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Palmer, S., Cox, S., McKinley, J., & Ofterdinger, U. (2014). Soil-Geochemical Factors controlling the Distribution and Oral Bioaccessibility of Nickel, Vanadium and Chromium in Northern Ireland Soils. *Applied Geochemistry*, 51, 255–267. DOI: 10.1016/j.apgeochem.2014.10.010

Published in:
Applied Geochemistry

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
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Accepted Manuscript

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PII: S0883-2927(14)00242-X

DOI: <http://dx.doi.org/10.1016/j.apgeochem.2014.10.010>

Reference: AG 3344

To appear in: *Applied Geochemistry*



Please cite this article as: Palmer, S., Cox, S.F., McKinley, J.M., Ofterdinger, U., Soil-geochemical factors controlling the distribution and oral bioaccessibility of nickel, vanadium and chromium in soil, *Applied Geochemistry* (2014), doi: <http://dx.doi.org/10.1016/j.apgeochem.2014.10.010>

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SOIL-GEOCHEMICAL FACTORS CONTROLLING THE DISTRIBUTION AND ORAL BIOACCESSIBILITY OF NICKEL, VANADIUM AND CHROMIUM IN SOILSherry Palmer^{*a}, Siobhan F. Cox^a, Jennifer M. McKinley^b and Ulrich Ofterdinger^a^a*School of Planning, Architecture and Civil Engineering; Queen's University Belfast, BT9 5AG, UK*^b*School of Geography, Archaeology and Palaeoecology; Queen's University Belfast, BT7 1NN, UK*^{*}*Corresponding author; spalmer04@qub.ac.uk, Tel. +44 (028) 9097 5606, Fax +44 (028) 9097 4278**Additional e-mail addresses; s.cox@qub.ac.uk, j.mckinley@qub.ac.uk, u.ofterdinger@qub.ac.uk*

Abstract: Geogenic nickel (Ni), vanadium (V) and chromium (Cr) are present at elevated levels in soils in Northern Ireland. Whilst Ni, V and Cr total soil concentrations share common geological origins, their respective levels of oral bioaccessibility are influenced by different soil-geochemical factors. Oral bioaccessibility extractions were carried out on 145 soil samples overlying 9 different bedrock types to measure the bioaccessible portions of Ni, V and Cr. Principal component analysis identified two components (PC1 and PC2) accounting for 69% of variance across 13 variables from the Northern Ireland Tellus Survey geochemical data. PC1 was associated with underlying basalt bedrock, higher bioaccessible Cr concentrations and lower Ni bioaccessibility. PC2 was associated with regional variance in soil chemistry and hosted factors accounting for higher Ni and V bioaccessibility. Eight per cent of total V was solubilised by gastric extraction on average across the study area. High median proportions of bioaccessible Ni were observed in soils overlying sedimentary rock types. Whilst Cr bioaccessible fractions were low (max = 5.4%), the highest measured bioaccessible Cr concentration reached 10.0 mg kg⁻¹, explained by factors linked to PC1 including high total Cr concentrations in soils overlying basalt bedrock.

Keywords: trace elements, bioaccessibility, geochemistry, factor analysis, human health risk assessment

1.0 Introduction

In Northern Ireland, nickel (Ni), vanadium (V) and chromium (Cr) are present in soils at high total concentrations, in some cases exceeding available statutory soil guideline values (SGVs) or generic assessment criteria (Environment Agency, 2009; Nathaniel et al., 2009). SGVs are intended for use as screening values; significant harm may not necessarily be present when a contaminant exceeds its SGV, but regulators may wish to seek additional evidence to determine if there is a high probability of significant harm to receptors from soil contaminant exposure under such circumstances (DEFRA, 2012).

Refining the human health risk assessment process with respect to oral exposure to soil borne contaminants plays an important role in sustainable development approaches. Informed land management practices and accurate risk communication can save local councils, land owners, and developers millions of pounds in remediation costs, in turn preserving natural soil resources (NERC, 2012). Soil bioaccessibility testing can be applied to complement a lines-of-evidence approach when assessing health risks from oral soil contaminant exposure (CIEH, 2009; DEFRA, 2012). In terms of risk estimation, *in vitro* oral bioaccessibility testing reduces reliance on total contaminant concentrations in soil, an approach which commonly will overestimate health risks due to the well-accepted concept that 100% of soil contamination is rarely bioavailable to receptors when ingested (Ruby et al., 1999; CIEH, 2009). Compared to *in vivo* animal bioavailability studies, *in vitro* testing is also less costly and can be completed in a shorter time frame while avoiding the ethical concerns of using live animals in research.

Over the past two decades, a considerable amount of effort has been invested across the scientific community in developing and validating a suitable standardised extraction method for estimating human oral contaminant bioaccessibility *in vitro* (Ruby et al., 1996; Ruby et al., 1999; Oomen et al., 2003; Wragg and Cave, 2003; Van de Weile et al., 2007; Wragg et al., 2009; NERC, 2012). The Unified BARGE (Bioaccessibility Research Group of Europe) Method (UBM) is a standardised physiologically based extraction technique which has been subjected to comprehensive inter-laboratory trials and validated for arsenic (As), lead (Pb) and cadmium (Cd) using *in vivo* swine data (Caboche, 2009; Wragg et al., 2011; Denys et al., 2012).

Previous trace element bioaccessibility research in Northern Ireland has shown that oral bioaccessibility is not primarily a function of total trace element concentrations in soil (Barsby et al, 2012; Palmer et al., 2013; Cox et al., 2013), diminishing the suitability of reliance on total soil contaminant concentrations as a driver for contaminated land management decisions. Following from these findings, specific geochemical factors accounting for the variability in trace element bioaccessibility across the country

require further investigation. Correlation studies exploring relationships between trace element bioaccessibility and other geochemical variables found statistically significant relationships which varied across different underlying bedrock types (Palmer et al., 2013; Cox et al. 2013). For example, sulphur measured as sulphur trioxide (SO₃) and loss on ignition (LOI) data showed strong positive associations with Ni and V bioaccessibility throughout Northern Ireland, whilst calcium appeared to exert either positive or negative influences over bioaccessibility depending upon the underlying bedrock type (Palmer et al., 2013).

Although several statistically significant intrinsic correlations between trace element bioaccessibility and a number of other geochemical variables have been previously confirmed, specific soil-geochemical associations are difficult to identify from correlation analysis alone. This paper therefore aims to more explicitly identify such soil-geochemical associations on a regional scale through a combined analysis approach. Exploratory data analysis (EDA), factor analysis and geostatistics were used to validate and identify common sources of variability across two data sets (Gooaverts, 1992; Abollino et al., 2011; Candeias et al., 2011; Giacomino et al., 2011), supporting the research aim of identifying geochemical factors that account for variability in the distribution and bioaccessibility of Ni, V and Cr in soils across Northern Ireland. Critically, such findings have applications beyond the study area as the diverse geology encountered in Northern Ireland extends stratigraphically beyond the immediate region.

2.0 Methodology

2.1 Study Area and Sample Selection

Northern Ireland hosts a wide variety of rock types relative to its small land area of just over 13,800 km² with most geologic time periods represented by the study area's diverse lithology (Fig. 1; Wilson, 1972; Jordan et al., 2007). Bioaccessibility research in this study area therefore provides the opportunity to increase the global understanding of the relationships between geochemistry and human health within both the scientific and regulatory communities.

The range of rock types represents three basement terranes: the Grampian, the Midland Valley, and the Southern Uplands-Down-Longford Terranes. As described in Mitchell (2004), the Grampian Terrane and associated rocks in the northwest represent the oldest rocks in the country, with their metamorphic igneous and sedimentary origins spanning the Proterozoic Era. Psammites and semi-pelites are the dominant rock type, with sandstone and conglomerate also present in this area. Following from the Proterozoic through to the Devonian, the Midland Valley Terrane hosts Palaeozoic igneous formations and Late Devonian-Early Carboniferous sedimentary rocks. Red sandstones, limestone and mudstones comprise the majority of rock types with a minor conglomerate component. Finally, granitic igneous intrusives and marine sedimentary rocks representing the Lower Palaeozoic Ordovician and Silurian

systems are found in the Southern Uplands-Down-Longford Terrane in the southwest. Lithic arenites and sandstones comprise the majority of bedrock in this part of the country. Portions of the Midland Valley and Grampian basement rocks in the northeast are covered by a large plateau of igneous Palaeogene basalts and lava-derived sedimentary clays originating from within the Permian to Cretaceous systems to a depth of up to 800 meters. Outside of this area, much of the basement rocks in Northern Ireland remain exposed. In contrast to the diverse range of underlying rock types, superficial deposits are dominated by glacial till, sand and gravel, and peat, and topsoil pH falls within a relatively narrow acidic range.

Eleven generic bedrock types as defined by the Geological Survey of Northern Ireland (GSNI; Smyth, 2007) are illustrated in Fig. 1. Geochemical and bioaccessibility data were separated into these groups prior to EDA with the aim of identifying potential differences in soil geochemistry and trace element bioaccessibility across different underlying bedrock types. Using generic bedrock types ensures that sample sizes remain sufficiently robust during analysis and EDA, as defining discrete minor geologic formations present in Northern Ireland would reduce sample sizes to a prohibitively narrow range of statistical significance. Such an approach also reduces variance and increases normality in the distribution of geochemistry data (Jordan et al., 2007; Zhang et al., 2007; Palmer et al., 2013).

Geochemistry data from the Northern Ireland Tellus Survey were provided by the GSNI. In excess of 6800 shallow profile soil samples from 5 – 20 cm depth were gathered during the Tellus Survey and analysed by X-ray fluorescence spectrometry (XRFS) for major oxides and trace elements. The complete Tellus Survey field methods and analytical methodology are described in Smyth (2007). Shallow soil samples from the Northern Ireland Tellus Survey soil archive were used for bioaccessibility testing and were selected to represent the diversity of rock and soil types across the study area.

2.2 Bioaccessibility Testing

The UBM is an *in vitro* extraction procedure for solid matrices designed to mimic the conditions of the human digestive system. The method incorporates saliva, gastric, and intestinal phases of digestion at a controlled temperature of 37° C. The full methodology is downloadable through the British Geological Survey (BGS) website (BARGE/INERIS, 2011).

Soil sub-sampling, solution preparation, UBM extractions and inductively coupled plasma mass spectrometry (ICP-MS) analyses were conducted in the Analytical Geochemistry Facility at BGS, Kingsley Dunham Centre, Keyworth, Nottingham during 2009 (Barsby et al., 2012) and 2013. Archived Northern Ireland Tellus soils from the < 2mm fraction were sub-sampled by coning and

quartering to ensure representative samples were obtained prior to extraction. The 2009 and 2013 bioaccessibility data sets were joined to ensure the diverse range of rock types present within the study area was adequately represented.

Fresh digestion fluids were prepared daily and one day prior to use to allow enzymes and pH to stabilise. Inorganic and organic solutions for each fluid were prepared in separate 500 ml glass volumetric flasks prior to combining in two litre non-reactive screw top Nalgene bottles to create one litre of digestive fluid. Additional solid reagents were weighed directly into the Nalgene bottles prior to adding the inorganic and organic solutions. Digestive fluids were immersed in the same warm water bath used for the extractions at 37°C for a least one hour prior to commencing extractions. The pH of each solution was checked and adjusted to the specifications outlined in Table 1 using either 37% HCl or 1M NaOH.

2.2.1 Extract Analysis and Quality Control

The UBM has been validated for As, Pb and Cd through *in vivo* studies (Caboche, 2009; Denys et al., 2012). It should be noted that, whilst the three trace elements presented in this paper have not been subjected to *in vivo* validation under the UBM, data for all trace elements of interest were subjected to rigorous quality control (QC) and quality assurance (QA) procedures as described below.

Extract analysis was carried out using an Agilent 7500cx series ICP-MS employing an octopole reaction system in combination with a CETAC autosampler. Sample introduction from the autosampler to the ICP is coupled to a CETAC flow injection valve. The instrument was calibrated at the beginning of every analytical run using a minimum of three standards and a blank for each trace element. Multi-element QC check standards containing the trace elements of interest at 25 µg/L were analysed at the start and end of each run and after a minimum of every 25 samples.

Accuracy and precision of UMB extract analysis is monitored at BGS by the on-going collation of BGS102 reference material data (Wragg, 2009). UBM results from ICP analysis were provided in µg/L with a dilution factor of 100 applied. Data were back calculated to mg kg⁻¹ of soil using Equation A, taking into account recorded soil sub-sample weights and total fluid volumes inclusive of HCl or NaOH additions used for pH adjustments.

$$C [mg/kg] = \{C [\mu g/L] \times \frac{V}{W}\} \div 1000$$

(Equation A);

where C = analyte concentration in units specified, V = total extraction fluid volume (mL) and W = total soil weight (g). Soils were pre-dried according to the Tellus methodology (Smyth, 2007); 100% solids were therefore assumed for calculating final concentrations.

For every seven unknown soil samples, one extraction blank, one duplicate soil and one BGS102 certified reference soil were included in the extraction procedure. Measured values for bioaccessible As and Pb were within one standard deviation of the certified reference value provided for BGS102. Overall mean gastric relative per cent difference for the analytes of interest was 11%. Values measured in blanks above daily detection limits were subtracted from measured sample values for each respective batch. Measured sample values below daily detection limits were reported as half the daily detection limit.

2.3 Geochemistry and UBM Data Analysis

Analysis of geochemistry and trace element bioaccessibility data relied upon a combined approach where intrinsic statistical relationships among variables were evaluated in the context of corresponding spatial outputs. Multivariate dimension reduction in the form of PCA was applied to link variables to a narrower range of soil-geochemical components such as specific soil or bedrock types. Conclusions were subsequently drawn about specific soil-geochemical influences causing variability in the geographical distribution and bioaccessibility of Ni, V and Cr.

Summary statistics were generated for XRFS geochemistry data in Microsoft (MS) Excel 2010 and IBM SPSS v.19.0. Boxplot figures were completed in R (R Core Team, 2013). PCA was conducted in R using the vegan package (Oksanen et al., 2013) and eigenvalue loading plots with eigenvectors were manually constructed using PCA eigenvalue factor loadings. Geochemistry variables, synonymous with factors for the purposes of PCA, were selected on the basis of their known potential to influence trace element bioaccessibility (Stewart et al., 2003; Subacz et al., 2007; Poggio et al., 2009; Meunier et al. 2010; Bradham et al., 2011) and consisted of eight major element oxides (%), pH, loss on ignition (%; LOI), and total Ni, V, and Cr (mg kg^{-1}).

To address issues of data closure encountered in compositional geochemical data, an additive log ratio transformation was applied to the data set using the robCompositional package in R (Templ et al., 2009). Titanium dioxide was chosen as the rationing variable for transformation (Reimann et al., 2009). Values for the thirteen geochemistry factors noted above from 6,862 sample locations were analysed by PCA using scaled Northern Ireland Tellus XRFS data for shallow soils. Scaling data corrects for variability in the magnitude of values that will naturally be present in a data set with multiple factors (Oksanen et al., 2013). To explore relationships between trace element bioaccessibility and Northern

Ireland geochemistry, UBM data inclusive of XRFS data from corresponding study set soil sample locations were also analysed by PCA following the same methods described above.

PCA is an unconstrained ordination method that is useful for dimension reduction in multivariate data. Data are transposed onto a three dimensional axis where the Euclidian distance between points is calculated in each direction. Similar to a one-dimensional linear regression, a line of best fit is calculated accounting for maximum variance between the data points; this vector is the first principal component (PC1). The second principal component (PC2) is the vector which lies perpendicular to PC1. Data are rotated in three dimensional space to repeat this process and derive subsequent components. Eigenvalues represent the proportion of factor variance accounted for by a particular component, providing the same level of information as an r^2 value in linear regression. In addition to factor eigenvalues, each soil sample location is assigned a unique site score. Site scores give an indication of individual data positions and resulting relative weightings along component vectors in three dimensional space. A higher score indicates more sample variance is accounted for by a prescribed component (Reimann et al., 2009; ESRI, 2010; Oksanen et al., 2013).

Geochemistry variables and PCA site scores were mapped in ArcMap v.10 using ordinary kriging. Semi-variograms were manually fitted to geochemistry data using an iterative process of varying search neighbourhoods until the model yielding the least mean prediction error and best fit semi-variogram was generated. Spatial PCA applies identical ordination methods as described previously, but additionally generates raster outputs of unique site scores against each principal component to facilitate interpolation of a site score surface. Final interpolated outputs show sample location variance accounted for by the specified principal component (ESRI, 2010; Candeias et al., 2011).

3.0 Results

3.1 Regional Trends in Geochemistry

Table 2 provides summary statistics for oxides, trace elements, pH and LOI. Ni, Cr and V concentrations are highest in soils overlying basalt bedrock types with their distributions controlled by a long-range ($a > 70$ km) spatial function aligning with the extent of basalts in the northeast of the study area (Figs. 2 and 3, Table 3). Ni and Cr exhibit low concentrations in soils overlying the 10 other bedrock types investigated compared to V, which displays more variability in its distribution across the study area (Figs. 2 and 3b). In particular, soils overlying sandstone and psammite & semi-pelite bedrock types exhibit high concentrations of V.

Magnesium (Mg), calcium (Ca), manganese (Mn) and iron (Fe) oxides show high relative concentrations in soils overlying basalt rock types (Figs. 4-6). Mg, Ca and Fe are present in the

minerals olivine, plagioclase feldspar and augite, which together account for approximately 90% of the minerals in underlying basalt bedrock (Hill et al., 2001). Mn is also known to be elevated in basalts as it readily substitutes for Fe in olivine (Wedepohl, 1978). Aluminium oxide (Al_2O_3) concentrations also appear to be controlled by underlying basalt, although Al distributions are not as strongly constrained by this bedrock type (Fig. 6b).

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Spatially, phosphorous pentoxide (P_2O_5) displays a high frequency of change in concentrations throughout the region, with little apparent association to underlying bedrock types (Figs. 4 and 6d). This small-scale spatial distribution is also displayed in Table 3, where P_2O_5 is controlled by a short-range spatial function ($a = 17$ km) with over half of its total variance (C) accounted for by a nugget effect (C_0). A large nugget variance and a short-range spatial function suggest that small scale processes not associated with underlying geology are influencing a modelled parameter (Dobermann et al., 1995; Einax and Soldt, 1999). Elevated P_2O_5 in shallow soils is likely to be the result of agricultural practices such as phosphate fertilizer applications, an observation which has also been noted by Jordan et al. (2001). Lastly, limestones, mudstones and sandstones underlie soils hosting high mean concentrations of silicon dioxide (SiO_2 ; Figs. 4 and 6c), characteristic of the parent bedrock material that will contribute to high sand and clay mineral content in soil (Sparks, 1995).

LOI, pH and sulphur trioxide (SO_3) are strongly correlated spatially across Northern Ireland, with distribution patterns aligning with acidic upland peat soil types which overlie mountainous formations comprised of acid volcanic and psammite & semi-pelite rock types (Figs. 6e and 7; Jordan et al., 2001). Whilst average pH and LOI remain relatively constant across bedrock groups in the study area, these parameters show more statistical irregularity in the acid volcanic and psammite & semi-pelite groups (Fig. 5). In addition to the highest observed proportions of LOI being located in upland peaty areas, intermediate levels of LOI could also be associated with the presence of clay minerals in other parts of the study area (Fig. 7), as the LOI method can result in structural water loss from clay in addition to providing an estimation of soil carbon content (Konen et al., 2002). The presence of sulphur compounds in peat soils may be indicative of microbial processes occurring under reducing, water-logged conditions or could be associated with atmospheric pollution sources (Campbell, 1996a; Campbell, 1996b; Nebel and Wright, 2000).

3.2 Ni, V and Cr Bioaccessibility

Mean and maximum bioaccessible fractions (BAF; %) for Ni, V and Cr were highest in the gastric phase. In line with best practice for ensuring human health risks are not underestimated, gastric data are therefore presented to provide a conservative estimate of the maximum amount of trace elements that would be potentially bioavailable. Nine generic bedrock classifications were captured by the bioaccessibility study set (Fig. 8). BAF are presented in Table 4

according to generic bedrock type with gabbro excluded due to the small sample size in this classification. BAF provide a preferred basis for comparison across bedrock groups due to normalisation by total element concentrations.

On average, approximately 12% of total Ni in shallow soils across Northern Ireland was solubilised by gastric extraction, equivalent to a mean bioaccessible concentration of 3.8 mg kg^{-1} . The highest quantity of bioaccessible Ni was measured at 30.7 mg kg^{-1} and occurred in the lithic arenite bedrock group; however, the highest proportion of bioaccessible Ni was observed in the psammite & semi-pelite group (max = 46.3%; Table 4). Soils overlying sedimentary limestones, sandstones and mudstones had higher mean proportions of bioaccessible Ni overall compared to soils overlying other rock types. Although the highest total Ni concentrations are observed in soils overlying basalt (Figs. 2 and 3), the lithic arenite and mudstone bedrock groups hosted up to twice (max = 30.7 mg kg^{-1}) and one and a half times (max = 24.2 mg kg^{-1}) as much bioaccessible Ni, respectively, than was measured in the basalt bedrock group (max = 15.7 mg kg^{-1}). Median Ni BAFs were lowest in the conglomerate and lithic arenite groups, however, while the highest median occurred in soils overlying sandstone.

Approximately 8% of total V was found to be bioaccessible on average across 145 sample locations, with measured average and maximum bioaccessible concentrations of 7.4 and 52.1 mg kg^{-1} , respectively. Maximum proportional bioaccessibility occurred in the sandstone group (23.1%), although this was only marginally greater than the maximum BAF of 22.5% measured in the basalt bedrock group (Table 4). Similar values were recorded in the mudstone group, with up to 22% of V rendered soluble during gastric extraction. Overall, the highest mean and median levels of gastric V bioaccessibility were recorded in soils overlying basalt bedrock, both in terms of proportional and absolute measurements. The median bioaccessible V concentration in soils overlying basalt bedrock was 11.5 mg kg^{-1} (BAF = 10.3%). Median V BAFs ranged from 5.0% to 8.6% across the remaining bedrock groups (Table 4).

Cr displayed a maximum BAF of 5.4% of its total concentration, with a mean and median BAF of 1.2% and 1.0%, respectively, across the study set (Table 4). Despite low proportions of Cr being bioaccessible, 9 - 10 mg kg^{-1} of gastric bioaccessible Cr was extracted from two samples, with measured bioaccessibility ranging between 5 - 6 mg kg^{-1} at a further three sample locations. Each of these five soils observed to have relatively high levels of Cr bioaccessibility occurred in samples overlying basalt bedrock. The maximum Cr BAF also occurred in the basalt bedrock group, although the mean BAF was highest in the granite bedrock group (1.7%; Fig. 8). Average total Cr bioaccessibility across the study area was measured at 1.5 mg kg^{-1} . Median bioaccessibility across all

bedrock groups ranged from 0.9% - 1.4% (Table 4), with the highest median BAF observed in soils overlying basalt. It should be noted that potential health risk from Cr in soil is highly dependent upon speciation which was not identified as part of this study (Nathanail et al., 2009).

3.3 Identified Principal Components

Principal component analysis of the full geochemistry data set with thirteen selected variables identified three components accounting for a cumulative variance of 79% across Northern Ireland. Analysis of the UBM data set found four components also accounting for 79% of variance (Table 5). Factor loadings for each component are presented in Table 6. PC1, linked to variables associated spatially with basalt, accounted for the greatest amount of variance (45%) in the data. A further 24% of geochemical variance from PC2 is explained by variables associated with sedimentary formations such as Ca, Fe and Mg (Table 6). Such elements are abundant in minerals of low hardness such as dolomite, calcite and chlorite (Tarbuck and Lutgens, 1999) although the presence of these specific minerals in the study area is not confirmed. In the UBM study set, Cr is the only trace element whose bioaccessible concentrations were weighted towards the same geologic component as its total concentrations, highlighting its definitive geogenic controls (Table 6). Bioaccessible Ni and V concentrations, however, were more closely associated with factors spatially related to acid peat soil chemistry such as SO₃ and LOI and also with factors suggestive of less recalcitrant minerals.

Eigenvalue loading plots may be used to illustrate both individual sample site loadings and factor loadings against identified principal components. Figures 9a and 9b illustrate factor loadings only for purposes of clarity due to the high number of soil sample sites analysed by PCA. Where obtuse angles are present between vectors in the plot, a negative correlation among two variables is expected. Conversely, acute angles suggest a positive relationship between two factors, with smaller degrees of separation indicating a stronger correlation (Reimann et al., 2009).

Total Ni, V and Cr and Fe and Mn oxides form a cluster of vectors in the bottom right quadrant of the plot in Fig. 9a, demonstrative of their geochemical co-occurrences in basalt. The presence of Al oxides is inferred by less than 90 degree angles between the eigenvectors of Al₂O₃, MgO and CaO, a solid phase which was also identified by Cox et al. (2013). Al maintains more than one geochemical association, however, demonstrated by its correlation also with SiO₂

in the loading plot, affirming the influence of clay minerals in the study area (Theng, 1974; Sparks, 1995; Cox et al., 2013). LOI and SO_3 are also strongly correlated, suggesting a soil-geochemical influence from peat soil types. The presence of sedimentary minerals is illustrated by the associations between Ca and Mg oxides in Fig. 9a (Tarbuck and Lutgens, 1999). Furthermore, oxides of these two elements are in closer proximity to Ni in the loading plot relative to Cr or V, suggesting that Ni resides in different host mineral phases than Cr or V.

Inspection of Fig. 9b inclusive of UBM extraction data shows that bioaccessible concentrations of Ni, V and Cr are still closely associated with their total concentrations, although this figure illustrates PC1 and PC2 only. Of particular note is the greater proximity of bioaccessible Ni concentrations to Ca and Mg oxides in the loading plot than total Ni concentrations, illustrating differing geochemical associations between total and bioaccessible Ni.

Component sample scores are spatially illustrated in Figs. 10a-c. In line with the above PCA interpretations, sample scores are heavily weighted to PC1 in the basalt regions, with minor variability also accounted for by underlying clay and sandstone rock types. Spatial patterns illustrated by PC1 indicate bedrock geology provides the primary basis for geochemical variability. PC2 conforms to a spatial pattern more closely aligned with regional variability in soil types, illustrating the additional importance of soil chemistry. Although Table 5 shows the third minor component accounts for only 10 and 9% of variance in the full geochemistry and UBM study sets, respectively, spatial PCA effectively illustrates the impact of soil-geochemical controls from PC3 relating to soil acidity (Table 6). The clarity of spatial patterns of PC3 in Fig. 10c additionally suggests that exploring geochemistry in the absence of strong sources of variance such as the basalts may reveal additional soil-geochemical components otherwise masked by the basalts.

4.0 Discussion

The minimum Ni BAF occurred in the basalt bedrock group. Total Ni, MgO, Al_2O_3 , P_2O_5 , MnO and Fe_2O_3 , previously observed by Palmer et al. (2013) to have significant negative correlations with Ni bioaccessibility, were also found to be present at high concentrations in soils overlying basalt compared to the other bedrock groups (Figs. 2 – 6). A significant proportion of variability in the above variables is explained by PC1, associated with basalt bedrock in the study area, supporting the conclusion that Ni in soils overlying basalt bedrock will have relatively low bioaccessible fractions irrespective of total Ni soil

concentrations. This is likely due to the presence of minerals of high recalcitrance such as olivine, quartz, feldspar or pyroxene (Lyle, 1980). The maximum Ni BAF was observed in soils from the psammite & semi pelite group. Associations with this bedrock group suggest a peat spatial influence rather than control from underlying bedrock itself, as this bedrock group is covered largely by upland peat soil types in Northern Ireland. As shown by Figs. 2 – 6, soils overlying psammite & semi pelite hosts low average total Ni, low average concentrations of Mg, Al, Si, Fe, and Mn oxides previously observed to negatively influence Ni bioaccessibility, and relatively high measured SO_3 and LOI. In the UBM data set the majority of variance in SO_3 and LOI, which had previously observed strong positive correlations with Ni bioaccessibility, was accounted for by PC2. Peat soils have high organic matter content and exhibit acidic soil pH, both of which are expected to increase Ni mobility, resulting in higher oral bioaccessibility. Ni possesses a high affinity for soil organic matter which can increase Ni soil mobility through the formation of soluble organic chelates (Alloway, 2005). In addition, Ni mobility increases with decreasing pH (Environment Agency, 2009; Poggio et al., 2009).

An investigation of Ni bioaccessibility in basalts in Northern Ireland using chemometric extraction data determined that a large proportion of bioaccessible Ni in soil samples overlying basalt was hosted by soluble carbonate phases, aluminium oxides and clay. A small proportion of bioaccessible Ni was associated with iron oxide, although the non-bioaccessible proportion was hosted by the remaining iron oxide minerals (Cox et al., 2013). While these findings were applicable in soils overlying basalt, the general regional trend observed across Northern Ireland appears to differ slightly from this, with variables associated with clay, Al and Fe oxides appearing to have a negative influence over Ni bioaccessibility (Palmer et al., 2013). Calcium arising from insoluble minerals present in basalts may be associated with reduced Ni bioaccessibility but Ca in soils overlying sedimentary limestones will account for higher Ni bioaccessibility.

The minimum V BAF occurred in the psammite & semi-pelite group, while low median V BAFs were observed in soils included in the limestone and lithic arenite bedrock groups. Higher mean and median V bioaccessibility (%) was observed in soils from the basalt bedrock sample group compared to other bedrock types, where total soil V was also the highest. Palmer et al. (2013) identified similar correlations between major oxides, SO_3 , LOI and bioaccessible V as were observed for bioaccessible Ni; however, results concerning more detailed factors controlling V bioaccessibility are less conclusive from this particular study. Based on previous correlation analyses, factors relating to V bioaccessibility were expected to be similar to those identified for Ni. Although both elements have a high affinity for organic matter in soil, V is understood to be more mobile in alkaline conditions, unlike Ni (USEPA, 2005;

Environment Agency, 2009). As shown by Fig. 3, total V in soils is less constrained by basalts across the study area when compared to Ni or Cr, with moderate V concentrations observed in soils throughout the western half of the study area. Published information regarding V bioaccessibility is limited, although factors linked to peat were previously positively correlated with V BAFs while Al and Fe oxides were negatively correlated to V BAFs (Palmer et al., 2013).

The minimum Cr BAF was observed in the psammite & semi-pelite bedrock group. This group hosts low average concentrations of total Cr, MgO, Al₂O₃, CaO, MnO, and Fe₂O₃ while having higher average levels of SO₃ and LOI compared to the other bedrock groups. The maximum Cr BAF occurred in the basalt bedrock group, which generally exhibits the opposite trends in major oxide abundance and LOI when compared to the psammite & semi-pelite group. Cox et al. (2013) found portions of total Cr were hosted by iron oxides in basalt and identified strong positive correlations between bioaccessible Cr and total Cr, MgO, Al₂O₃, P₂O₅, CaO, MnO, and Fe₂O₃, factors which were also associated with the basalt component as identified by PC1. Hill et al. (2001) found that Cr in the Antrim Basalts was associated with stable iron oxides and as a result was enriched during weathering, suggesting that Cr is not mobile and therefore unlikely to be bioaccessible. Similar trends in Cr have been noted previously with respect to its affinity to Fe and Al oxides and clay minerals in the soil environment (Rai et al., 1989; Frei and Polat, 2013). This is in contrast to Ni whose mineral associations are in a more bioaccessible form, an observation which may not be limited to soils overlying basalts but which may also apply to Ni in soils across Northern Ireland based on PCA findings.

5.0 Conclusion

Strong geogenic controls in Northern Ireland influence the spatial distribution and concentrations of major and trace elements in soils. However, the oral bioaccessibility of Ni, V and Cr is influenced by complex soil-geochemistry interactions that are not fully accounted for by underlying geology or total trace element concentrations. Higher Ni bioaccessibility was observed in soils over psammite & semi-pelite and limestone rock types, concluded to be linked specifically to the presence of acidic soil conditions, organic matter, and carboniferous sedimentary geology. High fractions of bioaccessible V were observed in soils overlying basalt and sandstone bedrock, although distinct controls from underlying bedrock over V bioaccessibility were not clearly

discernible. Both total and bioaccessible Cr concentrations showed the strongest associations to geologic factors, explaining in part its low bioaccessible fractions but high bioaccessible concentrations.

Acknowledgements and Disclaimer

2013 UBM testing was supported by the EU INTERREG IVA-funded Tellus Border project. The views and opinions expressed in this report do not necessarily reflect those of the European Commission or the SEUPB. Tellus Border is a €5 million cross-border project to map the environment and natural resources in the border region of Ireland and continue the analysis of data in the border counties of Northern Ireland. It is a joint initiative between the Geological Survey of Northern Ireland, the Geological Survey of Ireland, Queen's University, Belfast and Dundalk Institute of Technology. 2009 UBM testing was funded by the BGS University Funding Initiative.

The Northern Ireland Tellus project was funded by the Northern Ireland Department of Enterprise, Trade and Investment and by the Rural Development Programme through the Northern Ireland Programme for Building Sustainable Prosperity.

Special thanks to staff at the Analytical Geochemistry Facility at the BGS Kingsley Dunham Centre, especially Mr. Tom Barlow and Mr. Elliott Hamilton for their technical and analytical support. Thanks also to Mark Cave and Jo Wragg for their valuable assistance with 2013 UBM data QA.

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Figures

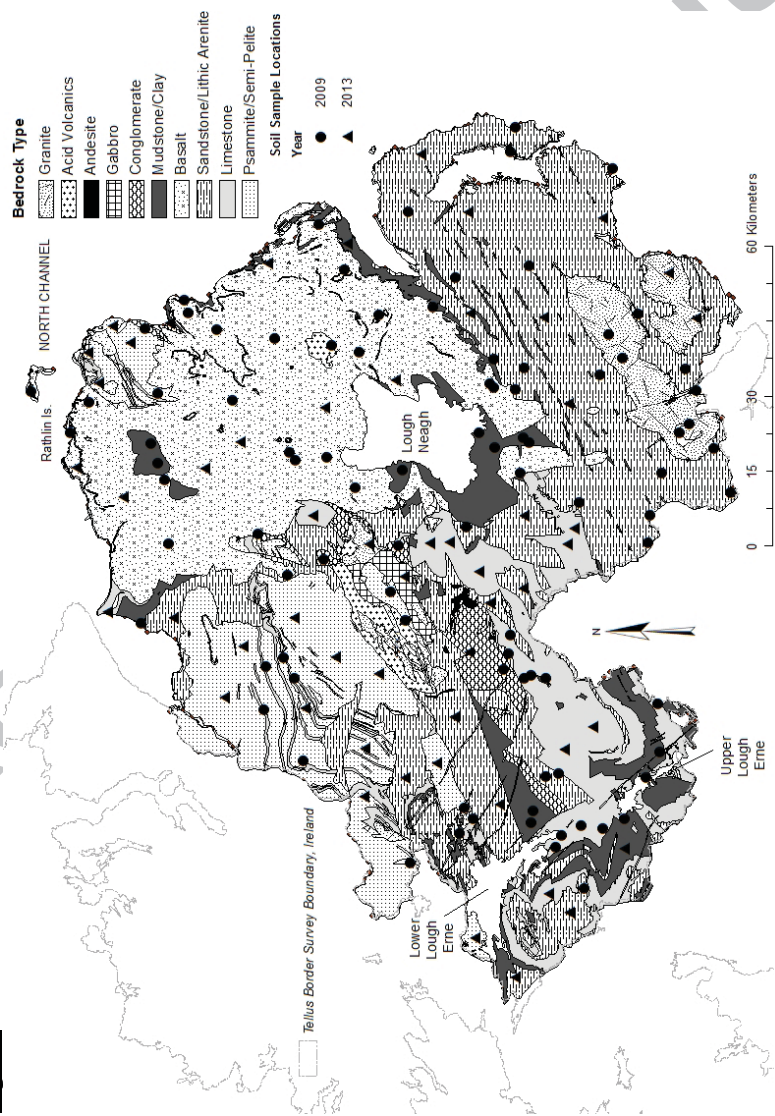
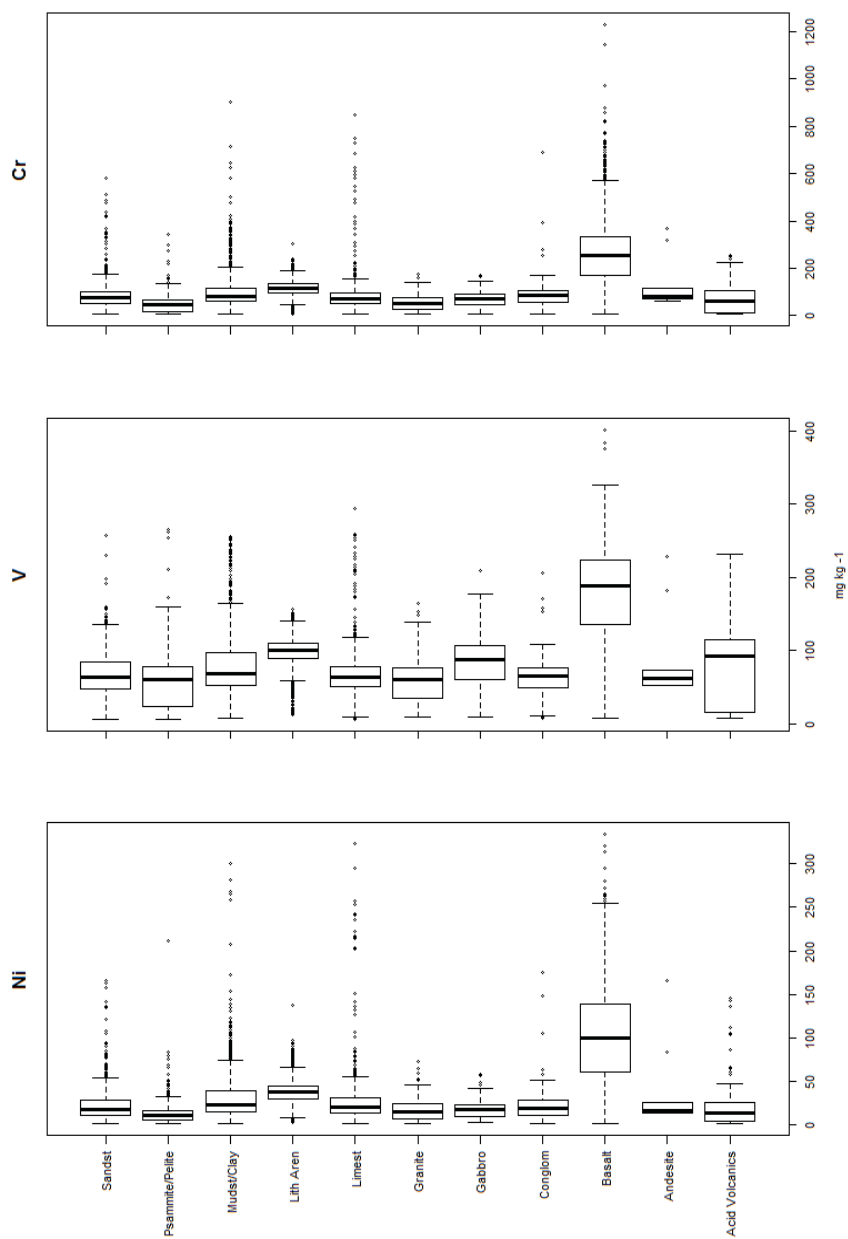
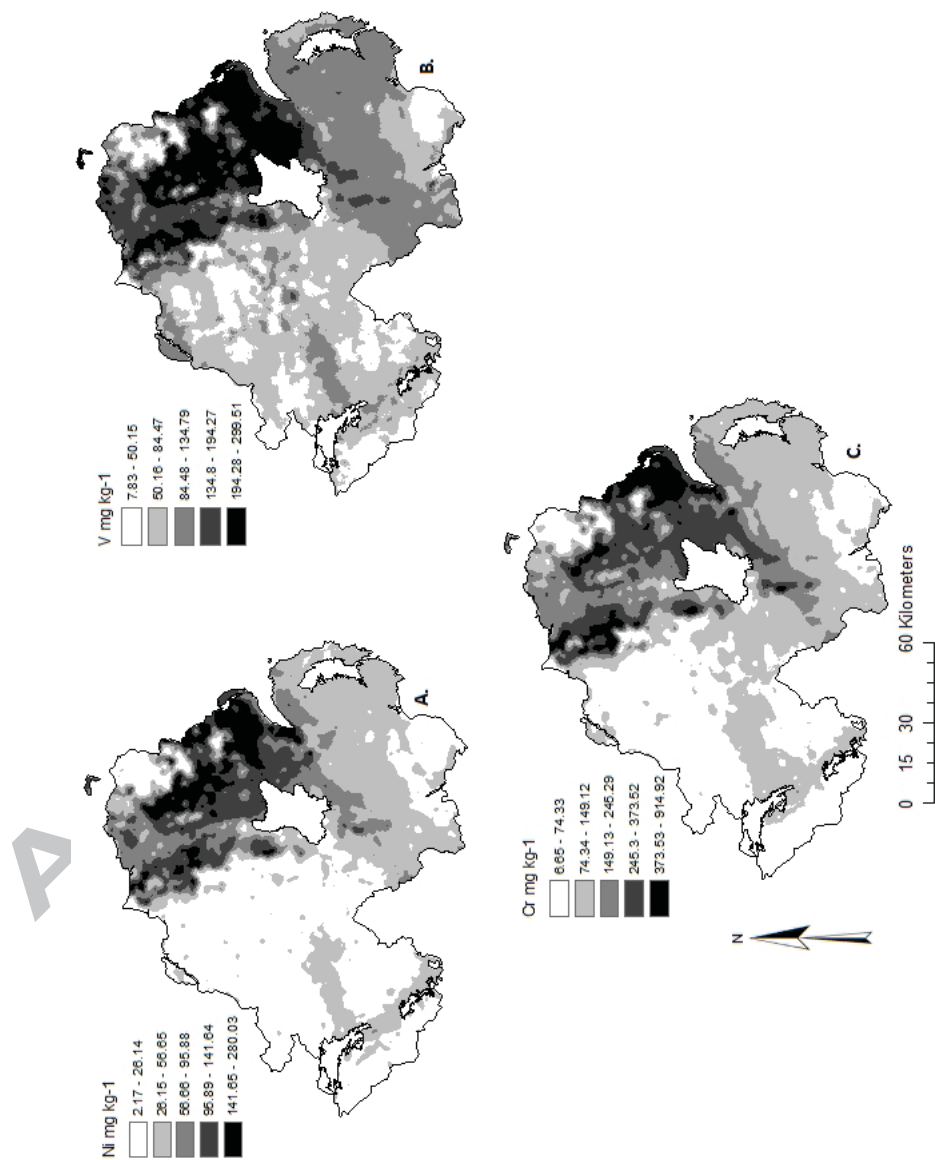


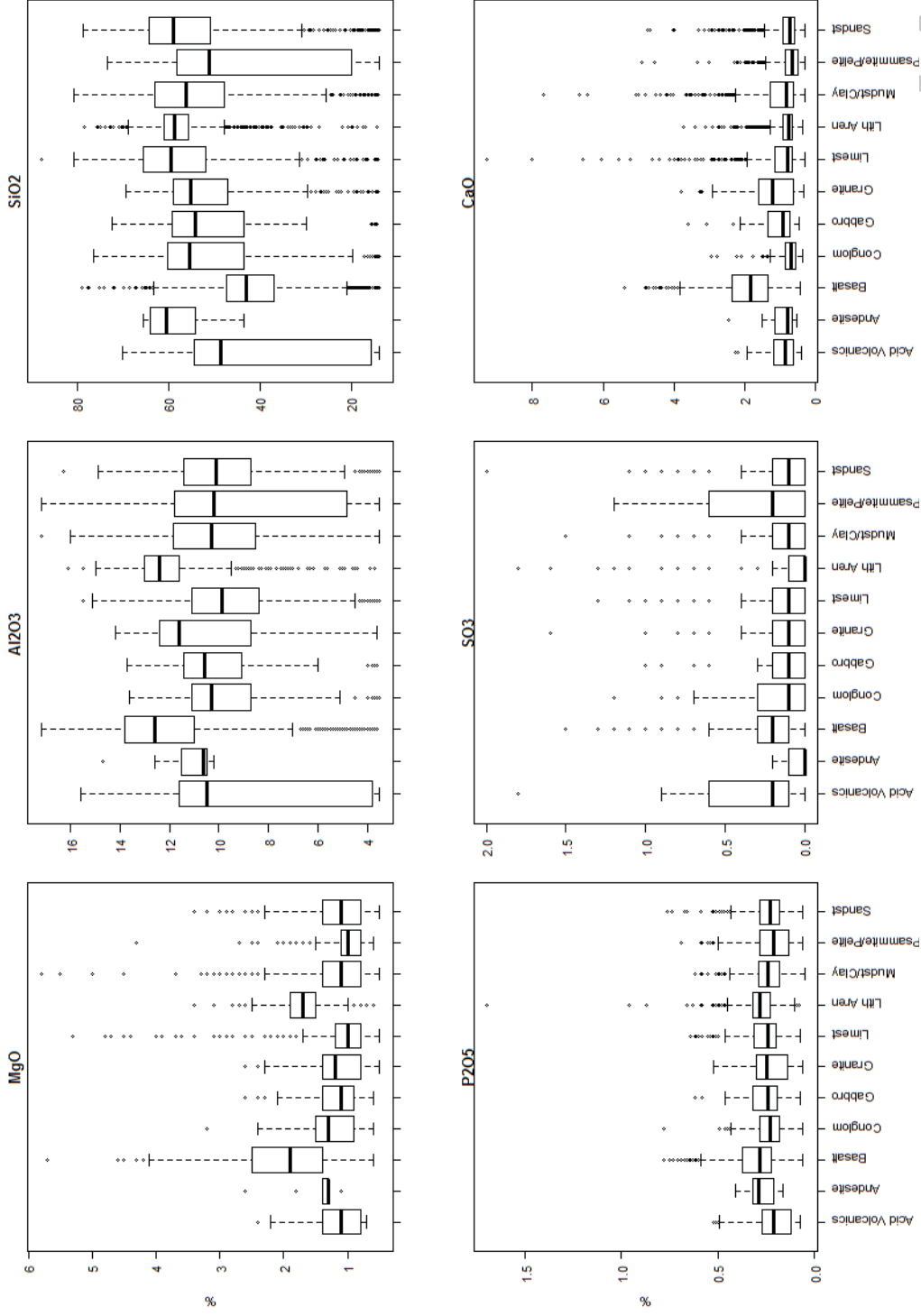
Fig. 1 Simplified geologic map of Northern Ireland and UBM sample locations, $n=145$. Simplified classifications based on Smyth (2007). Northern Ireland image used with permission from GSNI, Crown Copyright.



1
2 Fig. 2 Range of Ni, V and Cr total soil concentrations (mg kg^{-1}) across eleven generic bedrock groups present in Northern Ireland. All three elements have
3 higher concentrations in basalts, although V displays a greater degree of variability in its soil concentrations across the study area.

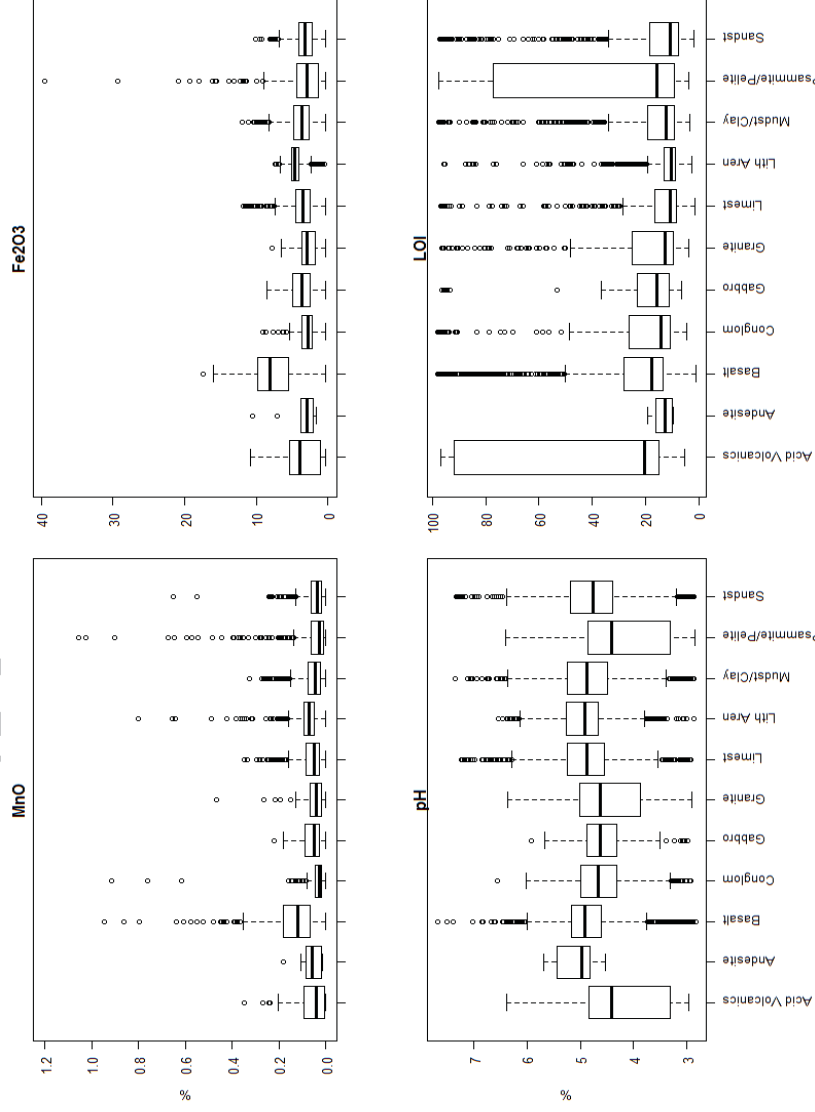


4
 5 Fig. 3 Total Ni, V and Cr soil concentrations across Northern Ireland interpolated by ordinary kriging. Intermediate concentrations of Ni, V and Cr can be
 6 observed in sandstones and lithic arenite in the southeast while relatively low concentrations are illustrated in upland locations relating to mountainous granite
 7 and psammite & semi-pelite, particularly for Cr and V.



8 Fig. 4 Box plots for six major element oxides expressed as percent total oxygen across eleven bedrock groups. Irregularity in the statistical distributions of
 9 some variables in soils overlying acid volcanics or psammite & semi-pelite may suggest the presence of sources of soil-geochemical variability not
 10 distinguished by the present grouping of data by generic bedrock type.
 11

12



13 Fig. 5 Box plots of MnO and Fe₂O₃ as percent total oxygen, pH and percent loss on ignition (LOI) with y-axis limited for MnO to permit illustration of
 14 statistical distribution. Lower average pH in psammite & semi-pelite and acid volcanic groups is the result of upland peat soils over these bedrock types.
 15 Irregularity in LOI distributions also in these two bedrock groups may suggest the LOI method is detecting multiple sources of combustion and water loss
 16 from both peat and clay soil minerals (Salehi et al., 2011).
 17

25

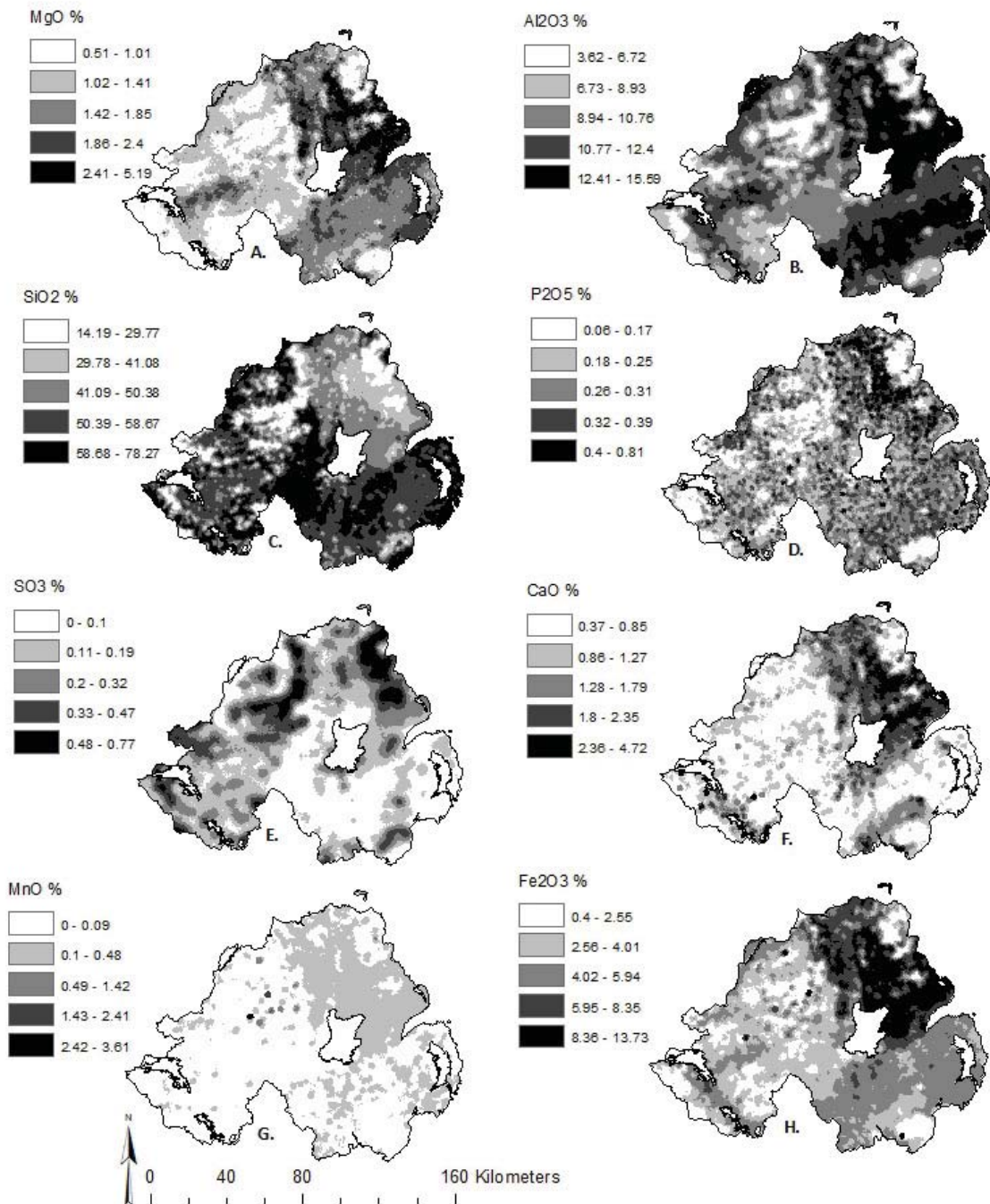


Fig. 6 Kriged major oxide distributions across Northern Ireland. MgO, CaO, and Fe₂O₃ are distinctly controlled by basalts in the northeast and most oxides with the exception of SO₃ display relative deficiency in mountainous upland peat soils. Al₂O₃ and SiO₂ show high concentrations in sandstone, lithic arenite, mudstones and limestones, whilst P₂O₅ is the only oxide whose distribution shows little apparent relationship to underlying geology.

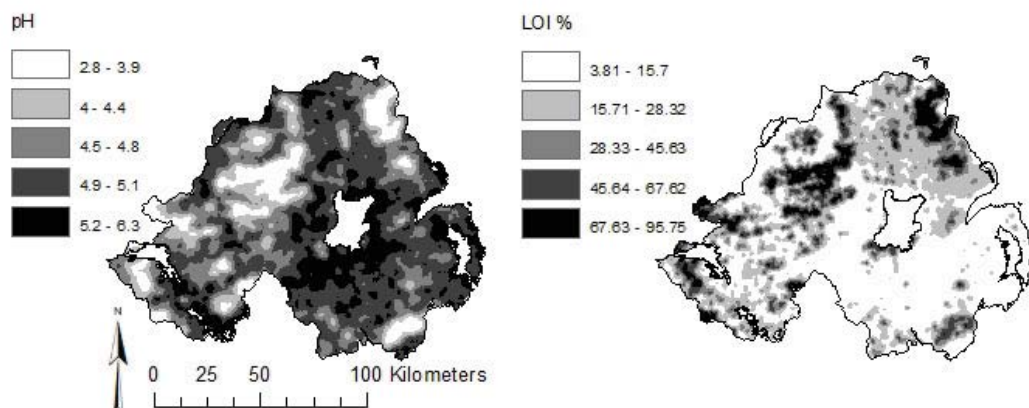


Fig. 7 Kriged soil pH and % loss on ignition across Northern Ireland. LOI gives an approximation of soil carbon content as illustrated by high values corresponding with spatial patterns of upland peat distributions, also related to acidic soil pH conditions as shown left.

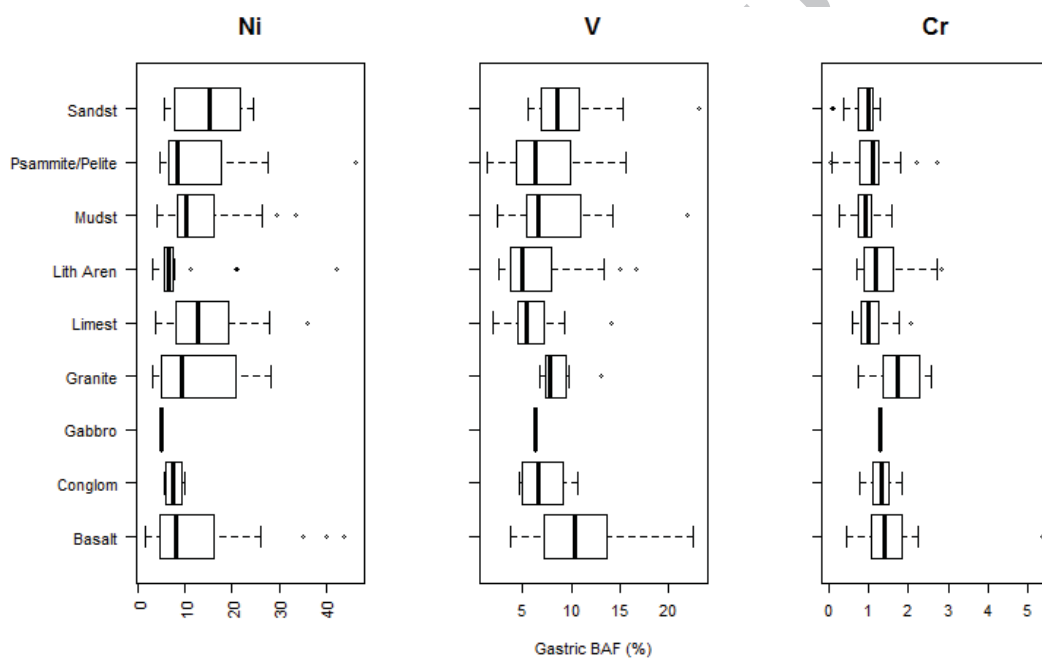


Fig 8. Boxplot distributions for gastric bioaccessible fractions of Ni, V and Cr according to nine underlying bedrock groups captured by combined UBM study set.

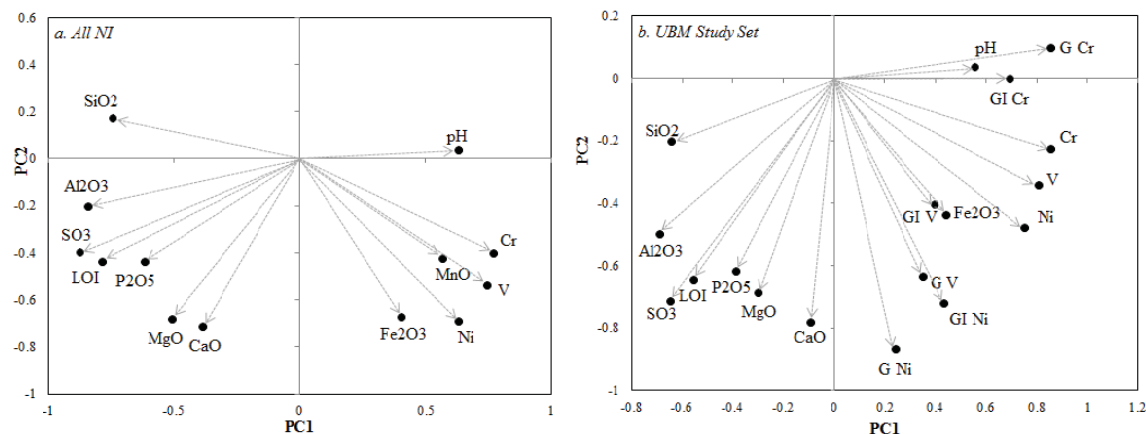


Fig. 9 Eigenvalue factor loading plots for principal components identified in full Northern Ireland geochemistry data set (a) and in UBM study set (b). Acute vector angles imply a correlation between factors while obtuse angles illustrate a negative relationship.

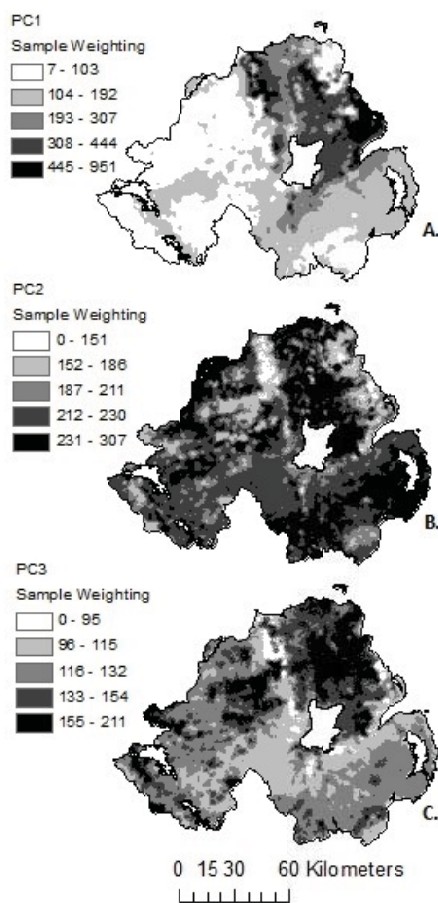


Fig. 10 Mapped soil sample site scores from PCA. First three components account for 87% of total geochemical variance from thirteen geochemical variables. PC1 is associated with variance from basalt bedrock, PC2 is linked to soil factor variance and remaining variance linked to PC3 is associated predominantly with a pH influence.

Tables

Table 1. pH tolerances for prepared digestive fluids.

Solution	pH Tolerance	Solution	pH Tolerance
Saliva	6.5 +/- 0.5	Duodenal	7.4 +/- 0.2
Gastric	1.0 +/- 0.1	Bile	8.0 +/- 0.2

Table 2. Summary statistics for trace elements (mg kg⁻¹), major element oxides (%), pH and LOI, $n = 6,862$ (Palmer et al., 2013).

	Ni	V	Cr	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	CaO	MnO	Fe ₂ O ₃	pH	LOI
Min	1.40	5.90	4.10	0.50	3.50	13.8	0.05	0.00	0.30	0.00	0.30	2.83	1.01
Max	334	402	1229	5.80	17.2	87.9	1.70	2.00	16.3	15.0	42.2	7.68	98.0
Mean	46.2	99.6	131	1.45	10.6	49.6	0.26	0.18	1.15	0.08	4.65	4.74	23.4
Median	29.1	85.0	94.1	1.30	11.4	54.1	0.25	0.10	0.85	0.06	4.19	4.82	12.9
StdDev	48.7	65.0	121	0.66	2.98	15.0	0.11	0.24	0.78	0.26	2.85	0.74	25.2

Table 3. Geostatistical summary of trace elements, oxides, pH and LOI. C_x = maximum variance accounted for by spatial function, C_0 = nugget variance not explicable within defined range of spatial function, a = maximum range of spatial dependence between sample locations in meters, Total $C_x = C_0 + C_1 + C_2$. Large C_0 : Total C_x ratios suggest micro-scale processes may influence spatial distributions (Einax and Soldt, 1999).

Variable	C_0	C_1	C_2	a_1	a_2	Total C_x	C_0 /Total C_x (%)
Ni	262.1	756.3	1885	9038	76,595	2903	9.0
V	697.8	1257	3014	13,816	74,194	4969	14.0
Cr	2223	11,604	3064	86,790	7038	16,891	13.2
MgO	0.02	0.12	0.02	1029	1872	0.16	12.5
Al ₂ O ₃	3.46	3.40	1.86	45,354	6720	8.72	39.7
SiO ₂	30.57	81.98	132.4	80,301	9927	245.0	12.5
P ₂ O ₅	0.006	0.004	--	17,233	--	0.01	60.0
SO ₃	0.04	0.02	--	36,438	--	0.06	67.7
CaO	0.32	0.51	--	177,902	--	0.83	39.5
MnO	0.06	0.03	--	31,404	--	0.09	67.7
Fe ₂ O ₃	2.71	6.86	--	96,708	--	9.57	28.3
pH	0.27	0.09	0.29	176,782	21,738	0.65	41.5
LOI	155.9	105.1	379.6	33,006	7886	640.6	24.3

1 Table 4. Ni, V and Cr gastric bioaccessibility (BAF = % of total concentration; mg kg⁻¹ = absolute measured bioaccessible concentration) across study area
 2 and by eight generic bedrock types according to combined 2013 and 2009 UBM extraction data (Barsby et al., 2012). Bold text indicates occurrence of
 3 maximum and minimum values from full-study set. Gabbro excluded due to small sample size.

BAF	Full Study Set			Basalt <i>n</i> = 29			Sandstone <i>n</i> = 16			Psammite & Semi-Pelite <i>n</i> = 22			Conglomerate <i>n</i> = 6								
	Mean	Med	Max	Mean	Med	Max	Mean	Med	Max	Mean	Med	Max	Mean	Med	Max						
Ni	12.4	15.2	46.3	1.4	12.1	8.2	43.8	1.4	15.2	15.2	24.4	5.6	12.8	8.2	46.3	4.7	7.6	7.5	9.9	5.5	
V	8.3	7.1	23.1	1.4	11.3	10.3	22.5	3.8	9.8	8.6	23.1	5.5	7.3	6.3	15.5	1.4	7.1	6.6	10.6	4.7	
Cr	1.2	1.0	5.4	0.03	1.5	1.4	5.4	0.4	0.85	1.0	1.3	0.05	1.1	1.1	2.7	0.03	1.3	1.3	1.8	0.8	
	Granite <i>n</i> = 7			Limestone <i>n</i> = 19			Mudstone <i>n</i> = 23			Lithic Arenite <i>n</i> = 16			Full Study Set mg kg ⁻¹								
BAF	Mean	Med	Max	Mean	Med	Max	Mean	Med	Max	Mean	Med	Max	Mean	Med	Max	Mean	Med	Max	Mean	Med	Max
Ni	13.2	9.3	28.3	3.0	14.4	12.9	35.8	3.6	13.3	10.3	33.6	4.1	9.3	6.6	42.2	3.0	3.8	2.4	30.7	0.3	
V	8.8	7.8	13.1	6.7	6.0	5.5	14.1	1.9	8.4	6.7	22.0	2.5	6.5	5.0	16.7	2.6	7.4	5.1	52.1	0.6	
Cr	1.7	1.7	2.6	0.7	1.1	1.0	2.1	0.6	0.9	0.9	1.6	0.2	1.3	1.2	2.8	0.7	1.5	1.0	10.0	0.004	

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Table 5. Eigenvalues greater than 1 explaining variance for component loadings.

Component	All Northern Ireland, <i>n</i> = 6862			UBM Study Set, <i>n</i> = 145		
	Value	% Variance	Cumulative %	Value	% Variance	Cumulative %
1	5.87	45	45	6.06	34	34
2	3.13	24	69	5.10	28	62
3	1.34	10	79	1.55	9	71
4	--	--	--	1.46	8	79

Table 6. Eigenvalue factor loadings for identified principal components in Table 5. MnO not identified as significant variable within UBM study set. Bold values indicate factor is most strongly weighted to indicated component, underlined values show where a large amount of remaining factor variance is accounted for by a secondary component.

Variable	Component								
	1			2		3			4
	All NI, <i>n</i> =6862				UBM Study Set, <i>n</i> =145				
V	0.742	<u>-0.534</u>	0.114	0.807	-0.342	0.224	-0.116		
Ni	<u>0.631</u>	-0.688	0.138	0.750	-0.478	0.019	-0.360		
Cr	0.770	-0.399	0.136	0.857	-0.224	-0.087	-0.175		
MgO	<u>-0.511</u>	-0.680	0.010	-0.299	-0.685	0.004	<u>-0.426</u>		
Al ₂ O ₃	-0.843	-0.200	<u>-0.340</u>	-0.689	<u>-0.497</u>	-0.386	-0.064		
SiO ₂	-0.747	0.174	<u>-0.521</u>	<u>-0.646</u>	-0.201	-0.662	0.121		
P ₂ O ₅	-0.620	<u>-0.436</u>	-0.362	-0.388	-0.617	<u>-0.430</u>	0.045		
SO ₃	-0.875	<u>-0.395</u>	0.155	<u>-0.649</u>	-0.712	0.143	0.093		
CaO	<u>-0.385</u>	-0.713	0.090	-0.097	-0.780	0.129	-0.018		
MnO	0.565	-0.422	<u>-0.512</u>	--	--	--	--		
Fe ₂ O ₃	<u>0.401</u>	-0.670	-0.249	0.443	<u>-0.435</u>	-0.049	-0.330		
pH	0.631	0.038	<u>-0.523</u>	0.555	0.036	<u>-0.531</u>	-0.092		
LOI	-0.787	<u>-0.438</u>	0.358	<u>-0.556</u>	-0.644	0.436	0.089		
G V	--	--	--	0.348	-0.634	0.280	<u>0.512</u>		
GI V	--	--	--	0.397	<u>-0.404</u>	-0.127	0.765		
G Ni	--	--	--	0.240	-0.866	0.043	-0.016		
GI Ni	--	--	--	0.433	-0.719	-0.193	-0.077		
G Cr	--	--	--	0.855	0.100	-0.162	0.120		
GI Cr	--	--	--	0.691	-0.001	-0.219	0.283		

Highlights

- Two soil-geochemical factors were identified accounting for 69% of total variance
- Low chromium bioaccessible fractions were linked to basalt bedrock factors
- Bioaccessible nickel was associated with peat and calcareous soil components
- The median vanadium bioaccessible fraction was 7%; chromium 1% and nickel 15%

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