Lability, solubility and speciation of Cd, Pb and Zn in alluvial soils of the river Trent catchment UK

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Alluvial soils can store a wide range of metal contaminants originating from point and diffuse sources. The biological health of these soils is important as they act as an interface between terrestrial and aquatic environments, therefore playing an important role in maintaining the quality of surface waters. The aim of this work was to examine the lability, solubility and bioavailability of Pb, Zn and Cd in the top (0-15 cm) 10 and sub soil (35-50 cm) of metal contaminated alluvial soils from the Trent catchment, U.K. Samples (n=46) were collected from within 10m of the river bank. Sources of contamination include historical mining, industry, sewage treatment works and energy production. Enrichment factors based on total metal concentrations showed that contamination in soils declined with distance from the mining areas before rising again as a result of general urbanisation and identified point sources (e.g. river dredging activities). 15 Pore waters were extracted and isotopic dilution and single extraction assays were undertaken on the soils to assess the lability and solubility of the metals. Multi-element isotopic dilution assays were used to determine the labile pool or E-value of these metals in the soil. E-value concentrations were found to range between 0.5-14 mg/kg, 11-350 mg/kg and 25-594 mg/kg for Cd, Pb and Zn, respectively. Comparison of the E-value assay with the EU standard extraction assay for trace element availability 20 (0.05M EDTA) showed that EDTA extractions generally over-estimated the E-value for Zn and Pb, with the difference being greater as contamination levels increased. Bioavailability of the metals was assessed by speciating the pore waters [M_{Sol}] using WHAM 7 to obtain estimates of free ion activities (M^{2+}). Values of (M^{2+}) were compared to published 'median critical limits' for soils that estimate levels of protection for 95% of biological species. For each of the three metals, (M^{2+}) was found to exceed these 25 critical limits at some sites. Solubility of the metals are reported using K_d values expressed using both the total and E-value as the solid phase. Finally we examine the use of different metal pools (total, E-value, EDTA-extractable) and different measures of Fe oxide pools (total, free total, free amorphous), in predicting [M_{Sol}] concentrations and (M^{2+}) using WHAM 7 in assemblage modelling mode. Overall best simultaneous model predictions for the three metals were obtained using the E-values. Larger over-30 estimates of [M_{Sol}] and (M^{2+}) were produced using the EDTA and total metal pools whereas a better fitting in the prediction was obtained when models used either the total or the free total FeOx pools.

Introduction

Alluvial soils act as archives for fluvially dispersed metal contaminants from numerous sources [1-5]. These soils are often 35 used in intensive agricultural systems. Several studies in the UK have previously noted the potential for metal transfer into cattle, when grazing grass grown on contaminated alluvial soils [6-7]. In addition, these soils play an important role in the biogeochemical cycling of elements as they provide an interface between 40 terrestrial and aquatic ecosystems. Thus, the biological health of these soils is important as their microbial populations are essential for many of the biogeochemical cycles that can improve the quality of surface waters. For example, the alluvial soils of the River Trent are considered to have some of the highest de-45 nitrification rates in Europe due to the high nitrate use in agriculture within the catchment [8]. Therefore understanding the solubility and bioavailability of metal contaminants in these soils is important in relation to (i) plant uptake (grazing and cereal production), (ii) the health of soil biota and (iii) the transport of 50 contaminants into surface waters or into shallow floodplain aquifers. Whilst many studies have identified alluvial soils in the UK as having high total metal concentrations, often as a result of historical metal mining within their catchments [9-10], relatively few have looked at their speciation. One exception is that of Bradley 55 and Cox [1] who used sequential extractions assays to assess solid phase speciation in Hamps and Manifold valleys of the Peak District that form part of the wider Trent catchment.

This paper reports on the solubility and bioavailability of Pb, Zn and Cd in a range of alluvial soils taken from the Trent 60 catchment in the UK, based on isotopic dilution assays and pore water extractions. The Geochemical Baseline Survey of the UK (G-BASE) identified alluvial soils of the River Trent catchment as having elevated concentrations of a number of trace metals including Cd (2-4 mg/kg), Pb and Zn (>200 mg/kg) [11]. Sources of 65 this contamination include the natural dispersion of metals from ore deposits in the Peak District, the subsequent mining of these deposits (from Roman times to the mid-20th Century), coal mining, power generation and industrial and urban inputs. In addition Pb concentrations have been enhanced from the diffuse 70 deposition of tetra-ethyl Pb and its combustion products, used in petrol and phased out in the year 2000. Previous work by Izquierdo *et al.* [2] in the Trent catchment examined the sources

and lability of Pb in these alluvial soils and whilst several point sources of contamination were identified, the diffuse enrichment of Pb from petrol Pb was found to be widespread.

There are several ways in which the solubility of metals can be expressed. Values of K_d are commonly used as a basis for the assessment of metal and radio-nuclide solid:solution partitioning in soil [12, 13]. K_d values still underpin the use of several soil and plant uptake models such as CLEA (Environment Agency) [14] which provides soil guideline values for metal contaminants. Whilst K_d values are site-specific, they can be considered representative of steady-state conditions where the soil metal has reached a pseudo-equilibrium. Soil characteristics such as pH, humic substances, metal oxides, clay and total and extractable metal concentrations have been used as variables in developing empirical linear regression models predicting K_d values for use in wider eco-toxicological and uptake models [12, 15]. These regression models have helped develop understanding of the robustness of the relationships between solution metal and soil characteristics [12]. More recently, the free metal ion concentration or activity has been identified as the solution species that provides robust predictions of plant and microbial uptake of metals based on the Free Ion Activity Model (FIAM) or Biotic Ligand models [16, 17]. Soil Critical Limits for Zn, Cd and Pb have been developed based on free ion concentrations in solution [18, 19].

Whilst assessments of bioavailability based on measurements provide the most accurate indications of metal toxicity, models (e.g. WHAM, Visual Minteq, ORCHESTRA) increasingly are being tested in their ability to predict solution metal concentrations $[M_{Sol}]$ and free ion activity (M^{2+}), from a range of soil characteristics such as pH, organic C, humic substances, FeOx, MnOx, clay and metal pools [3, 20, 21]. The development of these models will allow greater use of the increasing number of available spatial geochemical datasets, including National Datasets and archives (e.g. G-Base [22]) to be used for assessments of metal bioavailability. A major factor in using these models and obtaining realistic outputs is that they require an accurate estimate of the 'labile' or 'reactive' pools of metal, as this is in equilibrium with the soil pore water. The measurement of the labile pool using isotopic dilution (ID) assays is generally accepted as the most robust and mechanistically sound estimate of reactive metals [23]. Methods for Cd, Zn and Pb have used both stable and radio isotopes [24-31]. However, as a result of the ID assay being analytically challenging through the use of either stable isotopes or potentially hazardous using radio-isotopes, analogues of the labile pool have been suggested and these include 0.43M HNO_3 and the EU standard 0.05M EDTA extractions [32-34]. However, rarely have either of these extractions been compared to the ID assay as (i) extractants or (ii) in predicting $[M_{Sol}]$ or (M^{2+}) in assemblage speciation models.

In this work we assess the solubility and bioavailability of Zn, Cd and Pb in a set of alluvial soils from the catchment of the River Trent. To assess solubility we report (i) soil pore water metal concentrations and (ii) K_d values based on total metal concentration and the isotopically exchangeable pool of metal. We assess the bioavailability of these metals by speciation of the extracted soil pore waters using WHAM7 and compare predicted free metal concentrations with the critical limits concept of Lofts *et al.* [18] and the updated critical limits published by de Vries *et al.*

[19].

Lastly we assess the use of WHAM 7 to predict soil pore water concentrations from a range of soil characteristics. We compare predictions of $[M_{Sol}]$ and (M^{2+}) using different estimates of the reactive pool of metals (ID, 0.05M EDTA extraction, total metal concentrations) and different estimates of the metal oxides likely to bind metal (total, total free and free amorphous Fe, Al and Mn oxides), the aim being to provide information regarding the best extraction assays to use in these models.

Materials and methods

Study area

The River Trent flows north through the Midlands of the UK and has a catchment area of nearly 10 500 km^2. It has a number of tributaries, including the Rivers Dove and Derwent which drain the Southern Pennine Orefield, flowing over the Carboniferous Limestone Formation (Fig. 1) where mineral veins are hosted. The main ore minerals are galena (PbS), sphalerite (ZnS) and pyrite (FeS_2), with minor amounts of non-sulphide minerals including cerussite ($PbCO_3$), smithsonite ($ZnCO_3$) and pyromorphite ($Pb_5[PO_4]_3Cl$) [35-36]. Lead mining in the Southern Pennine Orefield was first documented during Roman times and peaked during the 18th-19th century [37]. Mining and smelting activities have caused widespread pollution. An estimated area of 250 km^2 of land in Derbyshire is considered to be affected by Pb contamination [38]. Metal-rich sediments still pulse into the Trent tributaries in their upper catchments [39] and can be stored in floodplain soils dowstream.

Samples were collected along a 50 km long reach of the lower River Dove and a further 180 km reach of the middle and lower River Trent. The lower reaches of the Dove and the whole of the sampled Trent catchment flow over the Mercia Mudstone formation (Fig. 1). The section of the Trent downstream from King's Mill, Castle Donington (Fig. 1) has been regulated for flood control and navigation [40]. In the lower Trent, Quaternary sand and gravel river terraces have been reworked to form alluvial deposits (locally up to 10 m thick) on which the Holocene alluvial soils rest [41]. There is evidence that the floodplain deposits along the River Trent have been reworked throughout their entire depth in historic times.[40]. The close proximity of the Derbyshire-Nottinghamshire-Yorkshire coalfields (Westphalian Coal measures, Fig. 1) suggests that mining, smelting and industry have been additional sources of Cd, Pb and Zn contamination to the Trent catchment, particularly since the 18th century with the development of coal-fired steam for factories, and a number of coal fired power stations. Local coal was also used for smelting iron ore mined at Scunthorpe [11], close to the river Trent outlet at Trent Falls. Agriculture in the Dove valley is dominated by pasture for grazing whilst from the confluence of the Dove and Trent, arable agriculture dominates.

Soil and soil pore water collection

Soil samples were collected at 27 sites, 7 of which were from the River Dove floodplain, one was at the confluence between the Dove and Trent and the remainder along the floodplain of the middle and lower Trent (Fig 1). Generally samples were collected on naturally accumulated alluvial soils and at roughly equal distances within each of the 4 sections. Samples were not

collected between Newark and Scunthorpe on the River Trent because of the construction of artificial embankments as flood defences. Five sampling sites were located in woodland, whilst the remaining sampling sites were predominantly on improved/rough pasture or arable land within 10 m of the river bank. At 19 sites, paired top and sub-soil samples were collected at depths of 0-15 cm (topsoil) and 35-50 cm (subsoil). The soil sample depths were chosen to be compatible with those in the national geochemistry baseline survey of the UK (G-BASE) [22]. Each sample consisted of ~1.5 kg of a bulked sample from five sub-samples collected at the corners and the centre of a 5 m² grid. A portion of soil was used to extract > 30mL pore water using quartz filters and following the centrifugation method of Kinniburgh and Miles [42]. Pore waters were filtered and kept for further analysis of non-purgeable organic carbon (NPOC), major and trace elements, major anions and pH. The remaining soil was dried (<30°C), sieved to <2 mm and used for soil characterisation.

Soil characterisation

Soil pH was determined in 0.01M $CaCl_2$ at a liquid/solid ratio=2.5 L/kg. Loss on ignition (LOI) was undertaken at 450°C as a measure of soil organic matter. Particle size analysis was determined using a laser diffraction particle size analyser after organic matter had been destroyed using H_2O_2 until no further reaction with fresh H_2O_2. Estimates of soil amorphous and poorly crystalline oxides [$FeOx_{amorph}$] was determined using 0.2M ammonium oxalate and 0.125M oxalic acid and shaken in darkness for 2h following a method adapted from Schwertmann [43]. Total free oxides [$FeOx_{free}$] in soils were extracted by shaking soils in a solution of 25% (w/v) Na-citrate and 10% (w/v) Na-dithionite [44]. The humic/fulvic acids were extracted by shaking soils with 0.1M NaOH. An aliquot of the supernatant was brought to acidic pH by adding 1.5M HNO_3 to allow fulvic acids to precipitate out. All extracts were subsequently centrifuged at 2500 rpm for 20 minutes, the supernatant being filtered through a 0.45 μm nylon filter. Duplicate samples and blanks were all prepared in a similar manner.

Total metal concentrations of soil samples

Approximately 30 g of soil was sub-sampled and ground in an agate ball-mill to produce a fine homogeneous powder for acid digestion. Sample digestion was performed by accurately weighing 0.25g of soil into a Savillex™ vial and adding HF, HNO_3 and $HClO_4$ concentrated and analytical grade acids, with a subsequent stepped heating program up to 170°C overnight, the purpose being the digestion of silicate and oxide phases. The dry residue was re-constituted after warming with MQ water, HNO_3 and H_2O_2, to 25 mL of 5% v/v HNO_3 and stored in HDPE bottles. Reference materials (NIST SRM2710, SRM2711, GSS-6, BGS102 and BCR-2), duplicated samples and blanks were all prepared in a similar manner to check accuracy of the analytical and digestion method.

EDTA extraction

In order to provide an assessment of bioavailable Cd, Pb and Zn in soil samples, an extraction with 0.05M NH_4-EDTA was performed following the BCR-EU standard method as described by Quevauviller [34]. The samples were shaken for 1 h at a liquid to solid ratio of 10L/kg and subsequently centrifuged and filtered through a 0.45 μm filter. Blanks and duplicated samples were all prepared in the same manner.

Isotopic dilution assays

Multiple-element isotopic dilution techniques were used to measure labile Cd, Pb and Zn simultaneously as described by Marzouk [45]. Previous experience of undertaking stable metal ID assays has demonstrated that the selection of the background electrolyte is of great importance. It must be able to solubilise sufficient labile-metal for robust analytical analysis whilst not dissolving non-labile metal[24]. Soils with large clay contents, relatively large organic C and circum-neutral pH values such as many of these alluvial soils have the potential for insufficient metal to be solubilised for robust isotopic measurement. We therefore examined two electrolytes, EDTA [24] and $Ca(NO_3)_2$ [45]. All samples were measured using 0.0005M EDTA whilst a subset of 22 samples were analysed using the 0.1M $Ca(NO_3)_2$ electrolyte. These 22 samples are marked in Table S2 (Supplementary Information). To determine the concentration of labile Cd, Pb and Zn, six replicates of 2.0±0.1 g <2 mm sieved soil were placed in centrifuge tubes and shaken in 25 mL of electrolyte for 3 days, after which equilibrium is assumed to be achieved. After this period, three replicates of each soil suspension were spiked with 0.4-0.6 mL solution containing ^{108}Cd, ^{204}Pb and ^{70}Zn, whilst the three remaining centrifuge tubes were used to measure the natural isotopic abundances of these elements. The spiked and unspiked suspensions were re-equilibrated for a further 3 days. All suspensions were then centrifuged at 2500 rpm for 30 minutes and filtered through 0.20 μm cellulose acetate filters. Samples were divided into four batches with similar levels of metal contamination based on total Pb, Cd and Zn analyses. The spike addition was chosen to double the natural ^{108}Cd, ^{204}Pb and ^{70}Zn concentrations of the most contaminated soil in each batch. Blanks were all prepared in a similar manner. The labile pool or E-value was determined using Eqn.1:

$$E - value = \left(\frac{M_M}{W}\right)\left(\frac{C_{spike} V_{spike}}{M_{M\,spike}}\right)\left(\frac{^{label}IA_{spike}{}^{ref}IA_{spike}R_{SS}}{^{ref}IA_{soil}R_{SS}-^{label}IA_{soil}}\right) \text{(Eqn. 1)}$$

where M_M is the average atomic mass of the metal, C is gravimetric metal concentration (mg/L), V is the volume of added spike (L), W is the weight of soil (kg), $^{label}IA$ denotes isotopic abundance of the isotopes used for spiking the soil (^{108}Cd, ^{204}Pb and ^{70}Zn) in the spike or soil, ^{ref}IA is the isotopic abundance of the isotopes used as reference (^{111}Cd, ^{208}Pb and ^{66}Zn) in the spike or soil, and R_{ss} is the ratio of the isotopic abundances of the labelling isotope over the reference isotope in the spiked soil supernatant.

Analytical procedures - Element concentrations

The concentrations of elements were determined on the total digests, pore waters and EDTA extracts using an Agilent 7500 quadrupole ICP-MS instrument. The instrument was calibrated using a series of synthetic chemical solutions diluted from multi-element stock solutions (SPEX Certprep™), the calibration was validated using synthetic chemical standards from a separate source. Similarly multi-element synthetic quality control

standards for calibration verification were produced in-house, but, where possible, from different sources to the calibration standards. The calibration and quality control standards were inserted every 20 samples to check possible drift over the run. Data were corrected for blank contribution and possible interferences by running a number of blanks and synthetic chemical solutions of Ba, Ce, Gd, Nd, Pb and Sm. Iron concentrations in the Fe-oxide extracts was analysed by ICP-OES (Perkin Elmer Optima 7300DU). Anions in pore waters were analysed by ion chromatography (Dionex ICS-5000). Non-purgable organic carbon in pore waters and humic/fulvic acid extracts was measured using a Shimadzo TOC-Vcph analyser. Solution pH and HCO_3^- were measured using a Radiometer Analytical TIM865 titration manager.

Analytical procedures - Isotope analysis

The isotope ratios of isotope dilution extracts were determined using an Agilent 7500 quadrupole ICP-MS instrument. The instrument was prepared for isotope ratio determinations before each analytical session, by plateauing of the detector voltage, cross-calibration of the pulse counting-analogue mode and updating of the dead-time correction factors. Isotope ratio determinations were on the basis of 10 replicate integrations of 30s. Prior to analysis, all test portions were diluted using 1% HNO_3/0.5% HCl to give a count rate as close to, but below, 800kcps to produce best counting statistics within the linear range of the pulse counting detector. The issue of mass bias in the isotope ratios was addressed by determining the measured isotope ratio for single element solutions (Cd, Zn) and NIST SRM981 (Pb) regularly throughout the analytical session and producing interpolated correction factors of sample isotope ratios with reference to the accepted isotope ratios (IUPAC). Quality control for isotope ratios was performed using synthetic chemical solutions diluted from multi-element stock solutions (SPEX Certprep™).

Solution speciation and predictive modelling using WHAM 7

Speciation of soil pore waters

To assess the potential toxicity of the metals in the centrifuged pore waters on soil biota we compared free ion concentrations obtained using WHAM 7 [21] against the 'critical limits' published by Lofts et al. [18] and de Vries et al. [19]. Input data to WHAM 7 included solution pH, temperature (277 K) and solution concentrations of Na, Mg, Al, K, Ca, Fe(III), Mn, Ni, Cu, Zn, Cd, Pb, Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, F^- and PO_4^{3-}. Colloidal fulvic acid was also included assuming that fulvic acid contains 50% non-purgable organic carbon (NPOC) and only 65% was active, the remainder being inert with respect to ion binding [46]. The possible existence of sub-micron FeOx and AlOx colloidal complexes was overcome by including the FeOx and AlOx precipitation option in WHAM 7 where the metals are allowed to precipitate out with a surface charge [47].

Prediction of soil solution [M$_{Sol}$] concentrations

WHAM 7 model can also be used in assemblage mode where predictions of soil pore water metal concentrations [M$_{Sol}$] can be made from soil and solution characteristics [48]. Input to the model consisted of solid phase properties including temperature (277 K) soil pH, particulate humic acid (g/L), particulate fulvic acid (g/L), particulate FeOx (g/L), particulate MnOx (g/L), particulate AlOx (g/L) and particulate clay (g/L). Solution phase properties included were those described in the previous section with the exclusion of Zn, Cd and Pb which were included as the concentration of labile metal. These three metals were then modelled between the solid (sorbed) and solution phases. Comparisons were made between total, isotopically exchangeable and 0.05M EDTA extractable Zn, Cd, and Pb in the different model runs. We also assessed the differences in using the FeOx$_{total}$, FeOx$_{amorph}$ or FeOx$_{free}$ in the model output. Table 3 describes the different model runs tested.

Description of the dominant sorptive surfaces for the labile pools

When predicting metal solution concentrations from solid phase properties in WHAM7, model output also allowed an estimation of the proportion of labile metal that sorbs to each individual solid phase i.e. oxides, clays or organic matter across the pH range.

Results and discussion

General soil characteristics

The measured range of soil characteristics for the dataset is shown in Table 1 and Table S1 (Supplementary Information). The pH of soil samples shows a relatively narrow range (pH 5.3-8.0), with the majority of soils being near-neutral probably due to the influence of the limestone bedrock in the upper Dove catchment or as a result of agricultural liming. Fig 2 compares these properties in the topsoil (0-15 cm) and subsoil (35-50 cm). The pH measured for paired topsoil and subsoil from the same profile were similar, although there was a trend for samples being slightly more alkaline with depth, possibly due to the consumption of surface-derived H^+ by reaction with soil minerals [13]. Concentrations of organic matter expressed as LOI (4-18%), and humic/fulvic acids (1-10 g/kg) were greater in the topsoil than in the paired subsoil, the topsoil being the sink for modern carbon inputs from plant growth or for fresh C associated with sediment being deposited in floodplains. A further possible influence on organic C concentrations at depth (50 cm) is that some sediments sampled may pre-date the early Holocene [49] with the sand being deposited when Net Primary Production was lower and therefore carbon concentrations of sediment were lower than those of modern day deposited sediment. Total free iron oxides (FeOx$_{free}$) in soils did not vary greatly, ranging from 15 to 40 g/kg. Amorphous iron oxides (FeOx$_{amorph}$) for which metals have a particular affinity, were in the 4-20 g/kg range. The proportion of clay varied between 168 and 544 g/kg. No distinctive trend with depth for paired samples was observed for these soil parameters (Fig 2). The similarity in the soil properties, with the exception of the LOI, FA and HA observations, reflects the similar provenance of the material and the consistent mechanism of soil development with time.

Total Cd, Pb and Zn pools in soil

The total concentrations of Cd and Zn in the soils span little more than one order of magnitude (1-22 mg/kg for Cd, 160-2000 mg/kg for Zn), whilst the range of Pb concentrations spans nearly two orders of magnitude (40-1300 mg/kg, Tables 1 and S1). For

many of the paired top and sub-soil samples the metal concentrations were reasonably similar (Fig 2). Again, this is likely to reflect the way alluvial soils develop (erosion and re-deposition) and the consistent long term source of major metal contamination (e.g. the Peak District ore deposits). In some samples, higher metal concentrations are found in the top soil compared to the sub soil which suggests that there has been an additional, more recent source of pollution (e.g. sewage, coal combustion). However, in a few paired samples this trend is reversed and more highly metal-enriched soil is found in the subsoil (sites 21 and 14). These are investigated further in the next section.

There is a positive linear correlation between total Pb and Zn (topsoil r=0.85 $p<0.0001$; subsoil r=0.92 $p<0.0001$), between total Pb and Cd (topsoil r=0.70 $p<0.0001$; subsoil r=0.83 $p<0.0001$) and between Zn and Cd (topsoil r=0.87 $p<0.0001$; subsoil r=0.95 $p<0.0001$). The slightly improved relationships found in the subsoil datasets suggest that these soils may have been deposited when the Pennine ore source was the only major source of metals in the catchment. No significant relationships were found between Cd, Pb and Zn concentrations and the content of potential sorptive surfaces i.e. FeOx, organic carbon (LOI), humic and fulvic acids and clays.

Spatial distribution and enrichment factors

Across the whole dataset (top soil and sub soil) the concentrations of Cd, Pb and Zn are generally showed strong correlation (r=0.80-0.93, $p<0.0001$), indicating a similar source of metals for most sites throughout the study area. If sampling sites 8-13 (River section II on Fig 1) are excluded from the whole dataset, linear relationships increase to r>0.96 ($p<0.0001$), which (i) supports similar origin for the three metals and (ii) suggests the occurrence of a point source of contamination accounting for differential enrichment in metals along section II. To assist in the identification of contamination patterns, enrichment factors were calculated using the method of Tye et al. [50] (Eqn. 2). These relate the concentration of a given element 'X' in soil to a crustal element (e.g. Al), and the ratio is then normalised to the ratio in the regional background i.e. percentile 0.75 of topsoils derived from the Triassic Mercia Mudstone as reported in the Geochemical Baseline Survey (G-BASE) of the UK [11]. Enrichment factors <10 cannot be unequivocally and confidently discriminated from the background [50].

$$EF = \frac{X_{soil}}{Al_{soil}} \times \frac{Al_{G-Base}}{X_{G-Base}} \quad \text{(Eqn. 2)}$$

The spatial distribution of Cd, Pb and Zn concentrations and EFs throughout the study area were split into 4 river sections (Fig 1 and 3, Tables 1 and S1), with the starting point (0 km) on the edge of the Southern Pennine Orefield, taken as the limits of the mineralised Derbyshire Carboniferous limestone. The distribution profiles (Fig 3) reveal a minor enrichment in Cd, Pb and Zn in the soils from the Dove catchment (Section I), with little difference between top and subsoils. This likely reflects the presence of Pennine ore-rich sediments carried down the river Dove from the mineralised Derbyshire Carboniferous Limestone upstream. This is supported by the Southern Pennine ore Pb isotopic signatures of these soils described in Izquierdo et al. [2]. Like other river systems in the UK, the metal concentration was found to decline with distance from the former mining area [51]. A rapid decrease in concentration was noted for the 3 metals, for which background concentrations (EFs<10) were determined in soils 15 km downstream. After the confluence of the Dove with the Trent (Fig 1), metal concentrations in most sub soils along Section II remain close to background levels (EF<5). By contrast, metal loadings in most topsoils increased to concentrations 3-6 times higher than the paired subsoil, with EF≈11-15 for Cd and Zn, whilst Pb enrichment in top soil compared to the paired subsoils was less significant (EF≈7). The presence of sewage works before this stretch of river that floods regularly should be considered as possible point pollution source of recent Cd and Zn inputs (and Pb to a lesser extent). Section III is characterised by soil profiles greatly enriched in metals, more prominently in subsoil (EF≈10-26) than in top soil (EF≈8-17). The distribution pattern along this section is identical for the 3 studied metals (Fig 3), strongly suggesting the same provenance. The lower River Trent was extensively used for commercial navigation until the 1950s. Historical records provide evidence of improvements such as large-scale dredging of a number of sections. Artificial riverbanks constructed with dredged sediments would act as historical reservoirs of metals from various sources, with possibly an important coal/ore contribution as these products were also transported on the river. Direct evidence for current and recent dredging and the subsequent storing of dredged material has been found at some of these sampling sites. This would account for the anomalous enrichment in metals at a number of sites along this section, with concentrations in the 300-2000 mg/kg range for Pb and Zn and 2-22 mg/kg range for Cd. These samples typically have greater metal concentrations in the sub soil strongly supporting the idea that these soil profiles have been anthropogenically modified. The progressive dilution of sediment and the absence of major point-source pollution directly affecting the southern bank of the Humber Estuary results in Cd, Pb and Zn concentrations close to background levels (EF<5) throughout the soil profiles in Section IV. A minor increase in the Pb and Zn concentrations in Site 27 (Humber Estuary) compared to Site 26 may be associated with local atmospheric deposition of particulate material from the Capper Pass smelter on its northern bank [50].

Extractable Cd, Pb and Zn pools

The extractable pools using 0.05M EDTA were strongly correlated with the total pools for the 3 metals (r>0.96, p<0.0001, Fig S1). Only 13-46% of Zn was extractable (interquartile range: 26-36%) with 0.05M EDTA. The slope of the linear correlation was ≈0.35 and suggests that a large proportion of Zn in soils is inaccessible and aggressive conditions are needed to release this metal. This is consistent with the findings of Tipping et al. [32] for a dataset of 98 soils. Greater slopes were determined for Pb and Cd (>0.50), suggesting that these elements are not as tightly bound to soil but exist in more available forms. It was found that between 23-67% of Pb (interquartile range: 42-57%) was extractable with 0.05M EDTA. Cadmium was the most available metal in the soil dataset as 46-80% (interquartile range: 63-73%) of the total Cd was found to be extractable. No clear relationships between the extractable concentrations and relevant soil parameters such as pH, LOI or free FeOx concentrations were

found.

E-values - method validation and comparison of suspending electrolytes

We tested 0.1M Ca(NO$_3$)$_2$ and 0.0005M EDTA as background electrolytes for the multiple element isotopic dilution assays. Results demonstrated that neither background equilibrating extractant was uniquely suitable for the analysis of Pb, Zn and Cd for all samples.

For Pb, 0.1M Ca(NO$_3$)$_2$ failed to solubilise a sufficient proportion of the labile pool to allow robust measurements of Pb isotope ratios (Coefficient of variation (CV) 1-22%). However, using 0.0005M EDTA as suggested by Atkinson et al. [24], allowed more analytically robust Pb isotope measurements to be obtained for all soils (E-values with CV <0.4-7%), as previously reported by Izquierdo et al. [2]. Thus, the final dataset for Pb modelling (Table S2) contains only E-values obtained using 0.0005M EDTA as the background electrolyte.

For Zn, 0.0005M EDTA as a background electrolyte solubilised sufficient concentrations for analytical purposes for all samples and the replicates showed low CV values (0.5-6%). However, for those soils where Zn <400 mg/kg, the concentrations of Zn extracted by 0.0005M EDTA were sometimes greater than the isotopically exchangeable pool (E-value). This indicates that non-labile Zn was being solubilised, therefore contradicting one of the fundamentals of isotope dilution [52]. Whereas the 0.1M Ca(NO$_3$)$_2$ electrolyte is unlikely to mobilise non-labile Zn, the variability of the replicates was greater (CV 1-23%) than using 0.0005M EDTA suggesting that it was not as efficient at solubilising sufficient labile Zn for isotope analysis. Thus, in the final dataset most E-values for Zn are those where 0.0005M EDTA was used as a background electrolyte with the exception of those indicated (Table S2). For three samples, reliable results were not obtained because neither background electrolyte was suitable (Table S2). For each of these soils, Ca(NO$_3$)$_2$ solubilised too little Zn to obtain accurate isotope measurements whilst EDTA was found to access Zn in non-labile forms.

For Cd, both background equilibrating solutions were found to solubilise sufficient Cd for isotope analysis and conform to the fundamentals required for ID assays [52, 53]. The EDTA extractant was found to be suitable for the determination of the E-values of Cd (CV 1-17%). Thus, in the final dataset most E-values for Cd are those where 0.0005M EDTA was used as a background electrolyte with the exception of those indicated (Table S2).

For those samples where both electrolytes produced robust measurements of isotopically exchangeable Cd (n=21), Pb (n=22) and Zn (n=14) we compared their values (Fig 5). Results showed excellent agreement in the concentration of labile metal between the two background electrolytes, although Ca(NO$_3$)$_2$ tends to slightly overestimate the labile Zn and underestimate the labile Cd compared to the use of 0.0005M EDTA (Fig 5).

E-values - concentrations

E-values strongly correlated the total pools (r=0.95, 0.84 and 0.97 for Cd, Pb and Zn respectively, p<0.0001). The labile pool (E-value) of Cd, Pb and Zn span more than one order of magnitude (0.5-14 mg/kg, 11-350 mg/kg and 25-594 mg/kg, respectively) (Table 1 and S2). Cadmium was found to be the most isotopically

exchangeable metal, with % E-values relative to the total metal pool in the 46-94% range. This high reactivity is in agreement with literature values for a range of unpolluted to heavily polluted soils i.e. 3-100% and typically 30-60% [25, 27-30]. Cadmium is often the most labile metal in soils [29, 31]. Lead displayed a lower reactivity and the lability ranged between 9-56%, which was on the lower range for %E$_{Pb}$ values in the literature i.e. 31-78% [17, 24, 26, 54-55]. Zinc was the least geochemically responsive metal, with only 13-37 % labile across the dataset. These values are in agreement with typical mean values in a range of polluted and unpolluted soils i.e. 10-33% [25, 27, 30].

Whilst the linear correlations between the total pools of Cd and Zn and their distribution patterns across the sampling area support a similar origin, their lability is decidely different. This suggests that, despite having similar input pathways accounting for similar enrichments, after entering the soil system the processes controlling their speciation varies. This is in line with the findings of Marzouk [45] for soils from a catchment similarly affected by former mining activities in the UK. They reported a relative lability decreasing in the order Cd>Pb>Zn, the suggestion being that Zn is fixed within the soil matrix e.g. occluded in Fe oxides. Römkens et al. [56] also found that whilst Zn become immobile due to fixation on oxyhydroxides, Cd tends to remain potentially available. Other authors have also reported greater fixation of Zn than Cd [25, 57, 58].

Despite a relatively narrow range of soil pH values within the dataset, a linear decline in Cd and Pb lability with increasing pH was observed (Fig 5) (r = –0.57 for Cd and r = –0.64 for Pb, p<0.0001). The trend was more parabolic around neutral pH for Zn, possibly as a result of several acidic soils from the Dove floodplain showing low values of labile Zn. Their provenance strongly suggests occlusion of Zn in ore minerals. If these 4 soils (topsoil site 4 and 7, topsoil and subsoil site 5) are excluded, a weaker but still significant (p<0.01) negative correlation between % E with pH was also determined for Zn (r = –0.40, p<0.01). Other authors have reported negative correlations between the lability (% E) of Cd, Pb, Zn and pH in acidic to near-neutral soils [25, 31, 58]. Cadmium, Pb and Zn adsorption onto oxides follow the basic trend of increased absorption with pH [59] and therefore the pH influences the E-value [23]. No strong correlations between %E and sorptive surfaces FeOx$_{total}$, FeOx$_{free}$, FeOx$_{amorph}$, humics and fulvic acids, LOI or clays were found. This is likely to reflect the fact that metal lability in soils depends on a combination of inter-related soil properties, with the greatest influence being pH. For Zn, there appears to be an additional total Zn concentration control on the % lability, which is probably source related. Whilst those soils with lower concentrations of Zn (<400 mg/kg) typically have a low % lability (13-20%), where the soil profiles have higher concentrations (Zn>500mg/kg), the %E value is invariably higher i.e. 20-40% (Fig S2). This suggests that large Zn inputs such as those attributed to dredging in several soil profiles along Section III are in relatively more labile forms. No obvious trend was observed for Cd and Pb, although their highest concentrations in soils are associated with their lowest lability (Fig S2), suggesting that high enrichments occur primarily in less labile forms.

There was little difference in % lability of Cd, Pb and Zn with depth, likely due to the soil characteristics involved in controlling

metal sorption (clay, organic matter, oxides, soil pH) not showing distinctive trends with depth (Fig 2). This may also result from soils close to the river banks being subject to continual erosion and deposition processes over time, thus it is likely that the metals in these soils have been in contact with the soil particles for significant periods of time and therefore have undergone long-term fixation processes.

Comparison of extractable and labile pools

We compared the final dataset of labile Zn, Cd and Pb with their corresponding 0.05M EDTA extraction values (Fig 6). EDTA can be a powerful extractant as it can mobilise metal adsorbents such as MnO_2, $FeOOH$ and $CaCO_3$ thus accessing the non-labile reservoir [30]. As described by Ahnstrom and Parker [60], comparison of E-values and EDTA extracts in the literature have yielded variable results. The effectiveness of EDTA as an analogue for the E-value appears to be metal specific and dependent on the concentration of EDTA used. For example, Gäbler *et al.* [27] reported a good agreement between the labile pool and a 0.025M EDTA extractable pool for a set (n=115) unpolluted soils (mean Cd 33% lability) and for polluted soil (>70% lability). However, Degryse *et al.* [25,] Nakhone and Young [28] and Young *et al.* [30] all reported mobilisation of non-labile Cd when concentrations >0.025M EDTA were used. In this study, a good agreement for Cd was found between the two assays, particularly at low concentrations. However for Zn, and particularly Pb the 0.05M EDTA extractant was found to over-estimate the E-value, particularly as concentration increased. The slopes (<1) in Fig 6 indicate that 0.05M EDTA accesses Pb and Zn hosted in non-labile forms and therefore cannot be effectively used as an estimate for the labile pool of metal.

Soil solution pools

Soil pore water properties and concentrations of Pb, Zn and Cd are shown in Tables 2 and S3. The pH of pore waters varied between 5.0 and 8.9 and showed little variation with depth. NPOC concentrations also showed little variation with depth and ranged between 14–63 mg/L. Concentration ranges for Pb (0.17 - 6.47 µg/L), Zn (17 – 786 µg/L) and Cd (0.12 – 8.73 µg/L) were generally similar in the top and sub soils, with exceptions being where there were significantly higher levels of contamination in either the top or sub soil. These overall patterns reflect the similar characteristics of the soil properties that contribute to controlling solubility (Fig 2). There were generally poor correlations between $[M_{Sol}]$ and solution pH, reflecting the significant contributions of other factors such as metal concentration, soil texture and the concentrations of other sorptive surfaces in the different soils. No significant correlations were found between Pb, Zn and Cd concentrations in pore solution and NPOC. There were strong relationships between $[Zn_{Sol}]$ and $[Cd_{Sol}]$ (r=0.89 and r=0.86 for the top and subsoils respectively, both $p<0.0001$). However, there were only poor linear correlations (r<0.50) between Pb and Zn or Cd.

K_d values

The liquid-solid partition coefficient K_d is used as a means to quantify the tendency of an element to bind to soil surfaces [13]. Values of K_d reported represent the specific solid-solution equilibria for specific sample sites (Eqn 3). These are generally expressed based on total metal concentration. However, for risk assessment models using K_d values, a more accurate assessment could be based on the labile metal that is in equilibrium with pore water, rather than the total metal concentrations [57].

$$K_d = \frac{M_{(total\ or\ labile)\ pool}}{M_{pore\ water}} \quad \text{(Eqn. 3)}$$

We present K_d values based on both total metal and labile metal pools (Table 2 and S3). For Cd and Zn, the range of values for the total pool was between log K_d 2.7–4.7 and for the labile pool was log K_d 2.0–4.2. Greater values were obtained for Pb, with log K_d 4.5–6.6 L/kg and 4.1–6.0 L/kg for the total and labile pools, respectively. This suggests that although 25% (on average) of the total Pb in the studied soils is labile, this fraction is not readily soluble but strongly adsorbed/bound to soil. The USEPA [61] reported log K_d in the 1.7–4.1 range for Cd, 0.7–5.0 for Pb and -1.0–5.0 for Zn.

Despite the large variability, the K_d based on both total and labile pools for Pb was greater than that for Cd and Zn (Table 2). The K_d values for the present dataset are on the high side relative to these literature values, which can probably be attributed to the circum-neutral pH in this study samples. K_d values using the labile pool for each metal is understandably lower than that for total pool, as the labile pool is only a proportion of the total. A narrower variation was observed for Cd due to its great lability (typically 70%). There were significant linear correlations (r=0.51–0.76, $p<0.0005$) between soil pH and Log K_d values for both the total and labile pools with Log K_d values increasing with pH, demonstrating the dominant effect of pH on solubility.

Metal speciation in solution

WHAM 7 was used to speciate the centrifuged pore waters to predict values of free ion activity (M^{2+}) for Cd, Zn and Pb. Whilst $[M_{Sol}]$ showed poor linear correlations with both soil and solution pH, better but still weak correlations of r= –0.49, –0.64 and –0.58 ($p<0.001$) were found between pore water pH and Cd, Zn and Pb metal activity respectively.

Values of (M^{2+}) were assessed in relation to the 'Soil Critical Limits' published by de Vries *et al.* [19], which are based on free metal ion concentrations (Fig 7). We use the 'median soil critical limit' for each metal which has been derived from toxicological test end point data for soil micro-organisms, plants and soft bodied invertebrates and aims to protect 95% of species and processes at a confidence interval of 50 %. Where (M^{2+}) is greater than the critical limit for a given pore water pH it would suggest that metal activity in solutions may be detrimental to soil biological life. Results show that for Cd and Zn, around half (50 and 58% respectively) of samples exceeded the median critical limit. This proportion was lower for Pb, with 37% of the soil samples above the critical limit. No particular difference between top and subsoils was observed.

Prediction of concentration of metals in pore water

We tested different soil metal pools i.e. total, labile (E-value) and extractable (0.05M EDTA) and different Fe, Al and Mn pools (total, free total and free amorphous) for their suitability in predicting $[M_{Sol}]$ simultaneously for Zn, Pb and Cd. The results

of the different modelling scenarios undertaken are reported using Residual Standard Deviation (RSD) and Mean Bias Error (MBE) (Table 3) as per the equations below (Eqn 4 and 5).

$$RSD = \sqrt{\sum \frac{(observed - predicted)^2}{n}} \quad (Eqn. 4)$$

$$MBE = \frac{(observed - predicted)}{n} \quad (Eqn. 5)$$

Overall the RSD and MBE are the lowest when the E-value is used in predicting $[M_{Sol}]$ for each metal. It is accepted that $[M_{Sol}]$ is derived from the labile pool of metal and the considerable improvement in model RSD and MBE values found when using the labile or the EDTA-extractable pools of metal compared to the total metal pool, confirms this hypothesis. Error in the prediction of $[M_{Sol}]$ was smaller for Zn and Cd using the E-value than when 0.05M EDTA was used. For Pb, the 0.05M EDTA pool appeared to give slightly improved estimates compared to the E-value. However, because the EDTA extraction greatly overestimated the labile Pb compared to the E-value (Fig 6), WHAM 7 appears to have compensated for the extra Pb sorption (particularly on FeOx and MnOx) by over prediction of Zn and Cd in solution $[M_{Sol}]$. Thus, the benefit of using the E-value is that (i) it provides a mechanistic basis for solid-solution equilibria and (ii) it does not lead to excessive extraction of one metal as demonstrated by the 0.05M EDTA extraction. Thus improved estimates of $[M_{Sol}]$ for multiple metals predicted simultaneously can be made because the concentration of metal used in the model does not result in over-consumption of sorptive surfaces. Differences in model predictions of $[M_{Sol}]$ were also examined using different Fe oxide phase pools. Overall, there was little difference when using either $FeOx_{total}$ or $FeOx_{free}$ pools in WHAM 7, largely because both pools are quantitatively similar. In most instances the $FeOx_{amorph}$ pools provided the greatest error in $[M_{Sol}]$ estimation (Table 3).

Fig 8 shows the best fit observed vs predicted graphs for the three metals using the E-value (Option 2; Table 3). Lead was found to be modelled most accurately followed by Zn and then Cd. There was no systematic difference in the ability of WHAM7 to predict $[M_{Sol}]$ in the top and subsoil samples. Whilst for Zn and Pb most predictions fell within ±1RSD of the model, there was a tendency for bias in the predictions. For example, Pb predictions had a slight bias to underestimate the concentration of $[Pb_{sol}]$ and for Zn there was a slight overestimation of $[Zn_{Sol}]$ with a Mean Bias Error (MBE) of 0.79. However, for all the different model runs, there was a greater overestimation of $[Cd_{Sol}]$. In addition, assuming that all the Fe in soil is present in forms onto which metals could bind (options 1, 4 and 7, Table 3) does not greatly improve $[Cd_{Sol}]$ predictions compared to those options where $FeOx_{free}$ or $FeOx_{amorph}$ are considered. Thus, we consider that the greatest source of error in the prediction of $[M_{Sol}]$, in particular for Cd, is in the relationship between the E-value and $[M_{Sol}]$. Thus the E-value used could be too great to accurately predict $[M_{Sol}]$ through (i) the presence of non-labile colloidal complexed metals in the equilibrating solution being included within the E-value measurement and (ii) the lack of a carbonate surface for

metals to bind on within WHAM7. The presence of non-labile colloidal metal being counted within the ID assay can result in a small overestimation of the labile pool of up to 5% and some researchers have used resins to separate the 'aqueous dissolved' from 'colloid/micro-particulate bound' metal before analysis [45]. Non-labile colloidal complexes of metals may include those with DOC or sub-micron FeOx. However, the use of EDTA as a background electrolyte prevents the resin step being taken as EDTA will compete strongly with the resin for the metals. The second potential source of error in the prediction of $[M_{Sol}]$ may derive from the absence of a calcite phase for sorption in the model. All three metals (Pb, Zn, Cd) are known to sorb onto calcite and will eventually precipitate if their Ion Activity Product is exceeded [62-65]. Cadmium in particular has a strong affinity for calcite as it has a similar ionic radius and hydration energy to Ca [66] and has been found to sorb in preference to Pb on calcite surfaces [67]. As a major source of the Zn, Cd and Pb in the alluvial soils are the ore bodies in the limestone of the Peak District (Fig 1), some calcite binding of metals is likely[68]. Recent work has described Cd sorbed on calcite as being either 'labile' or 'non-labile' where labile Cd sorbed to calcite is in immediate equilibrium with free Cd^{2+} ions whilst 'non-labile' Cd on calcite is kinetically restricted [69]. Thus in our work, whilst the isotope dilution assay will account for any labile Cd, Pb or Zn sorbed onto the surface of calcite, WHAM 7 does not include this surface within its database for the labile metals to be re-distributed in model predictions.

Prediction of free ion concentrations

A model's ability to successfully predict $[M_{Sol}]$ and (M^{2+}) will enhance their use in understanding the response to future changes in soils conditions. Such changes may include the long-term accumulation of metal via deposition or a major industrial spill. Output from models such as WHAM 7 can be linked to the Critical Limits concept [18-19] described earlier. Therefore, the predictions of free ion concentrations produced using the best fit model (Option 2, Table 3) were tested against the critical limits for each metal and in comparison to the free ion concentrations predicted by WHAM7 when speciated using only the porewater data (Fig 7). The predicted concentration of (M^{2+}) will be correlated with the prediction of $[M_{Sol}]$. Thus, the over prediction of $[Zn_{Sol}]$ and $[Cd_{Sol}]$ is reflected in the concentrations of free ions (Zn^{2+}) and (Cd^{2+}) predicted. This gives rise to conservative estimates of the number of soils that exceed the critical limits for these metals i.e. 60-70% of the topsoils and 100% subsoils. However, for Pb there is good agreement between the pore water speciated values of (Pb^{2+}) and the modelled predictions using the labile metal pools. Table 4 shows the MBE and RSD between the pore water speciation of metal ion concentration and the predicted metal ion concentrations using the best fit isotopic dilution (Option 2, Table 3) and 0.05M EDTA (Option 5, Table 3). Results again show that the estimation of the labile pool of metal using isotopic dilution gave slightly improved results as compared to the 0.05M EDTA extraction.

Prediction of dominant sorptive surfaces

Despite the lack of a carbonate phase in the model options it is informative to examine the solid phases that the labile pool of each metal is likely to favour across the pH range (Fig 9). For Pb,

it was found that sorption was almost entirely related to FeO_x and MnO_x; with sorption to FeO_x being greater at pH >7 and sorption to MnO_X being greater at pH < 7. Although Pb has a strong affinity to bind with organic matter, it has been suggested that it has far greater affinity for sorption to oxides than for organic matter [70, 71]. However, whilst labile Pb was found to bind predominately to the oxides, its ability to desorb is greater than that of Cd and Zn. The large ionic radius of Pb prevents it from being readily incorporated into the metal oxide structure during re-crystallisation and ageing processes, thus remaining primarily surface associated [72]. This may help explain the higher than intuitively expected lability of Pb found in this and other studies [24, 26] where previously it was assumed that Pb sorbs strongly both to poorly crystalline oxides and organic matter.

With Pb occupying many of the sorption sites on the oxides, the labile Cd and Zn are more evenly distributed in other binding phases. For Zn, sorption to the HA/FA phases was dominant below pH 7 with sorption to FeO_x increasing at pH >7. For Cd, MnOx accounted for up to ~60% of the sorption at pH 6 but this figure decreased with subsequent increasing pH, with FeOx becoming more important when pH >7. Whilst Fig 9 provides an indication of the preferred binding sites for the labile pools of Cd, Zn and Pb, other metals will also be present in the soil that may change the relative amounts of metal that bind to these surfaces and include Ni, Cu and Co.

Conclusions

We examined the bioavailability and solubility of Pb, Zn and Cd in a range of alluvial soils collected close to the river Trent, this area representing a major interface between the terrestrial and aquatic environments. Many of the soils within the dataset were enriched in Pb, Zn and Cd with the major historical source being the Peak district ores. A divergence between historical and modern contamination occurred downstream as the top soils developed higher enrichment factors indicating additional sources of contamination rather than just the Peak ore bodies. Pore-water extractions and speciation suggested that levels of contamination in some of these soils exceeded the 'critical limits' for the respective metals and could be detrimental to the soil biota. Soil extractions showed that the EU standard 0.05M EDTA largely overestimated the labile pools of Zn and Pb when compared to isotopic dilution assays, especially at high concentrations. This was reflected in the modelling exercise to predict [M_{Sol}] for the three metals, where reasonably accurate model predictions were obtained using the isotopically exchangeable pool of metal. This confirms the efficacy of isotope exchange methodologies when providing input data to geochemical models. However, further understanding of calcite surface sorption and non-labile colloidal metal is required. Results of this study show that although much of the contamination of the soil is historical, the concentrations of metals are such that significant bioavailability remains. This is likely to be the case in the alluvial soils of many other river systems draining historical mining and industrial areas in the UK.

Notes and references

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Table 1: Ranges of variation of general characteristics and lability of Cd, Pb and Zn of the alluvial soils sampled from the Trent Catchment, UK. The full dataset is reported in Tables S1 and S2.

| | units | Topsoils 0-15 cm | | | | | Subsoils 35-50 cm | | | | |
		min	p25	median	p75	max	min	p25	median	p75	p100
Clay	g/kg	179	281	336	443	544	168	290	356	404	500
Soil pH	-	5.8	6.5	7.1	7.3	7.8	5.3	6.8	7.1	7.5	8.0
LOI	% wt	6	9	11	14	18	4	7	7	9	14
$FeOx_{free}$	mg/kg	17141	23865	27649	31869	39228	15026	21818	30108	35382	40716
$MnOx_{free}$	mg/kg	733	1481	1576	1808	2809	775	1286	1463	1853	4730
$AlOx_{free}$	mg/kg	875	1284	1635	1938	2398	763	1269	1478	1964	2401
Humic ac.	mg/kg	1248	3974	6142	7685	10480	1048	1975	3188	4564	7136
Fulvic ac.	mg/kg	1782	3505	4376	7179	8773	1135	1610	2190	2928	4426
Total Pb	mg/kg	84	167	241	363	860	43	113	241	507	1282
Pb E-value	mg/kg	11	47	72	96	315	12	32	70	164	273
Pb % E	% wt	12	23	27	35	50	9	22	24	37	56
Total Zn	mg/kg	198	382	572	722	1474	158	290	419	999	2033
Zn E-value	mg/kg	25	77	150	194	412	37	65	180	303	594
Zn % E	% wt	13	21	24	28	37	13	23	26	30	35
Total Cd	mg/kg	0.8	3.8	6.2	8.0	16	1.0	2.3	5.3	10	22
Cd E-value	mg/kg	0.5	2.9	4.2	5.9	8.8	0.5	1.9	3.4	6.6	14
Cd % E	wt %	55	67	74	82	94	46	62	68	75	90

Table 2. Characteristics of extracted soil solutions including [M_{Sol}] and calculated K_d values for soils sampled from the Trent Catchment. The full dataset is reported in Table S3.

	Units	Topsoils 0-15 cm					Subsoils 35-50 cm				
		min	p25	median	p75	p100	min	p25	median	p75	p100
Solution pH	-	5.79	6.47	7.57	7.86	8.90	5.03	6.88	7.23	7.74	8.16
DOC	mg/L	19	23	27	32	62	14	22	30	37	63
[Pb_{sol}]	µg/L	0.2	0.5	1.0	2.1	6.5	0.2	0.4	0.9	1.3	2.6
[Zn_{sol}]	µg/L	17	30	53	92	786	22	38	67	83	396
[Cd_{sol}]	µg/L	0.1	0.5	0.7	1.5	8.7	0.1	0.5	0.7	1.0	3.3
Log Kd_{Tot} Pb	L/kg	4.5	4.9	5.5	5.7	6.1	4.6	5.0	5.6	6.0	6.6
Log Kd_{Tot} Zn	L/kg	2.9	3.6	4.1	4.3	4.6	2.7	3.6	4.0	4.3	4.7
Log Kd_{Tot} Cd	L/kg	2.9	3.6	3.9	4.0	4.3	2.8	3.8	3.9	4.1	4.2
Log Kd_{Lab} Pb	L/kg	4.1	4.5	4.9	5.1	5.5	4.1	4.6	4.8	5.3	6.0
Log Kd_{Lab} Zn	L/kg	2.4	2.9	3.4	3.8	4.0	2.0	3.0	3.5	3.8	4.2
Log Kd_{Lab} Cd	L/kg	2.8	3.5	3.7	3.9	4.1	2.7	3.5	3.8	3.9	4.1

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Table 3. WHAM 7 model scenarios tested and their prediction of [M_{Sol}]. Mean Bias Error (MBE) and Residual Standard Deviation (RSD) (Eqn 4 and 5) are shown for each model run.

Option	Soil Characteristics included	Cd		Zn		Pb	
		MBE	RSD	MBE	RSD	MBE	RSD
1	Labile Cd + Labile Zn + Labile Pb + Total Fe, Total Mn, Al$_{free}$	0.94	0.98	0.61	0.77	-047	0.67
2	Labile Cd + Labile Zn + Labile Pb + Fe$_{free}$, Mn$_{free}$, Al$_{free}$	0.96	0.98	0.65	0.79	0.44	0.65
3	Labile Cd + Labile Zn + Labile Pb + Fe$_{amorph}$, Mn$_{amorph}$, Al$_{amorph}$	1.20	1.20	0.79	0.92	-0.05	0.49
4	0.05M EDTA Cd + EDTA Zn + EDTA Pb + Total Fe, Total Mn, Al$_{free}$	1.02	1.06	0.78	0.92	-0.16	0.62
5	0.05M EDTA Cd + EDTA Zn + EDTA Pb + Fe$_{free}$, Mn$_{free}$, Al$_{free}$	1.03	1.08	0.81	0.94	-0.14	0.65
6	0.05M EDTA Cd + EDTA Zn + EDTA Pb + Fe$_{amorph}$, Mn$_{amorph}$, Al$_{amorph}$	1.29	1.34	0.97	1.10	0.27	0.70
7	Total Cd + Total Zn + Total Pb + Total Fe, Total Mn, Al$_{free}$	1.20	1.24	1.29	1.36	0.09	0.47
8	Total Cd + Total Zn + Total Pb + Fe$_{free}$, Mn$_{free}$, Al$_{free}$	1.24	1.28	1.33	1.41	0.13	0.53
9	Total Cd + Total Zn + Total Pb + Fe$_{amorph}$, Mn$_{amorph}$, Al$_{amorph}$	1.55	1.60	1.54	1.62	0.59	0.77

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Table 4: Comparison of MBE and RSD values (Eqn 4 and 5) when using WHAM 7 to predict (M^{2+}) by (i) pore water speciation and (ii) using either the ID or 0.05M EDTA pools of labile metal to predict (M^{2+}) when WHAM 7 is used in assemblage model mode.

	Isotopic Dilution		0.05M EDTA	
	MBE	RSD	MBE	RSD
Log (Zn^{2+})	-0.78	0.96	-0.90	1.07
Log (Pb^{2+})	-0.04	0.12	-0.32	0.43
Log (Cd^{2+})	-1.06	1.15	-1.13	1.18

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FIGURE CAPTIONS

Fig. 1   Geological map of the River Trent catchment with tributaries including the River Dove and sampling sites

Fig. 2   Scatter plots for a number of soil characteristics in paired topsoils and subsoils. The 1:1 line is shown.

Fig. 3   Distribution of enrichment factors (EFs) in the topsoil (black) and subsoil (grey). The calculation of Efs is described in Eqn. 2

Fig. 4   Comparison of E-values using two different suspending electrolytes i.e. 0.1M $CaCl_2$ and 0.0005M EDTA. The 1:1 line is shown.

Fig. 5   Comparison of E-values as a percentage of total metal concentration with soil pH.

Fig. 6   Comparison of 0.05M EDTA extractable and labile (E-value) metal concentrations (mg/kg). The 1:1 line is shown.

Fig. 7   Free ion concentrations, log (M^{2+}) in soil pore waters centrifuged from Trent catchment soils in relation to critical limits published by de Vries et al. (2007). Pore water speciation is plotted against the pore water pH whilst model prediction is plotted against soil pH.

Fig. 8   Comparison between observed and predicted concentrations of Cd, Pb and Zn in soil pore waters using WHAM7 (option 2 Table 3). The solid line represents the 1:1 line whilst dashed lines represent ±1RSD. (O) and (+) represent topsoils and subsoils, respectively.

Fig. 9   The solid phases that the labile pools of Cd, Pb and Zn are associated with, from predictions of WHAM 7 using modelling Option 2 (Table 3)
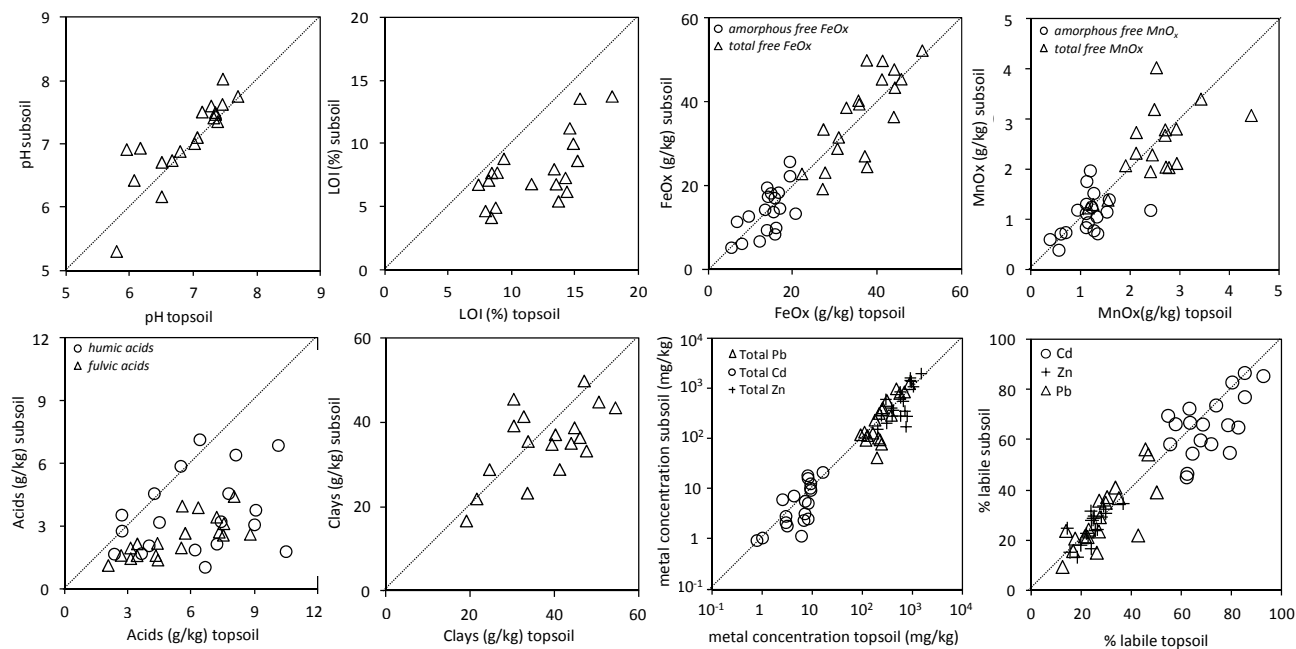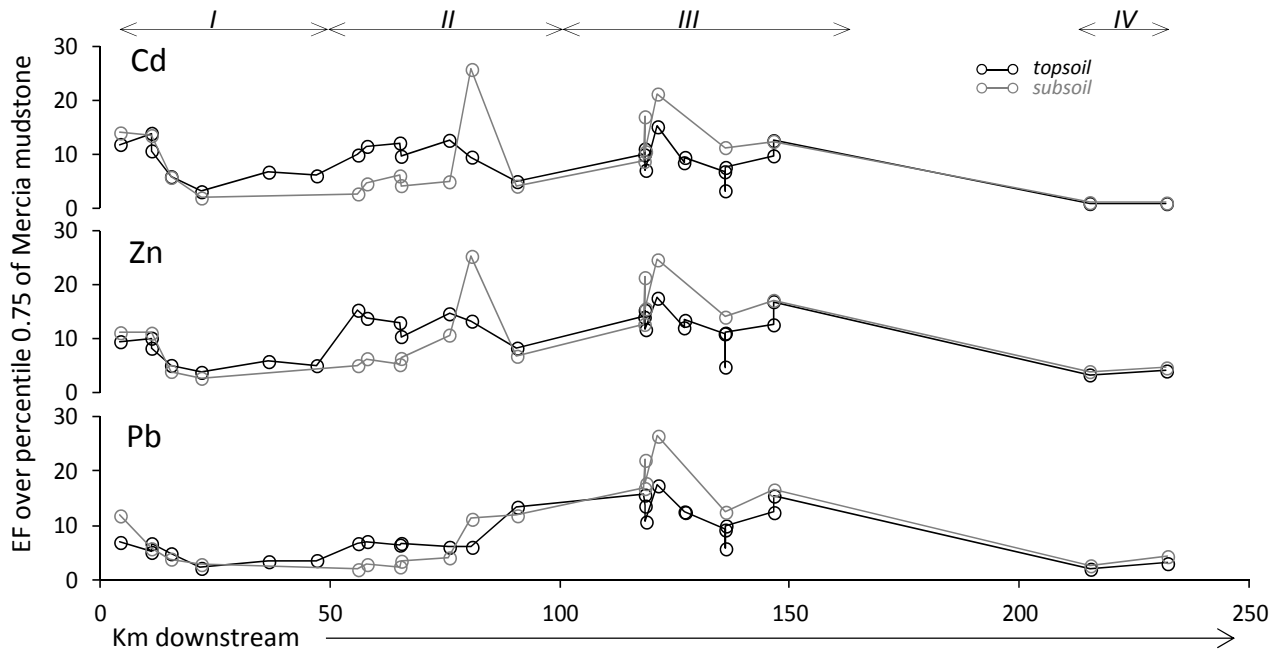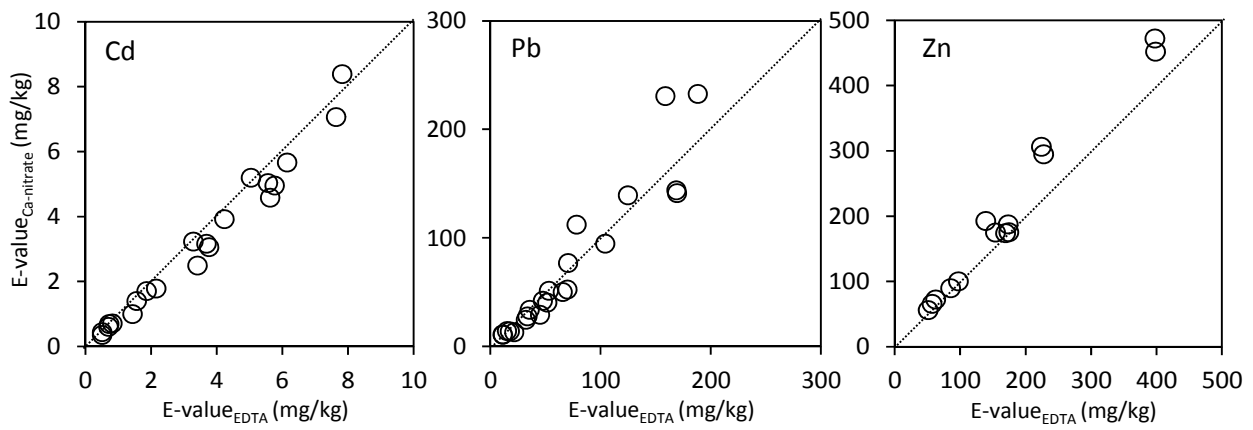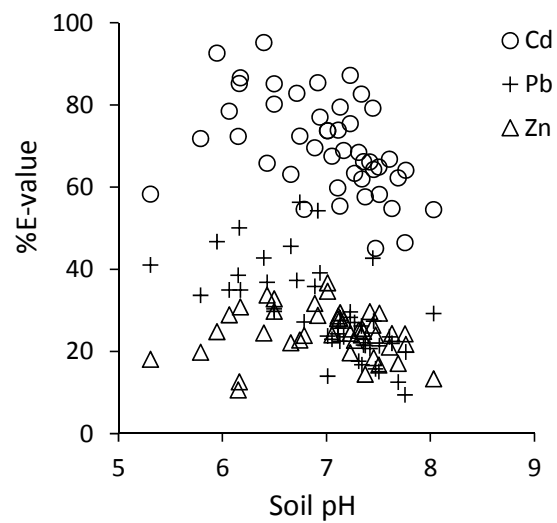
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9