



Speciation and leaching behaviour of inorganic contaminants in actively eroding historical coastal municipal solid waste landfills

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ABSTRACT

The erosion of legacy coastal municipal solid waste landfill sites will result in the dispersion of particulate material into nearby ecosystems with potential for effects on marine populations. Information on the speciation and solid phase associations of metal(loid) contaminants will help to predict contaminant behaviour and better understand ecosystem risks. Here, we investigate the solid phase composition of, and metal(loid) leaching from, fine fraction materials recovered from three actively eroding coastal landfill sites. High concentrations of a range of potentially toxic elements (As, Cd, Cr, Cu, Pb, Ni and Zn) were present in multiple samples, but metal(loid) leaching rates were very low ($\ll 1$ wt%) in both deionised water and seawater solutions. Therefore, particulate dispersion is the most likely mode of contaminant transport occurring at these sites. The fine fraction materials were dominated by fine sand sized (63–180 μ m) quartz grains and silt sized (< 63 μ m) matrix components, which were likely to be poorly retained on beaches and easily transported offshore. Four priority contaminants (As, Cu, Pb and Zn) were found to occur primarily in adsorbed or precipitate forms, as either coatings on other particles or as discrete < 10 μ m particles. Dilution of these fine-grained contaminated particles within natural pelitic sediments will likely reduce the overall ecosystems impacts; but the risks to filter and bottom feeding organisms, and the potential for biomagnification across trophic levels are poorly understood.

1. Introduction

Over the past century there has been a wide range of industrial, commercial, and municipal wastes disposed of in low lying coastal areas and estuaries with minimal containment and erosion protection (Brand et al., 2018; Nicholls et al., 2021). The erosion of legacy coastal landfill sites is of global concern due to the potential for climate impacts to increase both erosion rates and incidence of coastal flooding, which may lead to increased contaminant fluxes to coastal ecosystems (Brand and Spencer, 2020; Riley et al., 2024). The composition of the wastes present at individual sites is often poorly understood; a recent analysis of 2250 coastal legacy waste sites in England and Wales found that mixed,

undefined, household, and commercial wastes made up 63 % of the total waste area present (Riley et al., 2022). Many of these sites primarily received municipal solid wastes (MSW); the mixed wastes generated by households, businesses, and commercial activities; often combined during disposal and containing a biodegradable component) and are widespread in populated coastal areas (Brand et al., 2018; Cly, 2001; Riley et al., 2022).

Most UK historical landfills were closed in the second half of the 20th century with a small number of older sites active before the 1960s (Riley et al., 2022). Landfill closure age is relevant in terms of MSW composition. In the early 20th century coal ash was an important component of UK household wastes (~50 %), and MSW also contained more metal

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wastes (~20 %) than in other periods (Williams, 2013). Reduction of household coal burning in the 1960s and higher metal recycling, combined with the rise in the consumer society, led to disposal of more packaging materials (glass, plastics, paper) and increased biodegradable content as more food waste was produced (Williams, 2013). Recently, there has been advancement in understanding of the bulk composition of legacy landfills driven by landfill mining for value recovery, often the calorific (i.e. fuel value) and metal content have been quantified along with other physical and chemical properties (Hull et al., 2005; Kaartinen et al., 2013; Parrodi et al., 2018). Recovered MSW materials contain a large fine fraction component (<40 mm; average ~50 wt%; range 30–70 wt%), much of which is soil-type materials, stone fragments, inert (mineral), and construction and demolition wastes (Parrodi et al., 2018). The organic matter content of fresh MSW can be >40 wt%, but 30 years after disposal, biodegradable organics decrease as the waste become stabilised and an organic content of 5–10 wt% is commonly reported (Parrodi et al., 2018). A wide range of potentially toxic elements (PTEs) are ubiquitously discovered in the fine component, with As, Cd, Co, Cr, Cu, Ni, Pb, Hg, and Zn commonly present due to their presence in household items (Kaartinen et al., 2013; Parrodi et al., 2018; Slack et al., 2005). In leaching tests, low PTE solubilisation are typically apparent (Kjeldsen et al., 2002), but high Cu, Zn and Pb leaching rates have been reported at some sites (Gutiérrez-Gutiérrez et al., 2015; Kaartinen et al., 2013).

Contaminants from MSW can pose a wide set of risks to aquatic ecosystems. For younger materials, high oxygen demand from organic matter degradation may impact benthic ecosystems (Servais et al., 1999). Soluble PTEs may be taken up into marine algae, and particulates can be consumed by filter and bottom feeding organisms. Bio-accumulation of PTEs into higher trophic level animals is widely reported (Jakimska et al., 2011; Jitar et al., 2015), leading to ecosystem impacts (Jakimska et al., 2011). However, there is no established procedure to determine the potential impacts of eroding landfill materials in the marine environment (Dack et al., 2024). Therefore, it is important to understand the potential impacts on receiving environments if MSW landfills become subject to coastal erosion. Two modes of contaminant transport are typically considered: Erosion, breakup, and dispersion of the MSW solids; and leachate production by rain or seawater infiltration (Brand and Spencer, 2020; Brand et al., 2018). There is some evidence that leachate production alone is unlikely to result in harmful ecosystem effects in coastal waters due to high dilution rates (Brand and Spencer, 2020). However, the potential risks caused by dispersion of MSW particulates are poorly understood. There is a lack of data on the physical and mineralogical composition of eroded materials, and no information on the speciation and micro-scale solid association of PTEs; which are required to predict the likely environmental reactivity of MSW particles in coastal environments and potential uptake of PTEs into organisms (Pempkowiak et al., 1999).

Here, we seek to address this knowledge gap, providing detailed compositional data from actively eroding MSW materials to inform debate on the potential risks to receiving environments. The specific objectives of this study were to: investigate the compositional variation present in the fine fraction materials eroding from three coastal landfills sites; determine the micro-scale associations and chemical speciation of selected PTEs present in wastes (i.e. As, Cu, Pb, Zn); measure metal(loid) leaching behaviour of these materials in fresh and seawater solutions; and, to integrate this new data with existing literature to provide insight on the likely modes of contaminant dispersion and risks to coastal ecosystems.

2. Materials and methods

2.1. Sample collection

Solid wastes were recovered from three historical UK municipal waste landfills present within the coastal zone at Crosby Beach, Llanelli

and Withernsea (Fig. 1). These sites were selected as they were deemed high priority in national risk assessments (Riley et al., 2022) and field evidence showed all sites were actively eroding at the time of sampling (SI Fig. S1) causing dispersion of waste materials into the coastal marine environment. Multiple samples from each site were used for analysis. Crosby Beach (July 2021), four samples, CB1 CB2, CB2c and HRC. Llanelli (October 2022), four samples, LF1 LF2, LF3 and LF4. Withernsea (April 2021), five samples, WLF1, WLF2, WLF3, WLF 4 and WLF4.1. Each sample (~1 kg) was a pooled and homogenised composite of ~6 × ~150 g subsamples recovered along a 10 m section of exposed surface materials, up to a depth of no more than 30 mm below the surface, collected with plastic trowel and stored in plastic containers prior to homogenisation. Sampling targeted the fine-grained matrix component (<40 mm). Detailed descriptions and site histories are provided in SI section S1. Briefly, the Llanelli and Crosby beach landfills both received MSW from the 1970s to 1980s, but the Withernsea landfill was much older, operated for a longer period – 1860s to 1960s, and also contained ash-like materials and melted glass than indicate that some wastes had been incinerated before disposal.

2.2. Sample characterisation

For total elemental analysis, the MSW fine fraction materials were oven dried at 30 °C and sieved to collect the <10 mm fraction, and subsamples were produced by coning and quartering. Triplicate subsamples (after grinding to produce particles <125 µm) were then subject to a three-stage total acid digestion (SI Section S2; Table S1) and elemental concentrations were determined in the resultant solutions using an Agilent 7700× ICP-MS. Powder (<125 µm) X-ray diffraction (XRD) patterns were collected using a Siemens D500 diffractometer with an X-Ray tube at 1.5 kW and Cu-anode from 2 to 70° 2θ. Diffraction peaks were matched to standards in EVA v.18.0.0.0 using the JCPDS PDF-22004 database. Mineral morphology, association and quantification were determined using a QEMSCAN® 4300 automated scanning electron microscope. Approximately 1 g subsamples of selected waste materials (<2 mm) were mounted into 30 mm diameter epoxy resin blocks and carbon coated (25 nm). The QEMSCAN was operated at 25 kV and 5 nA beam using a tungsten filament under high vacuum and an X-ray count rate of 1000 counts from 4 EDS Bruker SDD detectors (Rollinson et al., 2011). The Fieldscan measurement mode was used for all samples with a 10 µm resolution. Observed phases were assigned to minerals based on the EDS chemical composition (SI Table S2) informed by phases identified by powder XRD.

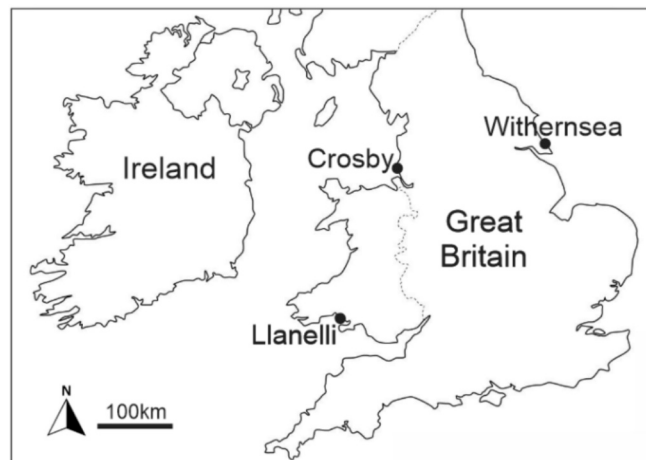


Fig. 1. Locations of historical MSW landfills at Crosby Beach, Llanelli and Withernsea.

Table 1

Average mineral concentrations (vol%) present in MSW fine fraction samples obtained from QEMSEM analysis; n.d. = not detected.

	Llanelli	Crosby	Withernsea
Quartz	44	77	28
Feldspars	10	10	12
Clays	33	3	22
Carbonates	5	4	6
Metal Oxides	2	1	16
Other Silicates	5	6	8
Sulfates	0.1	1	3
Sulfides	n.d.	n.d.	1
Other	<1	<1	4

2.3. X-ray absorption spectroscopy (XAS) and microfocus X-ray fluorescence (XRF) analysis

Samples of MSW fine fraction materials were prepared as either 8 mm diameter powder pellets (for XAS analysis), or as granular samples (<2 mm grain size) embedded in 30 mm diameter polished epoxy resin blocks (for microfocus XRF analysis). Blocks were polished used water a free lubricant. Standards were prepared as pressed pellets (diluted using cellulose binder and held in Kapton™ tape) from a wide range of laboratory chemicals and natural mineral samples (Table S2). Cu, Pb and Zn adsorbed to hydrous ferric oxide (HFO) standards were prepared by mixing 0.5 mL of 5000 mg L⁻¹ Cu²⁺ (as nitrate), Pb²⁺ (as nitrate) or Zn²⁺ (as chloride) with 0.5 g ferrihydrite precipitate (that contained goethite and hematite impurities; Cornell and Schwertmann, 2003), and adjusting to pH 7.5–8.0 with 0.1 M NaOH. After 24–48 h equilibrium, the solids were separated and dried at 40 °C.

X-ray Absorption near-edge structure (XANES) spectra were collected from powder pellets at the As, Cu and Zn K-edges (ca. 11,867, 8979, and 9659 eV respectively) and the Pb L₃-edge (ca. 13,035 eV) on beamline I18 at Diamond Light Source operating at 3 GeV with a typical current of 200 mA, using a nitrogen cooled Si(111) double crystal monochromator and focussing optics (Mossemans et al., 2009). A pair of plane mirrors was used to reduce the harmonic content of the beam and Kirkpatrick-Baez mirrors were used to produce either a focused or unfocused beam (0.005 mm or 0.1 mm diameter respectively at the sample) for microfocus or bulk sample analysis as required. For standards prepared as pressed pellets, XAS spectra were collected in transmission mode using ionisation chamber detectors. For samples and solutions, data were collected in fluorescence mode using a 4 element 1 mm thick sensor Vortex Si Drifts detector with CUBE pre-amps. All data collection was performed at room temperature (~295 K) within a He-

Table 2

Concentration (mean, mg kg⁻¹ ± 1σ) of selected elements in MSW fine fraction samples; n.d. = not determined; Eco-SSL = US-EPA ecological soil screening level for mammalian exposure (or *invertebrate exposure); PEL = Canadian marine sediments probable effects level; – = no standard data available.

	Llanelli	Crosby	Withernsea	Eco-SSL	PEL
Al	41,700 ± 8540	14,790 ± 2030	53,990 ± 9040	–	–
V	63 ± 12	61 ± 53	172 ± 27	1.59	–
Cr	172 ± 24	231 ± 128	130 ± 37	34	160
Mn	668 ± 58	225 ± 8	1047 ± 347	4000	–
Fe	39,970 ± 5200	15,380 ± 6620	125,600 ± 45,200	–	–
Co	n.d.	7 ± 0	239 ± 149	0.14	–
Ni	38 ± 7	21 ± 1	158 ± 44	13.6	42.8
Cu	82 ± 32	93 ± 82	819 ± 161	5.40	108
Zn	416 ± 35	440 ± 372	2060 ± 1140	*6.62	271
As	24 ± 6	13 ± 2	116 ± 19	5.70	41.6
Sr	n.d.	92 ± 1	262 ± 55	–	–
Se	n.d.	1 ± 0	6 ± 1	0.63	–
Ag	n.d.	1 ± 0	1 ± 1	4.04	–
Cd	1 ± 1	0.4 ± 0.0	8 ± 12	* < 0.40	4.2
Ba	n.d.	259 ± 20	1940 ± 350	1.04	–
Pb	374 ± 510	295 ± 85	1190 ± 450	0.054	112

filled bag (to lower the attenuation of low energy fluorescence X-rays). For the resin embedded blocks, multielement microfocus XRF spectra were collected from approximately 0.5 × 0.5 mm regions (spot size 0.005 mm). These were then processed by the beamline software in real time to produce elemental maps for Si, S, Ca, Cr, Fe, Cu, Zn and As.

Only single XANES spectra were collected (~10 min) from any one spot within samples and the sample stage automatically moved to expose an unaffected part of the sample before subsequent scans. For bulk analysis, multiple scans were then averaged to improve the signal to noise ratio using Athena version 0.9.26 (Ravel and Newville, 2005). For all XANES spectra, absorption was normalised in Athena over the full data range and plotted from approximately –20 eV to +30 eV relative to the edge position. Spectra were corrected E₀ using the data collected from the metal foil standards. Linear combination fitting (LCF) was performed in Athena using the full range of available standards (SI Table S3) to determine the most likely combinations of standards to best fit the sample. In the final LCF analysis, the number of standards used was limited to a maximum of 3 to reduce the degrees of freedom present. Standard choice was informed by principal component analysis (showing that 3 standards were sufficient to fit the sample data) and a screening exercise performed in Athena were samples where fit will all possible three standard combinations and only combinations with the lowest goodness of fit values (r-value) used in the final fitting. LCF often cannot directly identify the exact phases present in environment samples (as many phases can share similar molecular coordination environments) but can provide useful information on valence state and the dominant elemental bonding environments present.

2.4. Leaching tests

In accordance with BS EN 12457-2 waste leaching procedure (SI Section S3; BS EN 12457, 2002), air-dried MSW fine fraction samples were screened at <10 mm and then gently crushed in a pestle and mortar to produce samples with grain sizes <4 mm. For each MSW landfill, triplicate 90 g samples were contacted with 900 mL of deionised water or seawater (solid/solution ratio = 100 g L⁻¹) in a Heidolph REAX 20 end-over-end shaker at 10 rpm. Process blanks containing no solids additions were also produced (SI Table S4). Natural seawater (0.45 μm filtered) used in these tests was collected from the North Sea at Flamborough, North Yorkshire (54°06'14"N, 000°07'09"W) in August 2022 (Riley et al., 2024). After 24 h, solids and solutions were separated by settling. pH, oxidation reduction potential (ORP) and electrical conductivity were measured using unfiltered solutions using a Myron L 6P Ultrameter. ORP values were converted to Eh versus the hydrogen electrode by addition of 199 mV to the measured value. Specific elemental concentrations were determined in leachates after filtration (0.45 μm; cellulose nitrate) and acid addition (5 % v/v cHNO₃) using an Agilent 5800 Series ICP-OES or an Agilent 7700 Series ICP-MS as required. Anion concentrations (sulfate, chloride) were also determined using a Thermo Scientific Dionex Integriion Ion Chromatograph.

3. Results

3.1. Sample composition

The recovered MSW fine fractions were primarily composed of soil minerals: Crosby: quartz, microcline, orthoclase albite, and calcite; Llanelli: quartz, microcline, albite, calcite, dolomite, illite, and chlorite; Withernsea: quartz, orthoclase, albite, microcline, muscovite, biotite, microcline, goethite, hematite, gypsum, kaolinite, calcite, and ankerite. Semi-quantitate QEMSEM analysis (Table 1) indicates that quartz was the most common single-phase present, following by silicates (clays, feldspars), metal oxides, carbonate and sulfate phases. The mean grain size of quartz particles was between 80 and 200 μm and of other phases were typically <50 μm (SI Fig. S2). A wide range of trace elements were detected in the MSW fine fraction samples (Table 2). Trace element

concentrations were broadly similar in the Crosby Beach and Llanelli samples but were higher in the Withernsea samples. These concentrations exceed Dutch target values (Department of Soil Protection, 2000) for soil quality for multiple controlled elements and intervention values for As, Cu, Pb and Zn in many samples. PTE concentrations (As, Cr, Cd, Cu, Pb, V and Zn) in multiple samples also exceed ecological soil screening levels (US Environmental Protection Agency, 2005) for avian, invertebrate, mammals, and plants exposure. The MSW fine fraction samples also exceed Canadian probable effects levels aquatic sediment values for As, Cd, Cr, Cu, Pb, Ni, Zn (Persaud et al., 1993).

3.2. Trace element distribution and speciation

Microfocus XRF analysis (Fig. 2; SI Figs. S3, S4) allowed visualisation of the MSW fine fraction solids present. Silica was often present in discrete grains, ranging from $<50\ \mu\text{m}$ up to $500\ \mu\text{m}$, and as part of a fine-grained matrix phase. Fe also was found in discrete larger grains (up to $1000\ \mu\text{m}$) but was more commonly also present in the fine-grained matrix phase. In some samples, Ca was present in small $<50\ \mu\text{m}$ particles but was also found to co-occur with S and Si in particles in the Llanelli and Crosby samples. Selected elements such as As, Cu, Zn were not primarily found associated with any discrete particle types, but

instead were found in the Si-rich fine-grained matrix, occasionally as coatings on Fe-rich particles, and often in $<10\ \mu\text{m}$ elemental hot-spots. XANES spectra (Fig. 3) collected from the powder samples provided an average elemental speciation for each sample. There was a generally consistent elemental speciation for the four elements of interest in fine fraction samples collected from three distinct MSW landfill sites.

In LCF results the As K-edge XANES spectra were best fit by predominantly As(V)-O phases (89–92 %) with a minor contribution from As(III)-O phases (5–11 %), with no contribution from As(III)-S phases (Table 3). Cu K-edge XANES spectra were fit with three bonding environments. Cu(II) in inner sphere adsorption complexes (Cu(II)-ads; 41–66 %) was the most common speciation, but significant fractions of both Cu(I)-O (16–38 %) and Cu(I)-S (13–26 %) bonding were also present. Pb L₃-edge XANES spectra varied only slightly between different end member spectra; therefore, the LCF results presented are the least robust of the four elements of interest presented in this study. Nevertheless, adsorbed Pb(II) phases (38–50 %) were generally most common in LCF results from the Pb L₃-edge XANES spectra, except for one sample from the Llanelli landfill that was dominated by Pb(II)-SO₄ phases (Llanelli LF 1; 72 %). In other samples the presence of Pb(II)-SO₄ was predicted, albeit with a lower contribution (38–44 %). LCF also predicted a small contribution from Pb(II)-S phases (6–29 %) in all samples.

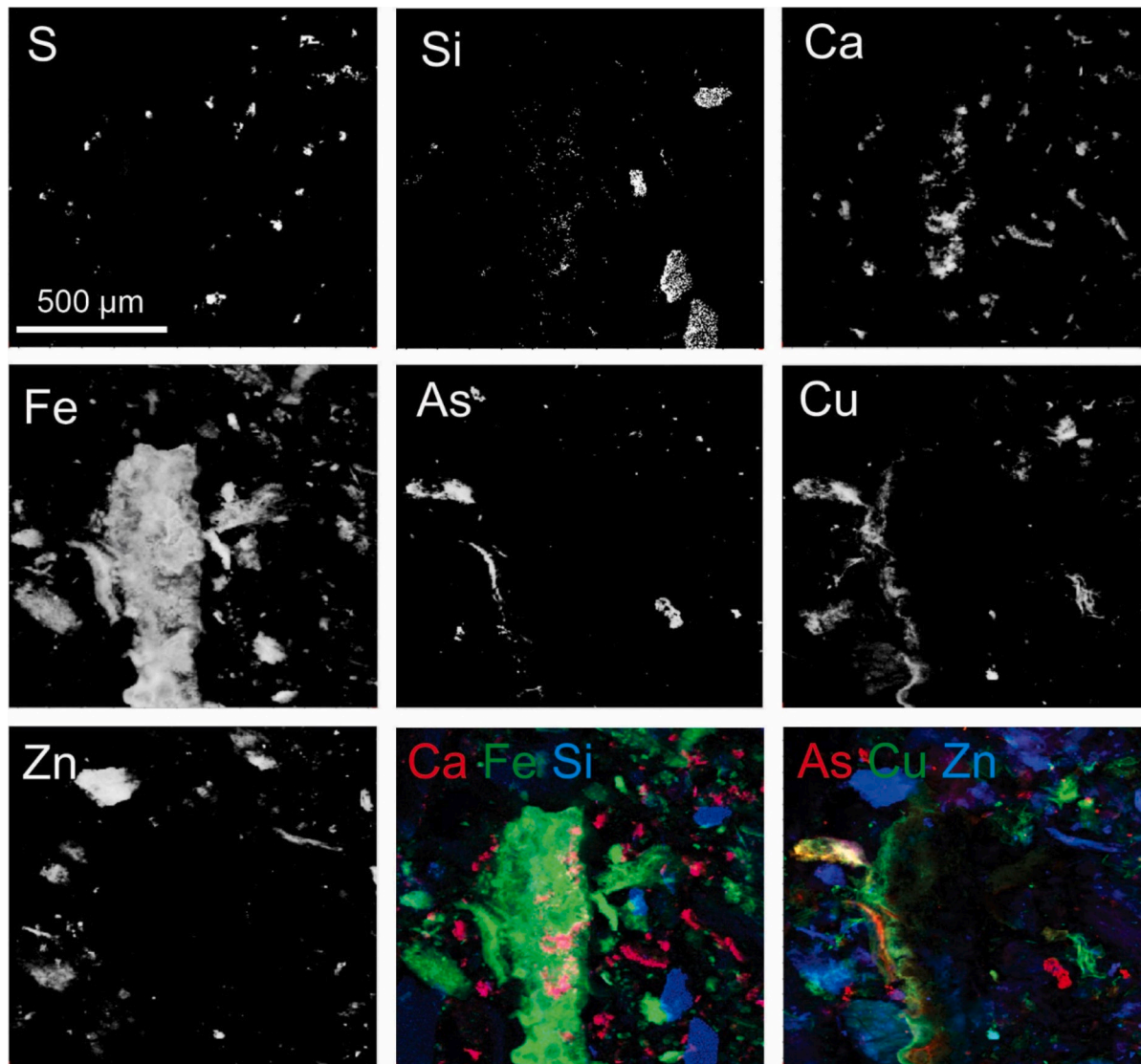


Fig. 2. μXRF elemental and false colour maps showing distribution of elemental K-edge X-ray emissions with respect to a selected particles within the Withernsea Landfill fine sediment fraction (Withernsea WS3).

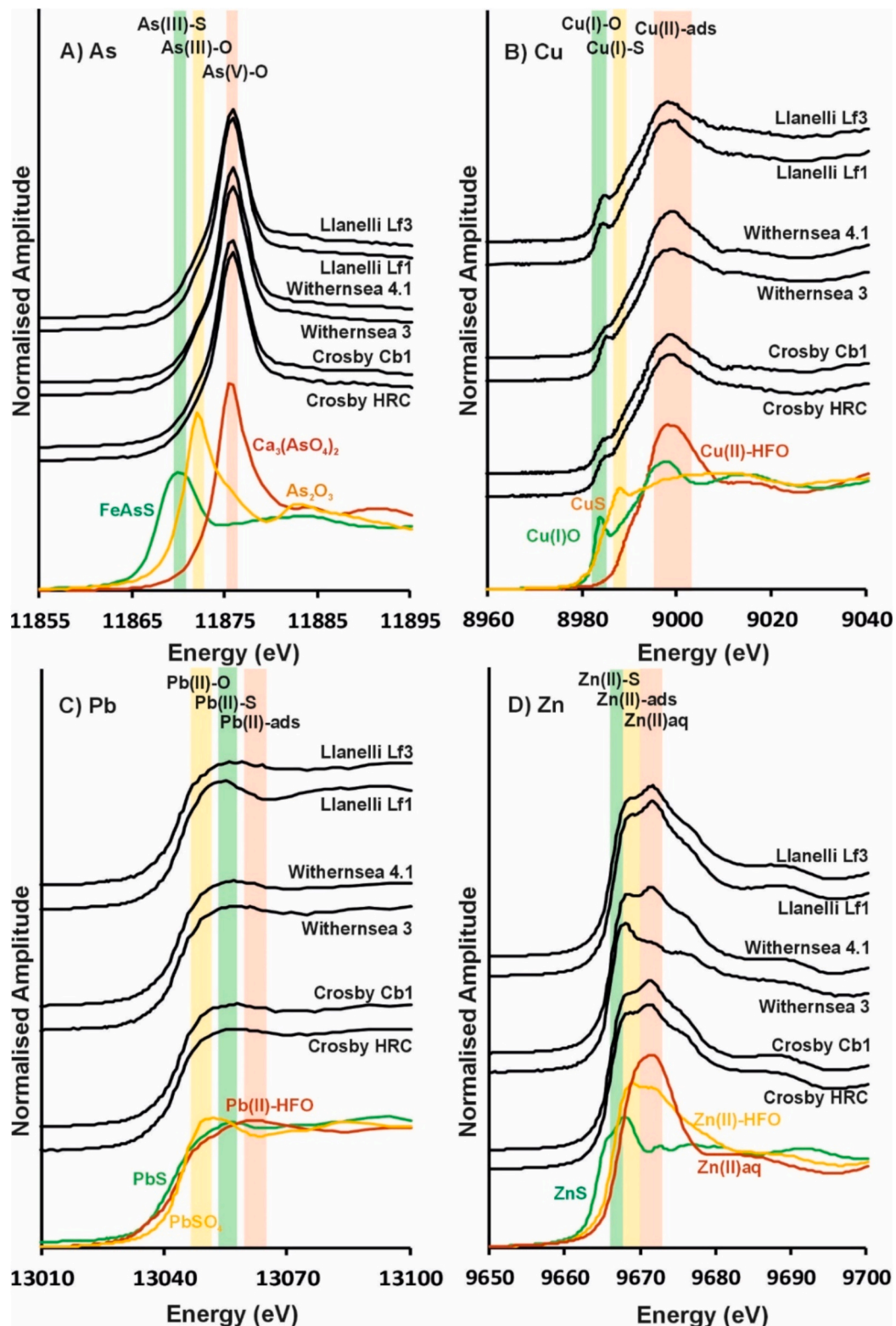


Fig. 3. As, Cu, Pb, and Zn XANES spectra collected from landfill fine fraction samples and selected standard spectra. The coloured bands are provided to guide the eye to significant spectral features present in standard spectra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Finally, LCF of Zn K-edge XANES spectra were dominated by Zn(II)-ads phases (63–100 %) with a small proportion of Zn(II) in complexes similar to the hydrated aqueous ion (which is also identical to Zn present in outer sphere adsorption complexes); one sample (Withernsea 3) also had a significant component of Zn(II)-S bonding present.

3.3. Leaching behaviour

Short term leaching behaviour was similar across all three MSW fine fraction samples analysed (Table 4). All samples produced near neutral to slightly alkaline leachate when subjected to leaching in either

Table 3

Linear combination fitting results (atom%) for As, Cu, Pb and Zn K-edge XANES data; uncertainty in last digit shown in parenthesis; r is the goodness of fit parameter.

As-XANES	As(V)-O	As(III)-O	As(III)-S	r
Crosby HRC	90 (1)	10 (1)	–	0.0103
Crosby CB1	91 (1)	9 (1)	–	0.0103
Withernsea 3	89 (2)	11 (2)	–	0.0139
Withernsea 4.1	95 (1)	5 (1)	–	0.0114
Llanelli LF1	92 (1)	8 (1)	–	0.0108
Llanelli LF3	89 (1)	11 (1)	–	0.0093

Cu-XANES	Cu(II)-ads	Cu(I)-O	Cu(I)-S	r
Crosby HRC	50 (2)	25 (1)	25 (1)	0.0011
Crosby CB1	53 (3)	28 (2)	19 (2)	0.0037
Withernsea 3	49 (4)	26 (3)	26 (3)	0.0094
Withernsea 4.1	66 (2)	16 (2)	18 (1)	0.0023
Llanelli LF1	48 (2)	38 (1)	13 (1)	0.0014
Llanelli LF3	41 (2)	37 (1)	22 (1)	0.0016

Pb-XANES	Pb(II)-ads	Pb(II)-SO ₄	Pb(II)-S	r
Crosby HRC	44 (2)	27 (3)	29 (2)	0.0003
Crosby CB1	38 (4)	42 (6)	19 (4)	0.0012
Withernsea 3	47 (4)	38 (7)	15 (4)	0.0015
Withernsea 4.1	50 (4)	44 (5)	6 (4)	0.0009
Llanelli LF1	5 (5)	72 (8)	24 (5)	0.0020
Llanelli LF3	43 (5)	42 (7)	15 (5)	0.0018

Zn-XANES	Zn(II)-ads	Zn(II)-aq	Zn(II)-S	r
Crosby HRC	100 (0)	0 (0)	–	0.0046
Crosby CB1	98 (3)	2 (2)	–	0.0045
Withernsea 3	63 (2)	–	37 (2)	0.0091
Withernsea 4.1	100 (0)	0 (0)	–	0.0043
Llanelli LF1	74 (2)	26 (2)	–	0.0030
Llanelli LF3	88 (2)	13 (2)	–	0.0029

deionised water (DIW; pH 7.7–8.8) or seawater (SW; pH 6.7–7.4) producing oxidising solutions (Eh 211–446 mV). Conductivity was higher in the SW solutions compared to those from DIW leaching. Within the DIW leaching results there were large differences in conductivity between the samples with the Withernsea samples producing much higher values than either Crosby or Llanelli samples (Table 4). SW leaching was dominated by seawater ions (Na, Mg, K, Ca, chloride, and sulfate) that were added with the leaching solution (SI Table S4). In DIW leaching was Ca and sulfate dominated (e.g. comprising >70 % of the total ionic strength present in the Llanelli sample leachates), or Na and chloride dominated (e.g. the Crosby samples). Leaching of trace elements was generally low, with only $\mu\text{g L}^{-1}$ concentrations of PTEs recovered regardless of the leaching solution, equating to specific mobilisations of $\ll 1$ % of the solid concentrations of PTEs (Table 2). There were no clear trends between DIW and SW leaching for many PTEs (including Al, V, Cr, Ni, Cu, As, Se, Pb). Zn, Ba and Mn concentrations, however, were all present at higher concentrations in the SW solutions (Co and Cd leaching by SW was also slightly enhanced). Iron was the only element with higher DIW leaching compared with SW leaching (Fe was below detection limits in the SW leachates). In terms of potential ecotoxicity, higher concentrations of Al, Fe, Mn and Zn ($>0.2 \text{ mg L}^{-1}$) were present in some DIW and SW leachates than for other elements measured (Table 4). However, PTE concentration values in all leachates were much less than UK waste acceptance criteria (BS EN 12457, 2002).

Table 4

Results from 24-h leaching tests using MSW samples in deionised water (DIW) and seawater (SW); solid/solution ratio = 100 g L^{-1} ; n.d. = not determined.

	Llanelli		Crosby		Withernsea	
	DIW	SW	DIW	SW	DIW	SW
pH, Eh; (mV) and Conductivity ($\mu\text{S cm}^{-1}$)						
pH	7.7	7.1 ± 0.1	8.8	7.4 ± 0.0	7.8 ± 0.2	6.7 ± 0.0
Eh	408 ± 6	414 ± 83	446 ± 7	211 ± 17	373 ± 6	379 ± 6
Conductivity	306 ± 1	51,630 ± 40	344 ± 9	49,650 ± 180	31,790 ± 610	51,600 ± 960
Major components (mg L^{-1})						
Chloride	29 ± 16	17,710 ± 360	75 ± 4	19,850 ± 1510	n.d.	n.d.
Sulfate	96 ± 27	2520 ± 50	26 ± 2	2650 ± 270	2080 ± 60	5390 ± 190
Na	9.6 ± 0.1	9220 ± 80	52 ± 1	10,210 ± 50	n.d.	n.d.
Mg	8.1 ± 0.1	1140 ± 10	3 ± 0.1	1180 ± 6	32 ± 2	1430 ± 40
K	8.2 ± 0.0	429 ± 3	4 ± 0.1	489 ± 2	n.d.	n.d.
Ca	33 ± 0.0	574 ± 4	12 ± 0.4	386 ± 9	810 ± 10	1460 ± 60
Si	3.5 ± 0.0	2.7 ± 0.0	2.5 ± 0.0	1.6 ± 0.0	n.d.	n.d.
Sr	n.d.	n.d.	n.d.	n.d.	2.5 ± 0.1	11 ± 0.6
Trace components ($\mu\text{g L}^{-1}$)						
Al	54 ± 7	4.6 ± 2.4	129 ± 16	<0.1	113 ± 6	205 ± 35
V	1.3 ± 0.1	0.9 ± 0.1	8.1 ± 0.1	2.5 ± 0.3	2.0 ± 0.0	2.0 ± 0.0
Cr	1.3 ± 0.2	1.3 ± 0.1	3.4 ± 0.4	<0.1	6.0 ± 1.7	3.7 ± 0.6
Mn	22 ± 1	313 ± 5	8.2 ± 1.4	85 ± 1	193 ± 6	923 ± 58
Fe	567 ± 56	<0.1	236 ± 22	<0.1	77 ± 21	n.d.
Co	0.3 ± 0.1	1.9 ± 1.8	0.2 ± 0.0	0.4 ± 0.1	6.0 ± 1.7	28 ± 4
Ni	2.5 ± 0.1	8.4 ± 4.5	2.1 ± 0.1	1.3 ± 0.6	6.0 ± 1.7	28 ± 4
Cu	18 ± 1	24 ± 2	30 ± 1	20 ± 1	13 ± 1	38 ± 7
Zn	13 ± 1	93 ± 13	14 ± 1	139 ± 17	49 ± 10	304 ± 26
As	3.8 ± 0.1	2.8 ± 0.1	12 ± 0.4	7.4 ± 0.8	4.0 ± 0.0	6.3 ± 0.6
Se	n.d.	n.d.	n.d.	n.d.	3.7 ± 0.6	3.7 ± 0.6
Ag	<0.1	<0.1	<0.1	<0.1	n.d.	n.d.
Cd	n.d.	n.d.	<0.1	5.4 ± 0.3	0.4 ± 0.0	17 ± 1
Ba	n.d.	n.d.	n.d.	n.d.	32 ± 2	1427 ± 42
Hg	<0.1	<0.1	n.d.	n.d.	<0.1	<0.1
Pb	1.8 ± 0.2	0.1 ± 0.0	15 ± 2	6 ± 2	1.7 ± 0.6	14 ± 1

4. Discussion

4.1. Composition of MSW fine fraction solids

The MSW fine fraction samples were composed of a similar range of primarily soil minerals such as quartz, feldspars, clays, carbonate, and iron oxides. The co-occurrence of Ca and Si in μXRF maps likely also relates to a fraction of anthropogenic particles, such as Ca-Si-hydrate from cementitious wastes (Rayment and Majumdar, 1982). Although the samples were sieved at 2 mm during preparation, they were mostly composed of fine sand sized (63–180 μm) quartz particles and a silt sized

(<63 μm) matrix containing the other phases present. This material is likely to have originated as soils used as waste cover during landfill construction (Tchobanoglous et al., 1993). Due to the large differences in density between MSW (150–300 kg m^{-3}) and soil cover (1300–1700 kg m^{-3} ; Tchobanoglous et al., 1993), closed MSW landfills can contain >50 wt% soil materials after compaction (Parrodi et al., 2018).

The fine fraction contained high concentrations of several PTEs, including As, Ba, Co, Cu, Ni, Pb and Zn, compared to background soil compositions. The range of elements present concentration ranges were similar to samples collected at two other UK coastal MSW landfills (Brand and Spencer, 2020) and a wide range of recovered MSW materials (Kaartinen et al., 2013; Parrodi et al., 2018). At Crosby and Llanelli, this may indicate that contaminated materials were co-disposed at these sites, but more likely the PTEs originated in other waste components (e.g. metals, electronics, batteries, paints) that were mobilised after landfill closure and accumulated within the fine fraction materials due to precipitation and sorption reactions. The chemical evolution of MSW landfills commonly includes a relatively short lived (1–10 years after closure; Pohland, 1982) period of acid generating anaerobic degradation in which low pH (≤ 5) and high concentrations of organic ligands (e.g. acetic acid) promote trace element mobility in leachates. The length of the acid generation stage is limited by the amount of fermentable organic matter present. Over time organic acids are consumed by anaerobic respiration, pH returns to neutral values, and any mobilised PTEs are sequestered in solids by precipitation and sorption processes (Kjeldsen et al., 2002). Leaching test results indicated that the legacy materials present at these sites were oxidised, neutral-slightly alkaline pH wastes consistent with matured MSW (Kaartinen et al., 2013). The micro-scale distribution of several trace elements (e.g. As, Cu, Zn, which were found as surface coatings, associated with fine-grained matrix materials, or very fine-grained distinct particles) was also consistent with redistributed metals within mature MSW. Linear combination fitting XANES of several trace elements present also indicated predominantly oxidised forms (e.g. As(V), Cu(II)) and significant fractions likely in adsorbed (e.g. Cu, Pb, Zn) or precipitated (e.g. Pb-sulfate) forms. Arsenic (V) is also likely to be present as arsenate adsorbed to mineral surface; however, given that mobile Ca is readily leached from these wastes, the presence of insoluble Ca-arsenate precipitates cannot be excluded (Bothe and Brown, 1999). The presence of metal sulfides (e.g. Cu, Pb, Zn) is also indicated in most samples. Hydrogen sulfide is produced by bacterial sulfate reduction (sulfate is likely to be present in gypsum-containing construction wastes) during the early phases of MSW maturation (Pohland, 1982; Rodrigo-Illari and Rodrigo-Clavero, 2020), and can readily react with M^{2+} ions to form metal sulfides. Later reoxidation of metal sulfides in the neutral pH mature landfill would likely result in production of adsorbed or precipitated phases like those detected in these samples.

Fine fraction samples collected from Withernsea had the highest concentrations of PTEs of the three studied locations. There was visual evidence that this landfill contained burnt wastes and ash layers, which may have concentrated any metal(loid)s originally present. However, these wastes are also reportedly much older than the other study sites. MSW composition has changed considerably during the 20th century, with a preponderance of domestic (coal) ashes in early 20th century wastes; this compares to modern MSW which contain much more biodegradable materials, plastics, and packaging materials (Williams, 2013). Ash from coal burning is enriched in a range of PTEs including, As, Cr, Pb, Fe, Cu and Zn (Jegadeesan et al., 2008), which closely match the range of trace elements that are enriched at this site. The mineralogical composition of the Withernsea samples is also more diverse than the other two sites, including higher amounts of metal oxides that may be derived from combustion wastes. Early 20th century MSW landfills make up a small percentage of known UK coastal legacy sites (Riley et al., 2022), therefore, the Withernsea site may represent an outlier in terms of composition. However, the range of contaminants present, their speciation and particle associations, and leaching behaviour was

generally in line with materials found at the other two MSW sites. Therefore, it is unlikely that knowledge of landfill closure date is required during consideration of the risks posed by PTEs to UK coastal ecosystems from legacy MSW landfills.

4.2. Implications and likely risks to coastal ecosystems

Leaching test results indicate that the fine fraction MSW solids recovered from these sites (dominated by fine sand and silt sized particles) produce neutral or slightly alkaline leachates with generally very low ($\ll 1\%$) mobilisations of PTEs present. It is not appropriate to compare leaching test concentrations with environmental quality standards for receiving coastal waters as high dilution factors and rapid dispersal are likely to dominate in these settings. Leaching test results are consistent with the metal(loid) phases found in LCF of XANES data which indicate a range of insoluble precipitates or adsorbed phases for metals such as As, Cu, Pb and Zn. These phases would be predicted to remain solid associated in either freshwater or seawater leaching scenarios as the inner-sphere metal adsorption complexes are not affected by potential changes in ionic strength. These PTEs would likely be susceptible to acidic leaching (Somani et al., 2023), however there is no plausible scenario where acidification could occur in their current locations. Therefore, it is likely that PTEs present in the fine fraction wastes will remain sorbed and if eroded into coastal environments will be dispersed as particulate contaminants.

Concentrations of many PTEs in the MSW materials are high enough to be of environmental concern as they enter coastal ecosystems. However, their fine-grain size will promote dispersal away from source areas (although accumulation of visible wastes, such as plastics, may also occur in the areas surrounding such sites). Also, unless the rate of shoreline retreat is very rapid (i.e. $>1\text{ m yr}^{-1}$), waste fluxes are likely to be small compared to natural sediment budgets (typically $1\text{--}10\text{ m}^3\text{ m}^{-1}$ shoreline yr^{-1} ; Davidson-Arnott et al., 2018). Therefore, high dilution rates are to be expected. This will likely result in generally low ecosystem impacts unless a specific bioaccumulation pathway occurs where marine organisms are consistently exposed to high concentration of waste derived particles. Filter and bottom feeding organisms are at particular risk from particulate associated PTEs as gastric pH is likely low enough to mobilise adsorbed contaminants (e.g. pH 2–6 in *Sparus aurata*; Yúfera et al., 2004). Although low erosion rates and high particle dispersion may mean that these sites remain of relatively low importance in terms of overall risk (beyond visual impact), this does present a moral hazard to site managers. Over 50 years of progress in waste management has resulted in a strong preference to avoid dilute and disperse as a disposal strategy, which is why these wastes were disposed in landfill to begin with. In addition, this work has only considered inorganic metal(loid) contaminants. Other pollutants, such as persistent organic compounds or asbestos, are known to occur at similar sites (Ochs et al., 2024; Somma et al., 2024) and may provide additional risks to human or ecosystem health. Climate risks such as increased sea levels and faster coastal erosion may increase contaminant fluxes at existing sites or increase the number of locations where erosion is observed. Therefore, while PTE emissions may not be substantially higher than environmental quality thresholds further research is required to understand both their impact in complex multi-contaminant systems, and the potential for biomagnification. When making site management decisions, coastal managers should also be informed by robust national scale risk assessments which consider the likely impacts from all contaminants present, and the cumulative impact of all known legacy waste sites within their regions.

5. Conclusions

This study highlights the complex composition and environmental behaviour of fine fraction solids recovered from legacy MSW landfills along the UK coast. Despite their heterogeneous mineralogy and

elevated concentrations of PTEs such as As, Cu, Pb, and Zn, the fine fractions typically contained these PTEs in stable, low-mobility geochemical forms under neutral to slightly alkaline conditions. These characteristics suggest limited leaching risks to coastal ecosystems under current environmental scenarios. While concentrations of some PTEs exceed threshold soil and marine sediment guideline values, their solid-phase associations are predicted to be as insoluble precipitates or strongly absorbed species. Therefore, these PTEs are likely to disperse as particulate pollutants upon erosion, rather than as soluble species. The Withernsea site, though chemically distinctive due to its age and ash content, showed broadly similar PTE behaviour to the other younger landfill wastes. Due to dilution within marine sediments, erosion and dispersion of fine fraction MSW particles may have limited ecological impact unless local conditions promote bioaccumulation, particularly in filter-feeding organisms. Nevertheless, the likely presence of other co-contaminants such as persistent organics and asbestos, as well as evolving coastal risks linked to climate change, underscores the importance of robust, regional assessments for coastal MSW landfills that should consider both current and future contaminant pathways.

CRedit authorship contribution statement

Ian T. Burke: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Patrizia Onnis:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **Alex L. Riley:** Writing – review & editing, Methodology, Formal analysis. **Catherine J. Gandy:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Violeta Ramos:** Methodology, Investigation, Formal analysis. **Gavyn K. Rollinson:** Methodology, Investigation, Formal analysis. **Patrick Byrne:** Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **Richard A. Crane:** Writing – review & editing, Supervision, Investigation, Conceptualization. **Karen A. Hudson-Edwards:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Elin Jennings:** Investigation, Formal analysis. **William M. Mayes:** Writing – review & editing, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **J. Frederick W. Mosselmans:** Writing – review & editing, Methodology, Formal analysis. **Adam P. Jarvis:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2025.118341> and includes; details of acid digestion process, leaching tests, synchrotron analysis and standards; Sample location photography; Additional μ XRF maps; QEMSEM analysis images and mineral determination; Process blanks and standards recovery data from acid digestion and leaching tests.

Data availability

Data will be made available on request.

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