, bottles and bottle tops, straws, cutlery, pellets, pens, cigarette lighters, cotton buds, food packages, toys, strapping and rope.

Recently, an additional type of non-manufactured marine plastic was described by Corcoran et al. (2014). “Plastiglomerates” are indurated, multi-composite materials made hard by the agglutination of rock and other materials with molten plastic, the source of the latter being attributed to the informal, open (e.g. campfire) burning of plastic waste. Plastiglomerates may be classified as in situ, where the material is adhered to a rocky substrate, or clastic, where conglomerates are discrete entities. This type of marine plastic is, therefore, composed of a melted polymeric matrix of unknown origin(s) that encapsulates sand, rock, shell fragments, wood and various pieces of anthropogenic debris, with a resultant bulk density of about 2 to 3 g cm⁻³.

Over the past two years, the Cornwall Plastic Pollution Coalition, a group of voluntary organisations, has reported the occurrence of plastics on beaches throughout the county of Cornwall, south west England, that have evidently undergone burning in situ or ex situ. Their appearance is similar to the plastiglomerates described by Corcoran et al. (2014) but encapsulated material is usually plastic (rather than rock or sand) and many samples do not appear to have agglomerated any significant quantities of extraneous material. Consequently, these samples have a relatively low bulk density and most will float in sea water. “Pyroplastics”, as they are hereafter referred to, may be encrusted on rocky outcrops towards the back beach and cliffs, or encountered along the strandline as distinct clasts exhibiting varying degrees of weathering, with crusts eventually breaking off and becoming a series of clasts.

In the present paper, a variety of pyroplastics collected from various beaches are described and defined, with particular emphasis on material retrieved from Whitsand Bay, a large, protected, sandy and south west-facing embayment to the west of Plymouth (Uncles et al., 2015; Fig. 1). A selection of samples is subject to analysis by Fourier Transform Infrared (FTIR) spectrometry in order to define their polymeric makeup and by x-ray fluorescence (XRF) spectrometry in order to identify inorganic additives and co-contaminants. Attempts are made to determine the origin and age of pyroplastics and to evaluate their potential environmental impacts and chemical hazards.

2. Methods

Through calls and descriptions on social media from mid-2018 to early 2019, pyroplastics were reported on and retrieved from sandy beaches throughout the county of Cornwall, including Whitsand Bay (Fig. 1), and then from places farther afield, both in the UK and overseas. As part of organised beach cleans or from informal beach-combing about 400 samples out of several thousand collected from the strandline, foreshore and rocky outcrops were forwarded to the University of Plymouth. Recording the abundance of pyroplastics was not an objective of the present study and was confounded by the difficulty in identifying material (especially where it assumed a distinctly geological appearance), but during a systematic clean of a beach on Whitsand Bay it was noted that several samples were often retrieved per metre of strandline.

In the laboratory, a subset of 165 samples from the beaches of Whitsand Bay and 30 samples collected from elsewhere were classified by density according to whether or not they floated in tap water at room temperature contained in a 30 cm diameter glass dish or a half-filled 30-L laboratory sink. Cleaned and dried samples were then photographed, weighed on a five-figure Sartorius Genius balance and measured for

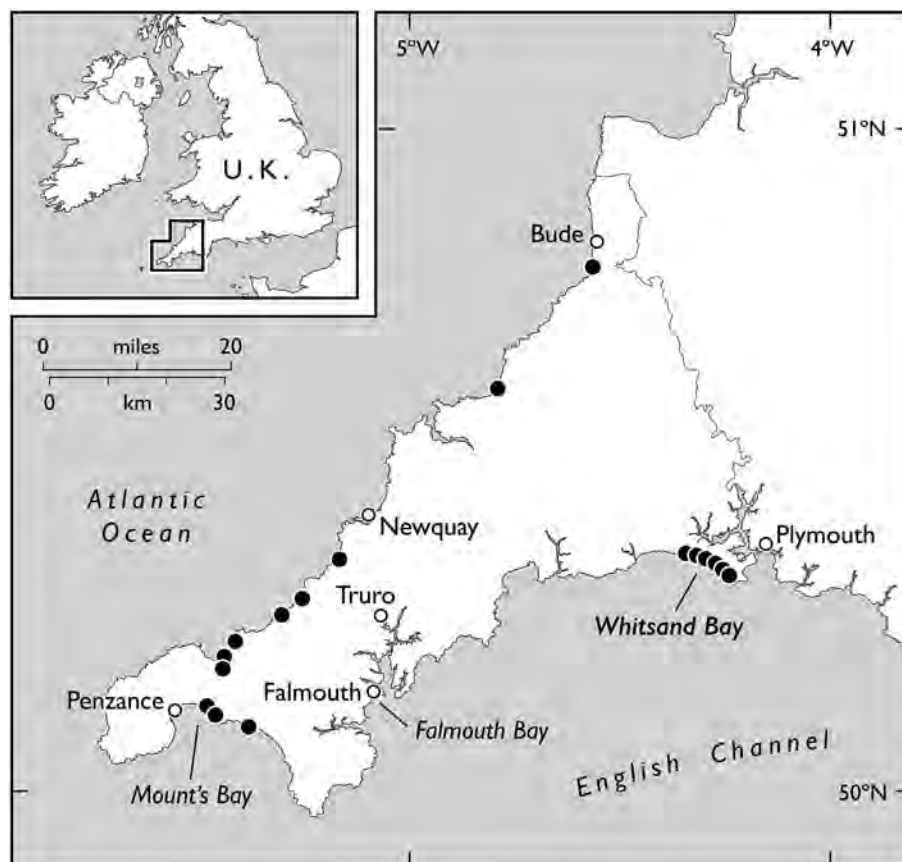


Fig. 1. Locations in Cornwall, south west England, where pyroplastics have been collected (filled circles) in relation to major embayments and centres of population.

primary diameter (longest axis; d_1) and secondary diameter (shortest axis but through the thickest part; d_2) using digital callipers. Samples were coded for colour (or colours) and the abundance and nature of encapsulated materials.

Samples were subsequently analysed for various elements that are indicative of additives, contaminants and extraneous material (Br, Cd, Cl, Cr, Cu, Fe, Pb, Sb, Zn) using a battery-operated Niton XL3t He GOLDD+ XRF spectrometer described in detail elsewhere (Turner and Solman, 2016). The instrument was configured nose upwards in a laboratory test-stand and activated remotely by a laptop. The region of the sample to be probed (usually the central part with the flattest and smoothest face) was placed above the detector window and counted in a standardless plastics mode with thickness correction (where sample thickness was <10 mm) for 20 s at 40 μ A and 50 kVp and 10 s at 100 μ A and 20 kVp. Spectra arising from sample counting were quantified by fundamental parameter coefficients to yield elemental concentrations in μ g g⁻¹ and a measurement error of 2σ (95% confidence). For pyroplastics too large to fit in the test stand (>20 cm in length) measurements were made likewise but the instrument was operated hand-held using the trigger mechanism with samples cradled in a folded radiation apron placed on a stainless steel bench. Elements were also determined in the calcareous worm tubes attached to two pyroplastics and, as a non-plastic control of similar density, a tarball. Here, the crushed contents of five ~100 mg deposits scraped from each sample were analysed by XRF in a higher density soils mode for counting periods of 45 s at 40 μ A and 50 kVp and 15 s at 100 μ A and 20 kVp.

For quality assurance and instrument performance purposes, two 13 mm-thick Niton reference plastics that had been impregnated with various elements (PN 180-554 batch SN PE-071-N and PN 180-619 LOT#T-18) were analysed at regular intervals throughout each measurement session; concentrations returned by the XRF were always within 15% (and usually within 10%) of certified values. Precision, evaluated by quintuplicate measurements of the same area of six samples of varying size, colour and appearance, ranged from <5% for Cl, Fe and Pb to about 15% for Cd and Sb.

Thirty of the Whitsand pyroplastics and five samples collected elsewhere that had been characterised above were analysed by attenuated total reflectance FTIR (ATR-FTIR) spectrometry using a Bruker Vertex 70. A stainless steel scalpel was employed to scrape a piece of a few mg from different regions of the surface and, in some cases, the subsurface (below 1 mm). Samples were clamped against the diamond crystal before spectra were acquired with 16 scans in the region 4000 to 600 cm⁻¹ and at a resolution of 4 cm⁻¹. After being smoothed, baseline-corrected and normalised via Bruker OPUS 7 software, spectra were compared with libraries of reference spectra for the identification of component polymers and were visually inspected for signs of polymer modification.

An experiment was also performed in the laboratory in order to observe changes effected to contemporary plastics when they were burned. Here, small, colourful plastic items, including bottle tops, pieces of cutlery, small toys and fragments of food packaging (and totalling about 150 mg in mass), were placed in a steel beaker suspended on a triangular pipe-clay and tripod in a fume cupboard and the contents heated over three Bunsen burners. The melted remains were subsequently transferred to a dish filled with tap water to replicate rapid cooling in the environment.

3. Results

3.1. Visual and physical characteristics

Pyroplastics were supplied from beaches in Cornwall and from the Orkneys (Scotland), County Kerry (Ireland) and north west Spain, and were reported on the coast of Vancouver (Canada). Samples were broadly similar in appearance, colour, size range and chemical makeup, but for the purposes of further classification and quantification,

pyroplastics are restricted to those from the beaches of Whitsand Bay where a greater number had been collected in a more systematic manner.

Fig. 2 and Fig. S1 illustrate pyroplastics collected from Whitsand Bay from which a subset was forwarded to the University, while Fig. 3 shows six larger clasts, graded according to degree of agglomeration and angularity, that had been sampled from this subset. Pyroplastics are distinctly different from manufactured plastics, having a geological or industrial appearance, often being agglomerated and heterogeneous, and generally being considerably thicker and less angular than secondary fragments. Pyroplastics are defined by an amorphous matrix that appears to be formed by the burning or melting of plastic and that is usually characterised by a single, neutral colour (black-charcoal-grey, off-white or brown), with occasional hues of green, blue, pink or yellow, and is accompanied by cracks and fractures, pits and cavities. Breaking the brittle matrix usually revealed a brighter and shinier internal structure (for example, a charcoal exterior would be accompanied by an anthracite-looking interior).

Samples (a) through to (f) in Fig. 3 are of similar dimensions but exhibit decreasing roundness and increasing angulation and roughness and an accompanying increase in apparent degree of association of the melted matrix with extraneous material. The more rounded pyroplastics of any sphericity (but usually high) that appear to contain relatively little agglomerated extraneous material (similar to samples (a) to (c)) could be considered as singular entities or “plastic pebbles”, while more angular pyroplastics of generally low sphericity (similar to samples (d) to (f)) could be described better as “plastiglomerates”. Agglomerated extraneous material is mainly plastic, and includes pellets, remains of straws, food packaging, bottle tops and rope, and fragments of unknown origin. Extraneous plastics of varied colours and shapes may be bonded (or fused) to the surface of the matrix or partially encapsulated, and may be intact or partly melted themselves.

Despite this classification, there is clearly a continuum of pyroplastics that makes distinction imprecise; moreover, occasional samples have additional characteristic features. For example, a few pebble-like pyroplastics had long filamentous plastic fragments fused to the matrix (Fig. S2), while some large plastiglomerates were extremely flat and rough and appeared to be composed of multiple matrices of different (but mainly neutral) colours or textures.

Table 1 shows summary statistics defining the mass and dimensions of the subset of 165 pyroplastics supplied from the beaches of Whitsand Bay. Distributions of all measures were skewed to the right with heavy tails or outliers. Mass ranged from <100 mg to about 270 g, with a median value that was about 350 mg and a distribution that was bimodal (with relatively few clasts between 5 and 10 g). Primary diameter (d_1) ranged from about 6 to 240 mm (median = 12.9 mm) and secondary diameter (d_2) ranged from about 4 to 40 mm (median = 6.6 mm), with the two measures combined to give aspect ratios (d_1/d_2) ranging



Fig. 2. Pyroplastics retrieved from the strandline at Whitsand Bay.

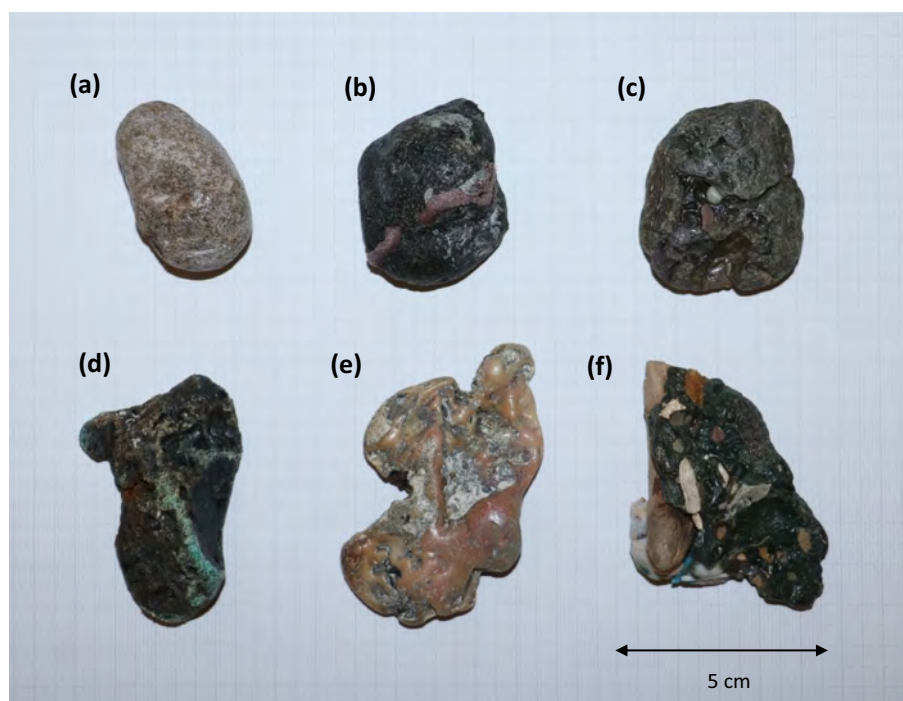


Fig. 3. A selection of samples collected from Whitsand Bay exhibiting increasing agglomeration and angulation from (a) through to (f).

from 0.42 to 7.5 (median = 2.0). In general, higher aspect ratios were accompanied by more angular plastiglomerates that appeared to contain relatively high quantities of visible extraneous agglomerated plastics while lower aspect ratios were associated with rounded pebbles containing relatively few (or no) visible extraneous plastics.

All pyroplastics were less dense than water at room temperature with the exception of five relatively large clasts. Three of the latter samples were plastiglomerates that had extensive and curved accumulations of calcareous deposits from the tube-building worm, *Spirobranchus triqueter*, on at least one face, with matted patches of what appeared to be the bryozoan, *Electra pilosa*, attached to one sample. The remaining two denser clasts were smooth and pebble-like with no visible extraneous material on their surfaces.

3.2. Chemical characteristics

Spectra arising from ATR-FTIR analysis of different regions of selected pyroplastics, and as exemplified in Fig. 4, revealed that the polymeric matrix consisted of either (or both) polyethylene or polypropylene, even in samples that were denser than tap water. FTIR results also suggested the presence of non-aromatic plasticisers and terminal methyl groups (indicative of chain breakage) in many cases, but no clear spectral differences were evident between the surface and interior of any sample tested.

XRF analysis of the entire subset of samples from Whitsand Bay indicated that no pyroplastics were constructed in whole of polyvinyl chloride (PVC), but that one distinctive object encapsulated by a large plastiglomerate was PVC-based. XRF also revealed a variety of elements

indicative of polymeric additives and residues and small quantities of inorganic extraneous matter (e.g. sand) in some cases. Concentrations of elements in the central surface region of the melted matrix (or in highly agglomerated samples, the most abundant matrix material) are shown in Table 2. Here, the number of cases in which each element was detected is shown along with an indicative range of detection limits (which vary for a given element dependent on sample thickness and composition), while statistical parameters are the same as those reported in Table 1.

Percentage detection ranged from about 7 for Sb to 100 for Fe, and median concentrations are greatest for Fe, lowest for Sb and similar among the remaining elements. Concentrations of each element are highly variable and span up to three orders of magnitude, and with the exception of Sb, distributions exhibit considerable skewness to the right and have heavy tails or outliers. Pearson's moment correlation analysis revealed that statistically significant relationships ($p < 0.05$) were restricted to the following elemental pairs: Cd-Sb, Cr-Pb and Cd-Fe; —; with the greatest number of co-associations and the strongest correlation between Cr and Pb and as illustrated by the linear regression results in Fig. 5.

XRF analysis of different areas of the same sample also resulted in variable elemental concentrations, and in particular where the matrix consisted of distinctly different components or colours or contained agglomerated material. Such heterogeneity is exemplified by the distributions of Pb and Cr concentrations in a large, multi-coloured plastiglomerate in Fig. 6. However, when elemental concentrations were normalised with respect to concentrations of an element exhibiting some general co-association or correlation (such as Pb and Cr; see above), ratios were rather consistent, as exemplified by the relationship inset in Fig. 6.

Lead was also detected in the calcareous tubes of *S. triqueter* attached to the plastiglomerate illustrated in Fig. 6 with a mean concentration of $12.2 \mu\text{g g}^{-1}$. By comparison, the mean Pb concentration in the worm tubes scraped from a pyroplastic whose Pb content was $<50 \mu\text{g g}^{-1}$ was $8.5 \mu\text{g g}^{-1}$ (but with no statistical difference noted between the mean tube concentrations according to a two-sample *t*-test; $p = 0.078$) and Pb in the tubes on a beached tarball was always below the detection limit of about $6 \mu\text{g g}^{-1}$.

Table 1

Summary statistics defining the mass and dimensions of the pyroplastic samples from Whitsand Bay ($n = 165$).

	mass, g	d_1 , mm	d_2 , mm	d_1/d_2
Median	0.358	12.9	6.58	2.04
Minimum	0.097	5.64	3.72	0.0422
Maximum	274	240	40.0	7.50
Kurtosis	69.9	31.6	6.18	11.3
Skewness	7.61	4.88	2.39	2.82

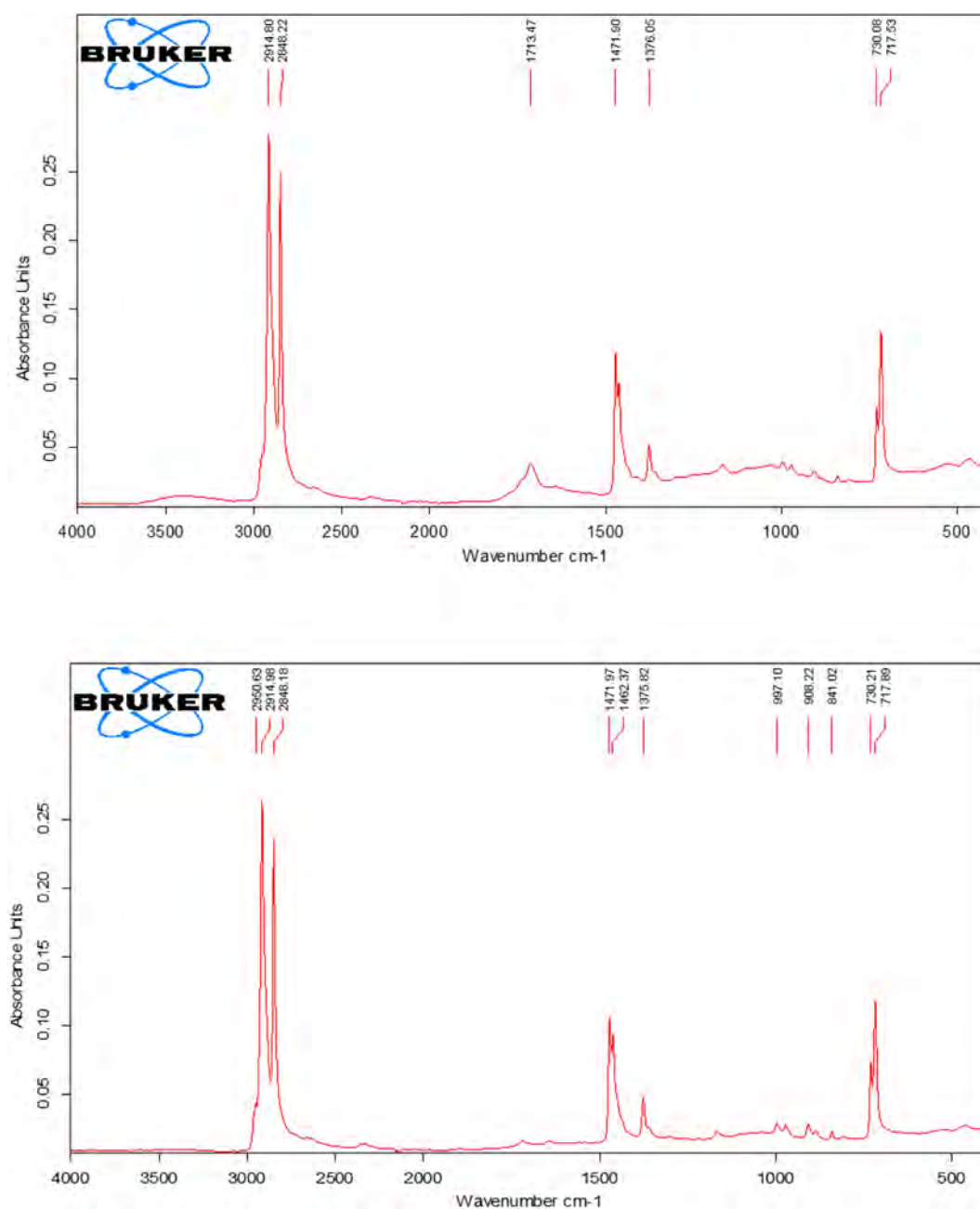


Fig. 4. FTIR spectra for the surface and subsurface (> 1 mm) of a charcoal-coloured pyroplastic from Whitsand Bay, which were library-matched from characteristic absorption bands at 2914, 2847, 1470 and 718 cm^{-1} to high density polyethylene.

Table 2

Detection frequency, indicative limit of detection (LOD) and concentration summary statistics for the elements in the pyroplastic samples from Whitsand Bay ($n = 165$). Also shown are the number of cases in which elemental concentrations exceed or potentially exceed their corresponding Restriction of Hazardous Substances (RoHS) limits (Br as certain brominated compounds $\sim 700 \mu\text{g g}^{-1}$; Cd = $100 \mu\text{g g}^{-1}$, Cr and Pb = $1000 \mu\text{g g}^{-1}$).

	Br	Cd	Cr	Cu	Fe	Pb	Sb	Zn
no. detected	120	46	72	93	165	128	12	137
LOD, $\mu\text{g g}^{-1}$	5–10	10–30	10–15	15–30	30–60	10–30	20–40	10–30
median, $\mu\text{g g}^{-1}$	7.8	62.4	53.5	31.4	773	76.0	54.8	62.3
minimum, $\mu\text{g g}^{-1}$	2.9	14.9	17.4	11.8	34.2	5.1	27.0	11.0
maximum, $\mu\text{g g}^{-1}$	346	1100	1430	581	45600	7510	196	2720
kurtosis	37.0	17.8	15.4	39.9	56.5	46.2	-0.83	24.5
skewness	5.71	3.89	3.52	5.59	7.05	5.98	0.95	4.84
no. exceeding RoHS	0	18	1			13		

4. Discussion

Pyroplastics are evidently formed from melting or burning of plastic and are distinctly different from manufactured (primary and secondary) marine plastics in terms of origin, appearance and thickness. Since pyroplastics have been retrieved by colleagues from Atlantic beaches in Spain and Pacific beaches of Vancouver, they are not a regional phenomenon, and it is suspected that their distribution may be widespread but that documentation is lacking because of a distinctly geogenic appearance. It is likely that the samples described here are related to the plastiglomerates derived from burning and reported on Hawaiian beaches by [Corcoran et al. \(2014\)](#), but a key difference is bulk density, with those retrieved from Hawaii agglomerating rocks and stones rather than other plastics. We did not observe significant agglomeration of dense material in our samples but it is possible that such clasts are more abundant on the seafloor offshore. Several of the

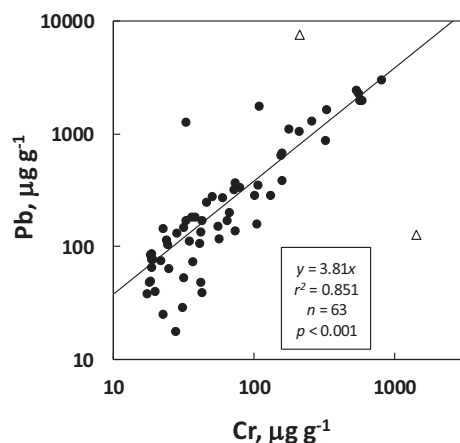


Fig. 5. Relationship between Pb and Cr in the pyroplastics from Whitsand Bay. The statistical summary defines the linear regression of the data excluding data points with the highest Pb content and the highest Cr content (shown as open triangles).

densest pyroplastics reported here returned relatively high concentrations of Fe, suggesting agglomeration of sand, and were partially covered in calcareous tubes of *S. triquetra*. The latter observation, coupled with the absence of more delicate fouling species, is consistent with a period submerged in the circalittoral zone that is subject to movement and disturbance through tidal and wave action.

The sources of pyroplastics are unclear but there are a number of possibilities. Corcoran et al. (2014) attribute plastiglomerate formation to the in situ burning of plastic and other waste in bonfires on beaches or rocky outcrops, with smaller clasts then formed by mechanical disintegration. There is clear evidence of bonfires on the beaches of Whitsand Bay, with encrustations of burned plastic on rocks towards the cliffs. It is suspected that fires are used as campfires or barbecues, or are employed to deliberately but informally burn beach waste or spent fishing equipment. This source is consistent with the occurrence of identifiable remnants of plastics typical of the marine environment, like nurdles and netting, agglomerated into pyroplastics, and could also introduce extraneous matter like sand and wood into the matrix.

More organised burning of waste, including plastics, appears to take place on many small islands where limited or primitive facilities for waste disposal exist. For example, inhabitants of some Caribbean islands are known to burn waste that results in partially melted plastics entering the sea (Witherington and Witherington, 2011). Although the fetch of Whitsand Bay to the south west extends across the North Atlantic, closer to Cornwall it has been reported that domestic waste burnt in open fires on the Channel Island of Sark (170 km south east of Whitsand Bay) has been dumped at sea from the harbour wall (Delaney, 2018). In such cases, pyroplastics would be expected to contain a more diverse array of plastics from the domestic waste stream, with possible agglomeration of buoyant marine plastics if material had not fully cooled on disposal.

In England there are about 20,000 landfills that had been constructed before the Control of Pollution Act in 1974, with many located on low value coastal land (O'Shea et al., 2016). Being poorly engineered, leakage of chemicals and materials has frequently been reported through both erosion and collapse (Pope et al., 2011; Njue et al., 2012). It is possible, therefore, that partially burned plastic dumped in historical coastal landfills or resulting from the more general burning of bulk waste and organic matter before disposal is able to escape into the littoral zone. Here, pyroplastics would be expected to be composed of an assortment of older domestic plastics but contain no marine litter.

The disposal of plastic garbage from ships, including incineration ashes generated onboard, has been prohibited since the implementation of the MARPOL 73/78-Agreement/Annex V (Regulation for the Prevention of Pollution by Ship Waste) of 1989, although only ships of 400 gross tonnage and above are required to carry out a garbage management plan (Chen and Liu, 2013). Current protocols typically involve reducing the volume of shipborne plastic waste, often by shredding and partial melting, and disposal of residual material in port. However, the rationale for the MARPOL agreement suggests that previous practice may have involved the direct disposal of large quantities of melted plastic into the marine environment, with the composition of resulting pyroplastics largely reflecting the contents of ship waste.

Regardless of the sources of pyroplastics and whether they are generated in situ, at sea or on land, many of those of positive buoyancy will end up in the turbulent swash zone where they are shaped by mechanical abrasion into more rounded and geogenic-looking pebbles. Evading

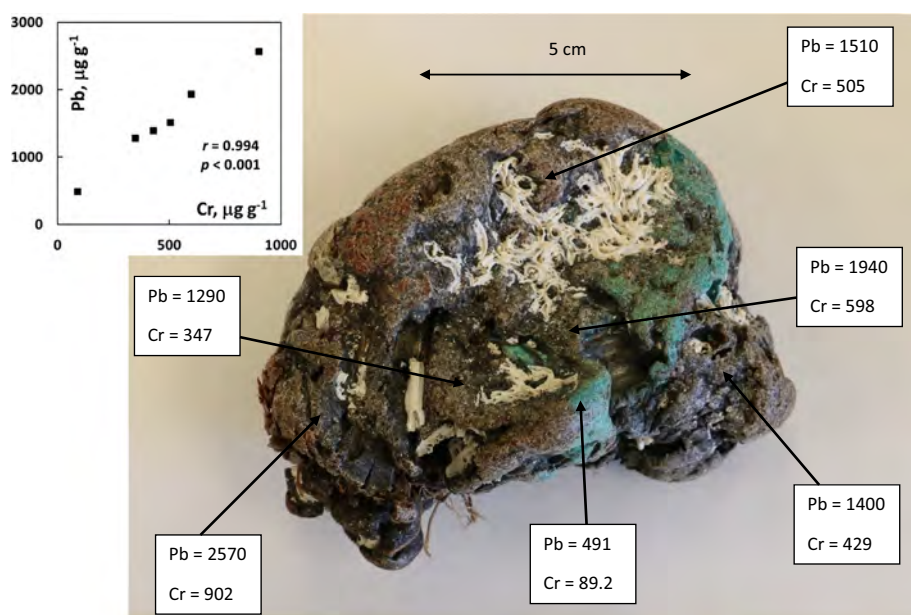


Fig. 6. Concentrations of Pb and Cr (in $\mu\text{g g}^{-1}$) across different regions of a pyroplastic hosting calcareous deposits of the tube-building worm, *S. triquetra*. Inset is the relationship between Pb and Cr concentrations in the sample.

ready recognition on the strandline, they are not classified under any category of marine litter according to OSPAR (2010) guidelines and potentially result in underestimates of the plastic inventory on beaches. Moreover, their brittleness means that they are a ready source of secondary microplastics and nanoplastics through impaction and shattering (Efimova et al., 2018), a characteristic that may well explain the bimodal size distribution we have observed.

Presumably, the age of deposition of pyroplastics is related to the degree of erosion and roundness and apparent agglomeration, although there is no clear means of quantifying this effect. With respect to age of manufacture of the plastic itself, a qualitative assessment may be gained from the distribution of certain additives within the matrix. Specifically, there is both a high occurrence and concentration of cadmium and lead among the samples, and in particular in the well-rounded clasts. These heavy metals are either no longer used or are highly regulated in consumer, electrical and packaging plastics, although small quantities appear in various goods through the recycling of improperly sorted historic waste (Turner, 2018). Significantly, limits for Cd and Pb in electrical plastics, defined by the Restriction of Hazardous Substances (RoHS) Directive (European Parliament and Council, 2003) as $100 \mu\text{g g}^{-1}$ and $1000 \mu\text{g g}^{-1}$, respectively, are exceeded in the pyroplastics analysed herein in 18 and 13 cases, respectively (Table 2).

Until a few decades ago, both Cd and Pb were used as heat and UV stabilisers in PVC and as pigments to colour most types of plastic. Given that PVC was absent among the pyroplastics and that there was no clear relationship between Cd or Pb and chloride (indicative of residual PVC), we surmise that the metals are present in the samples as pigments. The principal pigment of Pb used in plastics was lead chromate (PbCrO_4), effecting a range of reds, yellows and greens with high tinting strength and opacity by either itself or on mixing with other compounds. Among the pyroplastics there was a strong correlation between Pb and Cr concentrations determined by XRF (Fig. 5), with a gradient defining the linear regression of Pb versus Cr similar to the mass ratio of the metals in pure PbCrO_4 (~4); moreover, within the same sample, Pb and Cr exhibited a similar relationship that is exemplified for the pyroplastic shown in Fig. 6. Despite the presence of brightly-coloured leaded (and likely, cadmium-based) pigments, the matrix of pyroplastics assumes a neutral appearance (and most commonly grey or charcoal) through the mixing of multiple colours and hues. A simple laboratory test involving melting brightly coloured plastics in a steel beaker and rapidly cooling the contents in tap water resulted in a dark grey plastic matrix encapsulating various coloured streaks, as illustrated in Fig. S3.

Compared with contemporary consumer goods (Turner and Filella, 2017) and other beached plastics collected from the region that have undergone similar degrees of environmental exposure (Massos and Turner, 2017; Turner et al., 2019) there is a distinct lack of bromine and antimony in the pyroplastics. Specifically, the median concentration of Br is $7.8 \mu\text{g g}^{-1}$, Sb was only detected in twelve pyroplastics, and Br and Sb co-existed in just seven samples. Given the principal use of bromine in plastics is as brominated flame retardants (BFRs) in electrical and electronic housings and insulation, and that BFRs are usually associated with antimony as a retardant synergist, there is little evidence of electrical and electronic waste among the pyroplastic samples, either directly or through the presence of recycled material. This may reflect the fact that many pyroplastics pre-date the introduction of brominated flame retardants (the 1960s; Janssen, 2005) or the general recycling of electronic plastic into consumer goods, a practice that is currently not legal but that is exploited through a series of loopholes (Turner, 2018). Alternatively, it is possible that, because the presence of BFRs and Sb render plastic more difficult to burn, such materials are deliberately avoided in the first place or remain as more discrete (i.e. non-agglomerated) residues after burning. (Aside from its high density, this would also explain the absence of PVC in the beached pyroplastics, a material whose halogen content ensures an inherent flame retardancy.)

In addition to underestimating the stock of beached plastic and their propensity to readily form microplastics and nanoplastics, a concern of pyroplastics is the potential for heavy metals to be mobilised or enter the foodchain. The mobility of Pb was evaluated by determining its concentration in calcareous worm tubes on a lead-rich pyroplastic (illustrated in Fig. 6), a lead-poor pyroplastic and a beached tarball containing no detectable lead. That mean Pb concentrations in the tubes were greatest on the lead-rich pyroplastic and not detected on the tarball suggests that there is potential for transfer of additives or residues in plastic to organisms that use the material as a substrate. A similar conclusion was reached by Jang et al. (2016) for marine mussels inhabiting styrofoam that accumulated the flame retardant, hexabromocyclodecane, from the matrix but further studies in this area are required in order to evaluate the significance of contaminant transfer from plastics more generally.

In summary, pyroplastics are a non-manufactured type of marine plastic litter that appear to be derived from the informal or more organised burning of waste that may take place in situ or ex situ. They typically consist of a neutrally-coloured matrix agglomerating more distinct pieces of plastic and other debris, but weathering in the circalittoral zone shapes material into geogenic-looking pebbles that readily evade detection during beach-cleaning. Pyroplastics require their own classification within the umbrella of marine litter, and are a source of finer plastic particulates through mechanical breakdown and a potential source of contaminants for organisms that inhabit or ingest them.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.133610>.

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