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The importance of solid-phase distribution on the oral bioaccessibility of Ni and Cr in soils overlying Palaeogene basalt lavas, Northern Ireland

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ABSTRACT

Potentially toxic elements (PTEs) including nickel and chromium are often present in soils overlying basalt at concentrations above regulatory guidance values due to the presence of these elements in underlying geology. Oral bioaccessibility testing allows the risk posed by PTEs to human health to be assessed, however bioaccessibility is controlled by factors including mineralogy, particle size, solid phase speciation and encapsulation. X-ray diffraction (XRD) was used to characterise the mineralogy of 12 soil samples overlying Palaeogene basalt lavas in Northern Ireland and non specific sequential extraction coupled with chemometric analysis was used to determine the distribution of elements amongst soil components in 3 of these samples. The data obtained were related to total concentration and oral bioaccessible concentration to determine whether a relationship exists between the overall concentrations of PTEs, their bioaccessibility and the soils mineralogy and geochemistry.

Gastric phase bioaccessible fraction (BAF%) ranged from 0.4% to 5.4% for chromium in soils overlying basalt and bioaccessible and total chromium concentrations are positively correlated. In contrast the range of gastric phase BAF for nickel was greater (1.4 to 43.8%), while no significant correlation was observed between bioaccessible and total nickel concentrations. However nickel BAF was inversely correlated with total concentration. Solid phase fractionation information showed that bioaccessible nickel was associated with calcium carbonate, aluminum oxide, iron oxide and clay related components, while bioaccessible chromium was associated with clay related components. This suggests that weathering significantly affects nickel bioaccessibility, but does not have the same effect on the bioaccessibility of chromium.

Suggested keywords

oral bioaccessibility, nickel, chromium, basalt, sequential extraction, solid phase distribution

INTRODUCTION

Geochemical studies have reported elevated levels of potentially toxic elements (PTEs) in soils from both urban (Cicchella et al. 2005; Rodrigues et al. 2006; Okorie et al. 2011; Dao et al. 2012) and rural areas (Salminen et al. 2005; Cicchella et al. 2005; Barsby et al. 2012). These elevated PTE levels have been found to be due to geogenic (Wragg 2005) and anthropogenic (Dao et al. 2012) sources of contamination or a combination of both (Facchinelli et al. 2001; Zhang et al. 2008; Rodrigues et al. 2006; Mostert et al. 2012). Elevated nickel (Ni) and chromium (Cr) from geogenic sources have been identified worldwide (Quantin et al. 2008; Megremi 2010; Kierczak et al. 2007; Johnson et al. 2012; Barsby et al. 2012). Chronic exposure to Ni is known to cause lung fibrosis, cardiovascular and kidney diseases and cancer (Denkhaus and Salnikow 2002). Human health affects due to exposure to Cr depend on the speciation of Cr in the environment. In most natural soils Cr is stable as either Cr VI or Cr III. Cr VI is generally regarded as being highly carcinogenic, while Cr III is less toxic, and some instances is beneficial to human health (Costa and Klein 2006).

Most generic regulatory values for assessing risks from soil contamination to human health are based on the assumption that all the contaminants in the soil are readily taken up by the body. In the UK for example, the Environment Agency's Soil Guideline Values (SGVs) are developed based on this assumption (eg. EA 2009a). However, in truth only the bioavailable fraction of a contaminant is taken up by the body via the gastro-intestinal tract, respiratory system and skin (Ruby et al. 1999).

Bioavailability of contaminants in soil is not easy to measure directly, and therefore a number of in-vitro bioaccessibility tests have been developed to measure the oral bioaccessibility of a contaminant (how much of the contaminant that will be released into solution in the gastrointestinal tract). In 2002, Oomen et al. assessed and compared 5 in-vitro oral bioaccessibility testing methods. The Unified BARGE Method (UBM) (Wragg et al. 2011) was developed by the BARGE (Bioaccessibility Research Group of Europe) research group based on a method initially developed by Oomen et al. (2003). The

UBM method has been validated against in-vivo studies for As, Pd and Cd (Denys et al. 2012), and has been used for bioaccessibility studies of Cd, Pb and Zn (Pelfrène et al. 2012), Sb (Denys et al. 2009), Cr (Broadway et al. 2010), As, Cd, Cr, Cu, Ni, Pb and Zn (Okorie et al. 2011) and As, Cd, Co, Cr, Cu, Ni, Pb, U, V and Zn (Barsby et al. 2012).

Until recently, bioaccessibility studies have predominantly considered As and Pb. As a result, initial studies investigating the bioaccessibility of Cr, were concerned mostly with soil contamination due to the use of chromated copper-arsenate (CCA) (Stewart et al. 2003; Nico et al. 2006). More recently as understanding of As and Pb has developed, attention has shifted to other inorganic contaminants, including Ni and Cr. Investigations of Ni and Cr bioaccessibility have mostly been concerned with point and diffuse contamination in urban areas (Hamel et al. 1998 (Cr and Ni); Hansen et al. 2007 (Ni); Madrid et al. 2008 (Cr and Ni); Poggio et al. 2009 (Cr and Ni); Broadway et al. 2010 (Cr); Okorie et al. 2011 (Cr and Ni)). As a result, most of the studies listed have been principally concerned with the bioaccessibility of anthropogenic sources of contamination, and little attention has been paid to geogenic contamination. In 2012, Barsby et al. presented the first widespread investigation of bioaccessibility of inorganic elements from predominantly geogenic sources.

Bioaccessibility of contaminants in soil is controlled by aspects such as soil pH and organic matter content, mineralogy, particle size, solid phase speciation and encapsulation (Ruby et al. 1999; Cave et al. 2011). Therefore guidance in the UK has recommended that bioaccessibility testing should be supported by other lines of evidence including geochemical data and information relating to soil mineralogy (CIEH 2009). Although bioaccessibility studies have gathered relevant geochemical and mineralogical information for As contamination from both anthropogenic and geogenic sources (Meunier et al. 2010; Palumbo-Roe and Klinck 2007), little attention has been given to characterizing the geochemistry and mineralogy associated with geogenic Ni and Cr contamination to assess how these factors affect the oral bioaccessibility of Ni and Cr. Costa et al. (2011) investigated soil mineralogy associated with geogenic Ni and Cr contamination in Portugal, and recommended that further

bioaccessibility testing was required to fully characterise risks to human health.

The Tellus survey of trace metal concentrations in shallow soils in Northern Ireland (Smyth, 2007) revealed elevated Ni and Cr concentrations across a significant area of the Antrim Plateau (Barsby et al. 2012). These levels exceeded the current UK soil guidelines values (SGVs) for Ni in soils with a residential or allotment enduse (EA 2009b) and the LQM/CIEH Generic Assessment Criteria for Cr VI in soils with a residential, allotment or commercial enduse (Nathanail et al. 2009). On the basis of total concentration, these elevated Ni and Cr concentrations would therefore raise a cause for concern during human health risk assessment for redevelopment of these areas as residential, allotment or commercial landuses. However bioaccessibility testing undertaken by Barsby et al. (2012) indicated that these contaminants are not readily bioaccessible and therefore risks to human health are reduced. A greater understanding of both the mineral and chemical forms of Ni and Cr present in the soils overlying the Antrim Lava Group would facilitate more informed decision making during contaminated land risk assessments in Northern Ireland, and refine the assessment of risks posed by elevated geogenic Ni and Cr in soils worldwide.

The objectives of this study are therefore to: (1) investigate spatial trends in Ni and Cr oral bioaccessibility within the Antrim Lava Group and extend the correlation analyses of geochemical parameters undertaken by Palmer et al. (2012) to include Cr, (2) characterise the mineralogy of 12 soil samples collected from soils overlying the Antrim Lava Group during the GSNI Tellus Survey, using X-Ray Diffraction, (3) determine the distribution of trace elements amongst soil components of the finer soil fractions (<250 µm) in 3 soils using non specific sequential extraction and chemometric analysis as described in Cave et al. (2004) and (4) relate the data obtained to results of oral bioaccessibility testing undertaken by Barsby et al. (2012) to determine whether a relationship exists between the total concentrations of trace metals, their bioaccessibility and the soil's mineralogy and geochemistry.

MATERIALS AND METHODS

Study area

The Antrim Lava Group extends over an area of 4009 km² (Cruickshank 1997) in the north eastern corner of Northern Ireland. It comprises of Palaeogene basalt lavas, which have been divided into three formations, the Lower Basalt Formation (LBF), Middle Basalt Formation, including the Causeway Tholeiite Member (CTM) and Upper Basalt Formation (UBF) (Figure 1). Lyle (1979) concluded that volcanic activity that formed the basalts occurred in two cycles about 60 million years ago. The first cycle formed the LBF, with magma fractionation leading to the formation of the Middle Basalts at the top of this succession, while the second cycle lead to the formation of the UBF. Basalts from the LBF and UBF are olivine tholeiites, while the CTM are quartz tholeiites (Lyle 1979).

Collection, preparation and soil analyses

The Tellus survey consisted of a geochemical and geophysical survey of Northern Ireland. As part of the geochemical survey, surface soil samples were recovered every 2km² across Northern Ireland and analysed for a range of elements and major oxides (including Ni, Cr, Al₂O₃, CaO, Fe₂O₃, MgO, MnO, P₂O₅, SiO₂ and SO₃) using X-ray fluorescence (XRFS) as well as pH and soil organic carbon (SOC) (measured by loss on ignition (LOI)) (Smyth 2007). In total, 91 of the Tellus samples were randomly selected, as described in Barsby et al. (2012) for oral bioaccessibility testing using the Unified BARGE Method (UBM) (Wragg et al. 2011; Denys et al. 2012). Of these 91 samples, 23 overlie the Palaeogene basalt lavas of the Antrim Lava Group. Both the actual bioaccessibility of PTEs (mg kg⁻¹) and the bioaccessible fraction (BAF) for each contaminant were used in this study. BAF is the ratio of bioaccessible concentration from the UBM test and total concentration (by XRF) from the Tellus survey, reported as a percentage. In human health risk assessments a conservative approach is often adopted and therefore BAF is reported as the highest bioaccessible concentration from either the gastric or gastro-intestinal phase. To allow discussion of both the BAF as measured in the gastric and gastro-intestinal phase, both BAFs have been calculated and are presented in this paper. Details of quality control procedures employed for XRFS, pH and LOI analyses undertaken during the Tellus survey are

presented in Smyth (2007) and Barsby et al. (2012) provides full details of the use of reference materials, duplicates and blanks for UBM testing.

X-ray powder diffraction analysis (XRD) of bulk soil was carried out using PANalytical X'Pert (MPD) diffractometer with a $\text{CuK}\alpha$ radiation, on 12 of the Barsby et al. (2012) samples. These samples were described as basaltic soils (Jordan and Higgins 2009) and overlie the Upper and Lower Basalts and Causeway Tholeiite member formations on the 1:250k Solid Geology map of Northern Ireland (GSNI 1997). Samples were finely ground using a pestle and mortar and were run from 3° to 55° 2θ at a stepsize of 0.02° 2θ min^{-1} . Diffraction data was analysed using X'Pert High Score Plus software.

Chemometric Identification of Substrates and Element Distributions (CISED)

A non-specific sequential nitric acid extraction described in Cave et al. (2004) was carried out on three selected basalt soil samples shown in Figure 1. Samples of 4 g of dried and sieved soil ($< 250\mu\text{m}$) were placed in 40 mL polypropylene centrifuge tubes. Seven extractions were carried out twice on each soil sample yielding 14 leachates per soil. The first extraction was undertaken using 20 mL of ultrapure deionised water. Subsequent extractions were carried out using 20mL of nitric acid solution of increasing strength (0.01, 0.05, 0.1, 0.5, 1 and 5 M). The soil and extractant were shaken in an end-to-end shaker for 10 minutes prior to being centrifuged in a Sigma Centrifuge at 1039 RCF (relative centrifugal force) for 4 minutes. Extracted leachates were decanted, filtered using Minisart $0.2\mu\text{m}$ filters and refrigerated in 10mL Perkin Elmer Inductively Coupled Plasma (ICP) tubes at 4°C prior to analysis.

Leachates from CISED extractions were analysed by ICP - optical emission spectrometry (ICP-OES) for Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Si, Ti, V, Zn, Na, K using a Perkin Elmer 4300DV Optical Emission Spectrometer with Perkin Elmer AS93Plus Autosampler and Perkin Elmer Winlab32. 1.4kW forward power was applied and argon was used as both the coolant gas and auxiliary gas, at a flow rate of 15L min^{-1} and 0.2L min^{-1} respectively. Argon was also used in the nebulizer at a flow rate of 0.75mL min^{-1} and indium was used as an internal standard. Calibration was undertaken using multi-element

certified standards obtained from Inorganic Ventures and supplied by JVA Analytical Limited for all elements analysed. Certified standards of 1000 ppm were used to make standard solutions of 0.01 ppm, 0.1 ppm, 1 ppm and 10 ppm that were used for calibration. Blanks and quality control standards were run before and after the sample set. No duplicates were run, as the concentrations were an average of three analyses. A standard solution was run every 6 samples to check for calibration drift. All leachates were diluted by at least a factor of 10.

Chemometric processing of multi-element data from the extract analysis was undertaken using the method described in Cave et al. (2004). Selection of the number of components was carried out using the closely linked Akaike Information Criterion (AIC) and the Bayesian Information Criterion (BIC); as outlined in Wragg and Cave (2012). Samples were collected from geochemically similar areas (basalt soils overlying basalt geology) and therefore, in order to categorise the identified components into common sets of physico-chemical groupings (clusters), the composition (%) and profile concentration (mg kg^{-1}) data for each soil were subjected to cluster analysis in Matlab® as described by Wragg (2005). The outputs of the major element (Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, Ti, V and Zn) compositions of components and the proportion of each identified component leached from the CISED extraction and resulting mixture resolution algorithm were combined to form an input data matrix (component data matrix) for cluster analysis. The component data matrix was then mean centered and scaled on each variable so that all variables contributed the same weighting to the clustering procedure, before being subjected to a hierarchical clustering procedure to identify groupings/clusters. The final partitioning was determined by visualising the data matrix of components versus extraction profile and major element composition as a colourmap ordered into clustergram groupings. This allowed visualisation of the factors showing which major elements were dominant and where in the extractogram the component was removed, providing a means to relate clusters to geochemical sources and therefore cut the tree at a level which produced geochemically meaningful clusters.

Spatial mapping and statistical analysis

Geostatistical techniques comprising variography and kriging, were used to analyse and map the spatial distribution of Ni and Cr (mg kg^{-1}). Details of geostatistical analysis, adopted in this study, involving estimation of the variogram, fitting a model to this and use of the variogram model coefficients for spatial prediction (kriging) are provided in Barsby et al. (2012). Gstat (Pebesma and Wesseling 1998; Pebesma 2004), an open source programme for multivariate geostatistical modelling, was used to estimate variograms for the geochemical elements. Following production of the variograms using Gstat, the coefficients of the modelled variograms were used for kriging, conducted using the geostatistical functionality of ArcGIS version 10. Ordinary kriging (OK), which allows the mean of the measurements to vary spatially (Deutsch and Journel 1998), was used in this study. Exploratory data analysis, including compilation of summary statistics, and correlation analyses were carried out using IBM SPSS Statistics v19.0 software.

RESULTS AND DISCUSSION

Distribution of soil organic matter (SOC) and pH

The median pH determined during the Tellus survey for soils across Northern Ireland was 4.82. The median pH of soils overlying basalt bedrock was slightly higher at 4.91, with soils overlying the UBF having a lower median pH (4.87) than the LBF and CTM (4.95 and 4.85 respectively). This reflects the greater proportion of soils with lower pH that overlie the UBF (Table S1 in the supporting information).

The median SOC for soils across Northern Ireland was 12.92%, which is significantly lower than the median SOC for soils overlying basalts (17.69%). The median SOC in soils overlying the UBF (18.79%) is slightly greater than both the LBF (17.30%) and CTM (17.74%), this time reflecting a greater proportion of soils with higher SOC overlying the UBF (Table S1, supporting information).

Median values of pH and SOC in the subsample studied by Barsby et al. (2012) are similar to the overall Tellus dataset (Tables S1 and S2, supporting information), in all cases except the UBF, where median SOC is greater and median pH is less in the Barsby et al. (2012) samples. This may be due to the fact that a significant proportion (>30%) of the Barsby et al. (2012) sample locations overlying the UBF were identified as having peat as their soil parent material (Jordan and Higgins 2009), or had peat as the

superficial geology on the 1:250k Quaternary map of Northern Ireland (GSNI 1991).

Total and bioaccessible trace element concentrations for soils overlying Antrim Lava Group

Spatial distribution and summary statistics

Figure 1(a) shows the spatial distribution of total Ni concentrations determined during the Tellus survey. Table S2 in the supporting information summarises the Ni statistics for the full datasets, for samples which overlie basalt lithologies and samples which overlie the Upper and Lower Basalt Formations (UBF and LBF) and Causeway Tholeiite Member (CTM) on the 1:250k Solid Geology map of Northern Ireland (GSNI 1997). Table S2 shows that, for the whole Tellus dataset, Ni concentrations are higher in samples overlying basalt lithologies than for the remainder of Northern Ireland, with median concentrations in the UBF and LBF being 3 to 4 times higher those reported for the whole of Northern Ireland. The LBF has median total Ni concentrations that are slightly greater than the UBF (approx 20%). The highest Ni concentration recorded in the Tellus Survey (334 mg kg^{-1}) was reported for the LBF. In comparison, total median Ni concentrations in the CTM are 2 times greater than those reported for the rest of Northern Ireland. Lyle (1979) reported that olivine rich basalts (mostly the UBF and LBF) contained high concentrations of Ni, as Ni is preferentially absorbed by olivine instead of Mg, while the CTM contained less olivine and therefore had less Ni associated with them. Indeed Barrat and Nesbitt (1996) used Ni as an index of fractionation in Antrim Basalts due to their strong relationship. A similar trend is observed for total Cr concentrations (Figure 1(c) and Table S3, supporting information), which are generally about 3 to 4 times greater than total Ni concentrations, as also observed by Barrat and Nesbitt (1996).

Total median Ni and Cr concentrations for the subset of samples studied by Barsby et al. (2012) are similar to those for the complete Northern Ireland Tellus dataset. However when samples are divided into lithology or geological formation, although the same basic trends are observed as was seen with the whole Tellus dataset (i.e. concentrations are greatest in the LBF and least in the CTM), the absolute values are less in the Barsby et al. (2012) dataset. This suggests that the Barsby et al. (2012) dataset

contains a smaller proportion of samples of higher concentration, which is apparent in the box plots presented in Barsby et al. (2012).

As observed by Barsby et al. (2012), bioaccessible Ni and Cr was generally greater in extracts from the gastric phase than in the gastro-intestinal phase, with bioaccessible Ni being 1 to 2 times higher than bioaccessible Cr, despite higher total Cr concentrations. This is in contrast to the higher gastro-intestinal phase bioaccessibility observed by Okorie et al. (2011) for Ni and Cr in urban samples, perhaps suggesting an anthropogenic source in the Okorie et al. (2011) samples (Ljung et al. 2007). Samples overlying the LBF contained the greatest amount of bioaccessible Ni, with a mean concentration (gastric phase) of 6.17 mg kg^{-1} (compared to an NI mean of 4.58 mg kg^{-1}), while the UBF showed greater amounts of bioaccessible Cr (mean concentration (gastric phase) of 4.55 mg kg^{-1} , compared with an all NI mean of 1.79 mg kg^{-1}). The Ni and Cr bioaccessible fraction (BAF) was again greater in the gastric phase than in the gastro-intestinal phase, with Ni and Cr BAF values not varying significantly across lithology or geological formation. Ni BAFs were up to 8 times greater than Cr BAF.

Correlations

Table 1 shows the Pearson's correlation coefficients (r) for total Ni, total Cr, bioaccessible Ni (G and GI), bioaccessible Cr (G and GI) and Cr BAF (G and GI) correlated with total Ni, total Cr, Al_2O_3 , CaO, Fe_2O_3 , MgO, MnO, P_2O_5 , SiO_2 , SO_3 , SOC and pH for all bioaccessibility samples recovered from soils overlying the Antrim Lava Group (N=23). Pearson's correlation coefficients for correlations of Ni BAF (G and GI) and all elements/compounds except total Cr are taken from Palmer et al. (2012).

As indicated by their spatial distributions, total Ni and Cr are strongly correlated within the basalts ($r = 0.946$), as would be expected given their co-occurrence in the basalts (Barrat and Nesbitt 1996). Total Ni and total Cr also show significant ($p < 0.01$) positive correlations with MgO and Fe_2O_3 (accounting for greater than 65% of all variance), and to a lesser extent Al_2O_3 , MnO, P_2O_5 , CaO and pH. Significant correlation between MgO and Ni in the underlying basalt was observed by Lyle (1979), which can be

associated with olivine fractionation in the underlying bedrock, with greater olivine fractionation resulting in less Ni. Lyle (1979) also reported a negative correlation between MgO and SiO₂ in the basalt, as greater olivine fractionation was associated with increased quartz content, particularly in the CTM, which explains the lack of correlation between SiO₂ and total Ni and Cr.

Bioaccessible Cr (gastric phase) shows a similar pattern of significant ($p < 0.01$) positive correlations with total Cr, total Ni and Fe₂O₃ (accounting for approximately 75%, 65% and 57% of variance each), and to a lesser extent MgO, MnO, Al₂O₃, CaO and P₂O₅. Bioaccessible Cr from the gastro-intestinal phase also shows significant ($p < 0.01$) positive correlations with total Cr, total Ni and Fe₂O₃, but each of these account for less than 43% of variability, and is also positively correlated to a lesser extent with MgO. In contrast, Cr BAF from either the gastric or gastro-intestinal phase, is not strongly correlated with total Ni, any of the major oxides, pH or-SOC, indicating that Cr BAF, in both the gastric and gastro-intestinal phase, is independent of these factors.

As both total and gastric phase bioaccessible Cr are correlated with the same oxides (Fe₂O₃ and MgO), both total and gastric phase bioaccessible Cr are present either in these oxides or phases closely associated with them. This combined with the fact that gastric phase BAF for these samples is less than 5% indicates that Cr is not present in significant amounts in phases with high bioaccessibility that would dominate the bioaccessible fraction. Instead, the majority of gastric phase bioaccessible Cr appears to be derived from the oxide phases which contribute to the total Cr in the sample, however these oxide phases have low gastric phase bioaccessibility (less than 5%).

In contrast to the similar behaviour of total Ni and Cr and bioaccessible Cr, bioaccessible Ni shows very different correlations. Bioaccessible Ni in extracts from the gastric phase is not strongly correlated with total Ni, any of the major oxides, pH or-SOC, while bioaccessible Ni from the gastro-intestinal phase only shows significant positive correlations with Al₂O₃ and pH. However Ni BAF for the gastric phase shows significant ($p < 0.01$) negative correlation with Al₂O₃ ($r = -0.826$), Fe₂O₃ ($r = -0.718$) and MgO ($r = -0.712$) and to a lesser extent pH, MnO, Total Cr, Total Ni, CaO and P₂O₅ and SiO₂ and significant

($p < 0.01$) positive correlations with SO_3 and SOC. Ni BAF for the gastro-intestinal phase shows many of the same negative correlations (except pH and SiO), but is not significantly correlated ($p < 0.01$) with SO_3 or SOC. The strong positive correlations with SO_3 and SOC suggest that gastric phase Ni BAF is strongly controlled by the presence of peaty soils as observed by Palmer et al. (2012), but that peat does not provide such a significant control for the gastro-intestinal phase Ni BAF. This was confirmed when soil parent material (Jordan and Higgins 2009) was examined. Only 3 of the samples tested for bioaccessibility were identified as having peat as the soil parent material (Jordan and Higgins 2009), and these three samples had the highest gastric phase Ni BAF (all greater than 30%).

To determine whether other controls on gastric phase Ni BAF were present, correlations were rerun with the three peat samples identified above removed. On removal of these samples, Ni BAF for the gastric phase again showed significant ($p < 0.01$) negative correlations with Fe_2O_3 ($r = -0.665$), MnO ($r = -0.634$), MgO ($r = -0.624$) and Al_2O_3 ($r = -0.565$) but was not significantly correlated with pH, P_2O_5 , SiO_2 , SO_3 or SOC. This is a similar pattern to that observed for gastro-intestinal phase Ni BAF. The strong negative correlations of Ni BAF with Fe_2O_3 , MnO, MgO and Al_2O_3 combined with their positive correlation to total Ni and Cr suggest that the majority of total Ni is present in the oxides or other closely related phases, but these phases have low gastric phase bioaccessibility. However some Ni is hosted in other more soluble phases, which are more bioaccessible. In soil samples where there are high oxide contents, most of the Ni is in the oxide phases, giving a low BAF. However in samples with lower oxide contents, the other more bioaccessible phases dominate gastric phase bioaccessibility giving a higher BAF. This suggests that as well as gastric phase bioaccessible Ni being associated with peaty soils, bioaccessible Ni for both the gastric and gastro-intestinal phase is present in other specific mineral phases associated with lower Fe_2O_3 , MnO, MgO and Al_2O_3 concentrations, which have a lower total Ni concentrations, but a much higher Ni BAF.

Mineralogical evaluation of samples

Bulk XRD analysis was undertaken on a subset of 12 samples that were identified as having basalt as

their soil parent material (Jordan and Higgins 2009) to try to remove the effect of peaty soils on the analysis. XRD analysis showed that all samples were composed of quartz and plagioclase and alkali feldspars, with augite, hematite and montmorillonite also detected in all samples. Mica and clinocllore were identified in 8 of the samples, but there was no obvious correlation between samples that contained mica and clinocllore and total or bioaccessible Ni or Cr. This suggests that total and bioaccessible Ni and Cr are either influenced by Ni and Cr bearing minerals that are present at concentrations that were too low to be identified by conventional XRD, are controlled by non crystalline minerals that were not identified by the bulk XRD undertaken, or that they are present in the minerals identified by the XRD analysis (such as feldspar or pyroxene), but as these minerals are present in all samples, quantification is required to demonstrate their control on total and bioaccessible Ni and Cr. Olivine was not identified by XRD in any of the samples, probably because it weathers readily to clays (Nesbitt and Wilson 1992; Cruickshank 1997).

These findings are consistent with soils derived from weathered basalt. Lyle (1979) reported that the Upper and Lower Basalt Formation are comprised of olivine basalt composed predominately of plagioclase feldspars containing olivine phenocrysts and augite, while the Causeway Tholeiite Members are quartz tholeiites containing augite most abundantly, with plagioclase feldspars and small amounts on olivine and chloritic material.

All 12 samples showed similar XRD traces except for one sample which has the highest Ni BAF (22.5%) and a low total Ni soil concentration (36 mg kg^{-1}). The XRD scan for this sample showed a hump between 2 theta angle of 20 and 22, which was not present on scans for other samples. The pH of this sample was the lowest among the 12 samples (3.54 pH units) and it had the highest SOC value of 79.4%. These factors suggest this sample was in fact a peat.

Interpretation of sequential extraction data

Chemometric data analysis identified 6 components in sample A, 5 components in sample B and 7

components in sample C (See Figure 1 for sample locations). Following hierarchical cluster analysis of mean centered and scaled data, 6 geochemically distinct clusters were identified as shown in the dendrogram and associated colourmap in Figure 2. These clusters were identified as described by Wragg and Cave (2012) by considering the geochemical and mineralogical information already discussed and:

- The relative solubility of each component in the acid extracts (as illustrated on the right hand side of the colourmap)
- The major elemental composition (reported here as the median concentration) of each component (left hand side of colourmap), combined with ease of extractability

Residual pore water, possibly containing organics

This cluster is predominantly composed of Na, Ca, K and S and was mostly removed by the two water extractions, with a small amount extracted at higher acid concentrations (above 0.5M HNO₃). The ease of removal suggests it is associated with dissolution of residual salts from the original pore-water in the soil (Cave et al. 2004), however the small amount of this component extracted at higher acid concentrations may indicate that some organics are present, as humic acid type materials are oxidized and broken down at higher acid concentrations, releasing inorganics into solution (Cave et al. 2004).

Ca carbonate

Two clusters were assigned as Ca carbonate. Ca concentrations were very high in Ca carbonate cluster 1 (>85%) and which was extracted between 0.05 and 0.1M HNO₃. Ca concentrations are also high in Ca carbonate cluster 2 (70% for all components, except A-Ca-Mn which has a Ca concentration of 51% and a Mn concentration of 33%), which was extracted by addition of a weak acid (0.05M HNO₃). High Ca concentrations combined with removal on the addition of relatively weak acid, suggests these clusters are associated with the dissolution of a calcium carbonate phase (Wragg 2005; Wragg and Cave 2012). Although calcium carbonate was not identified in the XRD analysis (suggesting that any carbonates present in the samples are in amorphous form), both plagioclase feldspars and pyroxenes (augite), which

weather to Ca carbonate (Nesbitt and Wilson 1992), are known to be present in the underlying bedrock (Lyle 1979) and were identified in all samples in the XRD analysis.

Al oxide

These Al dominated components (c. 80% for A-Al and B-Al and c.30% for C-Al-Mg) are extracted with acid concentrations of between 0.05M and 0.5M and have been identified as an aluminum oxide. Al oxide is a weathering product of silicate minerals, including feldspars which were identified by XRD analysis, and gibbsite is known to be present in high concentrations in the weathered Interbasaltic Formation (Mitchell 2004), present between the LBF and UBF.

Clay related cluster

All these components have relatively high proportions of Al (35-65%) and Fe (15-65%), as well as Si (10-15%), and were extracted at moderate to high acid concentrations (0.1 to 5M). Relatively high concentrations of trace metals including Cu and Pb were contained in these components. The high acid strength for extraction, combined with predominance of Fe, Al and Si and presence of trace elements suggests components in this cluster are likely to be derived from clay like materials (Wragg 2005). Clays (both montmorillonite and chlorite (chlinochlore)) were identified during mineralogical analyses by XRD.

Fe oxide

All three components in this cluster have greater than 50% Fe and between 18 and 32% Al. In all cases except C-Fe-Al, Mg, P and Si were also identified. A-Fe-Al and B-Fe-Al are initially extracted at 0.5M HNO₃, and the amount extracted steadily increases up to 5M HNO₃. C-Fe-Mg-Si shows a slightly different profile, with some of the component extracted at lower acid concentrations, while C-Fe-Al is extracted at a slightly higher acid concentration. The dominance of Fe and high acid strengths required to extract these components has led to their identification as a Fe oxide and this correlates with the identification of hematite in all samples by XRD. The presence of Al and Si in all components apart

from C-Fe-Al suggests that the Fe oxide is perhaps intergrown with clays, as observed by Cave et al. (2004). Component C-Fe-Al was extracted at slightly higher acids concentrations (5M HNO₃) suggesting a purer oxide with less fine grains (Wragg 2005).

Relation of mineralogy and CISED to bioaccessibility

In all three CISED samples, gastric phase bioaccessibility was greater than gastro-intestinal phase bioaccessibility for both Ni and Cr. Total Ni concentrations were lowest in sample C (122 mg kg⁻¹) and highest in samples A and B (175 and 167 mg kg⁻¹ respectively), while gastric phase bioaccessibility was greatest in sample C (8.84 mg kg⁻¹; 7.27% BAF) and lowest in samples A and B (4.34 and 3.39 mg kg⁻¹ respectively; 2.0 - 2.5% BAF). Therefore although there is more total Ni present in samples A and B, this is in a less mobile form than the Ni present in sample C. In contrast, Cr gastric BAF was consistently between 1 and 2%, with sample A having the highest total Cr concentration (448 mg kg⁻¹) and sample C having the lowest total Cr concentration (293 mg kg⁻¹).

Median cumulative Ni and Cr extracted during the CISED extractions, ordered by ease of extraction for the five cluster types are shown in Figure 3. Element distribution observed for the two identified carbonate clusters has been summed as one single carbonate phase for the purposes of visualisation. Nickel and Cr gastric phase bioaccessibility for all three soils is also shown. This information provides an indication of the solid phase source fractions of bioaccessible and non-bioaccessible contaminants of interest (Wragg and Cave, 2012). For the three samples investigated, CISED extraction removed more Ni and Cr from the soils than the UBM, which is to be expected given the higher acid strengths used in the CISED extraction. However less than 15% of total Ni and Cr were extracted by the CISED method, suggesting that the majority of these elements are present in the less reactive alumino-silicate soil matrix as the silicate matrix is unlikely to be attacked by HNO₃ used in the CISED extraction (Cave et al. 2004; Ruby et al. 1999). The primary minerals quartz, feldspar and pyroxene (augite) were all identified in the XRD study and would be resistant to attack by HNO₃. Pyroxene is known to host both Ni and Cr (Wedephol, 1978). Utilisation of *aqua regia* has recently been shown to return 100% recovery of Ni in

similar extractions (Wragg and Cave 2012) and should be considered for further studies of Ni. However more concentrated acid strengths were needed to extract Ni in the Wragg and Cave (2012) study, which suggests that the additional Ni bearing phases extracted by *aqua regia* were not readily bioaccessible.

Figure 3 shows that gastric phase Ni bioaccessibility tends to increase with decreasing total Ni, while gastric phase Cr bioaccessibility decreases with decreasing total Cr. Figure 3 also indicates that the source of bioaccessible Cr is likely to be from the dissolution of this PTE associated with the clusters identified as residual pore water salts, carbonates, aluminum oxides and clays, with clays contributing the greatest proportion of bioaccessible Cr (greater than 85%). For Ni, it appears that the same soil components are the sources of the bioaccessible fraction of this PTE, in addition to some dissolution from the identified Fe oxide/hydroxide component present. However carbonate and aluminum oxide components contribute greater amounts of bioaccessible Ni (35 to 55%) than Cr (less than 10%). The Ni distribution for Sample C is noticeably different from Samples A and B, with a greater contribution of Ni coming from carbonate and clay components. This appears to cause the higher bioaccessibility observed for this sample, and supports the findings of the correlation analysis that in samples with lower total Ni concentrations, more soluble phases which contain a small proportion of total Ni dominate gastric phase bioaccessibility giving a higher BAF that is observed in samples with higher total Ni concentrations.

In their study of basalt weathering, Nesbitt and Wilson (1992) also found that Cr was predominantly present in primary Fe-Ti oxides, which are known to be the most resistant primary minerals during weathering of basalts, however once released from these primary phases, Cr became incorporated in clay and Al oxide. In contrast, they found that Ni was present in greatest amounts in olivine, which weathers rapidly, with some Ni leaching down through the soil horizons and remaining Ni being taken up by smectite and Fe oxyhydroxide. Quantin et al. (2008) and Kierczak et al. (2007) also found that Cr was less mobile than Ni in soils overlying ultramafic rocks, when studying the PTEs' bioavailability for plant uptake. Both authors concluded that Cr was tightly bound to recalcitrant primary Fe oxides and Quantin

et al. (2008) concluded that Ni was transferred more readily to secondary minerals during weathering.

CONCLUSIONS

This study investigated spatial trends in Ni and Cr oral bioaccessibility within the Antrim Lava Group using the bioaccessibility dataset produced by Barsby et al. (2012) and extended correlation analyses undertaken by Palmer et al. (2012) between total and bioaccessible Ni and major oxides to include total and bioaccessible Cr to identify principal controls on trace element bioaccessibility. Data from mineralogical testing of 12 selected soil samples using XRD and non specific sequential extraction and chemometric analysis on 3 of these samples were also related to results of oral bioaccessibility to determine whether a relationship exists between the overall concentrations of trace elements, the soil's mineralogy and their bioaccessibility.

XRD analysis showed that soils overlying the Basalts were composed predominantly of quartz, with plagioclase and alkali feldspars and smaller amounts of augite, hematite and montmorillonite, while chemometric data analysis identified 6 geochemically distinct clusters of components within the soils: residual pore water, Ca carbonate, Al oxide, a clay related cluster and Fe oxide.

Nickel and Cr concentrations are higher in samples overlying basalt lithologies than for the remainder of Northern Ireland, with Ni concentrations in the UBF and LBF being 3 to 4 times higher those reported for the whole of Northern Ireland. The LBF has total concentrations that are slightly greater than the UBF, while total concentrations in the Causeway Tholeiite Member are only slightly elevated compared to the rest of Northern Ireland. However not all Ni and Cr in soils overlying the Antrim Lava Group is bioaccessible, with Ni being generally more bioaccessible than Cr, despite higher total Cr concentrations. This can be linked to differences between the specific soil phases in which Ni and Cr exist, as shown by CISED results.

Cr appears to be present in soils in phases which are strongly associated with Fe_2O_3 and MgO, and have

an overall oral bioaccessibility of less than 5%. CISED results indicate that small amounts of Cr are associated with residual pore water salts, carbonates and Al oxides, however the majority of Cr is associated with iron oxides and clay components, with most bioaccessible Cr present in clay components. In contrast, in addition to the strong controls exerted on Ni BAF by geochemistry variables associated with peat (Palmer 2012), bioaccessible Ni for both the gastric and gastro-intestinal phase was found to be related to all identified soil components, with Ca carbonate and Al oxide components hosting a greater proportion of bioaccessible Ni than was observed with Cr. This combined with the findings of correlation analyses which indicated bioaccessible Ni is associated a number of more soluble phases, suggests that weathering significantly affects nickel bioaccessibility, but does not have the same effect on the bioaccessibility of chromium.

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REFERENCES

- Barrat, J.A., Nesbitt, R.W. (1996). Geochemistry of the Tertiary volcanism of Northern Ireland. *Chemical Geology*, 129, 15–38.
- Barsby, A., McKinley, J.M., Ofterdinger, U., Young, M., Cave, M.R., Wragg, J. (2012). Bioaccessibility of trace elements in soils in Northern Ireland. *Science of the Total Environment*, 433, 398–417.
- Broadway, A., Cave, M.R., Wragg, J., Fordyce, F.M., Bewley, R.J.F., Graham, M.C., Ngwenya, B.T., Farmer, J.G. (2010). Determination of the bioaccessibility of chromium in Glasgow soil and the implications for human health risk assessment. *Science of the Total Environment*, 409, 267–277.

- Cave, M.R., Milodowski, A.E., Friel, E.N. (2004). Evaluation of a method for identification of host physico-chemical phases for trace metals and measurement of their solid-phase partitioning in soil samples by nitric acid extraction and chemometric mixture resolution. *Geochemistry: Exploration, Environment, Analysis*, 4, 71–86.
- Cave, M. R.; Wragg, J.; Denys, S.; Jondreville, C.; Feidt, C. (2011). Oral Bioavailability, In: F. A. Swartjes (Ed.), *Dealing with Contaminated Sites* (pp. 287–324). Netherlands: Springer.
- Chartered Institute of Environmental Health (CIEH) (2009). Professional Practice Note: Reviewing human health risk assessment reports invoking contaminant oral bioavailability measurements or estimates. Chartered Institute of Environmental Health (CIEH).
http://www.cieh.org/library/Policy/Environmental_protection/Contaminated_land/Standing_Conference_on_Contaminated_Land/CIEH_PPN_Bioavailability_Final_June09.pdf. Accessed 13 December 2012.
- Cicchella, D., De Vivo, B., Lima, A. (2005). Background and baseline concentration values of elements harmful to human health in the volcanic soils of the metropolitan and provincial areas of Napoli (Italy). *Geochemistry: Exploration, Environment, Analysis*, 5, 29–40.
- Costa, C., Reis, a. P., Ferreira da Silva, E., Rocha, F., Patinha, C., Dias, a. C., Sequeira, C., Terroso, D. (2011). Assessing the control exerted by soil mineralogy in the fixation of potentially harmful elements in the urban soils of Lisbon, Portugal. *Environmental Earth Sciences*, 65(4), 1133–1145.
- Costa, M., Klein, C.B. (2006). Toxicity and carcinogenicity of chromium compounds in humans. *Critical Reviews in Toxicology*, 36, 155–163.
- Cruickshank, J.G. (1997). *Soil and Environment: Northern Ireland*. Belfast: Agricultural and Environmental Science Division, DANI and The Agricultural and Environmental Science Department, The Queen’s University of Belfast.

- Dao, L., Morrison, L., Zhang, C. (2012). Bonfires as a potential source of metal pollutants in urban soils, Galway, Ireland. *Applied Geochemistry*, 27, 930–935.
- Denkhaus, E., Salnikow, K. (2002). Nickel essentiality, toxicity, and carcinogenicity. *Critical Reviews in Oncology/Hematology*, 42, 35–56.
- Denys, S., Caboche, J., Tack, K., Rychen, G., Wragg, J., Cave, M., Jondreville, C., Feidt, C. (2012). In vivo validation of the unified BARGE method to assess the bioaccessibility of arsenic, antimony, cadmium, and lead in soils. *Environmental Science and Technology*, 46, 6252–6260.
- Denys, S., Tack, K., Caboche, J., Delalain, P. (2009). Bioaccessibility, solid phase distribution, and speciation of Sb in soils and in digestive fluids. *Chemosphere*, 74, 711–716.
- Deutsch, C. V., Journel, A.G. (1998). *GSLIB: Geostatistical Software Library and User's Guide*, Second ed. New York: Oxford University Press.
- Environment Agency (EA) (2009a). Updated technical background to the CLEA model. Bristol: Environment Agency (EA).
- Environment Agency (EA) (2009b). Soil Guideline Values for nickel in soil. Bristol: Environment Agency (EA).
- Facchinelli, A., Sacchi, E., Mallen, L. (2001). Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Environmental Pollution*, 114, 313–24.
- Geological Survey of Northern Ireland (GSNI) (1997). Northern Ireland. Solid Geology 1:250 000, Second ed. Keyworth, Nottingham: British Geological Survey.
- Geological Survey of Northern Ireland (GSNI) (1991). Quaternary Geological Map of Northern Ireland 1:250 000, Keyworth, Nottingham: British Geological Survey.
- Hamel, S.C., Buckley, B., Lioy, P.J. (1998). Bioaccessibility of Metals in Soils for Different Liquid to Solid Ratios in Synthetic Gastric Fluid. *Environmental Science and Technology*, 32, 358–362.

- Hansen, J.B., Oomen, A.G., Edelgaard, I., Grøn, C. (2007). Oral Bioaccessibility and Leaching: Tests for Soil Risk Assessment. *Engineering in Life Sciences*, 7, 170–176.
- Intawongse, M., Dean, J.R. (2006). In-vitro testing for assessing oral bioaccessibility of trace metals in soil and food samples. *Trends in Analytical Chemistry*, 25, 876–886.
- Johnson, C. C.; Ander, E. L.; Cave, M. R.; Palumbo-Roe, B. (2012). Normal background concentrations (NBCs) of contaminants in English soils: Final project report. Keyworth, Nottingham: British Geological Survey
- Jordan, C; Higgins, A. (2009). The AFBI Soil Classification Map of Northern Ireland at 1:50,000 scale. Based on information from Cruickshank, J.G. (Ed.) 1997, Soil and Environment: Northern Ireland. Agricultural and Environmental Science Department, Queen's University Belfast. Belfast: Agri-Food and Biosciences Institute.
- Kierczak, J., Neel, C., Bril, H., Puziewicz, J. (2007). Effect of mineralogy and pedoclimatic variations on Ni and Cr distribution in serpentine soils under temperate climate. *Geoderma*, 142, 165–177.
- Ljung, K., Oomen, A., Duits, M., Selinus, O., Berglund, M. (2007). Bioaccessibility of metals in urban playground soils. *Journal of Environmental Science and Health Part A*, 42, 1241-1250.
- Lyle, P. (1979). A petrological and geochemical study of the tertiary basaltic rocks of Northeast Ireland. *Journal of Earth Science*, 2, 137–152. Nesbitt, H.W. and R.E. Wilson (1992). Recent chemical weathering of basalts. *American Journal of Science*, 292, 740-778.
- Madrid, F., Biasioli, M., Ajmone-Marsan, F. (2008). Availability and bioaccessibility of metals in fine particles of some urban soils. *Archives of Environmental Contamination and Toxicology*, 55, 21–32.
- Megremi, I. (2010). Distribution and bioavailability of Cr in central Euboea, Greece. *Central European Journal of Geosciences*, 2, 103–123.

- Meunier, L., Walker, S.R., Wragg, J., Parsons, M.B., Koch, I., Jamieson, H.E., Reimer, K.J. (2010). Effects of soil composition and mineralogy on the bioaccessibility of arsenic from tailings and soil in gold mine districts of Nova Scotia. *Environmental Science and Technology*, 44, 2667–2674.
- Mitchell, W.I. (2004). *The Geology of Northern Ireland Our Natural Foundation*. Belfast: Geological Survey of Northern Ireland.
- Mostert, M.M.R., Ayoko, G.A., Kokot, S. (2012). Multi-criteria ranking and source identification of metals in public playgrounds in Queensland, Australia. *Geoderma*, 173-174, 173–183.
- Nathanail, P., McCaffrey, C., Ashmore, M., Cheng, Y., Gillet, A., Ogden, R., Scott, D. (2009). The LQM/CIEH generic assessment criteria for human health risk assessment. Nottingham : Land Quality Press.
- Nesbitt, H. W., Wilson, R. E. (1992). Recent chemical weathering of basalts. *American Journal of Science*, 292, 740-777.
- Nico, P.S., Ruby, M. V, Lowney, Y.W., Holm, S.E. (2006). Chemical speciation and bioaccessibility of arsenic and chromium in chromated copper arsenate-treated wood and soils. *Environmental Science and Technology*, 40, 402–408.
- Okorie, A., Entwistle, J., Dean, J.R. (2011). The application of in vitro gastrointestinal extraction to assess oral bioaccessibility of potentially toxic elements from an urban recreational site. *Applied Geochemistry*, 26, 789–796.
- Oomen, A.G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, C., Schoeters, G., Verstraete, W., Van de Wiele, T., Wragg, J., Rompelberg, C.J.M., Sips, A.J. a M., Van Wijnen, J.H. (2002). Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. *Environmental Science and Technology*, 36, 3326–3334.

- Oomen, A.G., Rompelberg, C.J.M., Bruil, M.A., Dobbe, C.J.G., Pereboom, D.P.K.H., Sips, A.J.A.M. (2003). Development of an in vitro digestion model for estimating the bioaccessibility of soil contaminants. *Archives of Environmental Contamination and Toxicology*, 44, 281–287.
- Palmer, S.; Ofterdinger, U.; McKinley, J.; Cox, S. F.; Barsby, A. (In review). Spatial analysis approaches to investigate the bioaccessibility of Nickel, Vanadium and Zinc in Northern Ireland, UK soils. *Environmental Geochemistry and Health*.
- Palumbo-Roe, B., Klinck, B. (2007). Bioaccessibility of arsenic in mine waste-contaminated soils: a case study from an abandoned arsenic mine in SW England (UK). *Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances and Environmental Engineering*, 42, 1251–1261.
- Pebesma, E. J. ; Wesseling, C.G. (1998). Gstat, a program for geostatistical modelling, prediction and simulation: *Computers and Geosciences*, 24, 17–31.
- Pebesma, E. J. (2004). Multivariable geostatistics in S: the gstat package: *Computers & Geosciences*, 30 (7), 683-691.
- Pelfrène, A., Waterlot, C., Mazzuca, M., Nisse, C., Cuny, D., Richard, A., Denys, S., Heyman, C., Roussel, H., Bidar, G., Douay, F. (2012). Bioaccessibility of trace elements as affected by soil parameters in smelter-contaminated agricultural soils: a statistical modeling approach. *Environmental Pollution*, 160, 130–138.
- Poggio, L., Vrscaj, B., Schulin, R., Hepperle, E., Ajmone Marsan, F. (2009). Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy). *Environmental Pollution*, 157, 680–689.
- Quantin, C., Ettler, V., Garnier, J., Sebek, O. (2008). Sources and extractibility of chromium and nickel in soil profiles developed on Czech serpentinites. *Surface Geosciences (Pedology)*, 340, 872–882.
- Rodrigues, S., Pereira, M.E., Duarte, A.C., Ajmone-Marsan, F., Davidson, C.M., Grcman, H., Hossack, I., Hursthouse, A.S., Ljung, K., Martini, C., Otabbong, E., Reinoso, R., Ruiz-Cortés, E., Urquhart,

- G.J., Vrscaj, B. (2006). Mercury in urban soils: a comparison of local spatial variability in six European cities. *Science of the Total Environment*, 368, 926–936.
- Ruby, M. V., Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., Mosby, D. E., Casteel, S. W., Berti, W., Carpenter, M., Edwards, D., Cragin, D., Chappel, W. (1999). Critical Review Advances in Evaluating the Oral Bioavailability of Inorganics in Soil for Use in Human Health Risk Assessment. *Environmental Science and Technology*, 33, 3697–3705.
- Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Á., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T. (2005). Geochemical Atlas of Europe. Part 1 - Background Information, Methodology, and Maps. Espoo, Finland: Geological Survey of Finland.
- Smyth, D. (2007). Methods used in the Tellus Geochemical Mapping of Northern Ireland. Keyworth, Nottingham: British Geological Survey.
- Stewart, M.A., Jardine, P.M., Brandt, C.C., Barnett, M.O., Fendorf, S.E., McKay, L.D., Mehlhorn, T.L., Paul, K. (2003). Effects of Contaminant Concentration, Aging, and Soil Properties on the Bioaccessibility of Cr(III) and Cr(VI) in Soil. *Soil and Sediment Contamination*, 12, 1–21.
- Wong, C.S.C., Li, X., Thornton, I. (2006). Urban environmental geochemistry of trace metals. *Environmental Pollution*, 142, 1–16.
- Wedephol, K. H. (1978). *Handbook of Geochemistry*. Berlin: Springer-Verlag.
- Wragg, J. (2005). A Study of the Relationship between Arsenic Bioaccessibility and its Solid Phase Distribution in Wellingborough Soils. PhD Thesis, University of Nottingham.

Wragg, J., Cave, M. (2012). Assessment of a geochemical extraction procedure to determine the solid phase fractionation and bioaccessibility of potentially harmful elements in soils: a case study using the NIST 2710 reference soil. *Analytica Chimica Acta*, 722, 43–54.

Wragg, J., Cave, M., Basta, N., Brandon, E., Casteel, S., Denys, S., Gron, C., Oomen, A., Reimer, K., Tack, K., Van de Wiele, T. (2011). An inter-laboratory trial of the unified BARGE bioaccessibility method for arsenic, cadmium and lead in soil. *Science of the Total Environment*, 409, 4016–4030.

Zhang, C., Wu, L., Luo, Y., Zhang, H., Christie, P. (2008). Identifying sources of soil inorganic pollutants on a regional scale using a multivariate statistical approach: role of pollutant migration and soil physicochemical properties. *Environmental Pollution*, 151, 470–476.

FIGURES

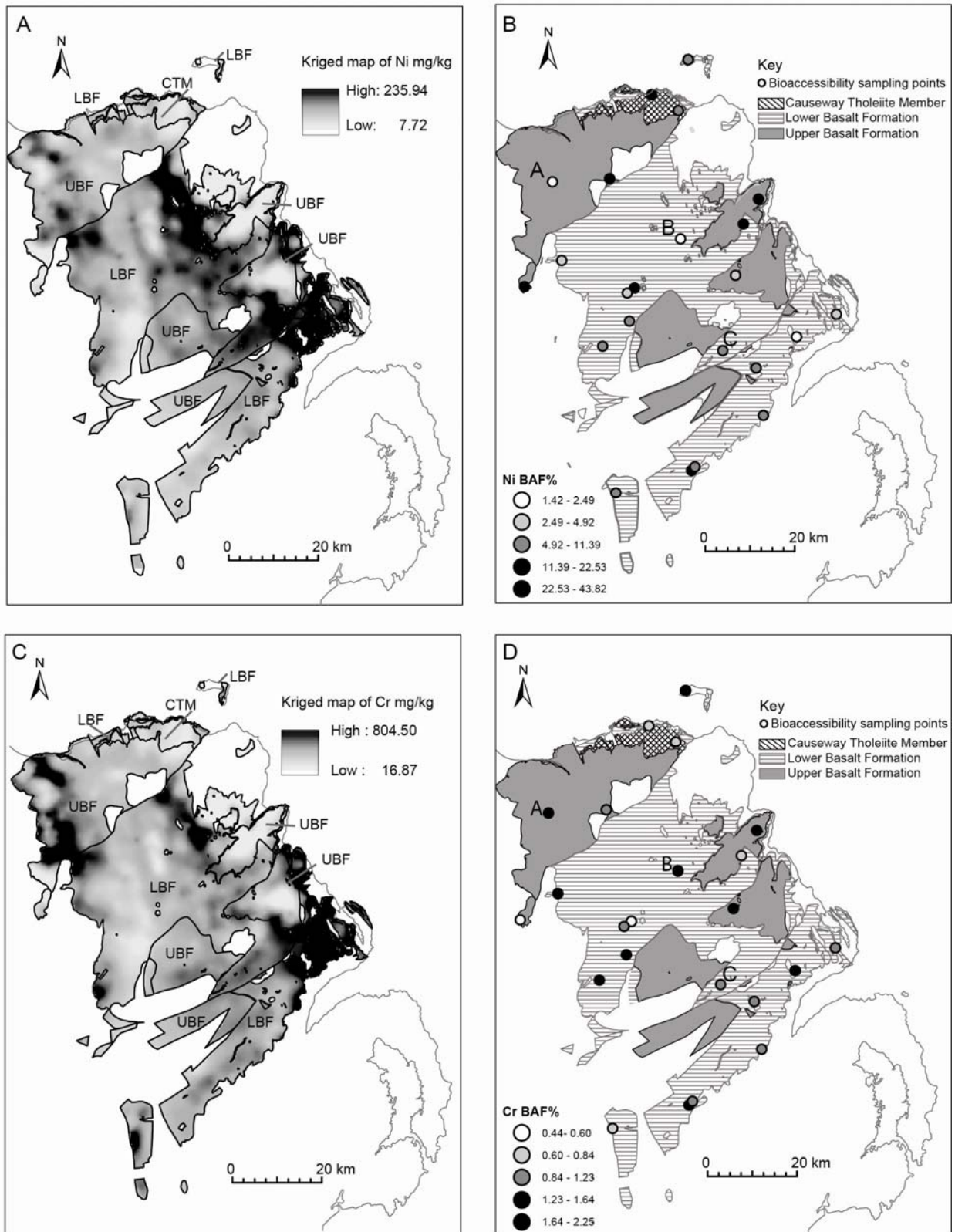


Fig. 1 Maps showing the spatial distribution of (A) total Ni, (B) gastric phase Ni BAF, (C) total

Cr and (D) gastric phase Cr BAF. (A) and (C) are total element concentrations by XRF (mg kg^{-1}) for all Tellus samples, while (B) and (D) are gastric phase BAF (%) for 23 Barsby et al. (2012) samples that overlie the Antrim Lava Group. CTM is Causeway Tholeiite Member; LBF is Lower Basalt Formation and UBF is Upper Basalt Formation. Samples locations (A, B and C) are identified and discussed in the text

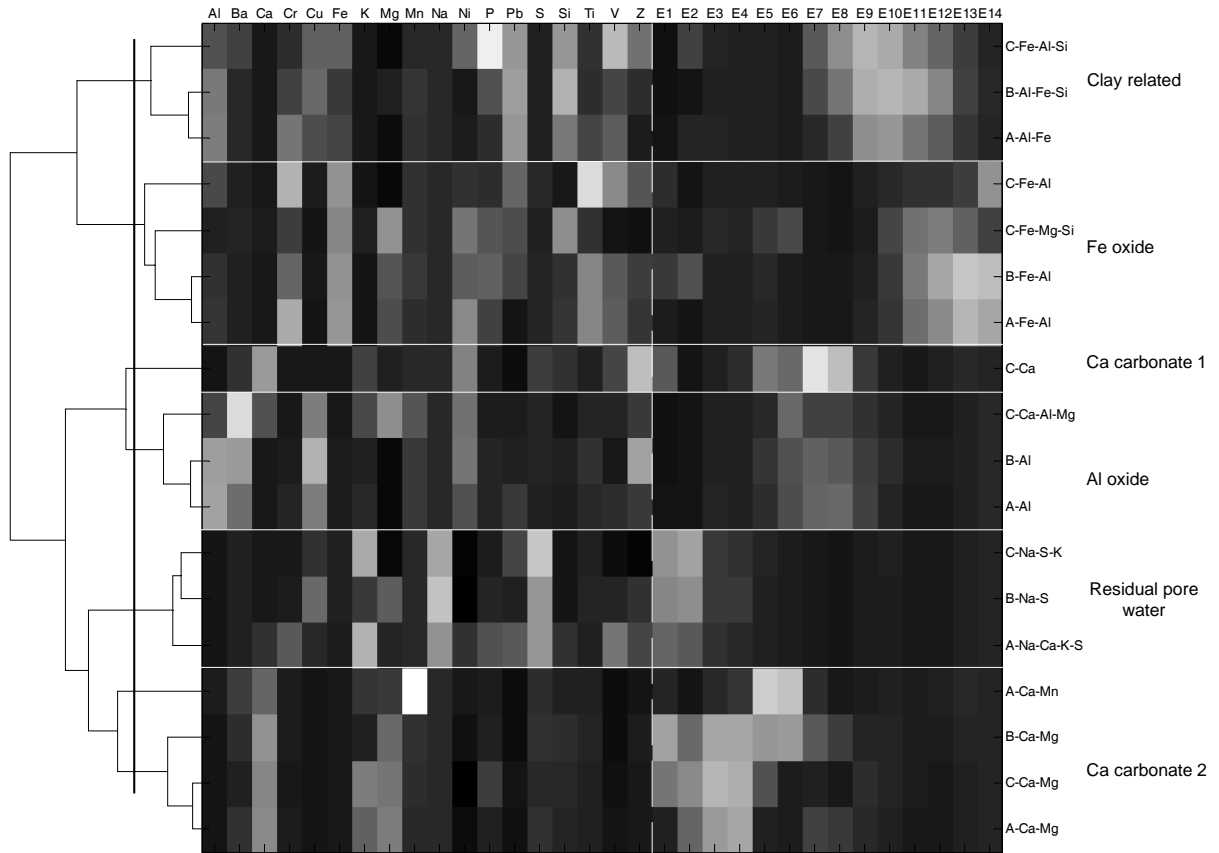


Fig. 2 Colourmap and associated clustergram for CISED extractable test soils. The dendrogram on the left hand side shows how individual components link together. The horizontal solid white lines divide the colourmap into clusters and the dashed vertical white line separates elemental composition data on the left hand side from extraction number data (E1-14) on the right. High concentrations are depicted by white/light grey and low concentrations by dark grey/black. Component names comprise a sample identification code (A, B and C) followed by the principal elements recorded for each component

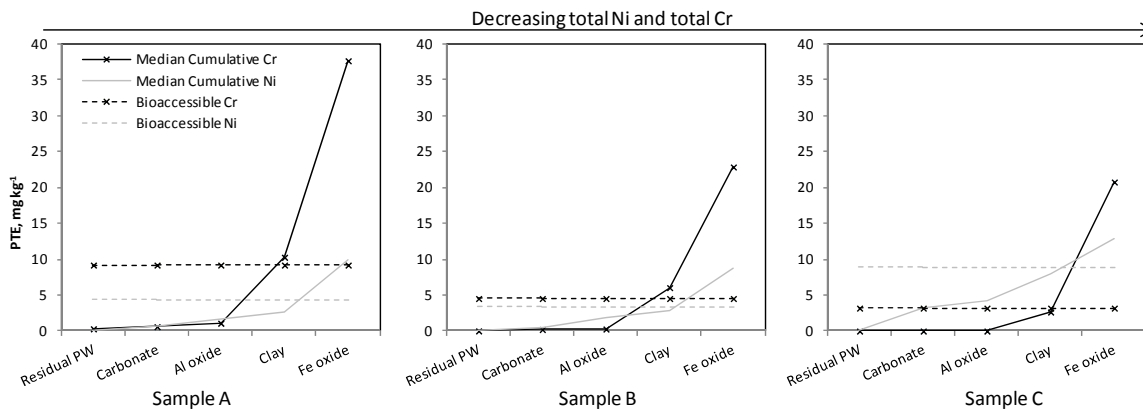


Fig. 3 Median cumulative Ni and Cr extracted during CISED extractions compared with *in vitro* gastric phase bioaccessibility as measured by UBM (mg kg^{-1}).

TABLES

	Total Ni	Total Cr	Fe₂O₃	MgO	Al₂O₃	MnO	P₂O₅	CaO	SiO₂	pH	SO₃	SOC
Total Ni	1	.946 **	.893 **	.901 **	.755 **	.778 **	.721 **	.688 **	.059	.611 **	-.302	-.442 *
Bio Ni-G	.240	.267	.074	.191	.186	-.028	.138	.255	-.047	.331	.087	-.057
Bio Ni-GI	.433 *	.471 *	.330	.473 *	.529 **	.236	.318	.397	.250	.618 **	-.324	-.423 *
Ni BAF-G^a	-.611 **	-.627 **	-.718 **	-.712 **	-.826 **	-.651 **	-.563 **	-.570 **	-.552 **	-.696 **	.677 **	.811 **
Ni BAF-GI^a	-.700 **	-.650 **	-.789 **	-.710 **	-.607 **	-.695 **	-.591 **	-.689 **	-.048	-.426 *	.214	.390
Total Cr	.946 **	1	.818 **	.863 **	.714 **	.660 **	.606 **	.608 **	.131	.612 **	-.339	-.480 *
Bio Cr-G	.809 **	.861 **	.759 **	.681 **	.571 **	.582 **	.535 **	.564 **	-.008	.401	-.207	-.353
Bio Cr-GI	.630 **	.675 **	.646 **	.531 **	.515 *	.508 *	.437 *	.474 *	-.018	.338	-.164	-.313
Cr BAF-G	.047	.083	.240	.155	.192	.157	.074	.347	-.001	-.080	-.050	-.166
Cr BAF-GI	-.239	-.217	-.014	-.127	-.054	-.047	-.131	.126	-.163	-.330	.139	.083

Table 1 Pearson correlation coefficient (r) for Barsby et al. (2012) samples which overlie the

Antrim Basalts (N= 23 for all correlations). ** Correlation is significant at the 0.01 level

(2-tailed). * Correlation is significant at the 0.05 level (2-tailed). ^a r values for correlation of Ni BAF

(G and GI) (mg kg⁻¹) with all elements/compounds except total Cr taken from Palmer et al. (2012)

Supporting information

		No of samples	Minimum	5th percentile	25th percentile	Median	Mean	75th percentile	95th percentile	Maximum
Soil pH (pH units) All Tellus data	All NI	6855	2.83	3.16	4.44	4.82	4.73	5.17	5.82	7.68
	Basalt	1733	2.83	3.29	4.60	4.91	4.80	5.17	5.67	7.68
	LBF	1033	2.92	3.49	4.70	4.95	4.89	5.19	5.67	7.68
	UBF	589	2.83	3.15	4.29	4.87	4.69	5.18	5.70	7.51
	CTM	47	3.81	3.90	4.67	4.85	4.82	4.98	5.36	6.14
Soil pH (pH units) Barsby et al subsample	All NI	91	3.14	3.76	4.49	4.78	4.83	5.20	5.97	6.61
	Basalt	23	3.14	3.16	4.19	4.76	4.59	5.00	5.89	6.05
	LBF	13	3.14	3.14	4.63	4.93	4.81	5.19	**	6.05
	UBF	6	3.26	3.26	3.47	4.42	4.22	4.80	**	4.92
	CTM*	2	4.38			4.48	4.48			4.57
SOC (%) Barsby et al subsample	All NI	6860	1.01	6.39	9.28	12.92	23.41	21.94	93.65	98.05
	Basalt	1733	1.01	8.54	13.39	17.69	27.82	28.29	93.50	98.05
	LBF	1033	2.54	8.05	13.22	17.30	24.13	24.09	86.02	97.32
	UBF	589	1.01	9.82	13.76	18.79	34.07	44.89	95.88	98.05
	CTM*	47	7.09	8.42	13.42	17.74	23.95	26.00	80.70	86.05
SOC (%) Barsby et al subsample	All NI	91	3.79	5.46	9.65	13.71	20.75	21.76	78.39	95.22
	Basalt	23	4.00	4.46	15.89	19.70	32.17	30.55	94.53	95.22
	LBF	13	4.00	4.00	10.98	16.69	26.64	25.18	**	91.79
	UBF	6	16.62	16.62	20.99	42.13	49.66	83.37	**	95.22
	CTM*	2	16.78			23.67	23.67			30.55

Table S1 Summary statistics for pH and SOC *Percentiles not reported, due to low sample numbers ** Percentile not reported as it exceeds max value

Nickel		No of samples	Minimum	5th percentile	25th percentile	Median	Mean	75th percentile	95th percentile	Maximum
Total Ni (mg kg ⁻¹) All Tellus data	All NI	6860	1.40	4.00	14.00	29.05	46.21	56.10	155.10	333.60
	Basalt	1733	2.30	8.20	60.90	100.20	102.22	139.15	201.63	333.60
	LBF	1033	3.20	16.99	72.45	110.90	112.58	148.45	210.20	333.60
	UBF	589	2.50	6.75	58.80	93.60	93.16	124.95	189.75	262.00
	CTM	47	7.00	12.72	35.20	45.40	58.54	69.80	160.84	226.50
Total Ni (mg kg ⁻¹) Barsby et al subsample	All NI	91	4.90	7.28	19.60	31.00	48.46	61.70	169.70	235.10
	Basalt	23	4.90	5.34	22.30	70.70	77.66	121.80	184.88	185.30
	LBF	13	7.10	7.10	25.30	77.20	80.83	121.70	**	183.20
	UBF	6	4.90	4.90	28.23	69.95	90.10	177.20	**	185.30
	CTM*	2	19.50			22.65	22.65			25.80
Bioaccessible Ni G (mg kg ⁻¹) Barsby et al subsample	All NI	91	.72	.93	1.67	3.06	4.58	6.03	12.43	30.70
	Basalt	23	.97	1.08	2.63	3.67	5.34	8.18	14.28	15.21
	LBF	13	.97	.97	3.18	5.67	6.17	8.59	**	15.21
	UBF	6	1.72	1.72	2.40	4.01	5.18	8.73	**	10.58
	CTM*	2	1.97			2.04	2.04			2.11
Bioaccessible Ni GI (mg kg ⁻¹) Barsby et al subsample	All NI	91	.37	.53	.89	1.52	2.16	2.45	5.97	11.10
	Basalt	23	.40	.44	1.12	1.89	2.43	4.28	5.79	5.88
	LBF	13	.60	.60	1.40	2.05	2.90	4.71	**	5.88
	UBF	6	.40	.40	.94	1.64	2.11	3.20	**	5.43
	CTM*	2	.97			1.11	1.11			1.25
Ni BAF G (%) Barsby et al subsample	All NI	91	1.42	2.99	5.55	8.16	12.16	16.29	35.41	43.82
	Basalt	23	1.42	1.54	4.55	8.16	12.32	16.23	43.08	43.82
	LBF	13	2.04	2.04	4.44	8.60	13.15	15.55	**	43.82
	UBF	6	1.42	1.42	2.22	10.58	13.79	25.68	**	35.13
	CTM*	2	8.16			9.13	9.13			10.09
Ni BAF GI (%) Barsby et al subsample	All NI	91	.60	1.68	3.31	4.79	5.50	7.33	11.04	14.45
	Basalt	23	.60	.70	2.08	4.11	4.49	6.68	9.65	9.98
	LBF	13	1.08	1.08	2.39	4.53	4.84	6.92	**	9.98
	UBF	6	.60	.60	1.21	3.57	4.26	8.16	**	8.33
	CTM*	2	3.75			5.07	5.07			6.39

Table S2 Summary statistics for Ni *Percentiles not reported, due to low sample numbers ** Percentile not reported as it exceeds max value

Chromium		No of samples	Minimum	5th percentile	25th percentile	Median	Mean	75th percentile	95th percentile	Maximum
Total Cr (mg kg ⁻¹) All Tellus data	All NI	6860	4.10	9.51	56.70	94.10	131.01	161.00	375.98	1228.80
	Basalt	1733	6.30	15.76	170.10	254.40	258.68	331.35	517.86	1228.80
	LBF	1033	6.50	42.40	192.10	269.70	276.87	344.65	511.43	1228.80
	UBF	589	6.30	11.20	169.25	244.50	250.73	321.10	538.65	879.30
	CTM	47	17.30	33.20	102.40	124.30	144.48	193.40	321.26	375.10
Total Cr (mg kg ⁻¹) Barsby et al subsample	All NI	91	13.00	30.24	66.00	96.60	132.73	169.80	413.68	510.20
	Basalt	23	13.00	14.42	85.10	195.00	205.71	288.30	505.64	510.20
	LBF	13	20.10	20.10	80.25	241.70	213.13	290.70	**	510.20
	UBF	6	13.00	13.00	110.50	190.85	245.47	457.63	**	487.40
	CTM*	2	68.30			82.45	82.45			96.60
Bioaccessible Cr G (mg kg ⁻¹) Barsby et al subsample	All NI	91	.08	.18	.73	1.20	1.79	2.24	4.84	9.96
	Basalt	23	.08	.09	.97	2.98	3.22	4.54	9.81	9.96
	LBF	13	.14	.14	.80	2.98	2.79	4.28	**	5.91
	UBF	6	.08	.08	1.45	3.08	4.55	9.39	**	9.96
	CTM*	2	.82			1.06	1.06			1.30
Bioaccessible Cr GI (mg kg ⁻¹) Barsby et al subsample	All NI	91	.08	.24	.56	.85	1.21	1.70	2.99	7.39
	Basalt	23	.08	.11	.97	1.83	2.10	2.97	6.78	7.39
	LBF	13	.25	.25	.62	1.77	1.75	2.55	**	4.35
	UBF	6	.08	.08	1.31	2.34	2.78	3.94	**	7.39
	CTM*	2	.97			1.05	1.05			1.13
Cr BAF G (%) Barsby et al subsample	All NI	91	.38	.58	.89	1.12	1.33	1.62	2.71	5.36
	Basalt	23	.44	.47	1.02	1.40	1.51	1.90	4.74	5.36
	LBF	13	.44	.44	.93	1.13	1.21	1.48	**	2.24
	UBF	6	.60	.60	.92	1.79	1.55	2.05	**	2.06
	CTM*	2	.84			1.37	1.37			1.90
Cr BAF GI (%) Barsby et al subsample	All NI	91	.37	.44	.62	.81	.98	1.25	1.90	4.44
	Basalt	23	.57	.57	.71	.88	1.14	1.28	3.88	4.44
	LBF	13	.58	.58	.67	.77	.86	.94	**	1.65
	UBF	6	.57	.57	.60	1.10	1.09	1.55	**	1.65
	CTM*	2	1.00			1.33	1.33			1.66

Table S3 Summary statistics for Cr *Percentiles not reported, due to low sample numbers. ** Percentile not reported as it exceeds max value