

# Measuring reactive pools of Cd, Pb and Zn in coal fly ash from the UK using isotopic dilution assays

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## ABSTRACT

Large volumes of coal fly ash are continually being produced and stockpiled around the world and can be a source of environmentally sensitive trace elements. Whilst leaching tests are used for regulatory purposes, these provide little information about the true geochemical behaviour and 'reactivity' of trace elements in coal ash because they are poorly selective. Isotopic dilution (ID) assays are frequently used in soil geochemistry as a means of measuring the reactive pools of trace metals that are in equilibrium with soil pore waters. This paper examines the applicability of multi-element ID assays in measuring the labile or reactive pool of Cd, Pb and Zn in a range of fresh and weathered fly ash, where pH is generally much more alkaline than in soils. The method generally worked well using 0.0005M EDTA as a background electrolyte as it provided robust analytical ICP-MS measurements as well as fulfilling the important principle of ID that non-labile metal should not be solubilised. Reactive pools were equivalent to 0.5-3% of the total Pb pool and 4-13% of the total Cd pool. For Zn, where samples had pH<11.5, the reactive Zn pool varied between 0.3 and 2%; when fresh ash samples with pH>11.5 were tested, the method failed as the spiked isotope appeared to be sorbed or precipitated. Ash weathering was found to exert little impact on the lability of Cd, Pb and Zn. We compared isotope dilution results with 0.43M HNO<sub>3</sub> and 0.05M EDTA extractions, these commonly being used as analogues of the ID assay, and concluded that these can be used as fast, cost-effective and simple proxies for the ID assays. Results suggest that ID methods can be used to enhance our knowledge of trace element behaviour in fresh and weathered fly ash.

KEYWORDS: isotope dilution, stable, isotopes, E-value, coal ash, metals, availability

# 1. INTRODUCTION

In order to fulfil the future world energy demand, all energy resources may need to be utilised. Despite the efforts and commitment for renewable power to account for a significant share of the total electricity supply, coal is still one of the most important electricity producing fuels particularly in China and India. With growing energy demand, many industrialised and developing countries will continue to rely on coal for power generation in the decades to come.

Coal-based power generation produces large volumes of fly ash worldwide. It is estimated that 780 Mt of coal ash are produced every year (WWCCPN, 2011). Fly ash has been successfully used for many years in a wide range of engineering applications including asphalt and concrete pavements, soil stabilization, road base, structural fill, embankments, mine reclamation, mineral fillers or fertilisers, production of zeolites and geopolymers and more importantly, as a high-performance substitute for portland cement and as a clinker addition in the manufacturing of portland cement. However, under 50% of world production is presently utilised (WWCCPN, 2011), with the remainder ash being either stored temporarily in stockpiles, disposed of in landfills or lagooned.

Whether fly ash is landfilled, disposed in surface impoundments, lagooned, recycled into ash based-products or mixed with soil, care should be taken as the total content of an element is not an accurate indicator of the potential environmental impact. The chemical properties of fly ash have been extensively studied and it is well known that fly ash contains a broad array of trace elements in concentrations  $>50$  mg/kg, many of which are of environmental concern such as As, Cr, Ni, Pb or Zn. Assessing the environmental performance of products based on the total concentration of elements present in ash would provide unreliable and highly overestimated predictions of the risk level which would inevitably limit any fly ash application opportunities. It is for this reason that the use of leaching tests or extractions as a means to provide a more realistic prediction of metal mobility has attracted considerable attention (Izquierdo and Querol (2012) and references therein).

There is a wide range of standardised extraction schemes with variable complexity, reactants/extractants, temperature, agitation method, liquid to solid ratio (L/S) or contact time, with additionally some other non standardised extractants appropriated for specific purposes. The procedures commonly used in the literature can be grouped in two main types based on the leaching agent: (i) deionised water extractions and (ii) acid extractions with a range of strength from mild to aggressive extractants (e.g. Chandler *et al.*, 1997; Kim, 2002; van der Sloot, 1997; Zandi and Russell, 2007). These extractions are limited in their ability to estimate the potentially bioavailable fraction. Metal solubility in water is strongly dependent on the pH of the ash-water system, which is not static but changes substantially over time due to CO<sub>2</sub> uptake or pH-controlling elements being liberated. In addition, acidic extractants are in general poorly selective and therefore they are likely to access inert pools. Thus, whilst being fast and cost-effective, simple extractions may not provide a true picture of the fraction of metal that is geochemically responsive and do not address the binding strength of metals in coal ash.

The reactivity of trace metals in soils has been extensively studied over the last decades and current research efforts have been directed at developing isotope dilution (ID) techniques as the most advanced method for accurately determining the reactive pool of elements, this being the pool of metal in equilibrium with the soil pore water (Hamon *et al.*, 2008; Smolders *et al.*, 1999; Young *et al.*, 2005). The current study assesses whether multi-element stable ID techniques can be similarly used to measure the 'labile' or 'reactive' pool of selected metals and develop our understanding on their binding strength in coal ash. The method may also develop an insight into the effects of ash weathering on the transfer of metals between accessible and inaccessible (inert) forms. Whilst ID has provided a reliable approach to determine the labile pools of metals in soil systems, the present work is, to our knowledge, the first attempt to use this advanced technique as a means of addressing the availability of metals hosted in an extensively used industrial by-product.

In this preliminary study we focus on Cd, Pb and Zn as exemplars. Generally, the water solubility of Cd and Pb in alkaline ash is low and is often not considered as posing a great risk to the environment, whilst Zn is slightly soluble in alkaline solutions. However, studies into metals

in soils have revealed that Cd, Zn and Pb, although traditionally considered as highly insoluble and tightly bound to soil, are not locked up but can be highly isotopically exchangeable and therefore reactive, typically >20% and often >50% of their total pool (Gabler et al. (2007) and references therein) depending on soil characteristics such as pH, organic matter and Fe oxide contents.

A further benefit of ID is that it can potentially provide increased understanding of the fixation and weathering processes that occur in both fresh and stored coal ash. However, although providing high resolution measurements of the *true* proportion of metal available, ID techniques may have some limitations for daily practice in ash management (e.g. execution time and isotope costs) where fast, cost-effective and relatively simple tests are needed for regulatory/quality control purposes (e.g. simple compliance tests to check results against parametric values previously established by the corresponding regulations). With this in mind, we tested three different single batch extractions (deionised water, EDTA and HNO<sub>3</sub>-based) with the aim of assessing and validating their suitability as a faster, more cost-effective and user-friendly analogue of the isotopic dilution assay to obtain a safe-side estimate of the geochemically responsive pools of the concerned metals.

## 2. MATERIALS AND METHODS

### 2.1. SAMPLING

Fly ash samples were obtained from 6 power stations in the UK shortly after being produced during 2012 (Table 1). Seven  $\approx$ 1kg fresh ash samples were collected from the top of delivery ash tankers. A sampling cone was forced into the ash to approximately 50 cm depth, following the approved method of taking samples from tankers by the British Standards Institute for Autocontrol samples. The sample was then transferred into a bucket with a lid, where it was then mixed and homogenised by rolling the bucket. Samples were stored in sealed buckets and used shortly after sampling to prevent ash undergoing reactions likely to change mineralogy. Another  $\approx$ 1kg three ash samples that have been lagooned for different periods of

time between 1.5 and 5-6 years were also collected from the lagoons. The lagooned ashes were dried at 40°C for at least 48h, grinded and kept in sealed containers before analysis.

As feed stocks in power stations change constantly, there is no evidence that their metal loading was originally the same. Therefore, differences in the total pool of metal may not necessarily reflect leaching processes during the waterlogged period, but are also likely to be attributed to the parent coal composition.

## **2.2. SAMPLE PREPARATION**

### **2.2.1. TOTAL DIGESTION OF ASH SAMPLES**

Sample digestion for total metal concentrations were performed by accurately weighing a portion of ash into a Savillex™ vial and adding concentrated HNO<sub>3</sub> acid before heating at 80°C overnight until dryness, the purpose being the digestion of reactive organic phases. These digests were then cooled prior to the addition of HF, HNO<sub>3</sub> and HClO<sub>4</sub> concentrated 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 with deionised ultrapure water, H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> to 25 mL of 5% v/v HNO<sub>3</sub>. Reference materials (GSS-6, BGS102, SRM1633b and BCR-2), duplicated samples and blanks were all prepared in a similar manner to check accuracy of the analytical and digestion method. A percent relative error <4% with respect to the certified values of the standard reference materials was determined for Cd, Pb and Zn.

### **2.2.2. ISOTOPIC DILUTION ASSAYS**

We used isotope dilution to determine the concentration of labile Cd, Pb and Zn in coal ash. For soils, the isotope dilution technique is based on the principle that when a given amount of stable isotope of an element is added, it will readily redistribute itself among the solution and the isotopically exchangeable phases i.e. the chemically reactive pool (Hamon et al. 2008), whilst it will not mix with inaccessible forms of the metal. The shift in the isotopic abundances of the element of interest in a soil suspension before and after the addition of the isotope spike gives an indication on the fraction of metal that is isotopically exchangeable, which is known as the *E*-

*value* or labile pool. It is a similar technique that is used for coal ash in this paper. Hamon et al. (2008) and Midwood (2007) have both written detailed descriptions of the principals of isotopic dilution assays which we refer the reader to.

Initially, preliminary tests on one fresh ash sample (1a) were carried out to assess the appropriate equilibrating electrolyte to use by testing 0.0005M NH<sub>4</sub>-EDTA, 0.1M Ca(NO<sub>3</sub>)<sub>2</sub> and 0.01M Ca(NO<sub>3</sub>)<sub>2</sub>. It was observed that EDTA was the most analytically robust and therefore it was subsequently used 0.0005M NH<sub>4</sub>-EDTA as the suspending matrix. For the assay, six replicates of 2.0±0.1 g fly ash 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 of the six replicates of each ash suspension were spiked with 0.5 mL solution containing <sup>108</sup>Cd, <sup>204</sup>Pb and <sup>70</sup>Zn enriched isotopes, whilst the three remaining were retained to measure the natural isotopic abundances of these elements. The spiked suspensions were re-equilibrated for a further 3 days and then centrifuged, the supernatant being filtered through 0.20 µm cellulose acetate filters to minimise sub-micron colloids in solution. Blanks were all prepared in a similar manner. The labile pool or E-value was determined using Eqn.1:

$$E - value = \left( \frac{M_M}{W} \right) \left( \frac{C_{spike} V_{spike}}{M_{Mspike}} \right) \left( \frac{^{light} IA_{spike} - ^{heavy} IA_{spike} R_{SS}}{^{heavy} IA_{ash} R_{SS} - ^{light} IA_{ash}} \right) \quad \text{Eqn 1.}$$

where M<sub>M</sub> 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 ash (kg), IA denotes isotopic abundance of a particular isotope in the spike or ash and RSS is the ratio of isotopic abundances of the lighter isotope over the heavier isotope in the spiked ash supernatant.

### 2.2.3. BATCH EXTRACTIONS

#### 2.2.3.1. WATER EXTRACTIONS

The EU compliance single batch leaching test EN 12457-2 (European Committee for Standardisation, 2002) was performed to determine the solubility of elements in water. This EN method is typically used to characterise wastes with views of their further acceptance at landfills

(Council Decision of 19 December 2002, Annex II to Directive 1999/31/EC). The ash samples were shaken in an end-over-end shaker for 24h using deionised ultrapure water at a liquid to solid ratio (L/S) of 10 L/kg. The supernatant, after centrifugation, was filtered through a 0.45 µm filter and the pH of leachates was measured immediately after with an Orion 720A+ pH meter and VWR pH probe.

#### 2.2.3.2. EDTA AND ACID EXTRACTIONS

We selected two simple extraction schemes regularly used in soil analysis to assess the bioavailable fraction of metals in soils, 0.05M EDTA and 0.43M HNO<sub>3</sub> (Tipping *et al.*, 2003, Ure, 1996). The extractions were performed by shaking ash with 0.05M NH<sub>4</sub>-EDTA (referred to as EDTA extraction in the following discussion) and 0.43M HNO<sub>3</sub> at L/S=10 L/kg for 1 hour and 2 hours, respectively. The supernatant after centrifugation was filtered through 0.45 µm filter and the pH of the extractions was measured immediately after with a an Orion 720A+ pH meter and VWR pH probe.

Although these extractants are poorly selective (Manouchehri *et al.*, 2006), it is considered that they provide the best non-isotopic measures of the geochemically active metal i.e. metal that enters into interactions with the soil solids that controls solution concentrations (Tipping *et al.*, 2003). Specifically the 0.05M EDTA extraction in soils has been harmonised and standardised (Quevauviller, 1998). EDTA is thought to extract metals in all the non-silicate-bound soil phases and it is likely to reflect the metal availability in both the short-term and relatively long-term (Ure, 1996). Compared to the isotope dilution assay, both generally overestimate the labile measurement (E-value), especially in contaminated soils. EDTA tends to dissolve Fe oxides, thus releasing non-labile metal whilst HNO<sub>3</sub> overestimates the labile pool by dissolving carbonate and some silicate matrices. However, the benefit of using these extractants is that they are reasonably well understood in relation to measuring E-values in soils and thus provide a reference to which to compare the efficiency of the isotope dilution measurements on the coal ash samples.

### **2.3. ANALYTICAL PROCEDURES**

### **2.3.1. ELEMENTAL CONCENTRATIONS IN ASH AND EXTRACTS**

The concentrations of a number of elements (>40) including Cd, Pb, Zn, Fe, Al and Si were determined on the extracts and the total digests (except for Si) and using an Agilent 7500 quadrupole ICP-MS instrument using a mixture of 'He collision cell' and 'no-gas' modes. Response suppression/enhancement effects being corrected for using a mixed internal standard containing Sc, Ge, In, Rh, Te and Ir. 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. The calibration and quality control standards were inserted every 20 samples to check possible drift over the run. Quality control standards yielded RSD typically <2%. 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.

### **2.3.2. ISOTOPE ANALYSES**

The isotopic composition of isotope dilution extracts were determined using an Agilent 7500 quadrupole ICP-MS using only 'He collision cell' mode to eliminate interferences on Zn and Cd isotopes. Correction for mass bias effects on the isotopes was derived from a SPEX Certprep™ multi-element standard for Zn and Cd, assumed to have a fixed natural isotopic abundance and SRM981 (NIST) for Pb due to variable natural isotopic abundance. The instrument was also calibrated for the simultaneous determination of concentrations of metals in the ash suspensions using a series of synthetic chemical solutions diluted from multi-element stock solutions (SPEX Certprep™). Response suppression/enhancement effects being corrected for using a single internal standard containing Rh found to be appropriate for Zn, Cd and Pb.

## **3. RESULTS**

The 0.05M EDTA-extractable, 0.43M HNO<sub>3</sub>-extractable and water leachable pools of Pb, Cd and Zn were plotted against their respective labile pools (Figure 1). Possible functional relationships among the studied pools across our dataset were sought. The pH of 0.05M EDTA extracts



ranged between 4.5 and 7.5, whilst for 0.43 HNO<sub>3</sub> the pH was consistently around 0.8 (Table I, Supporting Information). The concentration of metals solubilised by the 0.0005M EDTA background electrolyte used in the ID assays is also reported (Figure 1). These values are important because if the 0.0005M EDTA concentration exceeds the labile concentration of metal one of the principals of ID is violated. This being that the background electrolyte does not solubilise non-labile metal. The analytical techniques used in this preliminary study do not allow resolving the mode of occurrence of metals in ash, but correlations with the extractability of major elements can give an indication of the species likely to host metals.

### **3.1. ISOTOPE DILUTION VALIDATION METHOD**

#### ***Suspending electrolyte***

We undertook a preliminary test on one ash sample from Power Station 1 to investigate the optimum suspending electrolyte for alkaline ash. Three electrolytes commonly used in determining the isotopically exchangeable pool of metals in soils were evaluated: 0.1M and 0.01M Ca(NO<sub>3</sub>)<sub>2</sub>, and 0.0005M EDTA (Atkinson *et al.*, 2011; Gäbler *et al.*, 2007; Young *et al.*, 2000). The use of Ca(NO<sub>3</sub>)<sub>2</sub> (0.1M and 0.01M) does not risk mobilisation of non-labile metal, but it was found to mobilise insignificant amounts of Cd, Zn and Pb from ash, which resulted in analytically unreliable isotope measurements due to a poor contrast with the background. However, 0.0005M EDTA was found to be more analytically robust as it solubilised sufficient metal to obtain accurate isotope measurements. The coefficient of variation of E-values for 3 replicates was 2-6% (mean/median=4%) for Pb and 0.5-14% (mean/median=6%) for Zn. The E-values for Cd showed a slightly higher variability, with CV in the 0.1-49% range but typically 0.1-13% (mean=12%, median=9%). This is likely to be due to the very low total and labile pools of Cd in the ash. Atkinson *et al.* (2011) also investigated various suspending electrolytes for a range of contaminated soils and found that (i) 0.0005M EDTA solubilises sufficient Pb without accessing the non-labile pool and (ii) the use of a neutral salt as suspending electrolyte is less reliable at low Pb concentrations. Based on the above observations, we used 0.0005M EDTA as suspending matrix for our dataset.

### ***Method validation***

Atkinson *et al.* (2011) studied the influence of the EDTA concentration on the lability of Pb in 4 soils and reported that increasing concentrations mobilise non-labile Pb. Although they concluded that a 0.0005M concentration may provide a viable suspending electrolyte for soils, this finding may not apply to ash as it is very different in nature (particularly in pH range and organic carbon). Powerful chelating agents used to assess the availability of elements in soils such as DTPA or EDTA are likely to mobilise/dissolve or desorb non-labile metal (Degryse *et al.*, 2004, Nakhone and Young, 1993). This would violate one of the principles of isotope dilution in that the spiked isotope gains access to a chemically inert or non exchangeable pool, thus overestimating the E-value. In our dataset, the concentrations of Cd, Zn and Pb in the 0.0005M EDTA isotope dilution solutions were all lower than the E-values (Figure 1). This confirms that this electrolyte at this concentration does not bring non-labile metal into solution in this particular set of ash samples and suggests that it would be an appropriate electrolyte for highly alkaline by-products of thermal processes.

### ***Spike concentration***

The spike volume and concentration must be such that it causes significant change in the isotopic composition of the soil whilst keeping the ash-solution equilibrium and ash properties (essentially the pH) unaltered or perturbed to a minimum. Based on this principle, most studies in the soil literature spike with an amount of stable isotope around 0.1-12% of the total metal concentration in soil (Ahnstrom and Parker, 2000, Atkinson *et al.*, 2011, Degryse *et al.*, 2007, Hamon *et al.*, 2008, Nolan *et al.*, 2004), the concentration depending on the metal and the isotopic abundance of the spike in relation to the rest of isotopes.

As the metal isotope is originally dissolved in acid before dispensation, an excess of an acidified spike has been reported to cause alteration in the pH of soil-solution system, not only in poorly buffered soils but also in carbonate-bearing soils (Sterckeman *et al.*, 2009). This is not likely to have a large effect on ash suspensions due to their strongly alkaline nature and high buffering capacity of the ash samples. We chose the spike concentration to double the natural  $^{108}\text{Cd}$ ,  $^{204}\text{Pb}$  and  $^{70}\text{Zn}$  concentrations in the ash samples. Whilst this proved to be effective for Cd and Pb, it

was less effective for some of the Zn measurements where ash pH>11.5 as the Zn spike underwent absorption/precipitation processes and did not readily participate in the exchange equilibrium, as discussed below (see section 3.4).

## **3.2. LEAD**

### ***Lability***

The labile pool of Pb in ash ranged from 0.4 to 4 mg/kg, with 80% of values being >1 mg/kg (Table 1). The lability expressed as % E-value relative to the total Pb pool was consistently low: 0.5-2% for fresh ash and 2-3% for lagooned ash, which suggests that a prolonged period of waterlogging does not cause major changes in the ash mineralogy. A small transfer of Pb from the non-labile into the labile pool appears to have occurred. Whilst only up to 3% Pb is labile in the studied ashes, %E<sub>Pb</sub> values for soils and peat in the literature have been found to be between 9 and 78% (Atkinson *et al.*, 2011; Chenery *et al.*, 2012; Degryse *et al.*, 2007; Gäbler *et al.*, 1999; Izquierdo *et al.*, 2012; Tongtavee *et al.*, 2005). This difference in lability suggests that whilst Pb in soils is typically sorbed to poorly crystalline Fe oxides or organic matter (Atkinson *et al.*, 2011; Degryse *et al.*, 2007), Pb in fly ash appears to be primarily occluded and would therefore remain in geochemically inert forms even after an extended lagooning period.

### ***Extractability***

The water leachable concentrations of Pb were generally close or below the detection limit (0.002 mg/kg), reaching a minimum across the pH≈8.5-11.5 range (<0.002 mg/kg) and slightly increasing at pH >11.5 (0.002–0.17 mg/kg) (Figure 2) due to the formation of more soluble anionic hydroxo complexes (Jones, 1995). Lead often displays a U-shaped solubility curve against pH due to its amphoteric behaviour (Izquierdo and Querol, 2012). The water leaching yielded extremely low extractable proportions i.e. <0.05% of the total pool of Pb. Similar observations apply to the 0.0005M-EDTA extractable concentrations (<0.5%), measured in the equilibrating electrolyte of the isotope dilution measurement.

The extractable  $Pb_{HNO_3}$  ranged between 0.7 and 15 mg/kg (1-8% of the total pool) whilst  $Pb_{EDTA}$  was between 0.5 and 8 mg/kg (1-6%), with the lagooned ashes in the upper range for both extractants (3-8% and 4-6% for  $HNO_3$  and EDTA extractions respectively) (Figure 1). This indicates that <10% of the total pool of Pb could be available in the long-term. The extractable concentrations  $Pb_{EDTA}$  and  $Pb_{HNO_3}$  are well correlated ( $r^2=0.82$   $p<0.005$ ) if only fresh ash is considered (Figure 3). Tipping *et al.* (2003) also noted a good correlation for  $Pb_{EDTA}$  and  $Pb_{HNO_3}$  for a set of 98 soils. However, the whole dataset including lagooned ash showed a weaker  $Pb_{EDTA}$ - $Pb_{HNO_3}$  correlation ( $r^2=0.48$   $p<0.05$ ), due to Pb in weathered ash being more  $HNO_3$ -extractable than from fresh ash.

### ***Comparison of E-value with other extractants***

Both water and 0.0005M-EDTA extractable concentrations yielded extremely low and scattered values showing no consistent relationship with the labile pool  $Pb_E$  (Figure 1).  $Pb_{HNO_3}$  was found to provide an excellent estimate of the labile pool in fresh ash, with the dataset array falling along the 1:1 line (Figure 1) and showing a linear correlation ( $r^2=0.96$ ,  $p<0.001$ ). However, the weathered ash follows a different trend where  $Pb_{HNO_3}$  extractable concentrations largely overestimate the labile Pb pool. This is likely to reflect the glassy matrix degradation processes associated with prolonged periods of waterlogging, thus enabling  $HNO_3$  to dissolve more of the matrices and access otherwise non-labile/inert pools e.g. Pb locked in (alumino)silicates. Kim and Kazonich (2004) and Warren and Dudas (1988) reported a dominant silicate association for Pb in coal ash. Whilst this pool is highly insoluble in fresh ash, the strongly alkaline pH of fly ash in contact with lagoon water would enhance silica and alumina dissolution (Izquierdo and Querol, 2012), with the result that the fraction of metals hosted in aluminosilicate glass can be released. Zevenbergen *et al.* (1999) studied weathered ash and reported an initial glass dissolution step followed by the precipitation of noncrystalline <0.5 $\mu$ m clay-like aluminosilicates coating weathered ash particles, which were found to encapsulate metals and/or incorporate them within their structure. Thus, some non-labile Pb in fresh ash could be released into the labile pool and, as the pH decreases with  $CO_2$  uptake, this Pb would be subsequently transferred back to the non-labile pool by means of co-precipitation or encapsulation mechanisms. This

hypothesis would be supported by the higher HNO<sub>3</sub>-extractable Si and Al concentrations from lagooned ash (5-8 g/kg) compared to fresh ash (1-4 g/kg) (Table I Supporting Information), and the weak correlation between Al<sub>HNO<sub>3</sub></sub> and Pb<sub>HNO<sub>3</sub></sub> concentrations ( $r^2=46$ ,  $p<0.05$ ). Whilst any Pb hosted in these fine particle-sized neoformed amorphous clays could be mobilised by strongly acidic reagents such as HNO<sub>3</sub>, it would remain less accessible to weaker and/or non-silicate-selective extractants. Thus, Pb<sub>EDTA</sub> and Pb<sub>E</sub> measurements would remain essentially unaltered during the waterlogging period.

Pb<sub>EDTA</sub> overestimated Pb<sub>E</sub> only very slightly (by a factor  $\approx 1.5$ ) (Figure 1) and both pools were well correlated ( $r^2=0.80$ ,  $p<0.001$ ) across the whole dataset, which indicates that they are not affected by weathering. Therefore, a 0.05M EDTA extraction would be more accurate than a 0.43M HNO<sub>3</sub> extraction as surrogate for lability measurements on weathered ash and would provide a conservative estimation of the labile pool of Pb. The correlation between the EDTA-extractable concentrations of Fe and Pb suggests ( $r^2=0.63$ ,  $p<0.01$ ) that Fe oxides can host Pb likely to be labile (Figure 4).

### **3.3. CADMIUM**

#### ***Lability***

The labile pool of Cd in ash ranged between 0.02 and 0.37 mg/kg (typically  $\approx 0.15$  mg/kg, Table 1) i.e. 4-13% of the total pool of Cd is isotopically exchangeable, with no particular trend with ash weathering. Greater values are found in the literature for a range of contaminated soils i.e. 3-100%, with %Cd<sub>E</sub> typically 30-60% (Degryse *et al.*, 2004; Gabler *et al.*, 2007; Nakhone and Young, 1993; Smolders *et al.*, 1999; Young *et al.*, 2000). This may reflect a different mode of occurrence of Cd in ash compared to soils. Cadmium is often more highly available in soils due to a large proportion being adsorbed on Fe/Mn oxides or humic/fulvic acids (Nakhone and Young, 1993; Smolders *et al.*, 1999, Sterckeman *et al.*, 2009). Unlike soils, our ash dataset strongly suggests Cd fixation and most likely occlusion in oxides or the insoluble aluminosilicate glassy matrix as reported by Kim and Kazonich (2004). Exceptionally low levels of lability were

also reported for mine spoils (Ahnstrom and Parker, 2000; Nakhone and Young, 1993), due to Cd being primarily occluded in ore minerals and therefore being inert.

### ***Extractability***

The results suggest that Cd is the most mobile of the three studied metals. Although poorly soluble in water under alkaline conditions (0.001-0.006 mg/kg, <0.3% water leachable, Figure 2), 0.0005M EDTA extracts 3-6% of the total Cd, with no particular trend with weathering. The  $Cd_{HNO_3}$  and  $Cd_{EDTA}$  concentrations (0.05-0.59 mg/kg, 8-26% extractable) were very similar and strongly correlated for fresh ash (Figure 3), with a  $r^2=0.99$  ( $p<0.001$ ) and a slope  $\approx 1$  suggesting that the available pool of Cd occurs primarily in forms equally accessible to both extractants e.g. possibly oxidised metal species or adsorbed to oxides (Degryse *et al.*, 2004). These observations are in agreement with the findings of Tipping *et al.* (2003) for a set of 98 soils. The  $Cd_{HNO_3}$ - $Cd_{EDTA}$  correlation was only slightly worse when the whole dataset is considered ( $r^2=0.91$   $p<0.001$ ), which suggests that  $HNO_3$  ( $Cd_{HNO_3}=0.09-0.6$  mg/kg) does not extract significantly greater quantities of Cd out of weathered ash than EDTA ( $Cd_{EDTA}=0.05-0.5$ mg/kg).

### ***Comparison of E-value with other extractants***

No correlation was found between the water leachability and the labile pool. As shown in Figure 1, the water extractable concentrations were scattered and underestimated the E-value. The 0.0005M-EDTA concentrations do correlate with the labile pool ( $r^2=0.80$ ,  $p<0.001$ ) but they do not provide conservative predictions as data were consistently lower than the respective E-value. (Figure 1). Previous studies have revealed that an extraction with 0.05M EDTA may overestimate the labile pool from Cd-rich contaminated soils (Nakhone and Young, 1993), but it can give a good estimate of the labile Cd in non-contaminated soils (Fujii and Corey, 1986; Gabler *et al.*, 2007). EDTA can dissolve Fe-(hydr)oxides hosting occluded metals, which may account for non-labile Cd being released (Degryse *et al.*, 2004). Gray *et al.* (2003) found that EDTA solubilised on average 30% more Cd than labile forms measured by isotope dilution. Our dataset suggests that  $Cd_{EDTA}$  (0.05-0.5 mg/kg) could predict  $Cd_E$  lability (0.02-0.4 mg/kg) more realistically than water or  $HNO_3$  extractions (Figure 1), as both pools are correlated across the ash dataset ( $r^2=0.89$ ,  $p<0.001$ ). E-values ( $Cd_E$ ) were slightly overestimated but they can be

inferred with reasonable accuracy by applying a factor of x0.5 to  $Cd_{EDTA}$ . Weathering does not seem to affect the described trend as  $Cd_E$  was also about half the EDTA-extractable concentrations for lagooned ash.

The  $HNO_3$  extraction also releases some non-labile Cd (the extracted concentrations fall above the 1:1 line) but it was also found to be a reasonably effective tool to predict  $Cd_E$  for fresh ash ( $Cd_E-Cd_{HNO_3}$   $r^2=0.84$ ,  $p<0.01$ ). However, the correlation  $Cd_{HNO_3}-Cd_E$  was slightly worse ( $r^2=0.74$ ,  $p<0.01$ ) when considering the whole dataset. Similar glass dissolution and clay precipitation processes to those described above for Pb may also account for this behaviour. The fact that weathering-dependent  $HNO_3$  extractability was less apparent than for the other studied metals (Figure 1) suggests that whilst much of Pb and Zn are hosted in aluminosilicates, Cd may have a less prominent silicate association. This is supported by the lack of correlation between  $Cd_{HNO_3}$  and  $Al_{HNO_3}$  ( $r^2=0.11$   $p>0.1$ ). By contrast, the correlation between the EDTA-extractable concentrations of Fe and Cd ( $r^2=0.69$ ,  $p<0.01$ ) suggests that labile Cd may be associated with Fe oxides (Figure 4).

### **3.4. ZINC**

#### ***Lability***

The lability of Zn for samples with  $pH<11.5$  ranged between 0.3 and 5 mg/kg and decreased with increasing pH (Table 1 and Figure 5). Several studies have reported negative correlations between  $\%E_{Zn}$  and pH in acidic to near-neutral soils (Degryse *et al.*, 2004; Tye *et al.*, 2003). This trend is interpreted as a response to increasing adsorption with increasing pH. Sorption phenomena on Fe oxides are a recognised process that may reduce the mobility of trace elements in ash, as Fe oxides provide sites for metal binding (Izquierdo and Querol, 2012). Cadmium, Pb and Zn adsorption onto oxides follow the simplistic trend of increased adsorption with pH (Bradl, 2004) and therefore the pH is likely to influence E-value concentrations (Young *et al.*, 2007).

Regardless of the influence of pH, the above values yielded very low %Zn<sub>E</sub> in relation to the total pool. Only 0.3-2% Zn is isotopically exchangeable in the studied ash samples, whilst %Zn<sub>E</sub> in a range of polluted and unpolluted soils in the literature varied from 0.3 to 94%, with mean values in the 10-33% range (Degryse *et al.*, 2004; Gabler *et al.*, 2007; Young *et al.*, 2000).

For ash samples with pH>11.5, Zn revealed inconsistent and unrealistically large E-values i.e. 64 to 211 mg/kg (Table 1), which yields %E<sub>Zn</sub> up to 94% (Figure 5). These figures would be in line with the lability of Zn in soils reported above. However, it is highly unlikely that Zn<sub>E</sub> in ash exceeds Zn<sub>HNO<sub>3</sub></sub> (7-57 mg/kg), which is known to access non-labile Zn and can be taken as the worst case scenario. Rather, this overestimation is likely an 'isotope spiking artifact'. The concentration of Zn in 0.0005 M EDTA solution was sufficient to measure an analytically robust instrumental response, which rules out analytical inaccuracy as a possible cause. However, a low contrast between the isotopic ratios <sup>70</sup>Zn/<sup>xx</sup>Zn of paired spiked and unspiked suspensions was found for these specific samples. Whichever the stable isotope <sup>xx</sup>Zn (<sup>64</sup>Zn, <sup>66</sup>Zn, <sup>67</sup>Zn and <sup>68</sup>Zn) used in Eqn 1, invariably large E-values were obtained. This poor responsive behaviour suggests that the <sup>70</sup>Zn spike is being removed from the system before any isotopic exchange process has occurred. The hypothesis of spike adsorption/precipitation would be in agreement with the early findings of Tiller *et al.* (1972), who reported erratic and unrealistically high E-values e.g. >100% of the total pool in alkaline soils. These were attributed to the fixation of the isotope added due to the presence of vacant binding sites that sequester the introduced spike and impede the exchange process. In addition, the fact that samples 6a and 6b are from the same power station and have similar total metal concentrations (Table 1) and extractability but only differ in their pH (11.1, 12.7) and Zn<sub>E</sub> (0.3 and 110 mg/kg) would suggest that both parameters are closely related.

In contrast to the samples with pH<11.5, %E<sub>Zn</sub> for samples with pH>11.5 increases with increasing pH towards the highly alkaline end. This could be interpreted as a sharp increase in spike sorption with pH under strongly alkaline conditions, possibly on Fe-oxides. In addition, as depicted in Figure 5, the inflexion point in the %E<sub>Zn</sub> trend with pH is around pH≈11.5, which coincides with the onset of ettringite precipitation. Ettringite [Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O] is



usually formed during the reaction of alkaline ash with water (Hassett *et al.*, 2005) and can capture a number of trace elements (Jones, 1995). Bonen and Sarkar (1994) and Poon *et al.* (1985) found evidence for Zn immobilisation at the  $M^{2+}$  site in the structure of ettringite, which could contribute to spike scavenging. Moreover, the formation and precipitation of insoluble calcium zincate in alkaline soils has been reported (Bradl, 2004). For samples where the ash  $pH > 11.5$  it would therefore be necessary to modify the method. This could involve increasing the spike concentration so there is sufficient for robust Zn isotope exchange. This may require doing Zn isotope dilution assays singularly rather than as part of a multi-isotope approach, so that high acid concentrations are not introduced to the solutions.

### ***Extractability***

The water extractable concentrations were close to detection limit (0.008 mg/kg) for a number of samples and slightly increased towards the alkaline end due to Zn displaying a mild amphoteric behaviour (Figure 2). The 0.0005M-EDTA extractable concentrations were also low (typically <1% of the total pool) and scattered (Figure 1).

Although not being the most extractable metal in terms of proportion in relation to the total pool, Zn revealed the greatest absolute extractable concentrations (Figure 3). This element was more  $HNO_3$ -extractable for weathered ash (36-57 mg/kg, 12-23%) than for fresh ash (7-36 mg/kg, 4-9%). The narrower range of variation of EDTA extractability for the whole dataset i.e. 3-21 mg/kg (2-9%) indicates that  $Zn_{EDTA}$  is less sensitive to weathering than  $Zn_{HNO_3}$ . Based on these figures, only around 2-9% Zn would be long-term available in ash.

$Zn_{EDTA}$  and  $Zn_{HNO_3}$  are well correlated for fresh ash ( $r^2=0.95$   $p<0.001$ ) and for the whole data set ( $r^2=0.83$   $p<0.001$ ) (Figure 3). Tipping *et al.* (2003) reported a good  $Zn_{HNO_3}$ - $Zn_{EDTA}$  correlation with a slope  $\approx 1.0$  for a set of 98 soils. Zn in unpolluted or weakly polluted soils is often bound to Fe/Mn/Al-oxides and thus equally accessible to both extractants. The slope  $\approx 0.5$  for our dataset reflects a different binding state in ash. The fact that Zn is more extractable (by a factor of 2) with  $HNO_3$  than with EDTA would suggest an important silicate association in ash.

### ***Comparison of E-value with other extractants***

Both water and 0.0005M EDTA extractions gave a poor estimate of the labile pool as they had far lower concentrations and were uncorrelated with  $Zn_E$  (Figure 1). The 0.05M EDTA extraction overestimated the labile Zn by a factor of 3, but there was an excellent correlation ( $r^2=0.98$   $p<0.001$ ) between  $Zn_{EDTA}$  and  $Zn_E$  (Figure 1) for the subset of  $pH<11.5$  ash.

The  $HNO_3$  extraction also slightly overestimated the labile pool in the fresh ash samples where  $pH < 11.5$ . However, it provided greater overestimates of the labile pool in the weathered ash, similarly to Pb. Figure 1 shows lagooned ashes shifted away from the  $Zn_{HNO_3}$ - $Zn_E$  linear array for fresh ash ( $Zn_{HNO_3}$ - $Zn_E$   $r^2=0.79$ ,  $p<0.05$ ). This increased extractability after weathering can be taken as evidence for glass degradation processes and release of Zn otherwise inaccessible and non-labile. Zn appears to have a prominent glass association (50–60%) in UK fly ash (Spears, 2004) and US fly ash (Kim and Kazonich, 2004). The significant  $Zn_{HNO_3}$ -  $Al_{HNO_3}$  and  $Zn_{HNO_3}$ - $Si_{HNO_3}$  correlations ( $r^2=0.75$  and  $0.67$  respectively,  $p<0.001$ ) would strongly support this association.

According to the findings of Zevenbergen *et al.* (1999), it is likely that, upon weathering, Zn originally locked in the glassy matrix is released (due to a high initial  $pH \geq 11$ ) and subsequently fixed (as  $pH$  drops to  $< 9$ ) by the precipitation of non-crystalline clays in weathered ash, as previously described above for Pb. These authors reported Zn levels in the 0.02-0.2% range in such neoformed clays, either encapsulated or assimilated within the structure, which could account for the large non-labile pool of Zn.

## **4. CONCLUSIONS**

Isotope dilution techniques revealed that the 3 studied metals exhibited a very low reactivity in coal ash. Only 0.3-3% of total Pb and Zn in ash were geochemically reactive. This proportion can reach up to 13% for Cd, but this is not of such environmental concern as coal ash is typically depleted in this element. These observations are in line with the findings reported in the literature on trace element leaching in coal ash. The figures reported in this work are much lower than those reported for soils in the literature due to metals occluded primarily in

aluminosilicates or oxides. This suggests that high concentrations of the discussed elements in ash should not be a limiting factor in the use of coal ash as a raw material.

Ash weathering increases the accessibility of aggressive extractants to metals originally locked in silicates, which can be taken as evidence for ageing processes changing the crystallochemical status of metals in ash. It is likely that glass degradation during waterlogging releases hosted Pb and Zn, which are subsequently fixed via assimilation or encapsulation in neoformed clay-like aluminosilicates. Thus, a prolonged period of lagooning may change the ash mineralogy and the mode of occurrence of the studied metals, but these remain in chemically inert pools and the E-values are virtually unaffected. Cadmium availability and lability was less sensitive to weathering than Pb and Zn.

Our dataset suggests that 0.43M HNO<sub>3</sub> and 0.05M EDTA-extractable concentrations can act as surrogates for the labile pools of Cd, Pb and Zn much more realistically than water leaching or a 0.0005M EDTA extraction, for which extremely low and scattered concentrations were obtained. As expected, EDTA and HNO<sub>3</sub> extractions were found to release some non-labile metal, but their excellent correlations with E-values across the dataset suggest that the labile pool can be conservatively estimated with a reasonable accuracy. A simple EDTA extraction appears to be a reasonably effective extraction to estimate the labile pool of Cd, Zn and Pb regardless of their weathering level. The HNO<sub>3</sub> extraction failed in providing a reliable analogue of the labile pools of Pb and Zn in lagooned ash. A prominent silicate association of these metals in ash would account for their extractability being weathering-sensitive and overestimating E-values, whilst this is less apparent for Cd, which is more equally accessible to both extractants.

Isotope dilution proved to be a useful technique to resolve the reactivity and binding strength of Cd and Pb in coal ash, but was found to have limitations in the study of Zn. The erratic and unrealistically high E-values obtained for ashes with pH>11.5 strongly suggests spike precipitation/adsorption processes, which invalidates the present ID methodology as a reliable and effective method to determine the lability of Zn in strongly alkaline coal ash. However, adjustments to the method with respect to spike concentration should allow measurements to

be made. Further research should be devoted to develop isotope dilution methods to investigate the lability of surface-associated elements with low silicate affinity such as Mo, Sb or Se, which form oxyanionic species of major concern in coal ash.

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## FIGURE CAPTIONS

Figure 1. Labile pools of Cd, Pb and Zn ( $n=3$  for each data point, standard deviations reported in Table 1) against their extractable pool ( $n=2$  for each datapoint) in the dataset. Only reliable data for  $Zn_E$  and their paired extractable data are depicted. Diagonal lines depict slope=1 and  $\Delta$  denotes lagooned ash

Figure 2. Water leachable concentrations of Cd, Pb and Zn ( $n=2$  for each data point) against the leachate pH (EN 12457 leaching test).

Figure 3. Correlation between the 0.43M  $HNO_3$  extractable concentrations and 0.05M  $NH_4EDTA$  extractable concentrations of Cd ( $r^2=0.91$   $p<0.001$ ), Pb ( $r^2=0.48$   $p<0.05$ ) and Zn ( $r^2=0.83$   $p<0.001$ ) in the studied ash samples ( $n=2$  for each data point). Diagonal lines depict slope=1 and  $\Delta$  denotes lagooned ash.

Figure 4. Relationship between the 0.05M EDTA extractable concentrations of Fe in the studied ash samples and the extractable concentrations of Cd ( $r^2=0.69$   $p<0.01$ ), Pb ( $r^2=0.63$   $p<0.001$ ) and Zn ( $r^2=0.60$   $p<0.01$ ). ( $n=2$  for each data point)

Figure 5. Influence of pH on the lability of Zn expressed as %E over the total pool. ( $\Delta$  denotes lagooned ash;  $n=3$  for each data point). The semi-log scale should be noted.

Figure 1

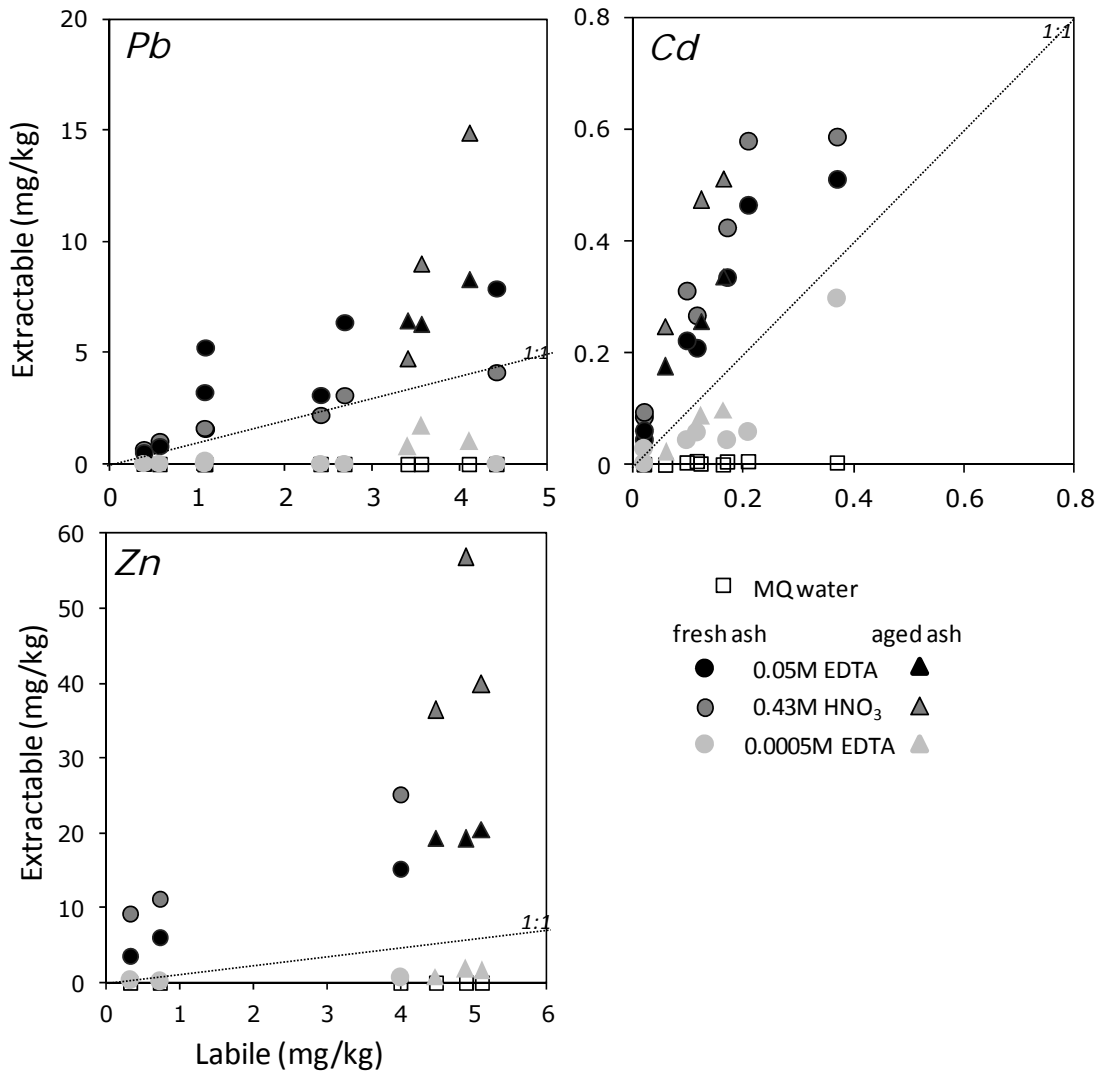




Figure 2

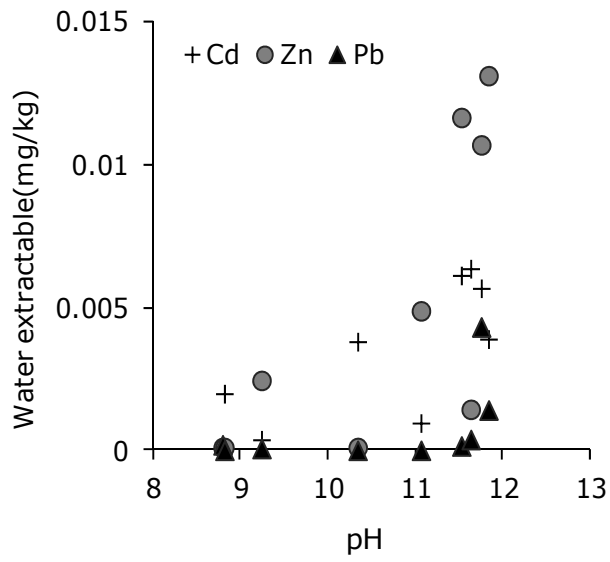


Figure 3

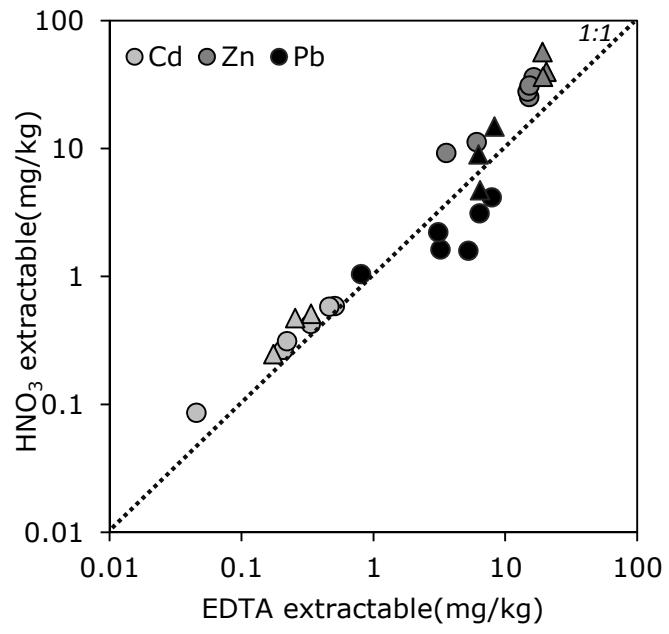


Figure 4

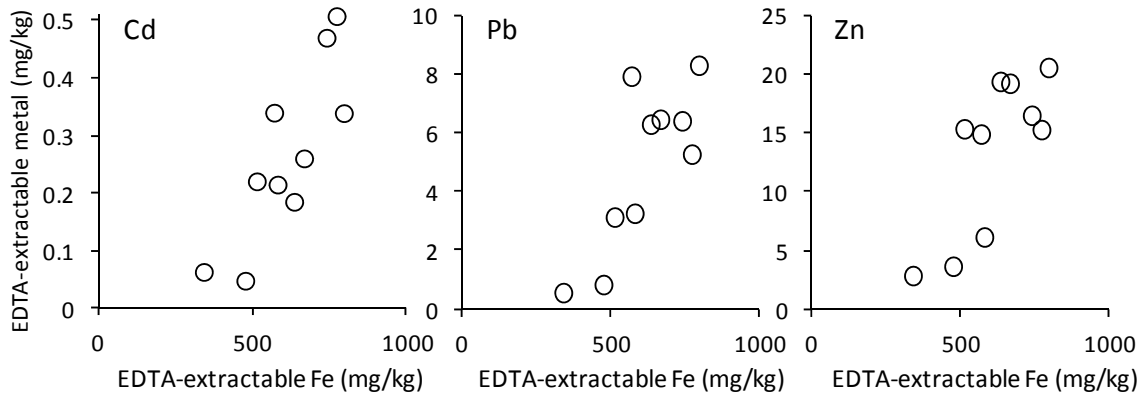


Figure 5.

