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CORRELATION ANALYSIS AS A TOOL TO INVESTIGATE THE BIOACCESSIBILITY OF NICKEL, VANADIUM AND ZINC IN NORTHERN IRELAND SOILS

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Abstract: Correlation analyses were conducted on nickel (Ni), vanadium (V) and zinc (Zn) oral bioaccessible fractions (BAFs) and selected geochemistry parameters to identify specific controls exerted over trace element bioaccessibility. BAFs were determined by previous research using the Unified BARGE Method. Total trace element concentrations and soil geochemical parameters were analysed as part of the Geological Survey of Northern Ireland Tellus Project. Correlation analysis included Ni, V and Zn BAFs against their total concentrations, pH, estimated soil organic carbon (SOC) and a further eight element oxides. BAF data were divided into three separate generic bedrock classifications of basalt, lithic arenite and mudstone prior to analysis, resulting in an increase in average correlation coefficients between BAFs and geochemical parameters. Sulphur trioxide and SOC, spatially correlated with upland peat soils, exhibited significant positive correlations with all BAFs in gastric and gastro-intestinal digestion phases, with such effects being strongest in the lithic arenite bedrock group. Significant negative relationships with bioaccessible Ni, V and Zn and their associated total concentrations were observed for the basalt group. Major element oxides were associated with reduced oral trace element bioaccessibility, with Al_2O_3 resulting in the highest number of significant negative correlations followed by Fe_2O_3. Spatial mapping showed that metal oxides were present at reduced levels in peat soils. The findings illustrate how specific geology and soil geochemistry exert controls over trace element bioaccessibility, with soil chemical factors having a stronger influence on BAF results than relative geogenic abundance. In general, higher Ni, V and Zn bioaccessibility is expected in peat soil types.

1. Introduction

Determining the bioaccessibility of potentially toxic elements in soil provides supporting information to more accurately constrain human health risk assessment approaches where oral soil borne contaminant exposure is the pathway of concern. While much research has been conducted in terms of the bioavailability and bioaccessibility of trace elements such as lead and arsenic, particularly from anthropogenic sources (Farmer et al. 2011; Meunier et al. 2010; Palumbo-Roe and Klinck 2007), a knowledge gap exists concerning the bioaccessibility of a wider range of metals and metalloids from geogenic sources.

Previous research suggests that toxic elements from geogenic sources may be less bioaccessible than those associated with anthropogenic contamination due to the solid phases in which they exist (Cave et al. 2007; Cave et al. 2003). Such findings have implications for human health risk assessments in the context of the United Kingdom's (UK) contaminated land legislation regime (DEFRA 2012), as better determination of specific health risks could avoid unnecessary soil remediation projects. In addition, correlating trace element abundance and bioaccessibility to specific soil types, geochemical parameters and parent bedrock geology can identify natural controls exerted over the bioavailability of geogenic contaminants, facilitating more accurate site-specific risk assessments.

In Northern Ireland, nickel (Ni), vanadium (V) and zinc (Zn), whose distributions are largely controlled by local geology, are present in soils at elevated levels, exceeding either Environment Agency (EA) Soil Guideline Values (SGVs) or other existing available generic assessment criteria (Barsby et al. 2012; EA 2009*a*; Nathanail et al. 2009). However, assessment criteria must be used with care, and particular attention should be paid to the derivation of such guideline values. For example, arsenic health criteria values and subsequent SGVs have been derived using toxicology data from exposure to soluble forms of arsenic in drinking water rather than from exposure via soil media (EA 2009*b*; EA 2009*c*). Where Ni is concerned, the inhalation pathway is considered to be the most significant exposure route capable of introducing human health risks, although toxicological information suggests some forms of Ni are still readily absorbed through the gastro-intestinal tract when ingested and, therefore, still capable of inducing toxic health effects (EA 2009*a*; EA 2009*d*). Such challenges regarding the accurate characterization of risks associated with soil-borne trace element exposure highlight the need for employing more detailed assessment techniques such as bioaccessibility testing, thus ensuring exposure pathways are relevant to specific toxic effects, land use scenarios and contaminant sources.

In response to these issues, much research has been conducted over the past two decades in order to refine a suitable methodology for bioaccessibility testing where ingestion of soil is the exposure pathway of concern (Wragg et al. 2011; Wragg et al. 2009; Wragg and Cave 2003; Van de Weile et al. 2007; Oomen et al. 2003; Ruby et al. 1999; Ruby et al. 1996). The most recently published methodology widely in use in the UK and European Union to date, the Unified BARGE (BioAccessibility Research Group of Europe) Method (UBM), has been validated against *in vivo* data for arsenic, cadmium and lead (Denys et al. 2012; BARGE/INERIS 2010; Caboche 2009). A recently published study by Barsby et al. (2012) was the first bioaccessibility investigation of its kind covering the region of Northern Ireland and employing the UBM. The findings of this study suggested that trace element bioaccessibility was specific to individual geologic formations within the region, thus unveiling a wider scope of investigation for determining in more detail the mechanisms governing this variability.

Specific soil properties such as redox potential, parent rock material, organic content, pH, nutrient content, and the co-occurrence of major element oxides can influence the mobility and bioavailability of toxic elements in soil. For example, Poggio et al. (2009) found soil organic matter was positively correlated with the bioaccessibility of several trace metals, including Ni and Zn. Where Zn is concerned, decreased bioaccessibility has been associated with the presence of aluminium oxides, and its mobility and resulting bioaccessibility may also be affected by the presence of organic matter (Pelfrêne et al. 2012; Nathanial et al. 2009; Poggio et al. 2009; ATSDR 2005). Less information is available to date concerning such relationships for V, although acidic pH has been found to reduce its mobility in soil (Nathanail et al. 2009), which is in contrast to other trace metals where solubility generally increases under acid soil conditions. Chemical conditions that are conducive to increased element mobility and solubility will in turn enhance bioaccessibility.

The aim of this paper is to illustrate how geology and geochemistry influence trace element bioaccessibility by using correlation analyses to identify relationships between Ni, V and Zn bioaccessible fractions (BAFs) in soil and selected geochemistry variables. With Northern Ireland's diverse geology, unsurpassed by any other country of a similar size (Jordan et al. 2007; Mitchell 2004; Wilson 1972), such a study has wider applications beyond the immediate study area when conducting site-specific human health risk assessments.

2. Methodology

2.1 Study Area

The range of bedrock types encountered in Northern Ireland forms a stratigraphic record which commences in the Mesoproterozoic era, comprising deformed and metamorphosed sedimentary and volcanic rocks formed at least 600 million years ago (Mitchell 2004). The region includes examples of all geological systems up to and including the Palaeogene period, comprising basalt lavas and lacustrine sedimentary rocks formed between circa 55 and 62 million years ago. Quaternary processes involved the advance of ice sheets and their meltwaters, resulting in a range of diverse superficial deposits including glacial till. As a result, superficial deposits such as glacial till and post-glacial alluvium cover at least 80% of bedrock in the region. The rock types encountered find stratigraphic distribution beyond Northern Ireland and, thus, findings in relation to pedological and geological controls on trace element bioaccessibility associated with specific soil and rock geochemical signatures has applications beyond the immediate region of Northern Ireland.

Data associated with sample locations presented for this study are divided into three generic bedrock types: basalt, lithic arenite and mudstone (Fig. 1). The rationale for selection of these groups is provided in Section 2.4. The basalt lavas of the Antrim Plateau are located in the northeast of the study region, with lithic arenite sample locations occurring predominantly in the southeast in the County Down area. In the southwest region of Fermanagh, sedimentary rock types are present, classified generally as mudstones.

2.2 Geochemistry Analyses

The GSNI (Geological Survey of Northern Ireland) Tellus Survey, conducted between 2004 and 2007, consisted of a comprehensive survey of stream sediments and stream waters, as well as rural and urban soils. Composite rural soil samples used for this research were collected from a total of 6,862 locations on a 2 km^2 grid from a depth of 5-20 cm below ground level (Smyth 2007).

Soil geochemistry data relating to trace elements, element oxides and other geochemical parameters including pH and loss on ignition (LOI; %) were determined as detailed in the Tellus geochemical mapping methodology report (Smyth 2007). Pseudo-total and total concentrations of Ni, V and Zn (mg kg^{-1}) were determined both by *aqua regia* digestion followed by inductively coupled plasma spectrometry (ICP), as well as by pressed pellet X-ray fluorescence spectrometry (XRF). Major element oxides (%) were determined also by XRF.

LOI, applied as an estimate of soil organic carbon (SOC), was determined by calculating sample weight loss after oven drying at 105°C for 4 hours followed by 4 hours in a 450°C furnace. While not a means of determining the precise carbon content of soils, the LOI method is recognised as a suitable, cost-effective approach to estimating regional trends in SOC and has been applied in other published research (Salehi et al. 2011; Elzinga and Cirmo 2010; Konen et al. 2002; Ball 1964).

2.3 Unified BARGE Method Testing

The UBM is a sequential extraction technique designed to mimic the conditions of the human digestive system. Three stages of the UBM aim to represent the salivary, stomach and intestinal exposure conditions of an ingested material. Two extracts are collected from the method: one following a one hour gastric digestion using synthesised saliva and stomach fluids, and a second extract is obtained after an additional four hours of gastro-intestinal digestion using synthesised duodenal fluid and bile. Details of the UBM protocol and required equipment and reagents are available on the BARGE web site (BARGE/INERIS 2010). UBM laboratory work was carried out at the British Geological Survey (BGS) in Keyworth, Nottingham. Methodology and quality control efforts used to obtain the bioaccessibility data referred to in this paper have been published previously (Barsby et al. 2012). For every 10 samples analysed by the UBM, one duplicate, one blank and one reference soil (BGS 102; Wragg et al. 2009) were extracted.

As described in Barsby et al. (2012), the trace element oral bioaccessibility was determined on a subset of archived surface soil samples from the original rural soil sampling programme of the GSNI Tellus Survey. Soil samples used for UBM testing, comprising 91 samples in total, were chosen with the aim of representing a broad spatial, lithological and pedological coverage across the region. Dried and sieved soil from the <250µm fraction was used for the UBM digestion.

Bioaccessible trace element concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS) following gastric (G) and the gastro-intestinal (GI) UBM extraction. BAFs (%) were calculated using bioaccessible concentrations determined from the UBM test (C_b) and the total XRF concentration in the soil sample as provided by the Tellus Survey data base (C_{pt}).

$$BAF\ [\%] = \frac{C_b[mg\ kg^{-1}]}{C_{pt}[mg\ kg^{-1}]} \times 100$$

(Equation 1).

XRF total concentrations were chosen for BAF calculation instead of ICP pseudo-total concentrations because of the ability of XRF analysis to detect insoluble traces of elements, providing a better understanding of total trace element bioaccessibility in terms of insoluble, geogenic mineral forms. Relative BAF results (%) were used for the correlation analyses as opposed to absolute UBM extract concentration values to provide a normalised basis for comparison of relative trace element bioaccessibility across geologic sub-groups.

2.4 Statistical Treatment and Grouping of Data

Correlation analyses were carried out using G- and GI-BAFs of the three trace elements against the following geochemical variables: oxides of magnesium (MgO), aluminium (Al_2O_3), silicone (SiO_2), sulphur (SO_3), phosphorous (P_2O_5), calcium (CaO), manganese (MnO), and iron (Fe_2O_3); total Ni, V and Zn concentrations; SOC; and pH. A two-tailed significance test was applied using the Pearson's correlation coefficient (r) in IBM SPSS Statistics v.19. Cut off points for critical r values were determined according to sample group sizes as defined in Triola (1998).

Initial exploration of distribution trends in the Tellus geochemistry data set indicated that, while all geochemistry data were not normally distributed when tested for skewness and kurtosis, log-transformation of the data did not substantially improve tendencies towards normal distributions. When Tellus geochemistry data were divided into geologic sub-groups, the tendency towards a normal distribution was increased. Parametric statistical testing was therefore deemed suitable for the purpose of these analyses.

Correlation analyses were first conducted on the complete bioaccessibility study set (n = 91). This sample set was subsequently divided into geologic sub-groups according to three generic bedrock types present in the study set in the highest proportions as defined by the GSNI Tellus Survey methodology (Smyth 2007). This was carried out with the aim of controlling for geogenic influences in the geochemistry data and reducing potential sources of variance which could be introduced from other soil properties or multiple rock types (Jordan et al. 2007; Zhang et al. 2007). In turn, it was anticipated that the likelihood of identifying geogenic controls over the BAF results would increase and correlation findings would be strengthened.

The rationale for using generic bedrock types as defined in the GSNI Tellus Survey rather than specific local formations was to ensure statistical robustness was maintained through the formation of sufficient sub-group sample sizes. The three generic bedrock types present in the bioaccessibility study set in the highest proportions were identified as basalt (n = 23), consisting of Upper and Lower Basalt formations, the Tardree Rhyolite Complex, the Causeway Tholeiite Member, and the Slieve Gullion Complex; lithic arenite (n = 17), inclusive of Gilnahirk, Gala and Hawick Sandstones; and the mudstone group (n = 18), represented by a mixture of sedimentary bedrock types including clays, limestones, mudstones and shales.

2.5 Spatial Data Analysis

Spatial interpolation by inverse distance weighting (IDW) was applied to the Tellus XRF geochemistry data set to illustrate geographic patterns in specific spatial variables of interest. Mapped outputs of total toxic trace element concentrations are presented in Barsby et al. (2012). IDW is a deterministic method, resulting in a clustering of values around data points on the surface through exact interpolation (Lloyd 2010). This effect is reduced in regularly gridded data such as the Tellus data used for this study. The IDW method assumes that sample points further away spatially will have a diminished influence over the interpolated value at a given location, while points closer to a specific location will have a greater influence over its predicted value (ESRI 2010; Matheron 1965).

ArcGIS v.10 was used to map the spatial distribution of selected geochemical variables from the complete Tellus geochemistry database (n = 6862) using IDW with a power function of 2, a variable search radius and an output cell size of 250. An iterative process was used to select the best fit model from four different possible single-sector search neighbourhoods of 8, 10, 12 or 15 neighbours. The function resulting in the best fit regression model of prediction was chosen based on values of mean prediction error, root mean square error and the slope of the regression function.

3. Results

When average BAF results were compared across the three generic bedrock types, differences in relative trace element bioaccessibility were observed (Table 1). The highest measured mean and maximum G-BAF for V was in the basalt group. However, the mean GI-BAF was greatest in the mudstone group. Zn G-BAF averages were also higher in soil samples located over basalt bedrock types, while differences in mean GI-BAFs were negligible, with the exception of the lithic arenite bedrock group where the lowest Zn GI-BAF was observed. Both mean G- and GI-BAF results for Ni were highest in the mudstone bedrock group, although the maximum G- and GI-BAFs occurred in soil samples collected over basalt and lithic arenite, respectively. The basalt group also displayed minimum G- and GI-BAFs where Ni was concerned.

Table 2 provides a summary of Pearson's correlation coefficients (*r*) for selected geochemical parameters and UBM BAF data. In general, total trace element concentrations were associated with reduced BAFs in the basalt sample group. The same trend was apparent for MgO, MnO, P_2O_5 and Fe_2O_3 within this bedrock group, with P_2O_5 revealing significant negative correlations to Ni, V and Zn BAFs in the basalt samples only. Al_2O_3 showed strong negative influences over all trace element BAFs, particularly for the basalt and mudstone samples. The effect of silicates expressed in the form of SiO_2 was less pronounced in terms of number of significant correlations; however, where this oxide was significantly correlated with Ni, V and Zn BAFs, it appeared to exert a negative control over bioaccessibility primarily in the gastric digestion phase. While SO_3 and SOC were consistently positively correlated with gastric BAFs, their effects were strongest across both digestion phases in the lithic arenite bedrock group.

3.1 Vanadium

When V BAF results were analysed for correlations with other geochemical properties within the bioaccessibility study sample set, significant negative correlations were found between gastric BAFs and MgO, Al_2O_3, SiO_2, MnO, and Fe_2O_3 ($p \leq 0.01$). Positive G-BAF relationships were observed with SO_3 and

SOC, also at the 0.01 significance level. Different effects on V BAFs were apparent in the correlation data when gastro-intestinal BAFs were analysed. GI-BAFs decreased in line with increasing total V and Ni content. MgO, MnO, Fe_2O_3 and Al_2O_3 continued to exert negative effects over V BAFs in the gastro-intestinal digestion phase, although the trend with SiO_2 observed in the gastric digestion phase was weakened to a point of non-significance. SO_3 and SOC exhibited a significant positive relationship with V GI-BAFs ($p \leq 0.01$), although Pearson's correlation coefficients were reduced when compared to the G-BAF data.

When BAFs were split into specific Tellus geology classifications, a number of previously observed correlations changed. Average absolute r values for G-BAFs against geochemical parameters were 0.58, 0.35 and 0.38 for the basalt, lithic arenite and mudstone groups, respectively, compared to an average correlation coefficient of 0.31 when correlations were conducted on the complete study set. Average absolute r values for GI-BAF correlations doubled in the basalt group, increased by 0.10 in the lithic arenite bedrock group, and improved by 0.16 in the mudstone bedrock group when compared to statistics obtained from the full study set prior to bedrock group division.

Overall, the greatest number of significant correlations between bioaccessible V and geochemistry variables was observed in the basalt bedrock group. Both G- and GI-BAFs were negatively correlated with total V, Ni and Zn ($p \leq 0.05$). MgO, Al_2O_3, P_2O_5, MnO and Fe_2O_3 also showed strong significant negative correlations with bioaccessible V in the gastric and gastro-intestinal phases ($-0.55 \geq r \geq -0.77$; $p \leq 0.01$). Increasing soil acidity appeared to result in increased V bioaccessibility according to G- and GI-BAF correlation values. SO_3 and SOC exerted the strongest positive influence over gastric bioaccessible V, although no significant r values were obtained for these variables within the basalt GI data.

The strongest negative correlations in soil samples overlying lithic arenite bedrock were observed with Al_2O_3 and Fe_2O_3, while the highest positive correlations were found with SO_3 and SOC. SiO_2 also appeared to have a negative effect over G- and GI-BAFs, though correlations were statistically significant in the gastric data only ($p \leq 0.05$). Correlations in this bedrock group did not vary substantially when gastric and gastro-intestinal digestion phases were compared.

In the mudstone bedrock group, MgO, Al_2O_3 and MnO showed consistent negative correlations with V BAFs in both the G and GI digestion phases. Significant correlations were observed for Fe_2O_3 and pH in the GI-BAF data only. In contrast to the inverse correlation observed between pH and BAFs in the basalt bedrock group, positive correlation statistics were obtained across these variables in the mudstone group.

3.2 Nickel

As shown in Table 2, bioaccessible Ni decreased in line with increasing total V and Ni, while the opposite was observed with total Zn. Within the complete study set, similar relationships were observed between Ni BAFs and oxides of Mg, Al, Mn and Fe, as were found in the V BAF data, with decreased levels of Ni bioaccessibility associated with their occurrence. In addition to this trend, SO_3 and SOC continued to exert a positive influence over Ni G- and GI-BAF results, with the largest *r* values obtained for the gastric BAF data.

In the basalt group, the average Pearson's correlation coefficient was 0.68 and 0.57 for the G- and GI-BAF data, respectively. Variables not producing significant correlations in this group were SiO_2, SO_3 and SOC, though this lack of influence was observed within the gastro-intestinal data only. Total Ni, V and Zn were inversely correlated to Ni BAFs ($p \leq 0.01$) in the basalt samples, while no such significant relationships were found in the other two bedrock classes.

Although the number of significant correlations in the lithic arenite group decreased when compared to the full study set results, average correlation coefficients still increased slightly for both gastric and gastro-intestinal Ni BAFs. This suggests the capability to identify correlations as significant was restricted due to the reduced sub-sample size rather than being a result of weakened absolute *r* values. Most notably in the lithic arenite group, SO_3 and SOC showed strong positive correlations with G-BAF data (r = 0.94 and 0.81, respectively), and also with GI-BAF results (r = 0.89 and 0.65, respectively; all $p \leq 0.01$).

The trends with sulphur trioxide and estimated organic content continued in the mudstone group, while oxides of aluminium and silica appeared to result in significantly reduced Ni bioaccessibility in the G-BAF data. The impact of Al_2O_3 was still significant in the GI digestion phase ($p \leq 0.05$), though this effect was reduced when compared to the G-BAF results. CaO was significantly correlated with Ni G-BAFs, with bioaccessibility appearing to increase in line with CaO concentrations. This impact was not consistent across the geologic formations, however, with significant negative correlations observed for this variable in the basalt bedrock group.

3.3 Zinc

Overall, Zn exhibited the highest mean and maximum G- and GI-BAFs compared to Ni and V, with up to a quarter of total Zn found to be potentially bioaccessible on average, reaching a maximum of 80% in the basalt group (Table 1). Following a similar pattern to V and Ni, oxides of Mg, Al, Mn and Fe were negatively correlated to Zn BAFs in both the G and GI fractions. Total V and Ni were also negatively correlated with bioaccessible Zn in the full study set; however, there was a weak relationship between total and bioaccessible Zn. SO_3 and SOC exhibited the strongest positive correlations with Zn G-BAFs, though significant correlation coefficients were still obtained across the GI-BAF data (maximum r = 0.95). pH was negatively correlated with Zn BAFs in the complete study set, and this relationship was more clearly displayed within the basalt bedrock group. However, this correlation was not significant in the other two bedrock groups ($p \geq$ 0.05).

In the basalt bedrock category, the only parameter not yielding a significant correlation with Zn BAFs was SiO_2 in the gastro-intestinal phase. The number of significant correlations was substantially reduced in the other two bedrock groups by comparison, although correlations with SOC, SO_3, Fe_2O_3 and Al_2O_3 remained strong overall. Additional significant negative correlations were observed between total V, total Ni and Zn GI-BAFs in both the lithic arenite and mudstone groups ($p \leq 0.05$). SiO_2 was associated with decreased gastric Zn bioaccessibility across all sample sets, while P_2O_5 and CaO appeared to exert strong negative effects over G- and GI-BAFs in the basalt group. In contrast, P_2O_5 and CaO yielded weakly positive r values in the mudstone bedrock group, although statistical significance was limited to CaO and the gastric bioaccessible fraction ($r = 0.76$, $p \leq 0.01$).

3.4 Spatial Trends

As shown by the correlation analysis (Table 2), SO_3 and SOC consistently exerted positive controls over the bioaccessibility of the three trace elements. In addition, SO_3 and SOC are strongly correlated to each other across Northern Ireland ($r = 0.86$, $p \leq 0.01$). As shown by Fig. 2c and d, SO_3 and SOC share similar spatial distributions across Northern Ireland, overlapping directly with the extent of acid upland peat soils. Overall, the range of pH values in Northern Ireland soils is relatively narrow (Fig. 2a), making definite correlations with BAF data difficult to distinguish in the absence of a wider range of pH values. Although soil pH did not appear as a factor affecting bioaccessibility as significantly as SOC and SO_3 through the correlation analysis, more acidic soil conditions are shown to be well-aligned spatially with peat soils in the region. In addition, spatial illustration of the distribution of aluminium oxide (Fig. 2b), which exerted consistent negative controls over Ni, V and Zn BAFs, shows lower relative abundances in peaty upland areas, with additional strong geologic controls over Al oxide distribution around the Antrim Basalts in the northeast of the country. Interpolation of other metal oxides associated with reduced BAFs such as Fe_2O_3 (not shown) resulted in similar spatial distributions to Al_2O_3.

4. Discussion

4.1 Geogenic Sources of Variance

Correlation analysis is a useful tool for identifying relationships between pairs of variables and for forming hypotheses on element sources, fate and behaviour.

Such analyses can also support the development of mathematical models to predict trace element bioaccessibility under certain conditions (Pelfrêne et al. 2012; Abollino et al. 2011; Poggio et al. 2009; Cave et al. 2007; Cave et al. 2003). It is important to note, however, that correlation does not necessarily imply causation (Triola 1998), and some of the geochemistry variables explored in this study may be mere micro-scale indicators of wider scale factors or processes bearing influence over trace element bioaccessibility. For example, some of the oxides studied are used as indicators of rock and mineral weathering processes which may be responsible for mobilising trace elements across large regional scales.

While correlation analysis can assist with understanding specific mechanisms that may influence trace element bioaccessibility, potential geogenic sources of variance in geochemistry data should be eliminated before these relationships can be effectively explored, particularly in Northern Ireland where such diversity in geology exists (Jordan et al. 2007). The increase in average correlation coefficients when the UBM data were split into the three dominant generic bedrock types indicates that variability was reduced within the geologic sub-groups. However, other sources of variability capable of weakening correlation statistics are still present within these data sets. Soil type, for example, is a variable that was not initially controlled for within the bedrock groups, although it is a variable that was revealed during the course of analysis, in the case of peat. At least eight distinctly different soil types are present within each of the basalt and mudstone sample groups, while shale soil types dominated in the lithic arenite division. Despite the variety of soil types in the basalt group, the high Pearson's correlation coefficients for most parameters suggests that a large source of variance in BAF data stems from geology in this area. Lower *r* values in the other bedrock groups suggest significant sources of variance are present in the results not accounted for by bedrock type. For example, soil type or localised physico-chemical factors such as soil moisture or redox conditions could also influence trace element mobility and bioaccessibility.

Differences in relative trace element bioaccessibility between the generic bedrock groups (Table 1) may be attributed to Ni, V or Zn existing in different solid phases over each bedrock type. For example, strong negative correlations between trace element BAFs and their total concentrations in the basalt bedrock group suggest most of the non-bioaccessible fraction of these elements is in an insoluble form in these soils, with a lesser soluble component accounting for the bioaccessible portion. This may be linked to the relative age of the basalt formations, which are among the youngest and least weathered rocks in Northern Ireland (Mitchell 2004). This conclusion is also supported by Cox et al. (2013), whose analysis of the solid phase distributions of Ni from the same study area found that soil samples containing greater proportions of Ni present in carbonate phases also hosted more bioaccessible Ni. Conversely, soil samples containing higher proportions of Ni hosted by Fe-oxides and clay had relatively lower Ni bioaccessibility. Previous comparison of ICP-derived trace element concentrations against XRF data for the same elements suggests that the relative solubilities of trace elements are influential in determining trace element bioaccessibility, with XRF concentrations commonly higher than ICP data due to the application of solvent-based *aqua regia* extraction versus the dry pellet analytical technique used for the XRF analyses (Barsby et al. 2012). Weaker negative correlations observed between BAFs and total trace element concentrations in the mudstone and lithic arenite bedrock groups may be related to their overall lack of relative abundance within these areas, illustrated previously by Barsby et al. (2012). The exception to this trend is illustrated by Zn BAFs, which were higher on average than the other two elements studied. Compared to Ni and V, Zn total distributions are controlled by a wider variety of rock types other than basalt, with high relative concentrations also found in soils over sandstone and limestone in the region.

While the overall trend in correlations with pH was weakly negative with respect to trace element BAF data (Table 2), the mudstone group provided a consistent exception to this result. A closer look at rock sub-types within this category shows a mixture of limestone, clay, argillaceous rock and mudstone. The presence of limestone in particular may have introduced variable results in the laboratory due to the release of calcium carbonate into solution, creating unstable pH conditions during *in vitro* UBM extractions. CaO also showed a similar trend to pH with respect to its variable influence over trace element BAFs, depending on how the data set was treated across the geologic classifications. Individual trends in CaO correlations were aligned with pH trends within the basalt and mudstone sample groups. Across Northern Ireland, CaO shows a significant positive correlation with pH (r = 0.436, $p \leq 0.01$). With respect to BAF correlation results, CaO and pH were both negatively correlated with BAFs in the basalt group, but positively correlated with BAFs in the mudstone group. Both basalt and limestone, included in the mudstone group, contribute to increased levels of calcium in Northern Ireland soils (Jordan et al. 2001). However, geogenic calcium in the basalt sample group may be in a less soluble form than calcium found in limestone parent material. Chesworth et al. (1981) found that the greatest proportion of calcium in basalt in Belbex, France was hosted by pyroxene and plagioclase minerals which were the least susceptible to degradation by weathering compared to other basalt minerals studied. This aligns with the finding by Cox et al. (2013), whose XRD analysis of basalt mineralogy in County Antrim, Northern Ireland confirmed the presence of the same weather and acid resistant, calcium-rich minerals. Conversely, trace metals associated with high carbonate soil components derived from calcium-rich parent material such as limestone are easily extracted when exposed to acid conditions, resulting in increased gastric bioaccessibility (Denys et al. 2007; Ljung et al. 2007; Nathanail et al. 2007; Cave and Wragg 1997). Despite the common acceptance that pH is largely influential over trace element bioaccessibility and mobility in the environment, demonstrating such a mechanism through the statistical methods applied here is difficult due to the highly controlled pH environment of UBM laboratory methods (Pelfrêne et al. 2012; BARGE/INERIS 2010).

The relative abundances of co-occurring metal oxides were also associated with increased variability in BAF results between the three groups, in particular where Al, Mg, Mn and Fe oxides are concerned. Al_2O_3 showed strong negative influences over all trace element BAFs, particularly for the basalt and mudstone samples. As shown by Fig. 2b, higher proportions of aluminium oxide in soil are spatially correlated with basalt bedrock in the northeast of the region. Additionally, aluminium compounds are expected to be higher in soils associated with mudstone bedrock due to the clay content of soils from these parent materials (Sparks 1995; Theng 1974). While the negative correlations found with aluminium oxide and Ni, V and Zn BAFs in this study may be due to geogenic or pedological co-occurrence, aluminium, iron, manganese and other metal oxides also participate in sorption and co-precipitation reactions capable of immobilising heavy metal cations in soils (Pelfrêne et al. 2012; Laveuf et al. 2009; Cances et al 2008; Cave et al. 2007; Ma et al. 2007; ATSDR 2005; Flynn et al. 2003; Ruby et al. 1999). In addition to chemically stabilising ionic forms of trace elements in soils, the presence of co-occurring metals and their associated oxides may provide an indication that trace elements are bound in insoluble solid phases of geogenic origin (Wragg et al. 2007; Jordan et al. 2001; Ruby et al. 1999). When studying the effects of weathering on element mobility in basalt, Chesworth et al. (1981) found that Al and Fe weathering products precipitated into crystalline mineral forms immediately after release from parent rock. In a study on the weathering products of basalt in South China, Ma et al. (2007) concluded that Al and Fe oxides and trace elements were mobilised during the weathering process, but subsequently were removed deeper in the soil profile through the formation of insoluble co-precipitates capable of encapsulating and storing trace elements. Considering that soluble forms of trace metals are more bioaccessible than insoluble ones, this supports the trend found in this study of reduced bioaccessibility in the presence of Al_2O_3 and Fe_2O_3. However, more detailed information is required about the precise mineral forms in which these oxides and trace elements exist.

4.2 Soil-Chemical Influences

Beyond geogenic controls over trace element bioaccessibility, which are important within wide spatial and time scales, more dynamic micro-scale chemical processes should also be regarded as highly influential. Soil chemistry including pH, organic content, microbial processes, redox potential and cation exchange capacity will significantly affect trace element bioaccessibility on variable spatial and time scales, regardless of total element concentrations (Abollino et al. 2011; Finžgar et al. 2007; Ljung et al. 2007; Hursthouse 2001). The time scales over which these factors can influence bioaccessibility are variable, with half-life sorption of metals onto humic materials in peat occurring within a time scale as short as 5 seconds (Sparks 1995). Seasonal variations in soil moisture and resulting redox changes can also affect trace element bioaccessibility and mobility, exemplifying the dynamic factors of influence that occur outside of geologic time and spatial scales.

One of the most consistent positive influences identified over trace element bioaccessibility was estimated soil carbon content. Poggio et al. (2009) found similar positive correlations between oral bioaccessible Ni and Zn and soil organic matter, and Nathanail et al. (2009) cite soil organic content as a key consideration when assessing risks to human health from soil-borne contaminant exposure. In contrast to these and previous findings, Pelfrêne et al. (2012) concluded that SOC had a negative impact over gastric Zn bioaccessibility. Despite this, the *absence* of organic matter deeper in the soil profile encourages Al and Fe to form insoluble co-precipitates with trace elements, while organic compounds present at the soil surface may form organic colloids that increase element mobility (Ma et al. 2007). Aluminium in particular freely moves from A to B soil horizons in acidic podzol soil types that are rich in organic humic material (Chesworth et al. 1981). Although the exact mechanisms by which SOC increases element bioaccessibility cannot be determined from this study, it is apparent that the presence of organic matter supports environmental conditions that are conducive to higher levels of oral trace element bioaccessibility.

While the presence of higher amounts of soil carbon is positively correlated with oral bioaccessibility results in this study, the effects of carbon in the human GI tract may be contrary to the *in vitro* trend. Ruby et al. (1999) suggest that the presence of organic matter in the form of food or soil particles in the GI tract may hinder trace element transport across the intestinal epithelium, effectively reducing trace element bioavailability. Further to this, organic matter has also been found to influence trace element speciation in the stomach phase of UBM digestion, which may in turn influence the final toxicity of an element after ingestion (Broadway et al. 2010). Ljung et al. (2007) also point out that soluble metals may be released from other compounds in the stomach acid, but that higher pH conditions in the intestine may cause insoluble precipitates to form, reducing bioavailability prior to intestinal absorption. This observation may help explain why correlation results for BAFs with SO_3 and SOC were stronger in the stomach phase of digestion than the in the intestinal phase. It is also anticipated that organic matter would be degraded to a high degree in the stomach acids, potentially reducing the effects of this variable once digestate reaches the intestinal phase.

Individual trace element chemistry and resulting behaviour in the environment should also be considered where element mobility and bioaccessibility is concerned. For example, higher Zn bioaccessibility when compared to Ni and V may be associated with the tendency of Zn to commonly occur as a free ion in natural systems (ATSDR 2005; CCME 1999). In a study of a suite of toxic metals in soils, Poggio et al. (2009) also found that Zn bioaccessibility was higher when compared to other metals studied. In nature, free Zn ions occur as Zn^{2+} which readily participate in sorption reactions with negatively charged soil particles, Fe and Mn oxides, clay minerals and organic matter. Low pH conditions discourage such sorption mechanisms from taking place, while Zn precipitates will form under alkaline conditions (Nathanail et al. 2009; ATSDR 2005; CCME 1999). Although ionic sorption reactions have the ability to immobilise trace elements in natural soil systems, such bonding mechanisms at the soil solution-particle interface are driven by relatively weak forces. As a result, these bonds may be easily broken by the acid conditions present in the human digestive system, re-mobilising ions for GI uptake.

Correlations between sulphur and carbon content in Northern Ireland soils have been explored previously by Jordan et al. (2001), where the narrow range of soil pH in the region was also observed. Peat soils possess many of the chemical characteristics frequently associated with elevated trace element bioaccessibility. Acidic and water-logged, reducing conditions erode soil parent material, mobilising trace and major elements into soluble ionic forms (Elzinga and Cirmo 2010; Imrie et al. 2008; Finžgar, 2007). Some elements may then either be leached out of the soil as a result, or retained by the high abundance of negatively charged organic matter (CCME 1999; Guo et al. 1997). If this mobilising effect causes major elements to be solubilised and subsequently leached, this renders them unavailable for participation in sorption reactions with trace elements, which may be the case where low abundance of metal oxides was observed in acid soils

(Fig. 2). Further to this, the absence of oxygen under reducing conditions may prevent the formation of metal oxides which require oxidative conditions (Wragg et al. 2007). Another mechanism for decreased major element oxide concentrations in water logged soils involves the biological and chemical reduction of these oxides into insoluble sulphuric and organic precipitates (Guo et al. 1997), where elements are effectively removed from soil solution and prevented from engaging in further chemical reactions. This mechanism is exacerbated in humus-rich peat soils, as organic matter has been found to prevent the oxidative release of metals from other compounds (Hursthouse 2001). In addition, acid pH conditions increase negative charges on organic soil particles, more strongly retaining cations through sorption mechanisms and ligand exchange (ATSDR 2005; Hursthouse 2001; Sparks 1995). This allows peat soils to potentially act as a sink for storing more bioaccessible ionic forms of potentially toxic elements.

Both Ni and Zn exhibit higher bioaccessibility in the presence of organic matter and are also actively mobilised under acid conditions (EA 2009*a*; Nathanail et al. 2009; Poggio et al. 2009; Imrie et al. 2008), although less information is available to clarify such trends for V. Nathanial et al. (2009) note that, unlike Zn and Ni, acid pH generally immobilises V in soil solution, although this trend could not be inferred from the data presented in this study. Previous mapping of the relative spatial distributions of Ni, V and Zn did not reveal higher trace element concentrations in areas of upland peat, but were instead spatially controlled by local geologic formations, particularly where basalt bedrock was present (Barsby et al. 2012). This, combined with the spatial illustration and correlations found with chemical parameters associated with peat soil types, suggests that total trace element concentrations are not necessarily an indication of the actual health risk present from toxic metal exposure. It can additionally be inferred that Ni, V and Zn bioaccessibility is likely to be elevated in peat soil types. Due to the precise geographic correlation of SOC and SO_3 with peat soil across Northern Ireland and the associated positive statistical correlations between SOC, SO_3 and trace element bioaccessible fractions, it is concluded that peat soil types provide the environmental conditions required to increase trace element mobility and bioaccessibility including acidic pH, high chemical reduction potential, elevated soil moisture and the presence of dissolved organic matter.

5. Conclusions

The strengthening of correlation statistics after division of BAF results into generic geologic sub-groups suggests that substantial variance is introduced into a data set when geochemistry is regarded collectively across a variety of rock formations. Such grouping decreases this variance and allows the influence of geology over trace element bioaccessibility to be more clearly exemplified. Strong correlation statistics observed for the Antrim Basalts in particular suggest a majority of variance in geochemistry and bioaccessibility is accounted for by the local geology. Fewer statistically significant correlations in the other bedrock groups indicate a higher degree of pedological or geogenic heterogeneity exists in these areas, producing more variability in the results.

While relationships between the bioaccessible fractions of Ni, V and Zn and other variables have been explored through correlation analysis and limited mapping techniques, a more detailed presentation of the landscape scale processes driving these relationships would further compliment this research. In addition, analysing UBM data in groups according to rock types that are more specific than the generic Tellus bedrock classifications may give clearer indications of geologic influences over trace element bioaccessibility and help further reduce variance in the data sets.

Geochemical mapping combined with correlation analysis in this study shows that Ni, V and Zn bioaccessibility is anticipated to be higher in peat soil types in Northern Ireland and is not necessarily a function of total trace element concentrations, which is the factor dominating the contaminated land risk assessment regulatory regime in the United Kingdom.

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Table 1 Summary statistics for BAF (%) results (from Barsby et al. 2012), total Ni, V, Zn (mg kg^{-1}) and oxide (%) concentrations

	Min	Max	Mean	St.Dev.	Min	Max	Mean	St.Dev.
Northern Ireland, n = 6862					Basalt Bedrock Group, n = 23			
Ni	1.40	333.60	46.21	48.65	4.90	185.30	77.66	59.65
V	5.90	401.60	99.66	65.04	18.10	280.00	157.88	88.98
Zn	2.80	2460.50	78.35	54.29	21.40	175.70	85.78	48.11
MgO	0.50	5.80	1.45	0.66	0.60	3.70	1.72	0.82
Al_2O_3	3.50	17.20	10.61	2.98	4.00	14.90	10.59	3.37
SiO_2	13.80	87.90	49.56	15.00	16.20	75.10	41.36	14.68
P_2O_5	0.05	1.70	0.26	0.10	0.08	0.56	0.25	0.11
SO_3	0.00	2.00	0.18	0.24	0.00	0.80	0.27	0.24
CaO	0.30	16.33	1.15	0.78	0.41	3.10	1.66	0.72
MnO	0.00	15.00	0.08	0.26	0.00	0.27	0.10	0.08
Fe_2O_3	0.30	42.25	4.65	2.85	1.26	11.42	6.26	3.34
Lithic Arenite Bedrock Group, n = 17					Mudstone Bedrock Group, n = 18			
Ni	21.20	72.80	41.64	14.09	13.80	153.20	47.25	38.50
V	74.50	124.30	95.55	14.46	36.40	234.10	90.82	53.46
Zn	73.80	2460.50	242.25	572.48	41.70	151.90	83.85	33.23
MgO	1.10	2.80	1.71	0.40	0.70	2.60	1.40	0.54
Al_2O_3	10.10	13.50	11.78	1.12	4.90	13.40	9.94	2.32
SiO_2	41.10	67.60	56.84	7.80	19.60	73.30	51.09	13.09
P_2O_5	0.15	0.48	0.31	0.09	0.18	0.55	0.28	0.09
SO_3	0.00	0.80	0.11	0.21	0.00	0.80	0.23	0.30
CaO	0.53	2.08	0.83	0.39	0.56	3.64	1.52	0.95
MnO	0.04	0.19	0.08	0.04	0.03	0.27	0.09	0.06
Fe_2O_3	2.96	6.31	4.37	0.85	1.76	10.21	4.40	2.20
Bioaccessibility Study Sample Set, n = 91					Basalt Bedrock Group			
V-G	1.92	22.50	8.72	4.59	3.82	22.50	11.19	5.65
V-GI	0.56	14.66	3.98	2.54	0.57	9.94	4.37	2.59
Ni-G	1.42	43.82	12.16	9.59	1.42	43.82	12.32	12.12
Ni-GI	0.60	14.45	5.50	2.92	0.60	9.98	4.49	2.66
Zn-G	4.28	80.76	22.17	17.63	6.92	80.76	26.85	22.42
Zn-GI	2.47	40.28	13.25	7.86	2.91	40.28	13.43	10.13
Lithic Arenite Bedrock Group					Mudstone Bedrock Group			
V-G	2.64	16.67	7.18	4.12	2.49	21.96	9.25	4.83
V-GI	0.95	8.35	3.33	2.20	1.25	14.66	4.94	3.46
Ni-G	3.01	42.17	9.87	9.77	4.13	33.62	14.50	8.71
Ni-GI	1.27	14.45	4.31	2.88	2.65	12.07	7.06	2.63
Zn-G	4.28	57.79	15.27	12.79	10.17	68.63	22.34	15.82
Zn-GI	2.47	16.45	7.62	3.37	4.98	24.06	13.34	5.50

Table 2 Pearson's Correlation Coefficients for Selected Geochemical Parameters and UBM Results (UBM data from Barsby et al. 2012)

	Total V	Total Ni	Total Zn	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	CaO	MnO	Fe_2O_3	pH	SOC[2]
Bioaccessibility Study Sample Set													
V-G	-.164	-.171	.127	-.331**	-.556**	-.379**	-.178	.542**	.121	-.414**	-.353**	-.143	.517**
V-GI	-.288**	-.305**	.125	-.413**	-.530**	-.134	-.029	.395**	.078	-.448**	-.473**	.022	.294**
Ni-G	-.447**	-.293**	.298**	-.511**	-.696**	-.536**	-.163	.754**	.006	-.396**	-.484**	-.310**	.723**
Ni-GI	-.511**	-.366**	.296**	-.543**	-.516**	-.102	-.080	.428**	-.090	-.355**	-.531**	-.057	.269**
Zn-G	-.433**	-.291**	.182	-.479**	-.805**	-.605**	-.177	.727**	.124	-.389**	-.462**	-.294**	.810**
Zn-GI	-.582**	-.550**	-.071	-.661**	-.707**	-.207*	-.331**	.376**	-.199	-.586**	-.619**	-.325**	.446**
Basalt Bedrock Group													
V-G	-.533**	-.606**	-.638**	-.612**	-.679**	-.410	-.581**	.606**	-.251	-.736**	-.690**	-.532**	.626**
V-GI	-.510*	-.696**	-.709**	-.676**	-.593**	-.138	-.547**	.394	-.355	-.766**	-.736**	-.473*	.406
Ni-G	-.749**	-.611**	-.682**	-.712**	-.826**	-.552**	-.563**	.677**	-.570**	-.651**	-.718**	-.696**	.811**
Ni-GI	-.784**	-.700**	-.757**	-.710**	-.607**	-.048	-.591**	.214	-.689**	-.695**	-.789**	-.426*	.390
Zn-G	-.761**	-.600**	-.676**	-.691**	-.890**	-.563**	-.588**	.724**	-.555**	-.649**	-.713**	-.743**	.854**
Zn-GI	-.828**	-.751**	-.834**	-.824**	-.828**	-.222	-.655**	.451*	-.762**	-.763**	-.833**	-.685**	.605**
Lithic Arenite Bedrock Group													
V-G	-.121	-.018	-.140	-.294	-.723**	-.493*	.054	.775**	.083	-.431	-.591*	-.165	.641**
V-GI	-.231	-.104	-.177	-.334	-.673**	-.430	.170	.764**	.055	-.441	-.652**	-.133	.607**
Ni-G	-.329	-.251	-.148	-.322	-.552*	-.585*	-.309	.943**	-.217	-.306	-.510*	-.407	.806**
Ni-GI	-.345	-.261	-.150	-.398	-.543*	-.383	-.284	.892**	-.291	-.274	-.559*	-.328	.649**
Zn-G	-.381	-.327	-.237	-.324	-.567*	-.529*	-.119	.952**	-.193	-.213	-.529*	-.382	.756**
Zn-GI	-.527*	-.506*	-.412	-.358	-.556*	-.445	.087	.842**	.007	-.299	-.602*	-.076	.666**
Mudstone Bedrock Group													
V-G	-.299	-.196	-.182	-.501*	-.730**	-.145	.257	.421	.436	-.500*	-.435	.463	.387
V-GI	-.434	-.330	-.263	-.532*	-.827**	-.118	.308	.378	.415	-.505*	-.558*	.474*	.399
Ni-G	-.264	-.136	.010	-.456	-.652**	-.750**	.351	.925**	.724**	-.405	-.364	.121	.871**
Ni-GI	-.356	-.241	-.066	-.403	-.550*	-.360	.144	.719**	.432	-.381	-.449	.196	.501*
Zn-G	-.345	-.225	.034	-.360	-.753**	-.645**	.438	.637**	.756**	-.380	-.428	.393	.854**
Zn-GI	-.717**	-.658**	-.560*	-.607**	-.878**	-.131	.250	.304	.268	-.658**	-.834**	.358	.381

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

[2]As estimated by loss on ignition

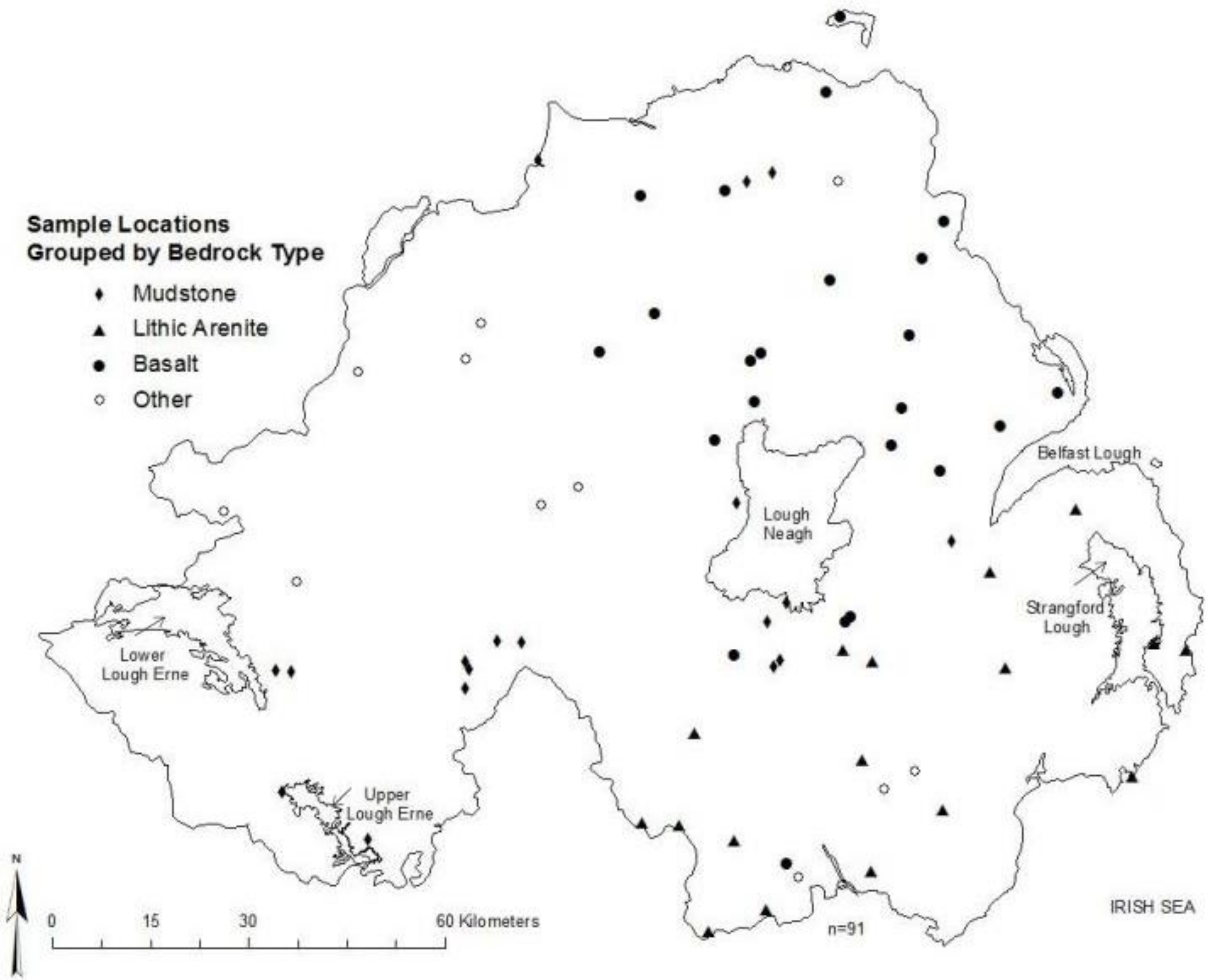

Fig. 1 Northern Ireland soil sample location map for bioaccessibility testing with bedrock classification

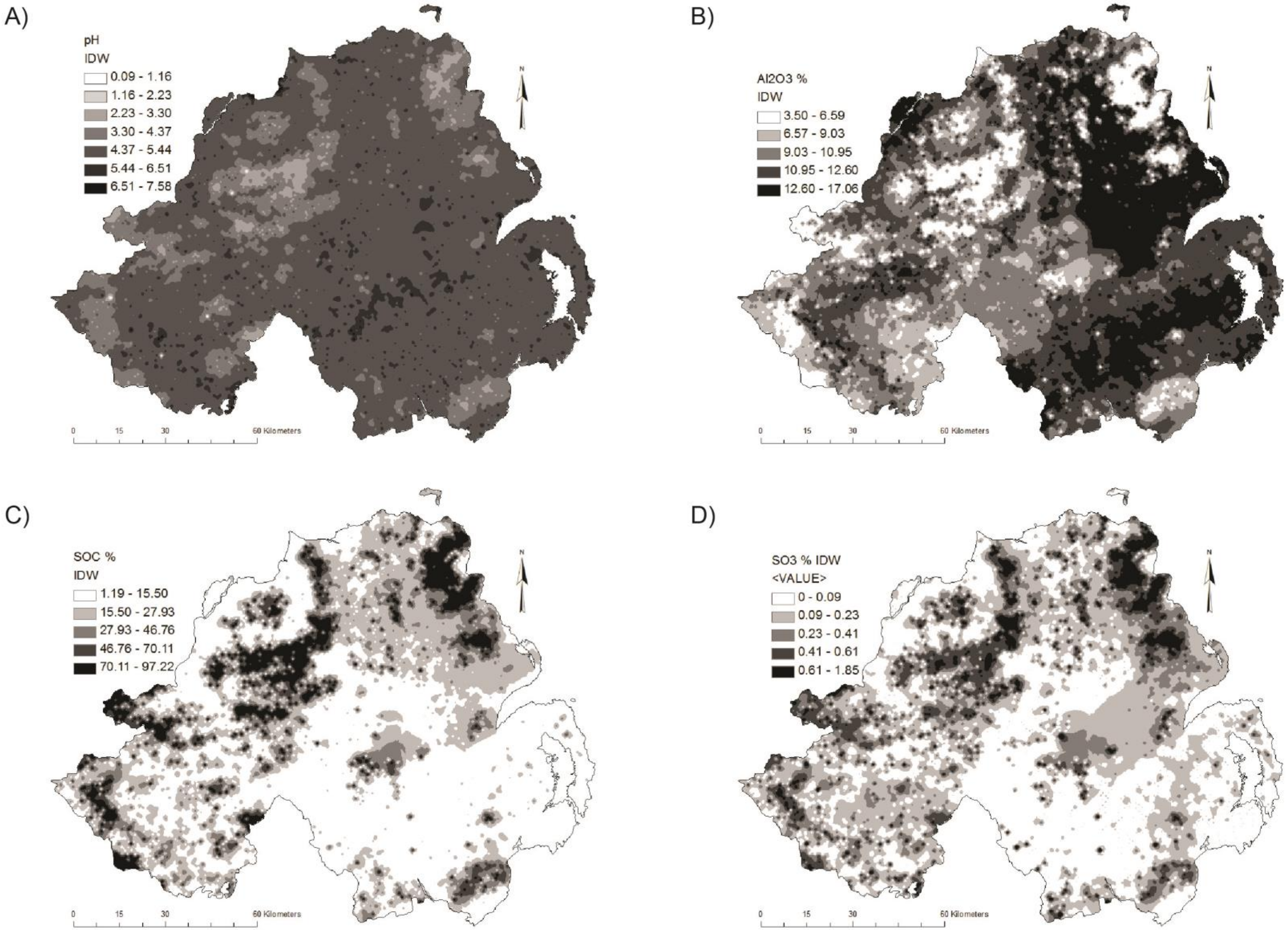

Fig. 2 pH, Al_2O_3, SO_3 and estimated SOC interpolated by IDW, 12 neighbours, showing highest and lowest proportional distributions and acidity in areas of upland peat deposits across Northern Ireland

Supporting Information:

Table A. Skewness and kurtosis values for Ni, V and Zn, demonstrating a general increase towards a normal distribution after bedrock group sub-division

	Skewness	Kurtosis
V N. Ireland	1.00	0.50
V Study Set	1.18	0.56
V Basalt	-0.24	-1.43
V Lithic Arenite	0.29	-0.57
V Mudstone	1.30	1.5
Ni N. Ireland	1.89	3.66
Ni Study Set	1.98	4.01
Ni Basalt	0.57	-0.90
Ni Lithic Arenite	0.67	-0.15
Ni Mudstone	1.20	0.12
Zn N. Ireland	14.28	556.89
Zn Study Set	8.97	83.44
Zn Basalt	0.27	-1.02
Zn Lithic Arenite	1.60	2.50
Zn Mudstone	0.73	-0.44

N. Ireland values, n = 6862; study set, n = 91; basalt, n = 23; lithic arenite, n = 17; mudstone, n = 18