**Supplementary Information**

Linkage between solid phase apportionment and bioaccessible arsenic, chromium and lead in soil from Glasgow, Scotland, UK

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**Table S1** Detailed description geochemical clusters and groupings

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| **Cluster name** | **Cluster number** | **Median composition (%)** | **Aqua Regia concentration range** | **Sample groups** | **Comments** |
| Residual pore salts | C1 | Na (37 %), S (37 %), Ca (4 %), Fe (3 %), Si (2 %), K (1 %) | DI | 1 & 2 | Extracted by de- ionised water only, this highly mobile cluster is likely to be derived from residual pore salts |
| Organic | C2 | S (70 %), Si (7 %), Fe (2 %) | DI–5.0M | 2 | The shape of the extraction profile is indicative of the presence of humic acid as the cluster is initially dissolved in de-ionised water becoming insoluble on the addition of acid. As the acid concentration increases and H2O2 added, humic acid is oxidised and breaks down, to be observed in the latter parts of the extraction profile. On the breakdown of this component the inorganic content of the cluster is released into solution, in this case Fe, As and Ni |
| Exchangeable | C3 | K (30 %), Mg (11 %) Ca (8 %), S (5 %), Na (4 %), Mn (2 %) | DI–0.01M | 1, 2 & 3 | The cluster only makes a small contribution to the total amount of solids extracted by the CISED method. Its composition and ease of extraction of this component is suggestive that the individual components associated with this cluster are exchangeable (Rowell 1994). |

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| **Cluster name** | **Cluster number** | **Median composition (%)** | **Aqua Regia concentration range** | **Sample groups** | **Comments** |
| Mg-dominated | C4 | Mg (62 %), Ca (20 %), Fe (6 %), S (4 %), K (2 %) | D –0.05M | 3 | The primary hosts of Cr (1398 mg kg-1) in the 27 soils. This is probably as a result of the presence of Mg-bearing minerals (e.g., brucite, MgOH2) and chromite (Fe, Mg)Cr2O4, which are constituents of COPR |
| C14 | Mg (53 %), Al (21 %), Fe (9 %), Mn (7 %), Ca (2 %), P (1 %) | 0.1–5.0M | 2 |
| C15 | Mg (45 %), Al (17 %), Fe (15%), Ca (12 %) | 0.01–1.0M | 3 |

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| **Cluster name** | **Cluster number** | **Median composition (%)** | **Aqua Regia concentration range** | **Sample groups** | **Comments** |
| Ca-dominated | C5 | Ca (90 %), Mg (6 %), Si (1 %) | 0.01–1.0M | 1 & 2 | The composition and ease of extraction identifies these as three separate clusters. Although only a small proportion of the samples were collected from sites containing the highly alkaline (Ca- and Mg-dominated) COPR waste, it has had an impact on the mineralogy of these soils. The increased acid strength along with the composition of C7 has given rise to the name ‘High Ca-Mg carbonate’. Previous application of the CISED extraction to other soils (e.g., Cave *et al*. 2015) has revealed that some physico-chemical components can be bound or encapsulated by another component. For example, a carbonate component encased by Fe-oxide would not be extracted until the application of higher acid strengths required for the dissolution of the Fe-oxide. That being the case, C7 is likely to be associated with a more acid-stable cluster, in this case possibly C15 or C16. The C7 cluster is only found in the Group 3 soil (Fig. 8), the single soil in this group from Rutherglen with COPR (with high concentrations of Ca and Mg) contamination. |
| C6 | Ca (69 %), Al (7 %) | 0.01–1.0M | The PHE were distributed within the combined carbonate clusters (C5+ C6 + C7) equating to 5.86 %, 4.98 % and 1.53 % of the total extractable element content. Potential host geochemical phases for As in this study are calcium carbonate minerals, but the amount of As accounted for compared to Fe-oxides is small. It is known, however, that As commonly substitutes for P in Ca-phosphate mineral phases e.g., apatite (Drahota & Filippi 2009; Smedley & Kinniburgh 2002). Several carbonate related clusters contain Cr (Table 4), a probable result of the use of lime in chromite ore processing (Hillier *et al.* 2003). Lead in the Ca-dominated phases may be associated with the presence of phosphates (Pb–PO4 minerals) and/or carbonates e.g. cerussite (PbCO3). A previous study of sequential extraction of heavy metals from Glasgow soils (Gibson & Farmer 1986) identified that although a large proportion of Pb was associated with residual geochemical phases, 13 % of the Pb was associated with the exchangeable and carbonate phases combined. |
| C7 | Ca (89 %), Mg (10 %) | 0.01–1.0M | 3 |  |

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| **Cluster name** | **Cluster number** | **Median composition (%)** | **Aqua Regia concentration range** | **Sample groups** | **Comments** |
| Al–Si-dominated | C8 | Al (36 %), Si (34 %), Ca (1 0%), Fe (10 %), Mg, Mn, P (1–5 %) | DI–1.0M | 2 | Two clusters were identified as alumino-silicate materials and make up the third largest cluster type; e.g., the cluster with the widest range (Fig. 7). Extraction of both C8 and C9 was less well defined compared to the other clusters. When combined, the Al–Si-dominated clusters (C8 + C9) are the primary hosts of Pb and a significant host of As (Table 4). Both As and Pb can be sorbed onto alumina-silicate minerals in soils (Alloway 2013; Goldberg 2002), with Pb showing the strong affinity to clays (Bradl 2004). |
| C9 | Al (53 %), Fe (11 %), P (2 %), Ca (2 %), Si (3 %), Mg and Mn (<1 %) | 0.05–5.0M | 1 & 2 |

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| **Cluster name** | **Cluster number** | **Median composition (%)** | **Aqua Regia concentration range** | **Sample groups** | **Comments** |
| Mn oxide | C10 | Mn (40 %), Al (21 %), Ca (20 %), P (4 %), Si (4 %) | 0.1–1.0M | 1 & 2 | Figure 6 shows that C10 has a high concentration of Mn and is first observed on the addition of H2O2 (step 7) to the system, a reagent known to readily dissolve Mn oxides, providing supporting evidence suggesting that C10 is derived from Mn oxides. The Mn oxide cluster was host to a small proportion 0.01 % and 1.88 % of the total extractable Cr and Pb respectively, but not As. This association is a likely result of the metal- absorbing capability of Mn oxides, in particular Pb (Alloway 2013; McKenzie 1980). |
| P-dominated | C11 | P (65 %), S (11 %), Fe (5 %), Al & Si (2–3 %) | 0.01–5.0M | 2 | Arsenic and Pb can both substitute into phosphate minerals especially apatite, with Pb forming phosphate minerals like pyromorphite (Alloway 2013). |

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| **Cluster name** | **Cluster number** | **Median composition (%)** | **Aqua Regia concentration range** | **Sample groups** | **Comments** |
| Fe-dominated | C12 | Fe (43 %), Al (20 %), Ca (14 %), S (6 %), P (4 %), Si (2 %), Mg (2 %), Mn (1 %) | 0.01–5.0M | 1, 2 & 3 | All of the clusters are dominated by the presence of Fe with smaller contributions from other elements ;e.g., Al (C16 and C12). C13 is extracted over a wider window than C16 and C12, which have narrow windows of extraction and observed later in the CISED scheme. The differences in the extractograms are likely to be a result of both physical and chemical differences in the cluster components; e.g., the other associated elements and the amount of each. The dominance of Fe with the mid-high acid strength required for their removal indicates that C16, C13 and C12 are likely to be Fe-oxides. Two of the clusters identified as Fe-oxides (C13 and C16) act as hosts for As, Cr and Pb in the soils (Table 4); Cr was the only PHE distributed within cluster C12. This association of As, Cr and Pb with Fe-oxides is shown widely in the literature; e.g., Fe-oxides form a particularly strong relationship with As (Alloway 2013; Goldberg 2002) and Fe-oxides exhibit a strong affinity with Cr and exert a predominant role on Pb adsorption in soils (Bradl 2004). |
| C13 | Fe (34 %), Mn (2 %) Al (1 %), P (1 %) |
| C16 | Fe (77 %), Al (10 %), Mg (3 %), P (3 %), S (2 %), Si (2 %) |

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