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Research article

Spatial variability of metal(loid) leaching from coastal colliery wastes under freshwater and saline water conditions

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A B S T R A C T

Historical disposal of coal mine wastes in the coastal zone has left a significant environmental pollution legacy. Climate change is increasing the likelihood that erosion of these wastes will lead to release of metal(loid)s to coastal environments. Whilst previous research has focussed on the generation of acidic, metal-rich waters from coal mine wastes in freshwater environments, a comprehensive investigation of metal(loid) leaching from such wastes in the coastal zone has not been undertaken. This study investigated the leaching behaviour of coal mine wastes under freshwater and saline conditions and determined the impacts of spatial heterogeneity of waste composition on such behaviour. The degree of leaching varied considerably within and between sites due to the heterogenous nature of the waste. Leachate pH varied from 1.80 to 6.99 with acidic leachates particularly enriched in Fe ($\leq$17,000 mg/kg dry waste) and sulfate ($\leq$48,000 mg/kg dry waste) due to dissolution of acid sulfate phases. Dissolution of Fe and Mn oxides, hydroxides and oxyhydroxides also led to release of surface adsorbed metal(loid)s such as As ($\leq$21 mg/kg dry waste), Zn ($\leq$86 mg/kg dry waste) and Cu ($\leq$14 mg/kg dry waste). Adsorption of As to high surface area minerals was confirmed by X-ray Absorption Near Edge Spectroscopy (XANES) analysis. Metal(loid) release was typically lower in the presence of seawater than deionised water due to the greater pH buffering capacity of seawater. This research provides an insight into the considerable challenges faced by coastal managers globally as they seek to mitigate the risks from such legacy pollution.

1. Introduction

Historical disposal of solid wastes from domestic and industrial sources in the coastal zone has led to considerable environmental legacies within coastal areas worldwide (Castilla, 1996; Nicholls et al., 2021). The presence of such legacy wastes poses a risk to human health and can cause adverse physical, chemical and biological effects on coastal ecosystems (Cooper et al., 2012). As the deposition of many of these wastes predated modern environmental regulation, there was no requirement for their management (Brand and Spencer, 2020). Given the often dynamic nature of the coastal zone these wastes are highly

susceptible to being mobilised via a range of physical and chemical processes, resulting in numerous negative impacts including turbidity and ecotoxic metal dissolution. With climate change leading to rising sea levels (Robins et al., 2016), increased rates of coastal erosion (Toimil et al., 2020) and increased frequency and severity of tidal flooding (Burningham and French, 2017), such releases are predicted to become more frequent (Brand et al., 2018). Evidence for the effects of climate change on metals release has already been observed in numerous locations worldwide, with extreme floods and the resultant increased erosion leading to the release of large volumes of toxic material to nearby waters (Nicholls et al., 2021).

Globally, mine waste represents one of the largest environmental concerns with several billion tonnes estimated to be generated per year (Rodríguez-Pacheco et al., 2023). Extensive deposition of mine waste has occurred in coastal environments worldwide (Castilla, 1996; Dold, 2007; Kwong et al., 2019), including in the UK which has a rich history of coal mining and mineral processing in such regions. Consequently, legacy coal mine wastes have been identified as the third most prevalent coastal legacy waste deposit in England and Wales, covering a total area of 4000 ha (Riley et al., 2022). The majority of this waste (56%) is located within the north east of England (Northumbria River Basin District (RBD)) (Fig. S1), which has the highest area of unprotected wastes in England and Wales (1807 ha), representing approximately 72% of the waste deposited along its coastline (Riley et al., 2022). Since closure of the coal mines in the 1980's to 2000's, legacy coal mine wastes in the coastal zone have been actively eroding at a rate of 0.5–2.0 m/year (Cooper et al., 2017).

Coal mine waste is highly heterogenous and, as such, its chemical properties vary widely, both within a single disposal site and between sites (Ahrens and Morrisey, 2005). It is commonly rich in pyrite (FeS_2), which is unstable when exposed to atmospheric conditions. The resulting oxidative dissolution of pyrite releases Fe and S, but also protons, resulting in generation of low pH drainage from such wastes (Younger et al., 2002). Trace metals and metalloids (hereafter referred to as metal(loid)s) may also be mobilised in this low pH environment. Iron in mine waste drainage may ultimately precipitate as Fe oxyhydroxides, along with sorbed or co-precipitated metal(loid)s (Kölbl et al., 2021). However, reductive dissolution of these minerals can mobilise and release Fe and associated metal(loid)s (Leyden et al., 2022), including into the coastal zone.

Whilst the generation of acidic, metal-rich waters from coal mine waste has been widely studied in freshwater environments (e.g. Younger et al., 2002), there is a paucity of investigations of these processes in the coastal zone. These are dynamic environments in which seawater as well as freshwater may interact with legacy wastes. Furthermore, physical processes of coastal flooding and erosion, increasingly severe due to climate change, have the potential to exacerbate the release of metal(loid)s via exposure of fresh sulfide minerals to atmospheric conditions. Seawater-induced metal(loid) release into the coastal zone was observed by Leyden et al. (2022). Reductive dissolution of reactive Fe and Mn in freshwater and acid sulfate soils, in combination with cation exchange processes, mobilised metals into pore waters. In north east England, intertidal sediments in areas affected by legacy coal mine waste have been found to contain elevated concentrations of metal(loid)s, especially Pb and Zn (Giusti, 2001). An assessment of the ecological impacts of coal mine waste disposal at coastal sites in the region has revealed an impoverishment of faunal communities in the vicinity of disposal sites, due partly to the presence of metal(loid)s (Hyslop et al., 1997).

Given the lack of data on the environmental behaviour of metal(loid)s associated with coal mine wastes deposited in the coastal zone, the research presented here seeks to address this important knowledge gap by linking the mineralogical composition of such wastes to their leaching behaviour in this environment, including quantitative determination of leaching behaviour under freshwater and saline conditions. The research had the following specific objectives: (1) characterise selected coal mine wastes with respect to metal concentrations and mineral phases; (2) quantify differences in leaching behaviour between coal mine waste subjected to standard leaching tests using deionised water and identical tests using seawater; (3) determine the impact of spatial heterogeneity of coal mine waste characteristics, both within sites and between sites, on leaching test results.

2. Materials and methods

2.1. Sample collection, preservation and preparation

Three legacy coal mine waste sites in north east England were

selected for sampling and analysis, in order to compare metal(loid) release processes across sites: (1) Lynemouth Bay, (2) Blackhall Colliery, (3) Dawdon Blast Beach (Fig. S1). At Lynemouth Bay, sampling was repeated on a further 2 occasions over a 20-month period to investigate spatial changes in metal concentrations and release at specific locations due to the continual erosion of the mine waste. These sites represent the most extensive coastal coal mine waste deposits in the region and scored highly in a national-scale GIS-based environmental risk assessment which considered a range of factors including rates of erosion (historical and future), risk of inundation and proximity to sensitive receptors (Riley et al., 2022). Further details on these study sites are provided in the Supporting Information (SI).

Four samples were collected from Lynemouth in September 2021 from the seaward edge of a vertical face of beach-deposited coal mine waste. A further two sets of samples were collected from the same locations in June 2022 and May 2023. At Dawdon, three samples were similarly collected from a vertical face of beach-deposited coal mine waste in February 2024 whilst at Blackhall four samples were collected in February 2021 from a range of exposed coal mine waste deposits across the site (Table S1). Each sample comprised a composite of 5 subsamples (each of approximately 500 g). Samples collected from a vertical face were taken from a horizontal depth of less than 10 cm into the face. All samples were collected using a plastic trowel and stored in polyethylene bags for transport to the laboratory where they were kept at 4 °C.

A representative subsample of approximately 20 g of each sample, collected by coning and quartering, was dried in an oven at 105 °C for determination of dry matter content and moisture content according to ISO 11465 (International Organisation for Standardisation ISO, 1993). The remaining portion of each sample was air-dried then passed through a 10 mm sieve and the >10 mm fraction discarded. Using coning and quartering, a subsample of approximately 20 g of the <10 mm fraction was then obtained for geochemical and mineralogical analysis. The remaining <10 mm fraction was prepared for leaching tests, according to BS EN 12457–2 (British Standards Institution (BSI), 2002), by gently crushing using a pestle and mortar until at least 95 wt% had a grain size of <4 mm. The <4 mm and >4 mm fractions were then combined, and subsamples taken for the leaching tests.

2.2. Composition

Using coning and quartering, 100 mg subsamples of each sample of Lynemouth and Blackhall waste were obtained and crushed until the grain size was <125 μm. The total metal(loid) concentration of each subsample was determined, in triplicate, by acid digestion followed by Inductively coupled Plasma-Mass Spectrometry (ICP-MS). The analysis of Dawdon waste was undertaken at a later date and it was not possible to conduct the same method as used for the Lynemouth and Blackhall samples. Each sample of Dawdon waste was prepared for microwave digestion according to BS ISO 11464 (BSI, 2006). Using coning and quartering, 20 g subsamples of the <2 mm fraction of each sample were obtained and crushed until the grain size was <250 μm. Following microwave digestion, cation analysis was conducted using an Agilent 5800 Series Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Full details of both methods are provided in the SI.

The samples of Lynemouth waste, together with a single sample of Blackhall waste (B2), were subjected to carbon and sulfur analysis with a LECO SC-144DR analyser at Wheal Jane Services Ltd. Samples were pulverised (<45 μm) and analysed for total sulfur, sulfur as sulfate, sulfur as sulfide, total carbon, organic carbon and inorganic carbon.

2.3. Mineralogical analysis

A subset of crushed (<125 μm) samples, with a focus on the Lynemouth waste but with a single sample of Blackhall waste (B2) for comparison (resource constraints precluded analysis of all samples), were

subjected to X-Ray Diffraction (XRD) to determine their mineralogical composition, using a Siemens D500 diffractometer with an x-ray tube at 1.5 kW and Cu anode. The diffractograms were interpreted using EVA v.18.0.0.0 software and the ICPDS PDF-2 (2004) database. Additionally, approximately 1 g subsamples of the <2 mm fraction of the same samples were mounted into 30 mm diameter epoxy resin blocks and coated with a 25 nm carbon coat for mineralogical analysis using a QEMSCAN® 4300 automated scanning electron microscope. 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 applied to all the samples using a 10 μm X-ray pixel spacing resolution. Observed phases were assigned to minerals based on chemical composition and XRD data. The mineral content detection limit was 1% by volume.

2.4. Microfocus X-ray absorption spectroscopy (XAS) and X-ray fluorescence (XRF)

Samples of Lynemouth waste (L2 and L3) were prepared for analysis as either 8 mm powder pellets held in Kapton™ tape (for bulk XAS analysis), or as granular samples (<4 mm grain size) embedded in 30 mm polished epoxy resin blocks (for microfocus XRF and XAS analysis). Bulk XAS spectra collected from homogenised powder samples was used to quantify the average element speciation present, while spot analysis was used to provide insight on the range of elemental speciation and (when combined with XRF mapping) information on solid phase associations. XAS spectra were collected at the As, Cu, Cr and Zn K-edges (11,867, 8979, 5989 and 9659 eV, respectively) on beamline I18 at the Diamond Light Source using a Si (111) double crystal monochromator and focussing optics. (full details in SI). XAS data was collected in fluorescence mode using a 4 element Vortex Si Drifts detector at room temperature (~295 K) within a He-filled bag. Multielement microfocus XRF spectra were collected from (~0.5 × 0.5 mm) regions of interest and processed in real time to produce elemental maps (for Si, S, Ca, Cr, Fe, Cu, Zn and As), which were used to choose points (spot size = 5 μm) for microfocus X-ray Absorption Near Edge Spectroscopy (XANES) spectra collection. All XAS spectra were then averaged, background subtracted and corrected for any drift in E0 using Athena version 0.9.26 (Ravel and Newville, 2005). Linear combination fitting (LCF) was also performed in Athena using a maximum of 3 standards in the final fits (uncertainty in LCF fits was < ±5 %).

2.5. Leaching tests

Leaching tests were undertaken in triplicate on 90 g subsamples of the <4 mm fraction (95% by mass) of the air-dried wastes according to BS EN 12457–2 (BSI, 2002). As prescribed by BS EN 12457–2, deionised (DI) water, to represent freshwater, was used as a leachant, but identical parallel tests used seawater as a leachant given the potential for seawater erosion and flooding at coastal legacy waste sites (see Table S3 in SI for summary hydrochemistry data). A leachant volume of 900 mL was used to achieve a leaching ratio of 10 L of leachant per kg of dry waste, to comply with BS EN 12457–2. A control test was performed for each sample using 950 mL of leachant but no sample. The samples were leached by agitating them on a Heidolph REAX 20 end-over-end shaker at 10 rpm for 24 h. After leaching, the samples were left to stand for 15 min to allow suspended solids to settle before sampling. For each leachant, temperature, pH, redox potential and electrical conductivity were measured prior to leaching using a pre-calibrated Myron L 6P Ultrameter. Equivalent measurements were also taken at the end of the leaching period. Two 30 mL samples of leachant were collected in polypropylene bottles prior to leaching and after leaching for filtered cation and filtered anion analyses (0.45 μm cellulose nitrate filters). The samples for cation analysis from the leaching tests on Blackhall waste and the seawater leaching tests on Lynemouth waste collected in 2021

were acidified with 2% v/v concentrated nitric acid and analysis was undertaken by a commercial laboratory using ICP-OES and ICP-MS. Cation samples from all remaining leaching tests were additionally acidified with 1% v/v concentrated hydrochloric acid and analysis was undertaken using a Agilent 5800 Series ICP-OES and a Agilent 7700 Series ICP-MS. Anion concentrations (sulfate, chloride) were determined using a Thermo Scientific Dionex Integrion Ion Chromatograph (IC). For the seawater leaching tests, leachate concentrations were corrected, prior to reporting all results, by subtracting the concentrations of each metal(loid) in the leachate of the control leaching test to account for the background concentrations in seawater. To comply with BS EN 12457–2, results were reported in terms of the mass of metal(loid)s released relative to the total mass of the sample, in mg/kg of dry waste. The mass of each metal(loid) released was calculated from its concentration (mg/L) in the leachate according to Eq. (1).

$$M = C * (L / M_D) \tag{1}$$

where M is the mass of metal(loid) leached (in mg/kg of dry matter), C is the concentration of metal(loid) in the leachate (in mg/L), L is the volume of leachant used (in L) and M_D is the dry mass of the sample (in kg). In the leaching tests described here, L was 0.9 L and M_D was 0.09 kg.

The proportion of each metal(loid) leached, as a percentage of the initial metal(loid) concentration within the waste, was also calculated. Statistical differences in the mass of metal(loid)s leached between sites in DI and seawater matrices were tested using the Mann-Whitney U test ($p = 0.05$). Analysis was undertaken using Minitab 21.4.2.

3. Results

3.1. Composition and mineralogy

Metal(loid) concentrations varied significantly between sample sites (Fig. 1, Table S4). Generally, samples from Blackhall had consistently lower metal(loid) concentrations than those from Lynemouth and Dawdon but there was considerable variation within sites. Iron and Al were the most abundant metals present in all samples; Fe concentrations ranged from 20,000 mg/kg (B4) to 180,000 mg/kg (L3) and Al from 6800 mg/kg (D2) to 71,000 mg/kg (L4). Lynemouth waste contained the highest concentrations of Zn (maximum 558 mg/kg (L3)), Cu (maximum 102 mg/kg (L3)) and Cr (maximum 114 mg/kg (L4)) whilst Dawdon waste contained the highest concentrations of Pb (156 mg/kg (D3) to 213 mg/kg (D2)) and Mn (maximum 270 mg/kg (D3)). Lynemouth waste also contained high As concentrations (68.1 mg/kg (L4) to 84.1 mg/kg (L3)), albeit the maximum As concentration was observed in sample D2 (91 mg/kg). Although Cd concentrations were low in all samples, they were at their highest in Dawdon waste (maximum 4.5 mg/kg (D2)). Generally, samples from Blackhall showed less variation between samples, except for Al which ranged from 14,000 mg/kg (B1) to 43,000 mg/kg (B3). For Lynemouth and Dawdon wastes, concentrations of some metal(loid)s varied by up to an order of magnitude between samples.

Total sulfur and carbon content also varied considerably between samples (Table S5). Total sulfur was generally higher in Lynemouth waste, ranging from 2.11% (L2) to 15.0% (L3) compared to 1.19% at Blackhall (B2). The high total sulfur content in sample L3 was mainly due to sulfide (10.9%) which is in contrast to the other samples in which sulfate exceeded sulfide. The highest total carbon content was observed in Blackhall waste (B2) (37.2%), whilst total carbon in Lynemouth waste varied from 4.69% (L1) to 34.3% (L2). In all samples, the percentage of total organic carbon far exceeded that of total inorganic carbon.

Lynemouth waste mainly comprised quartz and clay minerals with other minerals such as pyrite, biotite, Fe-bearing silicates, gypsum and jarosite also present (Fig. 2, Fig. S2, Table S6). However, the proportion by volume of each mineral varied significantly between samples. Samples L1 and L3 were dominated by quartz (54% and 42% respectively)
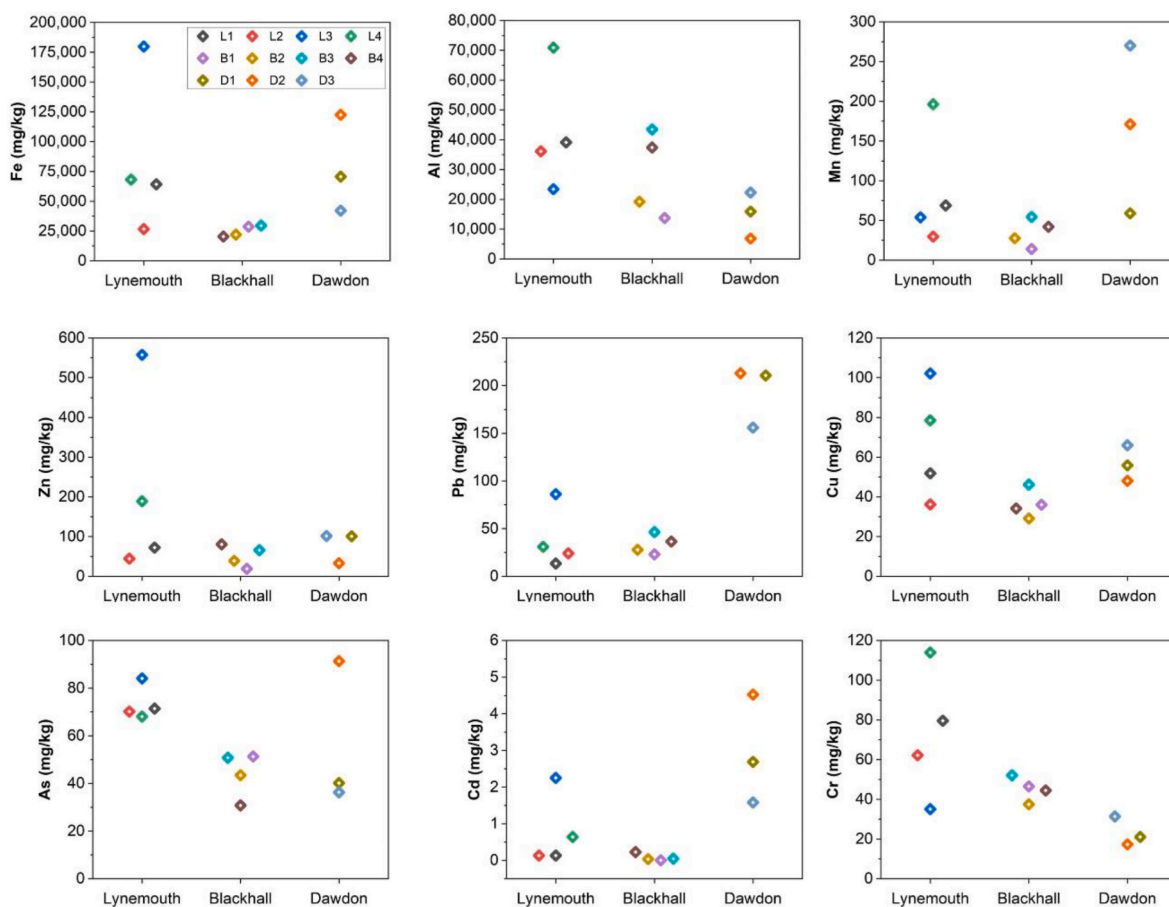
Fig. 1. Metal(loid) concentrations in samples of coal mine waste from Lynemouth, Blackhall and Dawdon.
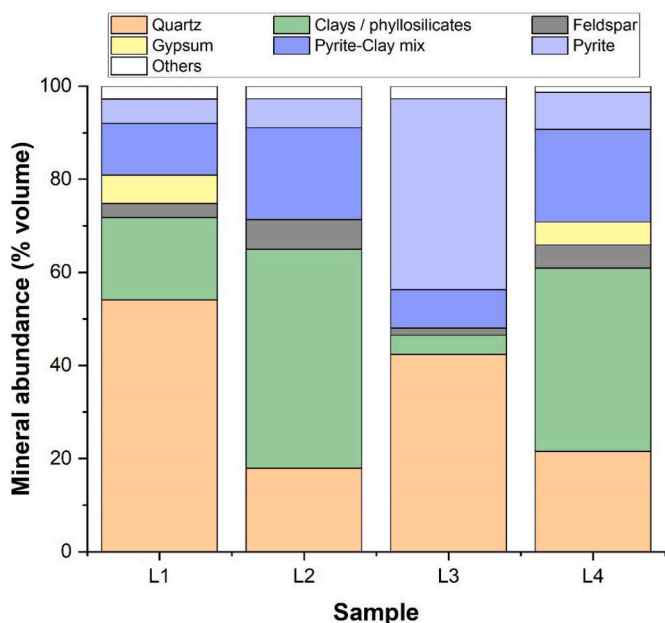

Fig. 2. Abundance of major mineral phases (percentage by volume) in samples of Lynemouth waste. Minerals shown are those in which volume was greater than 5% in one or more samples. "Others" refers to additional minerals present at volumes of 1–5% (QEMSCAN detection limit 1%).

with sample L3 also having a high pyrite content (41%). Samples L2 and L4, on the other hand, contained a higher proportion of clay minerals. Blackhall waste (B2) was also dominated by clay minerals, together with biotite and K-feldspar (Fig. S3, Table S6). In contrast to Lynemouth waste, B2 comprised only a small proportion (<3%) of Fe sulfides.

3.2. Metal(loid) speciation and distribution

Microfocus XRF analysis of Lynemouth waste (samples L2 and L3) allowed visualisation of the solid particles present (Figs. S4 and S5). Iron was found in discrete grains of pyrite and Fe-oxide minerals. Silicon was also found in large grains of quartz. X-ray Absorption Near Edge Spectroscopy (XANES) analysis enabled determination of the chemical oxidation states of selected metal(loid)s As, Cu, Cr and Zn (Fig. 3, Table S7). Arsenic was present predominantly as As(V)-O containing species, with a smaller contribution from As(III)-S and As(III)-O containing species. Arsenic(III) was associated with pyrite whilst As(V) was associated with Fe-oxide particles and fine matrix clays and grain coatings (Fig. S4). It is likely that As was originally mostly present as incorporated As(III)-S within sulfide minerals (e.g. pyrite, asenopyrite), due to the reducing environments of coal formation. Sulfide oxidation post-deposition probably produced As(III)-O and As(V)-O forms which were most likely adsorbed to mineral surfaces as arsenite and arsenate species. Copper, Cr and Zn, on the other hand, only occurred in fine-grained hotspots (Figs. S5 and S6). Copper was present primarily as Cu(I)-S phases, but there was also evidence for the presence of Cu(I)-O and Cu(II)-O species. Oxidation of Cu sulfides can produce a range of Cu(II) silicates, carbonates and adsorbed species (Peng and Zhao, 2011) and Cu(I)/(II) oxides are a common Cu sulfidfe oxidation product (Li et al., 2013). Therefore it is likely that primary Cu(I)-bearing sulphides
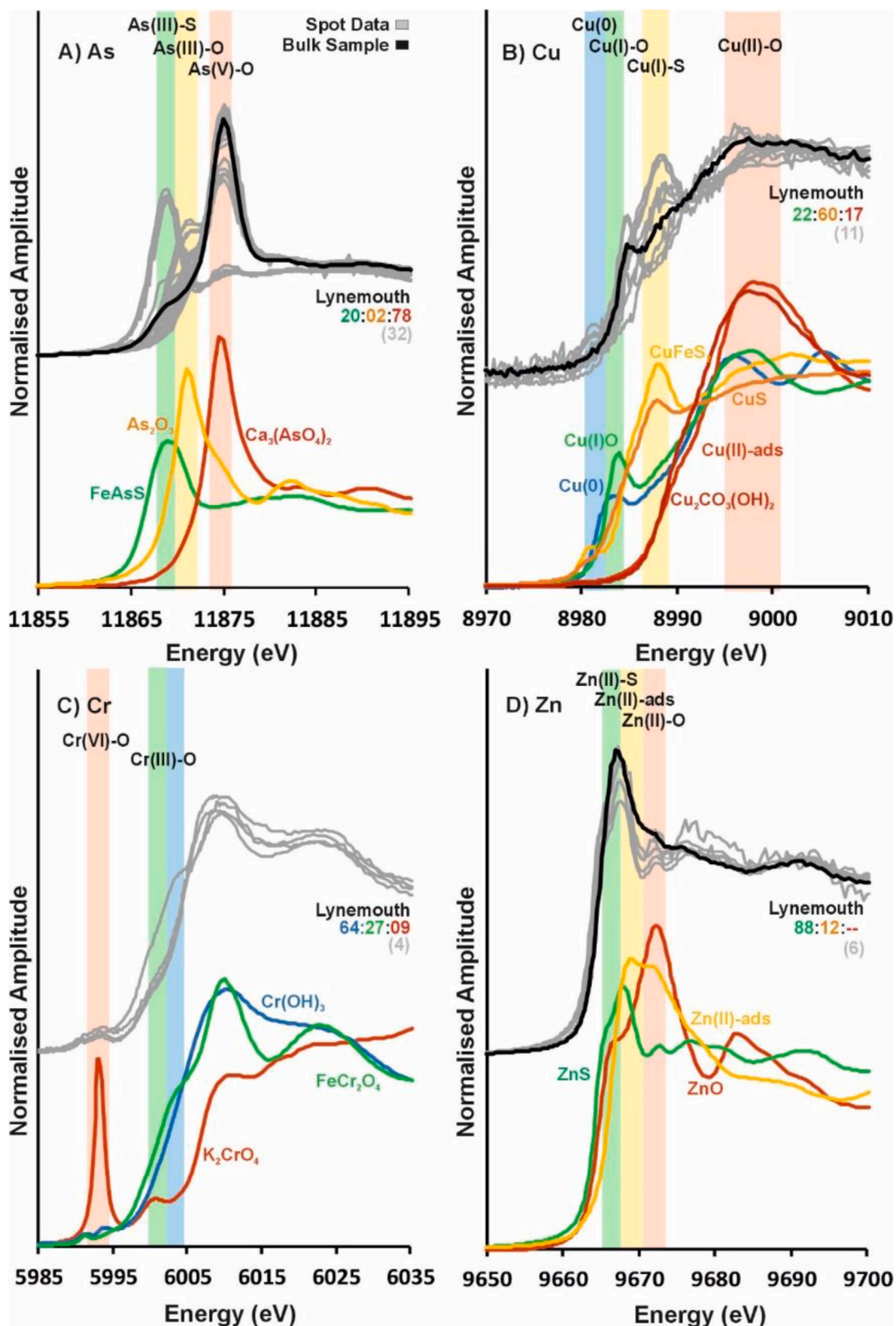
Fig. 3. Bulk average and individual spot K-edge XANES spectra for (A) As, (B) Cu, (C) Cr and (D) Zn in samples of waste from Lynemouth (L2, L3) and selected standards. Ratios presented below the sample data are results for Linear combination fitting (LCF) analysis of the bulk sample spectra (As, Cu, Zn) or the average LCF for the spot analyses (Cr); colours used match to the standards shown. The number in grey brackets is the number of spot analyses shown. The coloured bands are provided to guide the eye to significant spectral features present in standard spectra.

(e.g. chalcopyrite) have been partially oxidised and altered as the mine waste has weathered in situ post deposition. Only spot XANES data were available for Cr due to the low concentrations of Cr present meaning that bulk analysis was not possible. Chromium was present as Cr(III)-O species with some spot samples representing a 100% match to the Cr (III) hydroxide standard. Microfocus analysis revealed that some Cr (III)-O hotspots were found associated with Fe-oxide particles. Lynemouth waste contained significant amounts of Zn(II)-S containing phases with some spot sample analysis showing a 100% match to the sphalerite standard. The waste also contained some adsorbed Zn(II), indicating that primary Zn sulphides had also partially weathered in the post depositional environment at this site.

3.3. Leaching behaviour

Measurements of temperature, pH, oxidation-reduction potential (ORP) and electrical conductivity in the leachant ('*pre-leach*') and in the leachate after 24 h contact time with the wastes were recorded (Table S8). In both the DI water and seawater leaching tests, the pH decreased substantially after contact with the wastes, except for samples B2 and D3 in which pH increased slightly. In general, the pH of the DI water leachate was lower than that of the seawater leachate, likely due to additional carbonate alkalinity provided by the seawater (Leyden et al., 2022). Some variation in leaching behaviour of wastes from different sites was evident with the lowest pH obtained in leachates in contact with Lynemouth waste (range 2.11–2.68 (DI water); 1.80 to 2.93 (Seawater)). Contact with the wastes typically led to more oxidising conditions, as evidenced by an increase in ORP, which was generally more pronounced in the DI water leachate (range 213–497 mV) than the seawater leachate (range 179–490 mV). There was again some variation within and between sites with leachates in contact with Lynemouth waste showing the greatest rise in ORP and those in contact with samples B2, B4 (seawater only) and D3 becoming slightly more reducing. The electrical conductivity in the DI water leachant also increased
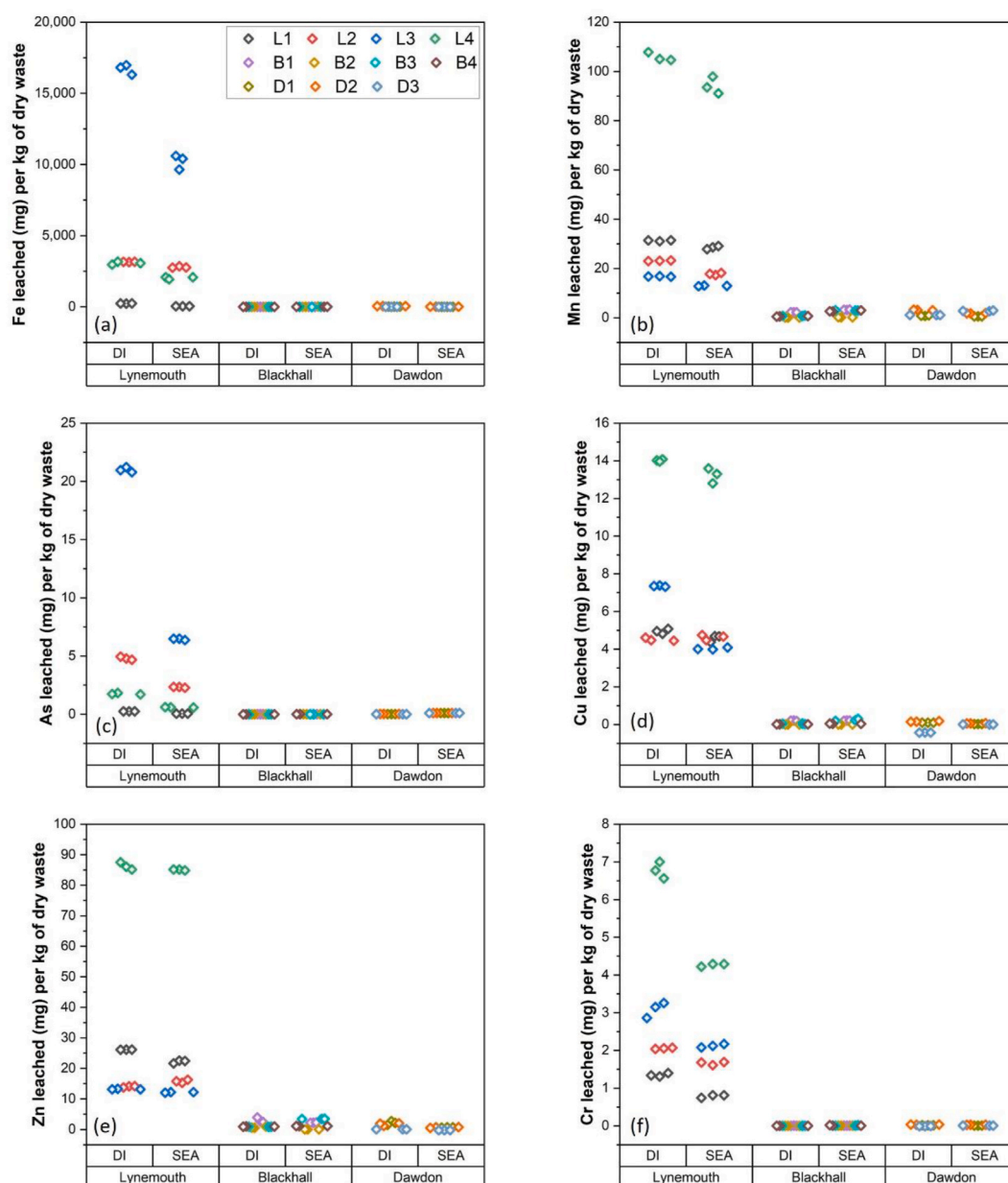

Fig. 4. Mass of Fe (a), Mn (b), As (c), Cu (d), Zn (e) and Cr (f) (mg) leached per kg of dry waste during leaching tests on coal mine waste from Lynemouth, Blackhall and Dawdon. DI = deionised water leachant; SEA = seawater leachant.

significantly after contact with the wastes, with the greatest rise again observed for Lynemouth waste (range 4114 to 6925 µS/cm). Whilst electrical conductivity in the seawater leachant was significantly greater due to the high salinity of seawater, increases in conductivity after contact with the wastes were more modest.

The DI water leachates were dominated by sulfate, Ca, Mg and Na (Table S9, Fig. S7). The seawater leachates were also dominated by sulfate and Ca but there was evidence of Mg, Na and K depletion after contact with many of the samples. The leaching of major ions, such as Ca, is related to weathering and demonstrated a positive association with initial concentrations within the waste (Fig. 1). Sulfate and Ca leaching were enhanced in the presence of seawater, except after contact with samples L3, L2 (Ca) and D1 (sulfate). The leaching of Na from samples L1, L2, L3 and D1 was also favoured by seawater. Magnesium and K leaching, in contrast, were greatest in the presence of DI water.

Lynemouth waste released a significantly greater mass of all metal

(loid)s of potential environmental concern in both DI water and seawater matrices (Mann-Whitney U test; $p < 0.05$) (Fig. 4, Tables S9 and S10). Leachates were particularly enriched in Fe and Al, which were also abundant within the waste (Fig. 1). Whilst more Fe was leached in DI water, Al followed the opposite trend with leaching more pronounced in seawater, albeit these differences were not significant (Mann-Whitney U test; $p > 0.05$). The mass of Fe leached from Lynemouth waste varied by two to three orders of magnitude between samples, ranging from 233 mg/kg dry waste (L1) to 17,000 mg/kg dry waste (L3) in DI water and from 40 mg/kg dry waste (L1) to 10,000 mg/kg dry waste (L3) in seawater. Conversely, the variation in mass of Al leached was modest, except for sample L4 in which a notably higher mass of Al was leached per kilogram of waste, although data are only available for DI water leaching for this sample. Fig. 4 also shows the mass leached per kg of dry waste for selected metal(loid)s. Considerably more As and Cr were leached from Lynemouth waste by DI water than by seawater, albeit the
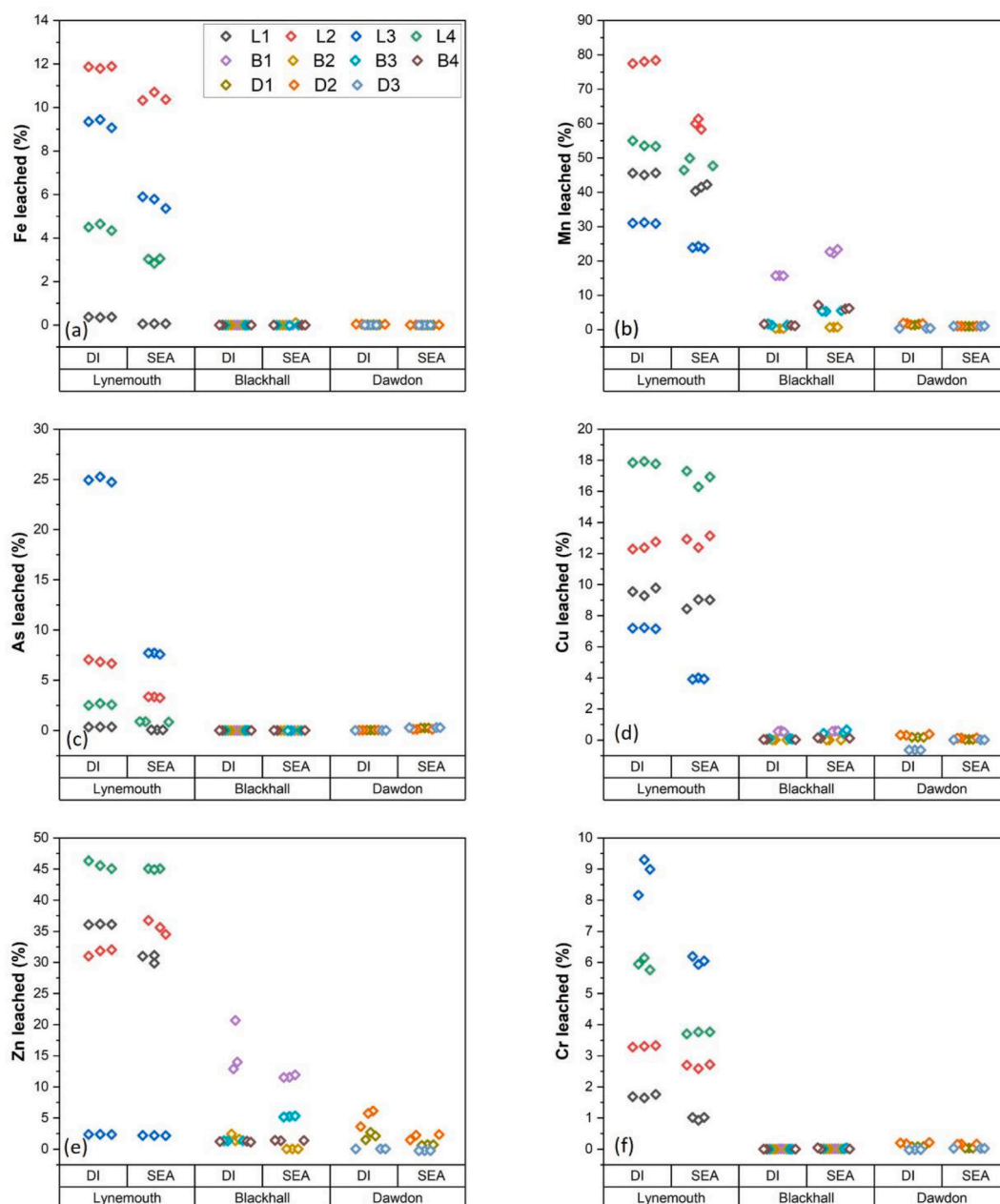

Fig. 5. Proportions of Fe (a), Mn (b), As (c), Cu (d), Zn (e) and Cr (f) (%) leached during leaching tests on coal mine waste from Lynemouth, Blackhall and Dawdon. DI = deionised water leachant; SEA = seawater leachant.

quantity released varied between samples. Although generally more Mn, Zn and Cu were also leached from Lynemouth waste by DI water, a slightly greater mass of Zn and Cu was leached from sample L2 by seawater. Differences between leaching matrices were not significant, however (Mann-Whitney *U* test; *p* > 0.05). Leaching behaviour varied between samples with the release of Mn, Cu, Zn, Cr and Ni greatest in sample L4 and leaching of As, Fe and Pb at their highest in sample L3 (Fig. 4, Tables S9 and S10). Typically, the lowest mass of each metal (loid) was leached from sample L1, although for Zn and Mn, leaching was at its lowest in sample L3.

Whilst Blackhall and Dawdon wastes also released a greater mass of Fe and Al than other potentially toxic metal(loid)s, leaching from these wastes was negligible compared to Lynemouth waste (Fig. 4, Tables S9 and S10). Despite the modest quantities of each metal(loid) released, leaching behaviour differed to Lynemouth waste, with significantly more Mn, Pb, As, Cd, Ni and Cr leached from Blackhall waste by seawater than DI water (Mann-Whitney *U* test; *p* < 0.05). More Cd and Pb were also released by seawater from Dawdon waste but the differences between matrices were not significant (Mann-Whitney *U* test; *p* > 0.05). Although the mass of sulfate released was generally one to two orders of magnitude lower from Blackhall and Dawdon wastes than from Lynemouth waste, sulfate leaching was enhanced by seawater in all wastes, except for samples L3 and D1 (Fig. S7).

The proportion of each metal(loid) released during the leaching tests is shown in Fig. 5 and Tables S11 and S12. Proportions were highly variable, but a higher percentage of all metal(loid)s was released from Lynemouth waste, with up to 78% of Mn, 46% of Zn and 97% of Cd originally present in the waste leached (albeit initial Cd concentrations were very low (Table S4)). Despite the high mass of Fe and Al leached from Lynemouth waste (Table S9), this equates to only a small proportion of the metal(loid)s present (<12 % Fe and <4 % Al) indicating that

the release of these metal(loid)s will persist longer-term. Although a greater mass of Al was leached from each waste by seawater than DI water, the difference in proportion released by each leachant was negligible. Similarly, only a slightly higher proportion of Cu and Zn was leached by seawater from sample L2. A significantly lower proportion of all metal(loid)s was released from Blackhall and Dawdon wastes, with only Mn, Zn, Pb (seawater only) and Cd having >1 % of the metal(loid) originally present in the waste leached. A particularly high proportion of Mn, Zn and Pb was leached from Sample B1 with 16% of the Mn and Zn present leached by DI water and 23% of the Mn, 12% of the Zn and 10% of the Pb leached by seawater (Fig. 5 and Table S12).

Samples of Lynemouth waste were collected on two subsequent occasions (in June 2022 and May 2023) to further assess spatial heterogeneity in waste composition and its effect on metal(loid) leaching. Whilst samples were collected from as close as possible to the locations sampled in 2021, ongoing erosion of the waste necessarily meant locations were not identical. Cooper et al. (2017) estimated the erosion rate at Lynemouth to be approximately 3 m/year. Metal(loid) concentrations within the waste varied considerably between sampling occasions (Fig. S8). Generally, concentrations of As, Cu, Zn and Cr were highest in the 2022 samples but there were exceptions such as sample L4 in which Zn and Cr concentrations were highest in 2023 and 2021, respectively. The variation in leaching behaviour between sample sets was also substantial (Fig. 6, Table S13). Arsenic, in particular, was leached considerably more from sample L3 by both DI water and seawater leachants in 2021 than in other years. In other samples, however, the mass of As leached was relatively consistent between sample sets. Similarly, the masses of Cu, Zn and Cr leached from sample L3 was considerably higher in 2021 whilst the greatest mass of these metals leached from samples L1 and L2 occurred in 2022. Although generally leaching was favoured by DI water compared to seawater, significantly more Zn was leached from

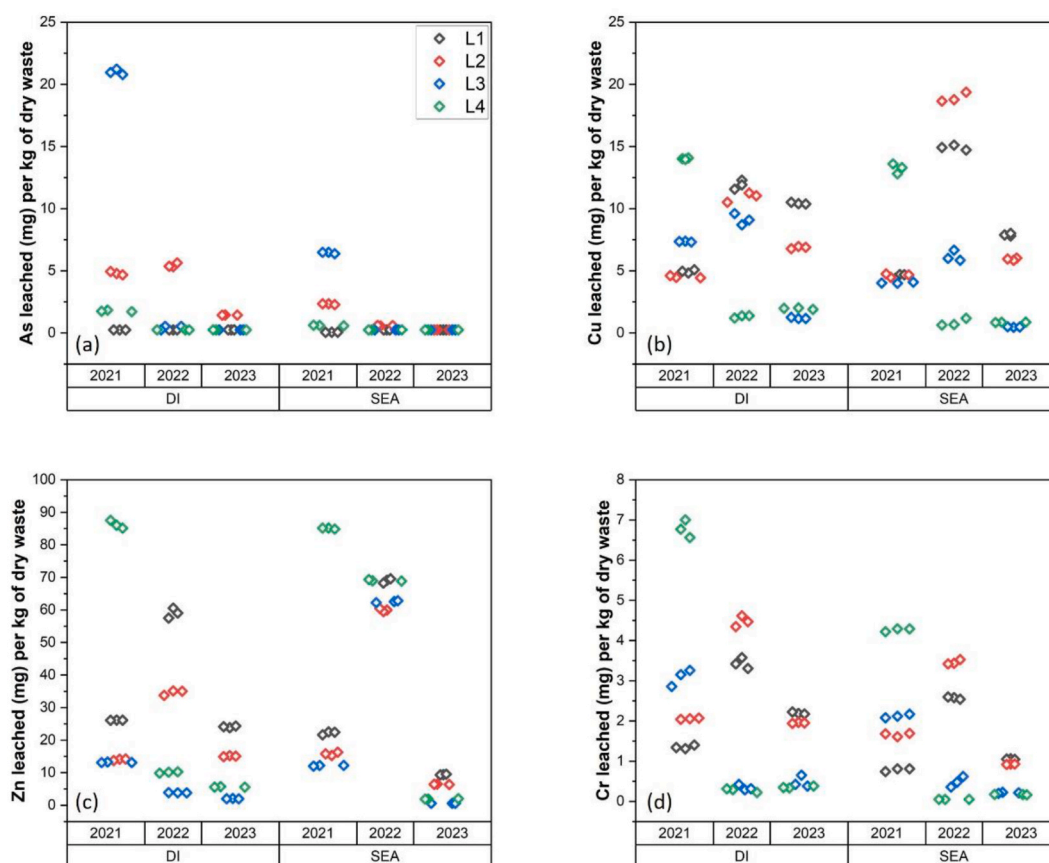

Fig. 6. Variation in mass of As (a), Cu (b), Zn (c) and Cr (d) (mg) leached per kg of dry waste during leaching tests on coal mine waste collected from Lynemouth in 2021, 2022 and 2023. DI = deionised water leachant; SEA = seawater leachant.

all samples by seawater in 2022 and more Cu was leached from samples L1 and L2 by seawater in this year. The proportion of each metal(loid) leached showed largely the same pattern (Fig. S9), except for Cr for which a higher proportion was leached by DI water from sample L3 in 2023. This is likely due to the low Cr concentration in this sample.

4. Discussion

4.1. Composition and mineralogy

The composition and mineralogy of the wastes is broadly similar to that reported by others for coal mine wastes, both in the UK (Giusti, 2001) and worldwide (e.g. Ahrens and Morrisey, 2005; Ciesielczuk et al., 2014; Ohki et al., 2004). The variation in metal(loid) concentrations between samples is also consistent with previous research (Ahrens and Morrisey, 2005) and is attributable to the heterogenous nature of coal mine waste. The composition of Lynemouth waste can largely be explained by its mineralogy, particularly the abundance of Al and Fe which corresponds to high clay and pyrite contents. Sample L3, in particular, had a high pyrite content (Fig. 2) which is consistent with elevated Fe and As concentrations in this sample. In contrast, sample B2 from Blackhall had a low proportion of Fe sulfide minerals and was dominated by Fe- and Al-bearing silicate minerals, which explains the high concentrations of Fe and Al within Blackhall waste. The presence of jarosite in Lynemouth waste provides evidence for pyrite oxidation, resulting in the formation of Fe oxyhydroxy-sulfate minerals (Johnston et al., 2011).

4.2. Leaching behaviour

Metal(loid) leachability from the solid phase is dependent upon a range of processes including their crystallinity and their strength of binding, which is governed by physical-chemical processes such as sorption/desorption and precipitation/dissolution (Acosta et al., 2011; Guo et al., 2016). If metal(loid)s are located within, or associated with, leachable minerals, then a positive correlation between their initial concentration and their resultant concentration in a receiving water is expected. For Lynemouth waste there was a clear link between degree of leaching and initial concentration for certain metal(loid)s, e.g. Ca, Fe, Al, Pb, As but for others, e.g. Zn, the relationship was less clear (Figs. S10 and S11). Whilst a positive correlation between mass leached and initial concentration was also evident for the major metal(loid)s in Dawdon and Blackhall wastes (Fig. S10), the limited release of trace metal(loid)s (e.g. Pb, As) from these wastes, particularly during seawater leaching, precluded identification of any trends (Fig. S11). Ohki et al. (2004) and Brand et al. (2018) also noted good correlations between leaching amount and metal concentrations in coal and landfill waste respectively.

Nevertheless, for all metal(loid)s the degree of leaching in both DI water and seawater was significantly greater for Lynemouth waste than for Blackhall and Dawdon wastes, despite certain metal(loid)s having a similar, or higher (e.g. Mn, Pb, Cd), concentration within Dawdon waste. pH is a key parameter governing metal(loid) mobility in wastes, with most metal(loid)-bearing phases solubilised under acidic conditions (Cappuyns and Swennen, 2008). The lower pH attained from the leaching of Lynemouth waste (1.80–2.99), compared to Blackhall (3.23–7.04) and Dawdon (2.81–6.68) wastes, is a probable factor in the greater release of metal(loid)s from this waste. There was a clear relationship between leachate pH and both Fe and sulfate release (Fig. S12), with the lowest pH (mean DI 2.11; mean seawater 1.80) and maximum mass of Fe (DI 17,000 mg/kg; seawater 10,000 mg/kg) and sulfate (DI 47,600 mg/kg; seawater 45,700 mg/kg) leached occurring for sample L3. Similarly, there was a positive correlation between the mass of Fe leached and the mass of sulfate leached (Fig. S13). Oxidative dissolution of pyrite results in the precipitation of various Fe(III) minerals, including oxyhydroxides and oxyhydroxy-sulfate minerals such as jarosite and schwertmannite (Johnston et al., 2011). The low pH, together with the

high mass of Fe released during leaching of the wastes, is likely attributable to the rapid dissolution of these acid sulfate phases, of which jarosite was present in Lynemouth waste but not detected in sample B2 from Blackhall. Sulfate release may be similarly linked to pyrite content as it is known to be the most important form of sulfur released during the oxidative dissolution of pyrite (Younger, 2000). Further evidence for this association is given by the positive correlation between the sulfur content of the waste and the mass of both Fe and sulfate leached (Fig. S14), with sample L3 also having the highest sulfur content (10.9% sulfur as sulfide) and the highest pyrite content (41 vol%) (Fig. 2, Table S6). There was no obvious relationship between TOC and leachable metal(loid)s. This is consistent with previous literature which found that sulfur content of the worked coal seams represents a better approximation of the severity of mine drainage (Younger, 2000). The coal seams worked at Lynemouth and Ellington collieries are known to have high pyrite and sulfur contents (Bullock et al., 2018; Turner and Richardson, 2004) and this may, in part, explain the higher mass of metal(loid)s leached from Lynemouth waste compared to Blackhall and Dawdon wastes.

Iron and Mn oxides, hydroxides and oxyhydroxides have long been recognised as playing an important role in the mobilisation of metal(loid)s such as As, Cd, Zn, Ni and Cu, in soils (Gasparatos, 2013). Their high surface area and high surface charge density give them a high sorption capacity but, upon contact with the acidic leachant, dissolution of these minerals likely also released any surface adsorbed metal(loid)s together with further protons (Kőlbl et al., 2021; Leyden et al., 2022). Adsorption of As to high surface area minerals present within Lynemouth waste was confirmed by XANES analysis.

DI water leaching typically resulted in a slightly lower pH than seawater leaching, due to the greater buffering capacity of seawater (Leyden et al., 2022). This led to marginally more favourable metal(loid) release by DI water for most metal(loid)s (especially from Lynemouth waste), which was also reported by Martín-Torre et al. (2015). These findings contrast with other published studies of metal leaching from wastes in seawater which have reported greater release of some metal(loid)s with increasing salinity (Brand and Spencer, 2020; Cabon et al., 2007; Riley et al., 2024). Cadmium, in particular, is generally more mobile under saline conditions due to its rapid complexation with chloride ions, forming highly soluble metal-chloride complexes (Acosta et al., 2011; Du Laing et al., 2008; Miranda et al., 2022). Increased Zn mobility in seawater has also been attributed to chloro-complexation (Du Laing et al., 2008; Guevara-Riba et al., 2005) whilst others have noted inhibition of Zn release (e.g. Yin et al., 2018). A high clay and silt content can inhibit the release of Zn and Cd in seawater (Acosta et al., 2011), together with the presence of sulfides (Du Laing et al., 2008), which may explain the reduced seawater mobility of these metals in Lynemouth waste relative to DI water leaching. Although more Cd was leached from Blackhall and Dawdon wastes under seawater conditions, the quantities released were negligible.

The behaviour of As, Cu, Cr and Zn during leaching tests was consistent with the XANES analysis showing As, Cu and Zn to be in forms in Lynemouth waste that can be mobilised as particulates in seawater and as aqueous species under low pH conditions or in the presence of high concentrations of competing ions. Similarly, the waste contained Cr (III) hydroxides that can be mobilised in solution at low pH.

4.3. Implications for metal(loid) release due to seawater inundation

Although metal(loid) release by seawater was similar or less favourable than that by DI water for most metal(loid)s, this study has highlighted the significant quantities of potentially toxic elements that could be released to the environment by both freshwater and seawater leaching of coastal colliery wastes. With global sea level rising at a rate of 3–4 mm/year and predicted to accelerate in the future due to climate change (Vitousek et al., 2017), the increased likelihood of coastal legacy wastes being inundated or eroded could exacerbate the release of metal

(loid)s to the coastal zone (Brand and Spencer, 2020). Inundation with saline water would change the geochemical environment within the waste, introducing oxygenated saline waters and potentially leading to increased mobilisation of certain metal(loid)s (Eggleton and Thomas, 2004). Many coastal mine waste deposits in the UK are threatened by increased coastal flooding and erosion. An almost 30 m landward retreat of the mine waste at Lynemouth has already been observed over a 10 year period (Cooper et al., 2017), and around 100,000 m^3 of coastal mine waste in the UK is predicted to be at risk of erosion within the next 20 years, rising to over 400,000 m^3 over the next 100 years (Riley et al., 2021). As such, there is the potential for both soluble metal(loid)s and solid waste to be released into the coastal zone (Brand and Spencer, 2018). Although dilution by coastal waters might minimise the risk to some extent (Ahrens and Morrisey, 2005), recent data for the north east England coast has shown that eroded wastes may be transported to, and deposited on, other beaches via processes such as longshore drift (Pitman et al., 2024). Coal mine wastes are particularly vulnerable since the low pH leachates generated result in a high risk of metal(loid) mobilisation, which could be a localised hazard in runoff and any ponded water on impacted beaches. However, neutralisation by seawater would likely promote (re)adsorption of some metal(loid)s to sediments within the littoral zone (Wong et al., 2010).

5. Conclusions

This study has highlighted the considerable variability in degree of metal(loid) leaching from legacy coal mine wastes deposited in the coastal zone. Variation in the mass of metal(loid) released can be attributed to the heterogenous nature of coal mine wastes. For most metal(loid)s there is a clear relationship between the degree of leaching and initial metal(loid) concentration. However, despite similar, or higher, concentrations of some metal(loid)s in Dawdon waste, the leaching of all metal(loid)s was greatest from Lynemouth waste. This can be attributed to the dissolution of acid sulfate phases which generates lower pH leachates and promotes the release of metal(loid)s. Furthermore, dissolution of Fe and Mn oxides, hydroxides and oxyhydroxides upon contact with the acidic leachates leads to release of surface adsorbed metal(loid)s. The larger proportion of acid sulfate phases in Lynemouth waste is associated with a high pyrite content.

Differences in leaching behaviour are also evident between DI water and seawater leachants. Whilst most metal(loid)s are less mobile in seawater due to greater buffering capacity, higher amounts of metal (loid)s were leached by seawater from Blackhall waste, albeit the quantities released were negligible (<4 mg/kg). Whilst both Cd and Zn can be more mobile in seawater, due to complexation with chloride ions, there is no evidence for this in the coal mine wastes investigated here. A high clay and silt content and the presence of sulphide ions, as typically found in coal mine wastes, appear likely causes of inhibited Zn and Cd release in seawater. Nevertheless, significant quantities of metal(loid)s may still be leached by seawater.

The spatial heterogeneity in metal(loid) concentration and mobility within legacy wastes poses challenges to accurately assessing the environmental risks to coastal waters from the release of metal(loid)s present. Relatively simple determination of metal content, at a small number of locations within a site, is unlikely to properly characterise risks associated with such legacy wastes. Continual erosion of the wastes means that samples collected from identical locations over a period of time will possess different characteristics in terms of metal(loid) concentration and leaching behaviour. Despite significant dilution by seawater, a thorough understanding of the complex biogeochemical processes occurring, and their impact on metal availability, will become increasingly important as sea level continues to rise in response to climate change. The fate and impacts of waste materials physically mobilised during coastal erosion remains poorly understood. Waste transport via processes such as long shore drift, and consequent impacts on beaches adjacent to those containing legacy waste deposits, warrant further investigation.

The historical use of the coastal zone for the disposal of wastes has left a significant legacy which looks likely to persist for centuries. The research presented here provides an insight into the considerable challenges faced by coastal managers as they seek to mitigate the risks from one type of legacy waste. Further investigations into the environmental risks posed by the release of metal(loid)s present in other legacy wastes should also be considered.

CRediT authorship contribution statement

Catherine J. Gandy: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Ian T. Burke:** Writing – review & editing, Visualization, Formal analysis, Conceptualization. **Patrick Byrne:** Writing – review & editing. **Nick Cooper:** Writing – review & editing. **Richard A. Crane:** Writing – review & editing. **Karen A. Hudson-Edwards:** Writing – review & editing, Funding acquisition. **William M. Mayes:** Writing – review & editing, Funding acquisition. **Patrizia Onnis:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **Alex L. Riley:** Writing – review & editing. **Adam P. Jarvis:** Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2025.124489.

Data availability

Data will be made available on request.

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