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Surface soil-dust contamination of *Phalaris arundinacea* grown on former lead mine sites: Implications for biomass use, phytoremediation and phytomanagement

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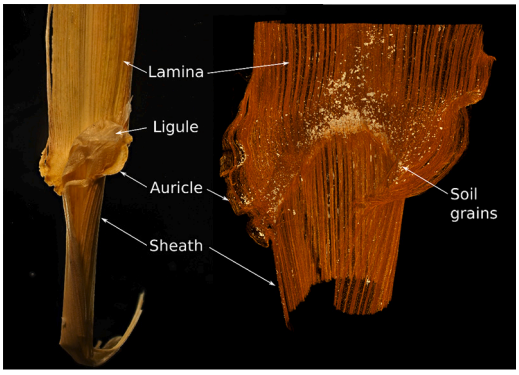
HIGHLIGHTS

- Contaminant "uptake" in phytoremediation studies might be due to surface soil dust
- Biomass imaging shows Pb-rich particles remain after HCl and Tween80 washing
- Washing methods are poorly reported in literature and need standardized protocols
- Phyto-management of Pb mine sites is more effective than phyto-extraction

GRAPHICAL ABSTRACT



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ABSTRACT

This study evaluated the contribution of soil dust deposited on the surface of reed canary grass (*Phalaris arundinacea*) grown on historic lead (Pb) mine sites to the overall contamination of the biomass, with implications for phytoremediation, valorization and utilization. By applying a novel combination of imaging of plant material using X-ray computed tomography (XCT) and scanning electron microscopy (SEM), with washing experiments and bulk analysis, the research aimed to distinguish between (a) Pb uptake through biological processes (phyto-extraction), and (b) surficial dust and physical entrapment of Pb-rich dust on plants cultivated in contaminated soils (surface-contamination). The study established the presence and distribution of Pb-rich particles, which were difficult to remove even by means of sequential washing in 1 M hydrochloric acid and surfactant. Analysis confirmed that the majority of Pb contamination was due to dust, but with significant levels remaining even after intense washing. This questions the effectiveness of phytoremediation in reducing bioavailable soil Pb levels through phyto-extraction, compared to achieving mechanical stabilization or reducing dispersion during phyto-management, and may represent a challenge to the viability of subsequent processing and use of the biomass product. Site-specific variations in contamination levels were observed, underscoring the influence of both local

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environmental conditions and plant morphology on dust accumulation. These observations highlight the necessity for standardized washing protocols to be adopted and for better reporting of the actual washing methods used in phytoremediation research, so as to correctly assess levels of contaminant uptake and actual remediation. The conclusion is that residual surficial dust contamination of biomass may have been overlooked in many previous phytoremediation studies and as a consequence the reported phyto-extraction potential has been overestimated.

1. Introduction

Waste disposal methods at former metalliferous mines have left a legacy of contamination that continues to negatively impact human and environmental health globally (Entwistle et al., 2019; Li et al., 2014). Practices such as the deposition of tailings or crushed rock dumps, where contaminated waste was once piled up in the nearest convenient location, have resulted in the contamination of the surrounding area of many historic mine sites (Rodríguez et al., 2009). Tailings consist of fine particles typically 63–2000 μm in diameter but which have been found to be as small as 1 μm (Csavina et al., 2012; Davies and White, 1981). In the UK alone, it has been estimated that there are in excess of 3000 abandoned historic metal mines (Jarvis et al., 2007). In 2023 legally binding targets were adopted to halve the length of English rivers polluted by abandoned metal mines by 2028 (The Environmental Targets (Water) (England) Regulations 2023, 2023). Historic mining tailings are typically too physically, chemically and biologically deficient to allow for natural vegetation regrowth, resulting in the continued dispersion of potentially toxic elements (PTE) to contaminate the surrounding area. Traditional remediation methods, such as soil removal and capping, are cost prohibitive when applied to historic mining sites where the distribution of PTE is often heterogeneous and spread over large areas (Gomes, 2012). In-situ biological and chemical immobilisation of PTE are therefore becoming increasingly considered as the best option when managing the risks associated with historic mining tailings (Bolan et al., 2014), with phytoremediation the most cost effective approach (Wang et al., 2017). However, the necessity for soil amendment to ensure adequate plant growth still represents a significant cost for such an extensive problem (Mendez and Maier, 2008). Furthermore, by reducing metal bioavailability, adsorption and plant uptake, soil amendment inherently favours phytostabilisation over phytoextraction as a remediation strategy for mine tailings, with the aim instead of creating a self-sustaining vegetative cap to minimise aeolian dispersion, water erosion and leaching processes. Recent applications to phytostabilisation of tailings have focussed on plant-soil-microbe interactions, organic amendments and field scale performance evaluation (Keith et al., 2024). Indeed, a longstanding challenge in phytoremediation has been to translate laboratory results to improve the efficiency of phytoremediation in the field, where a variety of additional stressors or complicating factors are encountered (Vangronsveld et al., 2009).

Another relatively unexplored area is the impact that wind-blown dust from historic mines have on the distribution of PTE and their effect on human and environmental health. Csavina, et al., found that windblown PTE impacted dusts were the least studied mobilisation mechanism (in terms of the number of peer reviewed papers) despite having the greatest transport time, spatial scale and potentially negative impact on human health of all other options (soil, water, biota)(Csavina et al., 2012). High concentrations of Pb in plant material are often reported from the vicinity of Zn/Pb mine sites, reflecting wind-blown or rain-splashed dust and soil (van der Ent et al., 2013). Operationalizing this phenomena Gil-Loaiza et al., 2018 found that establishing native vegetation on tailings led to deposition, measured as a net reduction in the mass of windborne dust flux crossing the site.

An emerging novel remediation option for historic metal mine sites is the growth of soil stabilising, second-generation biofuel energy crops such as reed canary grass (*Phalaris arundinacea*) (RCG), a perennial rhizomatous C3 grass species which is native to the UK (Jensen et al., 2018). This species exhibits useful characteristics including a tolerance to the biogeochemical site conditions typically found in historic mining areas of the UK, production of a relatively high biomass yield and the ability to quickly establish a fine binding network of rootlets capable of stabilising gravelly/sandy soil. Interest in RCG as a perennial grass bioenergy crop has grown considerably in recent years, especially in Northern Europe (Kołodziej et al., 2016; Lord, 2015; Šiaudinis et al., 2021; Smith and Slater, 2010; Strašil, 2012; Strašil et al., 2005; Wrobel et al., 2009). However, in direct field trial comparisons on lightly-contaminated brownfield sites with the two main UK candidate energy crop species, *Miscanthus* (MC) and short-rotation coppice willow (SRC), RCG showed lower concentrations of Cd and Zn, but higher Pb, in the unwashed above ground biomass (Lord, 2015).

The present study has employed X-ray computed tomography (XCT), an innovative technology that enables the penetration of materials to create 3D structural images, which has recently found applications in biomass analysis (Boigné et al., 2021; Sun et al., 2021). The production of X-ray attenuation images is intricately linked to the density of the sample, and this information can be extrapolated by analyzing the attenuation of specific scan regions with known densities.

The aim of the research reported here was to investigate the presence, form and distribution of lead in RCG grown on historic Pb mine waste impacted soils. The hypothesis tested was that harvested biomass fuel grown in this way could be contamination both by uptake and by surface-contamination but that these two effects might be distinguishable here by combining mineralogical and chemical analysis, with and without biomass washing. Thus, the specific goal was to determine whether the Pb concentrations measured by destructive chemical analysis of contaminated plant biomass were mainly the result of biological uptake of contaminants from the soil into the plant tissues, or from the physical entrapment of Pb-rich dust particles on the plant surfaces. It used XCT and scanning electron microscope (SEM) to confirm the presence of high density Pb-rich particles, to map their distribution and deduce their mineral form. This was followed by a series of washing procedures to attempt to remove them, followed by XCT, SEM or chemical analysis. The observation of discrete Pb-rich phases originating from the contaminated host soils adhering to the surface of biomass, and their persistence after intensive washing, has important implications, respectively, for the effectiveness of phytoremediation or phyto-extraction, and the subsequent valorization and utilization of biomass grown on highly Pb contaminated sites.

2. Materials and methods

2.1. Studied area

The Whiteheaps Mine and associated mineral processing complex is situated in the Northern Pennines, England, UK on the boundary between the counties of Northumberland and Durham on Bolts Burn (54.814 N 2.084 W) within the Derwent Valley (Pickin, 1992). The Northern Pennines are a classic example of a zoned orefield and area of Pb-Zn-Ag-Ba-F mineralization with historic mining activity over two millennia (Dunham, 1948). Mining, initially for Pb, took place at Whiteheaps from at least 1690 and ceased in 1989, at which time the site was predominantly used for the production of fluorspar (CaF_2). Early mineral processing operations at Whiteheaps were typical of the time and involved dammed water used to drive a water wheel that operated a

'crusher' that would break up ore (typically consisting of 5 % lead ore) into uniform sizes so that it could be separated in a process named 'washing' or 'dressing' (Milburn, 1987). Waste material from this process at Whiteheaps was later reprocessed to recover Pb and the fluorspar gangue mineral over the course of the 20th Century (Chambers, 1992). The crushing of the ore produced a fine material which was 'washed' to remove fluorspar with the lighter waste material discarded as 'slimes' (Morrison, 1998). Following closure of the mine site in 1989 the buildings were partly demolished and the processing wastes were regraded across the site, giving an appearance described as like 'a desert' (Fairbairn and Northern Mine Research Society, 2000). This was followed by topsoil capping, which has subsequently failed locally due to soil erosion and gullying. In 2018 a 2-year field trial was conducted to test the effects of organic waste soil amendments on the chemical mobility of PTE and growth of RCG at the Whiteheaps mine site (Nunn et al., 2023). The two 9 m × 9 m planting areas from this, each surrounded by rabbit-proof fencing, were re-used for the present plant growth and study.

2.2. Trial site soil analysis for PTEs

The purpose of soil sampling and bulk chemical analysis was to determine the PTE levels in the soils in which the plants were to be grown, to characterize the levels of contamination which were tollerated, and as the context for investigation of possible contamination of the biomass. The two trial sites had been previously identified as highly contaminated with Zn, Pb and other PTEs in surface soil sampling by Northumbrian Water. This was followed by confirmatory reconnaissance surface sampling and pseudototal analysis by microwave-assisted aqua regia digestion (MARS Xpress, CEM Microwave Technology Ltd., Buckingham, UK) and inductively-coupled plasma optical emission spectrometry (iCAP 6000 Series, Thermo Scientific, East Grinstead, UK, (Nunn, 2022)). At both trial areas (WH3 and WH5), ten 5 L surface soil samples collected from across the trial site to create a bulk sample for pot trials, were each subsampled and homogenized to provide a representative bulk sample for baseline analysis (NRM Laboratories, Bracknell, UK) in 2018 prior to any on site cultivation or amendment (Nunn et al., 2023). As part of the earlier trial, five additional samples of the unamended surface soils were collected at the centre and corners of each enclosed trial area in turn. These were submitted for analysis to Bureau Veritas Mineral Laboratories, Vancouver for analysis by aqua regia digestion and inductively coupled plasma mass spectrometry (method AQ250).

2.3. Trial site soil XRD mineralogical analysis

The purpose of x-ray diffraction (XRD) analysis was to give qualitative information on the mineralogy of the trial site soils, including the nature of any residual ore minerals or their alteration products. If detected this would give an indication of the chemical availability and particulate phases to be expected in any surface contamination. Portions of the same two composite bulk samples were used for XRD after further homogenisation in the laboratory (see Nunn et al., 2023) to ensure these were fully representative. XRD analysis was conducted with a Malvern Panalytical X'Pert3 diffractometer from 4.5 to 75° 2θ using a CuK radiation at 40 kV and 40 mA (X-Ray Mineral Services UK, Colwyn Bay). The samples were analysed for 60 min at a step size of 0.013. The mineral phase identification was performed using HighScore Plus (v.4.9 by Malvern Panalytical) and quantification using the Rietveld method was undertaken with BGMN AutoQuan software. XRD analysis was conducted on a Philips PW1730 Generator from 3 to 35° 2θ using a CuKα radiation at 40 kV and 40 mA and quantification was performed using a Reference Intensity Ratio based (RIR) method (Moore and Reynolds, 1998).

2.4. Field trial establishment

In Spring 2022 the experimental sites each received a surface application of the same source segregated green-waste compost prepared to Publicly Available Standard (PAS) 100 (DJ & SJ Enderby, Codlaw Farm, Northumberland) with a target application rate of 50 t $ha^{-1.}$ (as received, at approximately 63 % dry matter content). The compost was delivered to site in 20 kg bags (31 at area WH3 and 32 at WH5) and lightly raked by hand evenly across the two enclosed trial areas (118 m^2 and 98 m^2 respectively, hence 52 $t.ha^{-1}$ and 65 $t.ha^{-1}$ actual application rates respectively). RCG was hand-seeded on 15th March 2022 at a rate of 40 kg ha^{-1} using non-certified seed (Watsons Seeds, Dunbar). This resulted in a good strike and first year establishment at both areas.

2.5. Plant material preparation and washing for imaging with XCT and SEM

XCT scans and SEM imaging was completed on unprocessed green RCG cuttings (stem and leaf) sampled from the WH3 and WH5 trials in August 2022. Plant samples were taken on site using a clean pair of scissors and placed in a zip-lock bag. Both 'washed' and 'unwashed' samples were then prepared for scanning. For XCT five blades were placed in each tube, one tube each for the washed and unwashed material from each of the two sites (total 4 tubes and 20 blades). For SEM imaging one sample of each, both washed and unwashed were scanned for areas of interest (total four samples). Unfortunately, it was not possible to use the same samples before and after washing for XCT and SEM. The reagents and sequential washing method used were the optimum methods identified during a PhD study to evaluate different washing procedures and reagents for biomonitoring plants (Neelam Manzoor, pers. Comm.). In each case the reagent was poured into a clean container and the sample was submerged in the reagent for 30 s followed by 30 s rinse with distilled water to remove reagent from the samples. The first washing reagent was an appropriate volume (enough to submerge the sample) of freshly prepared 1 M HCl (Thermo Fisher Scientific, UK). The second washing reagent was Tween-80 (0.1 %, non-ionic detergent, Sigma-Aldrich, UK). After washing, the samples were air dried for one week before being sealed in 50 mL centrifuge tubes awaiting scans.

2.6. Unwashed plant bulk analysis

In order to obtain fully representative samples of biomass from the naturally variable sites, the entire biomass growth was collected. In January 2023, at WH3 all available senesced material above 5 cm from the ground was cut carefully with scissors and placed into buckets and homogenized (total wet mass 153 g). At plot WH5 all plants were cut by the same process but at 10 cm (total wet mass 188 g). This was allowed by the greater plant height at WH5 compared to WH3. Scissors and buckets were cleaned between the sites. All biomass from each site was placed into zip lock sample bags and returned to the laboratory where they were dried to a constant mass at 105 °C in a Heratherm OGS400 laboratory oven (Thermo Scientific, Runcorn, Cheshire, UK). The dried plant material (WH3 123 g, WH5 144 g) was then all milled to <1 mm particle size with a knife mill (GM300, Retsch, Haan, Germany) to homogenise in preparation for analysis. The elemental analysis (Alfred H Knight, Dundonald, Scotland) was completed on a 5 g sub-sample of the above-ground biomass directly by using an extraction based on ISO BS EN16968:2015 (British Standards, 2015). In this method the analysis sample is digested in a closed vessel made from a fluoropolymer using nitric acid, hydrogen peroxide, and hydrofluoric acid in a microwave oven or a resistance oven or heating block. The digest is then diluted and the elements are determined with suitable instruments, in this case by inductively-coupled mass spectrometry (ICP-MS, AHK method SM044). Bulk biomass collection, drying, homogenisation and analysis was repeated in September 2023 using identical methods at WH3 (419 g dry

matter) and WH5 (1094 g). However RCG root analysis was not attempted due to the difficulty of separating the highly contaminated soil from the fine network of rootlets (A. Colantoni, pers. comm.) and our own concern that even the smallest residues of such a contaminated soil would compromise the analysis of such small quantities of dry weight biomass.

2.7. X-ray computed tomography

A Nikon Metrology X-ray micro-CT (XCT) system fitted with a 180 kV X-ray source was used to scan and compare washed and unwashed samples. The resulting 3D data sets were used to visualize the structure of each blade of grass and identify any particles of soil and metal- containing minerals based on their higher densities relative to the grass tissue. The 4 centrifuge tubes were first XCT scanned together at 50-μm resolution, 80 kV energy, and with 3141 projections over a 360° rotation. This scan data was then reconstructed as a 32-bit 3D data set using Nikon CT Pro software. This data set gave a low-resolution overview of an 80 mm length along the samples and was used for screening purposes.

Each tube was then scanned individually at 18-μm resolution, producing an analysis volume 28.8 mm in length centered on the middle of the tube and overlapping with that portion of the 50-μm scan. 2 mm diameter glass beads with a nominal density of 2.5 g.cm^{-3} were fixed to the outside of the centrifuge tubes before scanning (see Fig. 1). These glass beads, together with an assumed density of the polypropylene centrifuge tube of 0.92 g.cm^{-3} (Gahleitner and Paulik, 2014) were used to create a 2-point calibration linearly relating X-ray attenuation values to approximate sample density.

Finally, single blades of grass from the washed WH3 and WH5 samples were removed from the 50 mL centrifuge tubes and placed in individual 6 mm diameter tubes then scanned at a resolution of 5.25 μm and centered on the leaf node collar with an analysis region 8.4 mm in length. These high-resolution scans enable visualizing the internal leaf structure, but could not be scanned with the glass bead and plastic tube within the field of view hence results are presented in terms of x-ray attenuation rather than sample density.

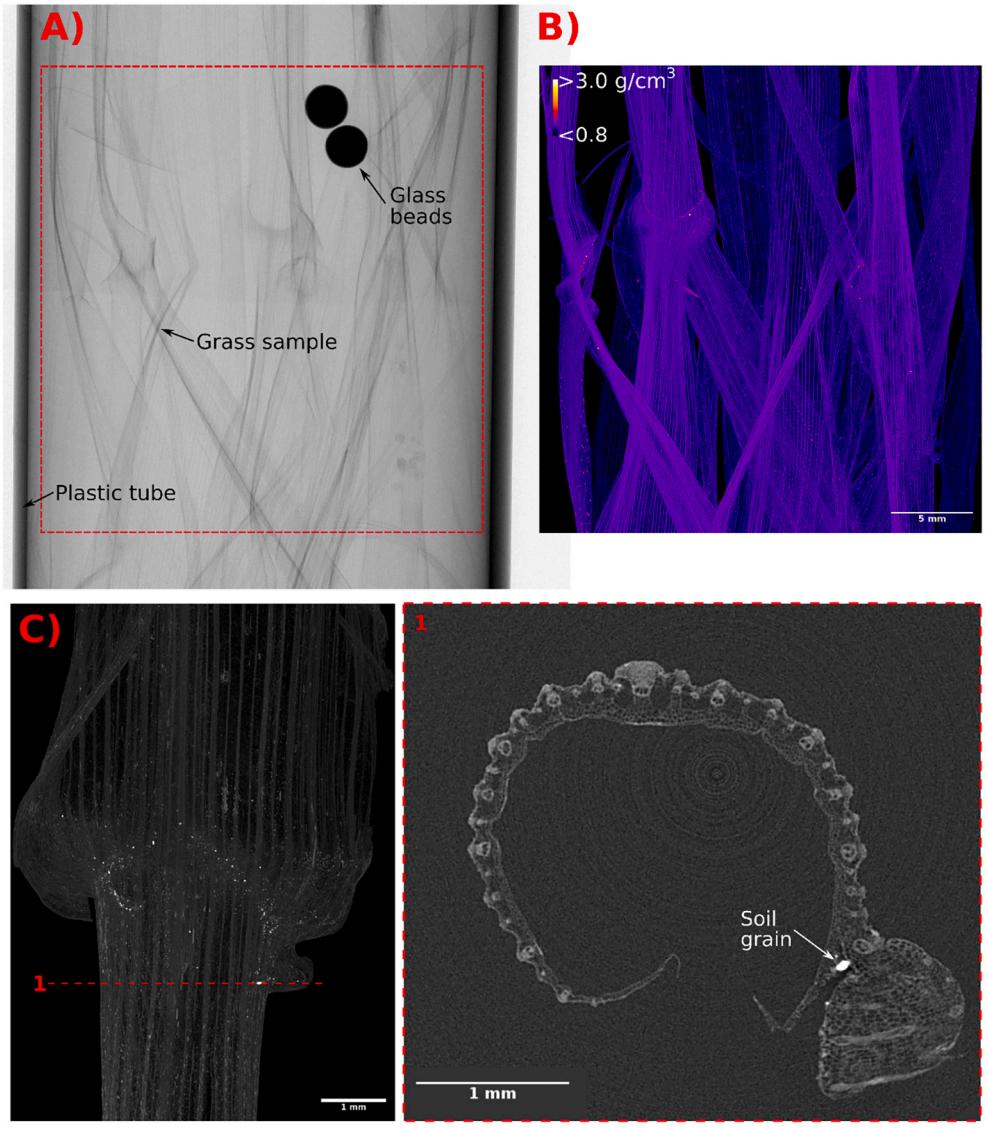

Fig. 1. XCT Images of RCG from Whiteheaps WH5. (A) An X-ray projection showing the central portion of the 50 mL centrifuge tube as it is scanned at 18-μm resolution. The reconstructed volume that is suitable for analysis is denoted by the red box. (B) Reconstructed volume after calibration for density based on the attenuation values of the plastic tube and the glass beads. A small number of particles are significantly denser than 3 g.cm^{-3}. (C) A single leaf node collar at 5.25-μm shown as a vertical map of max X-ray attenuation (left) and a cross section through the 3D volume (right). High density particles are visibly wedged into bifurcations and pockets formed by the collar.

2.8. Scanning electron microscopy imaging

After air drying, 3 to 5 washed and unwashed WH3 and WH5 grass leaves were cut into 2 × 2-cm sections. Multiple representative sections were cut from various parts of the leaves ensuring that leaf margins and mid rib were included in each sample. All the samples were cut using sterilized plastic scissors while wearing nitrile gloves. SEM sample preparation and analysis was performed at the Continuous Manufacturing and Advanced Crystallization (CMAC) hub, University of Strathclyde using an EM ACE 200 sputter (20 nm gold layer, Leica Inc.) and a TM4000 Plus SEM (Hitachi High-Technologies Corporation, accelerating voltage of 10 kV, observation and backscattered electron (BSE) modes). The magnifications used are shown with the images.

2.9. Biomass powder washing experiments, analysis of floated and settled fractions

Initially, only unwashed biomass was chemically analysed for bulk contaminant concentrations, so an additional washing experiment was devised to investigate the effectiveness of washing in reducing bulk chemical contamination. For this 5 g of ground dried biomass from WH3 and WH5 was added to 50 mL centrifuge tubes in triplicate, each containing 45 mL of a mixed washing solution (1 M HCl and 0.1 % Tween-80 prepared as previously discussed). Sequential application was not considered practical for the powdered biomass, due to the potential losses from separation by any means other than settlement. The centrifuge tubes were then shaken by hand for 1 min to mix the biomass with the solution and then allowed to settle. Floating biomass was removed using a clean spatula and the remaining liquid was poured out. The settled material was then removed using a clean spatula. These samples were then dried to a constant mass at 105 °C. 0.15 g each of the floated and settled biomass were then digested in 10 mL of nitric acid (PrimarPlus-Trace analysis grade, > 68 % HNO_3, Fisher Scientific, Loughborough, UK) with a microwave digestion system using the manufacturer recommended conditions for "plant material" (MARS Xpress, obtained from CEM Microwave Technology Ltd., Buckingham, UK). The digestates were analysed using ICP-MS (Model 7700×, Agilent Technology, Cheshire, UK) alongside a certified reference material for analytical quality control ERM-CD281 (rye grass). Results were analysed using IBM SPSS Statistics v 30, using a one-way ANOVA and Bonferoni post-hoc test to compare the significance of differences in Pb concentrations between the unwashed, floated, settled and lost biomass fractions, with the data for samples WH3 and WH5 analysed separately to avoid influence of large differences in the initial concentrations of Pb.

3. Results

3.1. Soil PTE contamination

Analyses of the mine soils used for cultivation of the biomass collected at the various stages of the trials (Table 1) illustrate the extreme levels of contamination present and the local heterogeneity: Phytotoxic effects are to be expected from the Cu and Zn levels at both sites, whereas the levels of Cu or Pb at either site, and Zn at WH5, could harm grazing livestock (ICRCL 70/90, 1990). The observed Cd, Cu and Zn are still within acceptable levels for human health exposure during public open space access (Nathanail et al., 2015). Since there is no Suitable for Use Level (S4UL) available for Pb, comparison instead to the more precautionary Category 4 Screening Levels (C4SL) (CL:AIRE, 2024) indicates that levels of Pb are roughly an order of magnitude higher than those for which there would be no significant possibility of significant harm. The range of values obtained illustrates the difficulty of obtaining a single value for soil concontaminant concentration, such as might be needed as a quotient to calculate bioconcentration factor (van der Ent et al., 2013). Accordingly, these quantitative data are used to qualitatively indicate the extreme levels of Pb and Zn contamination

Table 1
PTE analyses of mine soils at trial sites used for plant cultivation, including initial reconnaissance grab samples (WH3R, WH5R), representative bulk samples (WH3B, WH5B), range, mean and standard error of 5 in situ samples (WH3S, WH5S), compared to various proposed trigger values (mg.kg^{-1}).

	WH3R (n = 1)	WH3B (n = 10)	WH3S (n = 5) range (mean ± SE)	WH5R (n = 1)	WH5B (n = 10)	WH53S (n = 5) range (mean ± SE)	ICRCL 70/90 trigger (crop growth)	ICRCL 70/90 trigger (grazing livestock)	C4SL POS_{PARK}	S4UL POS_{PARK}
Cd	6	5.07	5.1–11.3 (7.6 ± 1.1)	22	6.3	5.9–12.3 (10.1 ± 1.2)	50	30	560–880	560
Cu	605	545	385–559 (446 ± 31)	1770	890	459–2030 (1110 ± 269)	250	500		44,000
Pb	14,300	13,900	9490–10,000* (9860 ± 99*)	6730	9110	6410–10,000* (8780 ± 765*)	–	1000	580–1400	N/a
Zn	2440	1850	1540–2730 (2002 ± 201)	14,300	5150	2920–10,000* (6260 ± 1210*)	1000	3000		170,000

* values included exceed calibration range of 10,000 mg.kg^{-1}.

present in the plant growth soils.

3.2. Soil mineralogy and Pb-rich phases

The XRD whole rock results for mine soils WH3 and WH5 are shown in Table 2. The main Pb bearing phase in WH3 was found to be cerussite ($PbCO_3$). Cerussite contains approximately 78 % Pb by mass. The sample from WH3 was found to contain 0.8 % cerussite which corresponds to approximately 0.6–0.7 % Pb equivalent to 6000–7000 ppm. In WH5 the concentration of cerussite could not be quantified but the scan verified the presence of a trace amount (<1000 ppm Pb). In both samples, the amount of Pb bearing phases was lower than that expected from the elemental analysis shown in Table 1 but the relative concentrations (WH3 > WH5) agreed.

3.3. Unwashed biomass contamination

The plants sampled at WH5 were generally greater in height by up to 50 cm, and on average approximately 10 cm, than those at WH3. Clear differences in the concentrations of Cu and Pb, shown in Table 3, were also found in the unwashed bulked biomass from the two trial sites, which cannot easily be explained by the differences in PTE soil concentrations alone. For example, Pb concentrations found in plants from site WH3 (3220 $mg.kg^{-1}$) were greater by a factor of 100 compared to those found at WH5 (43 $mg.kg^{-1}$), whereas soil concentrations at the first site were only c.50 % higher. Conversely concentrations of Zn are relatively similar in the two biomass samples, in spite of the differences in soil concentrations. The concentrations of Pb observed at WH3 in naturally grown biomass were of note here and warranted further investigation, since concentrations above 1000 $\mu g.g^{-1}$ (or $mg.kg^{-1}$) if found internally in washed leaf biomass might otherwise suggest hyperaccumulation status (van der Ent et al., 2013). Repeated sampling in the following growth year gave moderately consistent results.

3.4. XCT imaging of washed and unwashed grass

Figs. 1 and 2 show XCT images of the washed and unwashed RCG with areas of higher density particles, the majority of which are smaller than sand grains in size (<63 μm). In all of the XCT images the greatest density of particles occurs in the ligule where the collar of the leaf joins the stem. This part of the plant's anatomy forms a potential trap for particulate surface contamination.

Dried leaf bulk or envelope density ranges between 0.1 and 0.6 $g.cm^{-3}$ across a range of species (Poorter et al., 2009), but the absolute or skeletal density is closer to 1.3 $g.cm^{-3}$ (Brewer et al., 2014). The absolute density of silica is 2.6–2.7 $g.cm^{-3}$ while that of metallic lead is 11.37 $g.cm^{-3}$. The mineral forms observed in the Whiteheaps mine soil (Table 2) have slightly lower densities of approximately 6–7 $g.cm^{-3}$ (e.g. galena (PbS) 7.2–7.6 $g.cm^{-3}$, cerussite ($PbCO_3$) 6.58 $g.cm^{-3}$) and are of similar density to many other metallic minerals commonly found in soil samples e.g., iron oxides (5.24 $g.cm^{-3}$).

Table 2
XRD analysis (in % by mass) of representative composite samples of mine soils from site WH3 and WH5 (TR – Out of tolerance range).

Sample	WH3B	WH5B
Illite/Smectite	0.0	1.9
Illite+Mica	4.8	11.2
Kaolinite	TR	0.8
Chlorite	0.0	0.0
Quartz	49.7	47.5
K Feldspar	0.0	0.0
Plagioclase	0.0	0.0
Calcite	0.0	0.0
Dolomite	0.0	0.0
Siderite	1.3	1.0
Cerussite	0.8	<0.1
Fluorite	43.0	37.2
Galena	0.0	0.0
Sphalerite	0.4	0.3
Pyrite	0.0	0.0
Total	100	100

Table 3
Analysis of bulked and homogenized RCG biomass taken from Whiteheaps mine site (on dry basis) for 2022 and 2023 growth seasons ($mg.kg^{-1}$).

Sample	WH3		WH5	
	2022	2023	2022	2023
Cd	3.39	2.11	1.28	0.80
Cu	109	17.1	11.8	6.79
Pb	3221	896	43.0	21.5
Zn	1173	1169	885	767

Spatially resolved density in the XCT images have been estimated in the 18-μm resolution scans here by measuring the average attenuation of the polypropylene centrifuge tube (21.7 m^{-1}) and the glass bead (200.4 m^{-1}), which have densities of approximately 0.92 and 2.5 $g.cm^{-3}$ respectively. By extrapolation, those parts of the images with an attenuation rate of over 1038 m^{-1} should have a density of approximately 10 $g.cm^{-3}$. The density plots shown in the unwashed grass image from WH3 (Fig. 2) confirm that a number of regions have densities of approximately 6 $g.cm^{-3}$. For the WH5 grass there are several regions with densities above that of the plant material, consistent with silica soil particles in terms of size, shape, and density, although there are only a handful of denser regions consistent with metallic minerals.

Care should be taken when extrapolating density from X-ray attenuation as many lab X-ray sources such as the Nikon scanner used here produce a polychromatic energy spectrum with the result that X-ray interactions with minerals are not truly linear (Maire and Withers, 2013). Additionally, quantification of small particles approaching the scan resolution is hampered by "partial volume" effects in which a grain of metallic mineral with a density of 5.2 $g.cm^{-3}$ would return a density of 2.6 $g.cm^{-3}$ if it was divided between two voxels in the 3D scan and could therefore not be distinguished from a silica mineral. Such partial volume effects are evident when moving from the initial 50-μm screening scans (data not shown) to 18-μm scans of regions of interest, and then to 5.25-μm scans of a single leaf node. As resolution increases, more high-density particles are evident, the contrast between particles and leaf tissue increases (Fig. 1C) and contrast between high- and low-density particles becomes apparent (Fig. 2 bottom).

Based on the XCT scan data alone, it is not possible to conclude that lead bearing minerals such as cerussite and galena are present within the samples. However, as there is such a large difference in density between grass (1.3 $g.cm^{-3}$), many non-metallic minerals such as silica (2.65 $g.cm^{-3}$) and the metallic minerals (5–7 $g.cm^{-3}$), it is clear 1) that soil particles are present in the unwashed samples, 2) that after washing these particles remain wedged into bifurcations and pockets in the plant tissue primarily around the leaf node collar, and 3) that some particles have a high density consistent with metallic minerals.

3.5. SEM images of washed and unwashed grass plants

The SEM images (Fig. 3), show that angular foreign objects with sizes in the range of 10–50 μm can be found on the leaf material of both washed and unwashed plant samples from site WH3. Material of a similar size and shape were found on the unwashed WH5 plants. The SEM image of a washed WH5 plant shows a different texture, indicative of a difference in mineralogy or perhaps an etching effect from the washing procedure.

3.6. Floated and settled biomass contamination

For plant material from both WH3 and WH5 the settled 'washings'

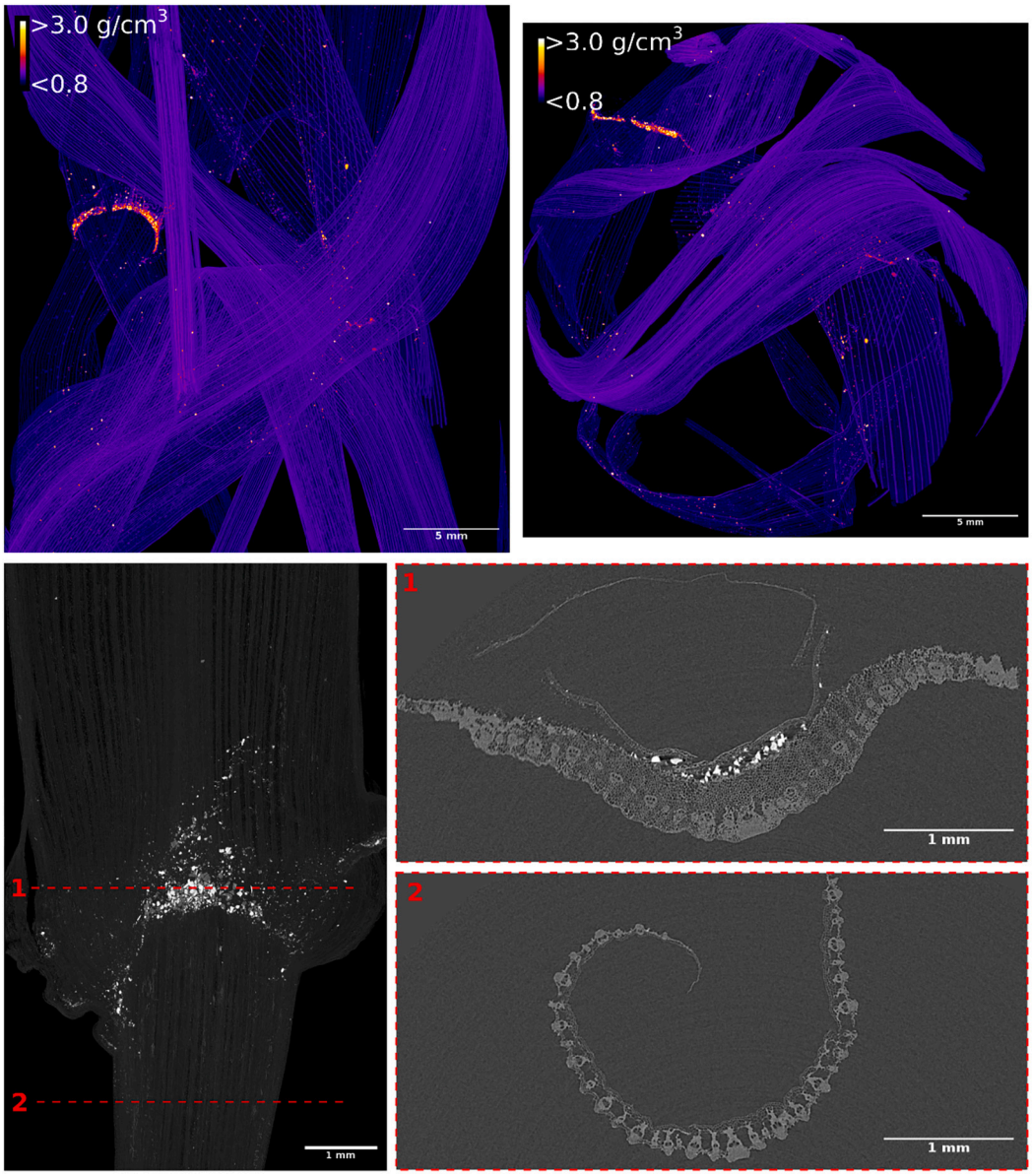

Fig. 2. XCT Images of RCG from Whiteheaps WH3 (Top): Maximum density maps in vertical (left) and horizontal (right) planes at 18-μm resolution. Shows the distribution and clustering of soil grains throughout the samples. Bottom: A single node collar at 5.25 μm shown as a maximum attenuation map (left) and as cross sections through the 3D volume at position 1 where many soil particles are trapped in a crevice within the node, and at position 2 where no soil particles are visible at this resolution.

were found to contain considerably higher concentrations of Pb than the floating plant material (Fig. 4), with the highest concentrations represented by the mass of Pb in the eluted biomass, as calculated by difference (Table 4). Statistical testing showed that the differences in Pb concentrations found between unwashed, floating, settled and eluted fractions were significant in all case at the 99 % level for each sample. Mass balance calculations (Table 4) suggest that the bulk of the Pb (90–87 %) was removed by intensive washing. In both cases, however, roughly half of the Pb contained in the original sample was not recovered as either floating or settled plant material, presumably lost with the decanted washings, either in solution or as fine suspended particulate material. These results indicate that the bulk of the Pb was present as particulate material on the plant structure, with no more than 13 % actually within the lignocellulosic plant material and hence protected from washing or strong acid solution. This matches studies of leafy greens grown in urban soils, where aqueous washing was able to remove 75–94 % of Pb from lettuce (Egendorf et al., 2021).

4. Discussion

Combining phytoremediation with energy crop production offers a nature-based solution to both the legacy of soil contamination and the need to increase local production of biomass by sustainable and ethical means (Lord, 2015). However, a weakness of this approach for highly contaminated sites is the possibility of the biomass inheriting a “non-negligible degree of contamination”, as is demonstrated here, which might potentially threaten its non-waste or by-product status if it cannot “be used directly without any further processing other than normal industrial practice” (Fermeglia and Perišić, 2023). Although “normal industrial practice” might generally include drying, washing, filtering and modification to the size and shape, of these only washing is likely to achieve valorization of biomass contaminated with PTE and would rarely be practical or indeed normal. Furthermore, transfer of contaminants off-site as soil particles via adhering dust equates merely to relocation rather than to sustainable in situ remediation or improvement

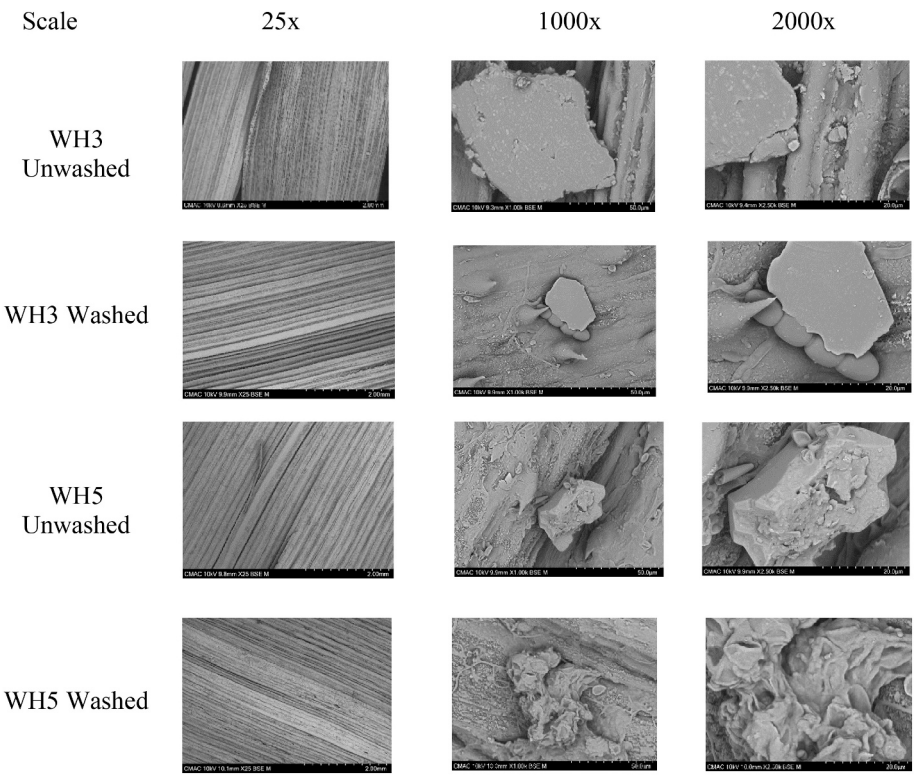

Fig. 3. SEM images of surface particles on washed and unwashed RCG from Whiteheaps mine sites WH3 and WH5.

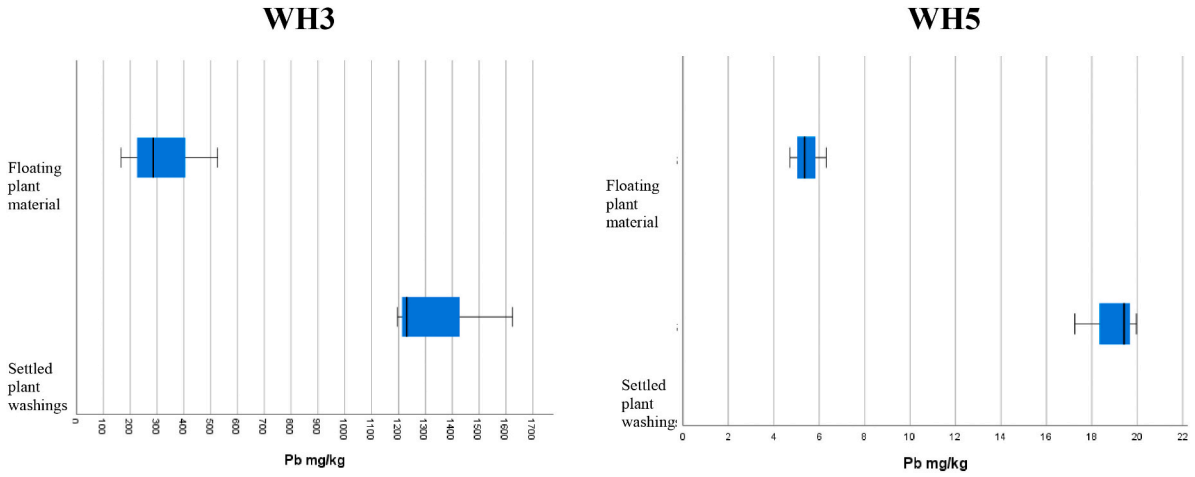

Fig. 4. Analysis of floating and settled plant material following 1-min wash in 1 M HCl and 0.1 % Tween 80 ($n = 3$).

of soils at the contaminated site. Indeed, downstream processing or use of the biomass – for example its combustion – could lead to further environmental dispersion of contaminants. Thus, the questions addressed by this study, specifically whether contamination found in the biomass of plants grown at historic mine sites is biologically absorbed or reflects the presence of surficial soil dust particles, and whether these can be removed by washing, is of fundamental importance to the viability of combining phytoremediation with biofuel production.

4.1. Nature of contamination found in plants grown on historic mine sites

Crushed mining waste from historic Pb mines is often found in particle sizes of 10–50 μm and typically contains a greater concentration of Pb than larger size fractions found at the same site (Csavina et al., 2012; Davies and White, 1981; Drahota et al., 2018; Jesús Eulises et al., 2021). The XCT images clearly show that, even following a thorough washing, high density particulate material remains on the plant. This material is largely found in the (pocket shaped) ligule of the grass plant (see Fig. 5). The SEM images show that some of this material is trapped on the surface of the plant and the shape (angular edges) and size (>50 μm) is that expected of crushed mining waste. Not all of these were removed by vigorous washing, with mineral grains remaining on the surface of the washed plant. The combination of results from the two scanning techniques and the washing procedure indicates that a significant amount of the Pb contamination in the unwashed biomass is attributable to adhering dust, which is also very difficult to remove completely from the plant surface. Similar differences between Pb analyses of washed and unwashed samples of wild plants have been observed from around mine tailings sites with the percentage removal after washing ("phytobarrier indices") calculated as a measure of the attenuation of windblown dust

Table 4
Mass balance calculated for floating and settled plant material following 1-min wash in 1 M HCl and 0.1 % Tween 80). Results for two biomass samples (WH3, WH5), each with 3 replicate washings (Fig. 4) showing concentration levels and mass balance fractions for Pb and biomass as percentages (in brackets), mean (n = 3) and standard error of the mean (S.E.M). Washing efficacy is the percentage of total mass of Pb originally present in the biomass which was removed by washing (Fig. 7).

Site	Unwashed Pb concentration, mg. kg^{-1}	Washing experiment replicate	Floated biomass: Pb concentration $mg.kg^{-1}$ (Pb %, biomass %, by mass)	Settled biomass: Pb concentration $mg.kg^{-1}$ (Pb %, biomass % by mass)	Eluted material: Pb concentration $mg.kg^{-1}$ (Pb %, biomass %) by difference	Washing efficacy (settled+ eluted/ total Pb %)
WH3	3220	1	526 (16.3, 31.3)	1196 (37.1, 36.9)	4702 (46.5, 31.9)	83.7
		2	165 (5.1, 34.1)	1625 (50.5, 36.4)	4861 (44.4, 29.4)	94.9
		3	286 (8.9, 34.2)	1231 (38.2, 31.8)	5021 (52.9, 33.9)	91.1
		Mean	*326 (10.1, 33.2)*	*1351 (41.9, 35.0)*	*4864 (47.9, 31.7)*	*89.9*
		S.E.M	*106 (3.3, 1.0)*	*138 (4.3, 1.6)*	*92 (2.5, 1.3)*	
WH5	43	1	4.7 (11.0, 28.9)	20.0 (46.5, 35.0)	50.6 (42.5, 36.2)	89.0
		2	5.4 (12.5, 29.8)	19.4 (45.1, 33.3)	49.5 (42.4, 36.9)	87.5
		3	6.3 (14.7, 29.0)	17.2 (40.0, 36.9)	57.2 (45.3, 34.1)	85.3
		Mean	*5.5 (12.7, 29.2)*	*18.9 (43.9, 35.1)*	*52.3 (43.4, 35.7)*	*87.3*
		S.E.M	*0.5 (1.1, 0.3)*	*0.9 (2.0, 1.1)*	*2.4 (1.0, 0.8)*	

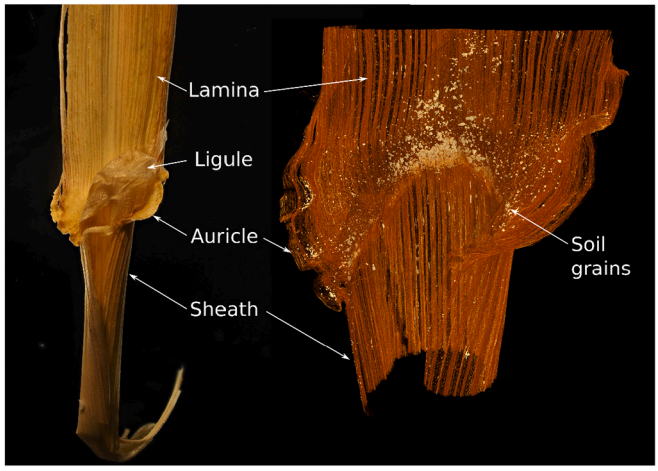

Fig. 5. Photo of area of the grass plant scanned (left) next to XCT image (right) to highlight area where grains of soil dust collect.

(González-Chávez et al., 2023).

4.2. Elemental and site-specific differences

For plants grown at WH3 the surface contamination levels were greater and more likely to remain following washing, whereas for plants grown at WH5 there was limited evidence of mine dust found after washing. This is likely the result of differences between the two sites. The plants sampled at WH5 were up to 50 cm taller, and on average approximately 10 cm taller, than those at WH3. This could mean there was less opportunity for soil to splash onto the taller plants at WH5 and also possibly also there was less wind-blown dust as WH3 is in a location more exposed to the dominant (westerly winds), while soils at WH5 in the stream valley bottom remain wet from water draining from a mining adit throughout most of the year. The range of monthly average wind speeds for the nearest available similar location (Slaley) is 16.3–24.5 $km.hr^{-1}$ (Weather Spark, 2024). Furthermore, the plants at WH3, shown in Fig. 6, are in general more stressed, showing stunting and reddened leaves (presumably anthocyanins) so the high concentrations may also potentially be due to the breakdown of basic plant physiological function (Liu et al., 2023; Pourrut et al., 2011).

The concentrations of Cd and Zn in biomass samples from both sites were relatively similar (Table 3). Although the Cd concentrations in the soil were also similar (Table 1), those of Zn were very different. This may indicate that Cd and Zn are being absorbed by the plant via a biological function and reaching a maximum tolerable concentration. Selective uptake of Zn and Cd is a well-known phenomenon in phytoremediation trials using other fast-growing energy-crop species, such as *Salix* and *Populus* (Dickinson et al., 2009). Although this was less pronounced in RCG compared to other energy crop species grown on the same brownfield sites (Lord, 2015) the grass has been shown to act as a phyto-indicator for Cd and Zn (Polechońska and Klink, 2014). Furthermore, the plants taken from WH5 were found to have lower concentrations for all elements considered, even in the case of Zn where soil concentrations at site WH5 were considerably greater. It is possible that taller and better developed plants have less ligule parts per gram of dry biomass, especially after stem elongation, hence fewer places that dust can become trapped and thus potentially a lower metal concentration per gram of dry biomass. In agricultural systems over-wintering of mature RCG before harvesting can be used to improve fuel quality by leaf loss and alkali leaching which raises the ash melting temperature, but this also leads to an increase in silica content, attributed to contamination with soil (Lewandowski et al., 2003), a process which our observations

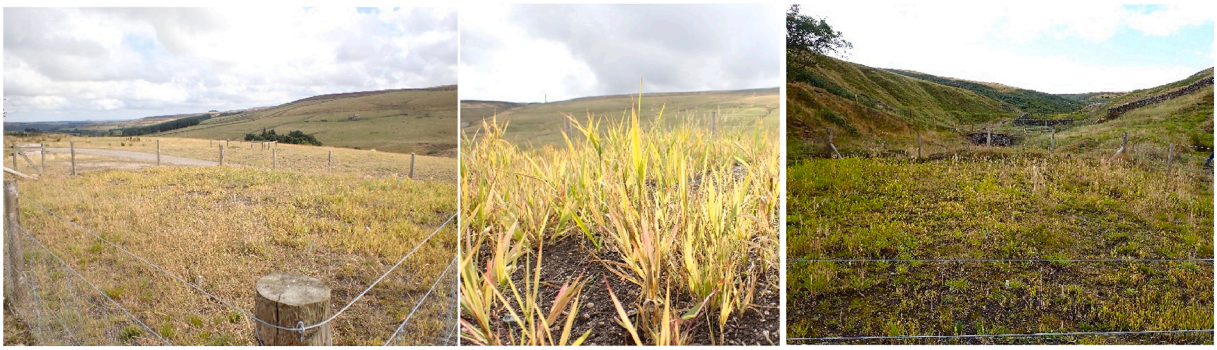

Fig. 6. Trial sites WH3 (left) WH5 (right) at Whiteheaps mine complex with evidence of stunting and reddened leaves at WH3 (centre).

support.

4.3. Under reporting of washing methods in phytoremediation studies

The findings of this study suggest that the manner in which plants are collected and washed has a marked impact on the concentrations of PTE measured in their biomass and attributed to phytoremediation. For example, when considering possible (hyper-) accumulation, "passive accumulation via air-borne deposition on plant leaves" should be discounted (van der Ent et al. (2013) with greenhouse studies preferred to those outdoors on highly contaminated sites to avoid surface contamination with soil. In spite of this potential pitfall, washing procedures are still often poorly reported in published methodologies, with a greater focus directed towards the digestion reagents or analytical instruments used. For example, a review of examples of published works (here including only studies of lignocellulosic perennial biomass plants grown on land or soil contaminated with PTE) found that most of such studies either omitted to mention whether any washing procedure was used or reported the procedure ambiguously (Table 5). One study explicitly and deliberately analysed unwashed material to assess soil particle adhesion as a potential contamination source in biomass fuel (Lord, 2015). The current study indicates that the lack of attention given to this potentially crucial step in plant elemental analysis (especially for plants grown on historic mine sites) is a critical gap. It suggests that some of the literature data used so far to support the proposed combination of phytoremediation and biofuel production may have inadvertently overestimated plant uptake, particularly for Pb at high soil concentrations and in smaller species growing close to the ground with plant geometries favoring the trapping of windborne dust. Although total biomass Pb concentrations in *Phalaris* initially exceeded 3000 $mg.kg^{-1}$, our intensive washing process reduced this for powdered biomass to well below the qualification thresholds of a 1000 $mg.kg^{-1}$ shoot concentration set as the primary requirement for effective phyto-extraction, which in turn lowered the [shoot]/[soil] concentration ratio or Bioconcentration Factor to below 1, and by so doing failed the second requirement (Egendorf et al., 2020; van der Ent et al., 2013). Even after serial washing with strong acid and surfactants, our XCT images provided prima facie evidence that Pb was retained as ore particles and effectively trapped within the plant structure, rather than adsorbed and phyto-extracted.

Table 5
Examples of washing procedures reporting in the literature for studies growing reed canary grass (RCG), short-rotation coppice willow (SRC) and Miscanthus (MC) on land or soil contaminated with PTE.

Washing procedure	Reference	Potentially toxic elements measured in biomass	Species
Not described	Antonkiewicz et al., 2016	Co Cu Fe Pb Zn	RCG
	Barbu et al., 2013	Co Pb	MC
	Fijalkowski et al., 2018	Co Cr Cu Ni Pb Zn	MC
	Kocoń and Jurga, 2017	Cd Cu Pb Zn	MC
	Laval-Gilly et al., 2017	Cd Cr Cu Ni Pb Zn	MC
	Mayerová et al., 2017	Cd Co Cr Cu Ni Pb Zn	RCG
	Rosikon et al., 2016	Cd Cr Cu Ni Pb Zn	RCG
	Smith and Slater, 2011	Cu Fe Mn Zn	RCG
	Strašil, 2012	Cd Co Cr Cu Ni Pb Zn	RCG
No washing procedure used intentionally	Lord, 2015	Cd Cr Cu Ni Pb Zn	RCG MC SRC Willow
Ambiguous procedure e.g. "washed carefully" or "brushed and washed"	Baum et al., 2006	Cd Cu Pb Zn	SRC Willow
	Jensen et al., 2009;	Cd Cu Pb Zn	SRC Willow
	Korzeniowska and Stanislawska-Glubiak, 2015	Ni	RCG
	Leung et al., 2007	As Co Cu Fe Pb Zn	MC
	Meers et al., 2007	Cd Cr Cu Ni Pb Zn	SRC Willow
Washed with distilled/ deionized water	Badmos et al., 2015	Cu Cr Pb Zn	RCG
	Hartley et al., 2009	As	MC
	Kacprzak et al., 2014	Cd Cr Cu Ni Pb Zn	MC
	Korzeniowska and Stanislawska-Glubiak, 2019	Cu Ni Zn	MC
	Krzyżak et al., 2017	Cd Pb Zn	MC
	Pavel et al., 2014	Cd Pb Zn	MC
	Polechońska and Klink, 2014	Cd Co Cr Cu Fe Mn Ni Pb Zn	RCG
	Pulford et al., 2002	Cd Cu Ni Zn	SRC Willow
	Vervaeke et al., 2003	Cd Cu Pb Zn	SRC Willow
	Vysloužilová et al., 2003	Cd Zn	SRC Willow
	Wang et al., 2012	Cr Cu Pb Zn	MC

5. Conclusions

This study investigating the nature of lead (Pb) contamination found in (or on) RCG grown at two areas of a historic Pb mine site has given critical insights into the effectiveness of combining phytoremediation with biofuel production:

1. Combining XCT/SEM imaging of unwashed biomass reveals extensive surficial contamination. These areas of high-density, angular dust particles are resistant to vigorous serial washing with concentrated strong acid and laboratory surfactants, remaining physically trapped between leaf and stems, with eluted fractions contributing significantly to the total contaminant loading. This observation has important implications for the use and possible valorization of phytoremediation biomass, together with the understanding of heavy metal uptake by plants and the relative effectiveness of phyto-extraction versus phyto-stabilization of highly contaminated sites.
2. Variations between elements and trial sites were seen, with lower concentrations on taller, healthier plants, in more sheltered areas, suggesting that the soil conditions, physical location and condition of the plants also play a role in PTE-rich dust accumulation. The implication is that smaller plants with complex geometries grown on highly contaminated sites may have a disproportionately high level of surficial contamination, compared to assimilated contamination, but which still cannot be removed by simple washing.
3. The relative importance of surficial particulate contamination, coupled with the difficulty of achieving full decontamination by washing procedures, highlights the need for improved reporting of washing methods used and further study of their effectiveness. In this study our intensive washing reduced contamination levels in the floated biomass by a factor of 9 on average (Fig. 7). In the absence of a demonstrably effective standardized washing procedure, it is possible that analyses of naturally grown plants on actual contaminated sites may have over-estimated plant uptake by a similar factor, by inadvertently including surface contamination with PTE-rich soil.

CRediT authorship contribution statement

Benjamin Nunn: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Richard Lord:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **James Minto:** Writing – review &

Fig. 7. Summary of biomass powder washing experiment results showing concentrations of Pb in washing fractions (with standard errors for 3 experiments), split of biomass (average, n = 3) and calculated Pb mass-balance between fractions (average, n = 3).

editing, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Christine M. Davidson:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Neelam Manzoor:** Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Richard Lord reports financial support, equipment, drugs, or supplies, and travel were provided by Northumbrian Water Ltd. Richard Lord reports financial support, equipment, drugs, or supplies, and travel were provided by European Union. Benjamin Nunn reports financial support, equipment, drugs, or supplies, and travel were provided by Northumbrian Water Ltd. Benjamin Nunn reports financial support, equipment, drugs, or supplies, and travel were provided by European Union. If there are other authors, they 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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Data availability

The data that has been used is confidential.

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