THE EFFECTS OF LEAD SOURCES ON ORAL BIOACCESSIBILITY IN SOIL AND IMPLICATIONS FOR CONTAMINATED LAND RISK MANAGEMENT

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Abstract

Lead (Pb) is a non-threshold toxin capable of inducing toxic effects at any blood level but availability of soil screening criteria for assessing potential health risks is limited. The oral bioaccessibility of Pb in 163 soil samples was attributed to sources through solubility estimation and domain identification. Samples were extracted following the Unified BARGE Method. Urban, mineralisation, peat and granite domains accounted for elevated Pb concentrations compared to rural samples. High Pb solubility explained moderate-high gastric (G) bioaccessible fractions throughout the study area. Higher maximum G concentrations were measured in urban (97.6 mg kg^{-1}) and mineralisation (199.8 mg kg^{-1}) domains. Higher average G concentrations occurred in mineralisation (36.4 mg kg^{-1}) and granite (36.0 mg kg^{-1}) domains. Findings suggest diffuse anthropogenic and widespread geogenic contamination could be capable of presenting health risks, having implications for land management decisions in jurisdictions where guidance advises these forms of pollution should not be regarded as contaminated land.

Keywords: lead, anthropogenic pollution, geogenic contamination, oral bioaccessibility, human health risk assessment, soil

1. Introduction

Lead (Pb) is a toxic trace element that has been the subject of extensive human health research. Its neurotoxic effects from the oral exposure pathway, particularly in children, are well documented (EFSA, 2010; ATSDR, 2007; Ryan *et al.,* 2004; CCME, 1999; Rosen, 1995). Some studies also suggest Pb exposure may be associated with increased incidences of violent crime (Meilke & Zahran, 2012; Nevin, 2007; Nevin, 2000). Whilst many known toxins have quantifiable threshold exposure levels above which toxic health effects could occur, Pb is currently regarded by the global scientific community as a non-threshold toxin. Non-threshold toxicity indicates that laboratory studies have not identified a minimal risk level (MRL) or a no observed adverse effect level (NOAEL). Adverse health effects could potentially occur at any blood Pb level (EA, 2009; ATDSR, 2007; USEPA, 1988). Therefore, it is arguable that no amount of Pb exposure can be regarded as safe based on available research to date.

Elevated Pb in the environment is attributed to a number of human activities and industrial processes such as fuel combustion, mining, agricultural slurry spreading, and incineration of municipal wastes (Alloway, 2012; Nriagu & Pacyna, 1989). The reported natural abundance of Pb in the earth's crust ranges from 12 -14 mg kg^{-1} (Rose *et al.*, 1979; Lee & Yao, 1970; Krauskopf, 1967; Taylor, 1964) although globally reported normal background concentrations (NBC) in soil can substantially vary. The United States Environmental Protection Agency (USEPA) suggests natural Pb concentrations in the United States range from 50 to 400 mg kg^{-1} (USEPA, 2013). The Canadian Council of Ministers of the Environment (CCME) provides a mean range of 12 – 25 mg kg^{-1} for Canadian Soils (CCME, 1999). The average reported concentration in rural soils in the United Kingdom (UK) is 52.6 mg kg^{-1}, ranging from as low as 2.6 to as high as 713 mg kg^{-1} (EA, 2007). In Northern Ireland (NI), Jordan *et al*. (2001) reported a mean total Pb soil concentration of 23.2 mg kg^{-1}. More recently, the Tellus Geochemical Survey of NI measured a higher average total Pb concentration of 41.7 mg kg^{-1}, with a maximum extractable Pb concentration exceeding 3,000 mg kg^{-1} near the Belfast metropolitan area. In rural parts of NI, McIlwaine *et al.* (2014) reported a typical threshold value (TTV) of 63 mg kg^{-1}.

Due to the global variability in Pb NBCs and also with regards to its non-threshold toxicity, identifying a starting point for contaminated land assessment in a human health context is challenging. The CCME provides a soil quality guideline of 140 mg kg^{-1} in a residential land use setting (CCME, 1999). Following its non-threshold toxicity classification, the generic Pb soil guideline value (SGV) (DEFRA & EA, 2002*a*) was withdrawn in the UK. Whilst a selection of provisional Category 4 screening levels (pC4SL) for Pb were recently published (Harries *et al.*, 2013), final C4SLs have not been issued for any soil contaminant. A C4SL denotes a lower tolerable limit for a contaminant in soil, beneath which human health risk is unlikely to be present.

Although Pb concentrations in the wider environment have declined since its removal from petrol in the last century, its ubiquitous anthropogenic presence still persists in soils, particularly around urban centres (Harries *et al*., 2013; Appleton *et al*., 2012*a*). Previous research worldwide has highlighted areas of elevated soil Pb concentrations outside of areas where geogenic associations are known to exist, including within the Republic of Ireland (ROI) and NI (Barsby *et al*., 2012; Bourennane *et al.*, 2010; Jordan *et al.*, 2007; Ljung *et al.*, 2006; Zhang, 2006). Such findings demonstrate how anthropogenic pollution sources substantially contribute to elevated soil Pb concentrations. In NI Pb is found in highest total and extractable concentrations around the Belfast urban area and in soils overlying mineral deposits, with high soluble Pb measured in peaty upland areas (Jordan *et al*., 2001). This latter observation may be accounted for by atmospheric deposition of anthropogenic Pb through rainfall, as precipitation is the primary moisture source in upland peat soils.
The large surface area and number of acidic functional groups that are common to peat make it an ideal substrate to bind trace elements either as sedimentary, deposited, particulate matter or as sorbed or complexed metal ions (Brown et al., 2000). The major sources of metals in the peat mass of ombrotrophic peat bogs has been shown to come from atmospheric precipitation (Steinnes and Friedland, 2006) which has been specifically illustrated in Ireland (Coggins et al., 2006). Whilst the ability of peat to accumulated trace metals has been well documented there is little data on the bioaccessibility of the trace elements in this peat rich soils.

Four Pb source domains were previously identified in NI accounting for elevated soil Pb concentrations (McIlwaine *et al.*, 2014). A domain is an area where a distinguishable factor is recognised as controlling the concentration of an element. Urban, peat, granite and mineralisation Pb source domains were related to elevated concentrations of Pb, with typical threshold values (TTV) higher than the TTV calculated for the remaining rural domain. TTVs aim to identify the threshold between diffuse and point source anthropogenic contamination, thereby giving an indication of typical concentrations within defined geographical areas. Urban Pb source domains are likely to be directly attributable to anthropogenic activity. Some anthropogenic pollution sources are potentially more soluble in the environment and resultantly more bioavailable (Ljung *et al*., 2007; Appleton *et al*., 2012*b*), in turn posing a greater risk to human health.

Not all toxins that are rendered bioaccessible will be bioavailable, but *in vitro* bioaccessibility tests can better refine the contaminated land risk assessment process by reducing reliance on total soil contaminant concentrations. Such reliance may overestimate health risks (CIEH, 2009; Scheckel *et al.,* 2009; Nathanail & Smith, 2007; Nathanail, 2006; Ruby *et al*., 1999). The Unified BARGE (Bioaccessibility Research Group of Europe) Method (UBM) is therefore a useful extraction method to employ in risk assessment scenarios where oral contaminant exposure is expected to contribute to toxic health effects. The UBM is a robust soil extraction technique that measures *in vitro* the oral bioaccessibility of contaminants by mimicking the conditions of the human stomach and upper intestine (BARGE/INERIS, 2010). The method has been validated for Pb, arsenic (As) and cadmium (Cd) using *in vivo* swine data (Denys *et al.*, 2012; Caboche, 2009) and has also been subjected to global inter-laboratory trials (Wragg *et al*., 2011). Data obtained from UBM extractions provide an indication of what fraction of a contaminant may be solubilised in the gastro-intestinal (GI) tract (the bioaccessible portion) and therefore potentially available for absorption resulting in toxic health effects (the bioavailable portion).

The aim of this research was to measure the oral bioaccessibility of Pb in soil and attribute findings to different Pb sources through solubility estimation and source domain identification. This aim was met through 1) exploratory geochemistry data analysis (EDA) to identify areas of elevated soil Pb concentrations and examine associated spatial structures, 2) comparison of total and extractable Pb concentrations to estimate Pb solubility and 3) source domain identification to determine whether elevated Pb concentrations are the result of geogenic or anthropogenic processes. Lastly, measured oral bioaccessibility was compared across the identified Pb source domains.

2. Methodology and Study Area

2.1 Study Area

The study area is located in the UK and Ireland, consisting of NI and neighbouring County (Co.) Monaghan in ROI (Fig. 1). The estimated cumulative population of NI and Co. Monaghan is 1.9 million, with a low average population density of 130 per km^2 (ONS, 2013; CSO, 2011). Current and historical industrial activities concentrated around the Belfast metropolitan area include textiles manufacturing, shipbuilding and aerospace engineering. In addition, quarrying activities are widespread throughout the region with active mines also present, particularly near the Antrim Glens in the northeast (GSNI, 2014). Outside of the larger urban areas of Belfast and Londonderry, land is largely rural and used for agricultural purposes, with metropolitan areas accounting for less than 4% of land use across the study area (European Environment Agency, 2012). As a result, the study area is perceived to be relatively unspoiled from an anthropogenic pollution perspective (Zhang, 2006).

Soil types present in the study area include peats, humic and sand rankers, brown earths, podzols, mineral gleys and alluviums. Soil pH falls within a narrow acidic range of approximately 5.0 to 6.0 (Jordan *et al.*, 2001), with the NI Tellus geochemical survey more recently recording an average pH of 4.7. This decrease in pH over time suggests acidification of soils may be increasing in the study area. The climate is temperate and average annual rainfall ranges from a low of 800 mm in the eastern region to a high of over 1900 mm in the west. The Antrim Glens in the northeast, the Sperrin

Mts. in the west and the granitic Mourne Mts. in the southeast intercept much of the precipitation borne by air currents which have travelled over the Atlantic Ocean, although the western half of the study area is most significantly affected by these Atlantic weather patterns (Met Office, 2012).

2.2 Geochemistry Data Analysis

Total and extractable Pb concentration data from the NI Tellus and Tellus Border geochemical surveys were provided by the Geological Survey of Northern Ireland (GSNI) and by the Geological Survey of Ireland (GSI), respectively. Rural NI Tellus Survey soil samples were collected on a 2 km^2 grid at depths of 5 – 20 cm ('A') and 35 – 50 cm ('S'). 'A' samples were analysed for total Pb concentrations by x-ray fluorescence spectrometry (XRFS) and for extractable concentrations by inductively coupled plasma mass spectrometry (ICP-MS) following an *aqua regia* digest. 'S' NI Tellus Survey soil samples were also digested by *aqua regia* and analysed by ICP-MS. Tellus Border 'A' samples were collected on a 4 km^2 grid and analysed only by ICP-MS following an *aqua regia* digest to yield extractable concentration data. Full analytical and field methods employed by these comprehensive regional geochemical surveys can be found in Smyth (2007) and Knights and Glennon (2013).

As part of this research, additional XRFS analysis was conducted at the British Geological Survey (BGS) Analytical Geochemistry Facility on a sub-set of 18 Tellus Border 'A' samples in Co. Monaghan according to the same methods described in the NI Tellus Survey methodology (Smyth, 2007). The additional XRFS data was required for solubility estimation and for calculation of UBM bioaccessible fractions (BAF) in Co. Monaghan. Geochemistry data were handled in SPSS v.19.0, R (R Core Team, 2013) and MS Excel 2010.

2.3 Geostatistical Analysis and Interpolation

Interpolation by ordinary kriging (OK) (Matheron, 1965) was conducted in ArcMap 10.0 (ESRI, 2010). The OK model yielding a mean prediction error closest to zero was selected as the final model for generating interpolated surfaces and geostatistics (Lloyd, 2010). Geostatistical outputs can be influenced by a nonparametric data distribution (Lloyd, 2010; Clarke, 2001; Einax & Soldt, 1999). Total and extractable Pb concentration data were therefore log-transformed prior to interpolation. OK models were checked for robustness using cross validation statistics and a visual assessment of the best fit semi-variogram using a maximum search neighbourhood of 12 nearest sample locations.

Semi-variogram parameters give an indication of the spatial structure that exists within a data set. This in turn can help explain geochemical or environmental processes that affect the spatial distributions of elements (Goulard & Voltz, 1992; McBratney *et al.,* 1982). The semi-variogram sill (C_1) is synonymous with the sample variance and represents the maximum variance that exists between measured sample values within the range of spatial correlation (*a*). Beyond the distance *a*, samples are no longer spatially correlated (Clarke, 2001; Gringarten & Deutsch, 2001). The nugget variance (C_0) is attributed to micro-scale variance outside of sampling resolutions. Although the nugget effect is commonly regarded as an indication of measurement error or random semi-variogram behaviour, micro-scale processes which control element distributions may also be accounted for by the nugget variance. For example, Imrie *et al*. (2008) found that factors attributed to anthropogenic land use patterns were accounted for by a nugget effect. Dobermann *et al.* (1995) concluded buffalo excrement influenced soil chemistry over a range that occurred within the nugget variance. Functions with a high proportion of total variance ($C_o + C_1$) accounted for by the nugget variance may therefore be indicative of anthropogenic processes or land use behaviours which are significantly affecting element distributions but occurring over short spatial scales not detected by the primary range (*a*) of the function.

OK yields results which increase in accuracy in line with increasing sample numbers (Einax & Soldt, 1999). Due to lower sample numbers than were available for total and extractable Pb concentration data, bioaccessible Pb concentrations were interpolated using inverse distance weighting (IDW) with a maximum search neighbourhood of five neighbouring sample locations. IDW is an exact interpolator (Lloyd, 2010) and this method therefore yielded a more accurate range of Pb bioaccessible concentration values across the interpolated surface.

2.4 Pb Solubility Estimation

A method for estimating element solubility in soil at a regional scale was applied to the NI Tellus and Tellus Border XRFS and ICP-MS data, similar to approaches used previously in Finland (Jarva *et al.,* 2009) and Cyprus (Cohen *et al.,* 2012). XRFS measures total element concentrations in soils whereas ICP concentrations rely on the antecedent *aqua regia* acid extraction. Although *aqua regia* acid is said to effectively leach many metals (Gill, 1997), the solubility of elements will affect how easily they are leached from the soil (Delgado *et al.,* 2011). Therefore, by comparing the concentrations measured by the two methods, element solubility at a regional scale can be estimated. Elements which are more soluble in the environment generally exhibit higher oral bioaccessibility (Finžgar *et al.,* 2007).

ICP extractable concentrations were plotted against XRFS total concentrations using the R statistical software package (R Core Team, 2013) to explore the relationship between the two analytical methods. The ratio of XRFS/ICP Pb concentrations was mapped by OK to illustrate geographical trends in Pb solubility. The classes on the map were defined by the boxplot classes method (McIlwaine *et al*., 2014) with an additional class added where the ratio was equal to one, i.e. where the two analytical methods are equal. Boxplot classifications retained the appropriate amount of detail to allow a direct comparison with the mapped bioaccessibility results.

2.5 Pb Domain Identification

Domains were previously identified for Pb in NI as described in McIlwaine *et al*. (2014). Total XRFS concentrations in shallow soils were mapped using empirical cumulative distribution function (ECDF) classes and compared to the main factors identified as controlling element concentrations—bedrock geology, superficial geology, land use classification and mineralisation. Elevated concentrations of Pb were attributed to urban, granite, mineralisation and peat source domains in NI with the remaining rural domain hosting lower Pb concentrations.

Additional Co. Monaghan data were obtained to identify Pb domains across the extent of the study area for this research. Bedrock geology data were obtained from the GSI 1:500000 Bedrock Geology map (GSI, 2005). Superficial peat cover was identified using the Irish Environmental Protection Agency Soils and Subsoils Mapping Project data completed by Teagasc (Fealy & Green, 2009). The Corine land cover data (European Environment Agency, 2012) was used to identify urban and rural land use within the study area. Areas of known or suspected mineralisation in Co. Monaghan are identified in the Tellus Border prospectivity map (Coulter and Stinson, 2013).

Data used for identifying the mineralisation source domain in NI and Co. Monaghan relied upon prospectivity maps (Coulter & Stinson, 2013; Lusty *et al.*, 2012) and not the locations of working or historic mines. The mineralisation domain and associated soil Pb is therefore regarded as geogenic and naturally occurring for the purposes of this research.

2.6 Oral In Vitro Bioaccessibility Testing

UBM extractions were carried out in 2009 (Barsby *et al*., 2012) and 2013 at the BGS Analytical Geochemistry Facility following the published method (BARGE/INERIS, 2010). The 2009 and 2013 data sets were joined to create a UBM data set of 163 samples for this research. Samples (< 2 mm fraction) were selected from the NI Tellus Survey and Tellus Border soil archives to cover a wide range of soil and underlying bedrock types present in the study area.

Standard BGS internal laboratory procedures were followed during UBM extraction and analysis according to UK Accreditation Service national laboratory requirements. Reagents were sourced by BGS from Merck, Sigma, Baker and Carl Roth. Saliva, gastric, duodenal and bile solutions were prepared one day prior to soil extractions to permit stabilisation. Solution pH was adjusted as required according to UBM specifications using either 37% HCl or 1M HNO_3 (Table 1). Soils not adhering to pH specifications (pH < 1.5) after one hour of gastric extraction were discarded and re-extracted at a later date.

Extracts were analysed by an Agilent 7500cx series ICP-MS employing an octopole reaction system in combination with a CETAC autosampler. The instrument was calibrated at the beginning of every analytical run using a minimum of three standards and one blank for each trace element. Multi-element quality control check standards were analysed at the start and end of each run and after every 25 samples at minimum.

One blank, one duplicate and one certified BGS102 reference soil (Wragg, 2009) were included in the extraction run for each of seven soils extracted in 2013. The BGS102 certificate of analysis provides certified UBM values for acceptable ranges of gastric (G) Pb concentrations. Average measured G Pb in reference soils was within one standard deviation of the certified BGS102 value. The mean relative per cent difference (RPD) for gastric Pb in study area soil samples was 8%. In line with the available BGS102 certified reference value for G Pb, G data are presented in the following results as it is common practice to report the results yielding the highest bioaccessibility to ensure health risks are not underestimated. This approach also adheres to the precautionary principle advocated by UK contaminated land legislation and guidance (DEFRA, 2012). Details of quality control for 2009 extractions are similar to the above and are described in detail in Barsby et al. (2012).

3. Results

3.1 Lead Soil Concentrations

The highest extractable Pb concentrations are found in soils along the northeast coast near the Antrim Glens, extending south into the Belfast metropolitan area and Ards Peninsula, with the occurrence of elevated Pb concentrations continuing along the southeast NI-Co. Monaghan border (Fig. 1, Fig. 2A). Peat soils overlying the Sperrin Mts. in the northwest also host elevated concentrations of Pb. It is this part of the study area that receives the most precipitation borne from Atlantic Ocean air currents

(Met Office, 2012). The maximum measured extractable Pb concentration occurs near the greater Belfast metropolitan area (> 3000 mg kg^{-1}).

Although no SGV is currently available for Pb in the UK, Table 2 provides an overview of how Pb concentrations compare against historic withdrawn and current provisional soil screening criteria. Fig. 2B illustrates where extractable Pb concentrations exceed the lowest published pC4SL of 30 mg kg^{-1} by at least 10%. This criterion is applicable for a female child in an allotment setting (Harries *et al.*, 2013). Pb concentrations were flagged as exceeding the pC4SL only where the concentration met or exceeded 33 mg kg^{-1} to ensure the measured Pb concentration was sufficiently above the pC4SL. Extractable Pb concentrations exceed the pC4SL at over 2,208 of 7,234 NI Tellus and Tellus Border soil sample locations in the study area (Fig. 2B). When total XRFS Pb concentrations are compared with the pC4SL, the number of occurrences where the screening criterion is exceeded increases to 2,629 (not illustrated).

Given the withdrawn and provisional nature of the Pb SGV and pC4SL, respectively, it would not be possible to assess the potential level of health risk from the values presented in Table 2 and Figs. 2A-B alone. Although Fig. 2B shows a geographically widespread occurrence of extractable Pb concentrations exceeding the lowest published pC4SL, it is important to note that individual sites must be assessed on a case by case basis taking relevant land use scenarios and all likely risk exposure pathways into account.

XRFS Pb concentrations were mapped previously by Barsby et al. (2012) and exhibit similar spatial patterns to extractable Pb concentrations. Extractable Pb concentrations are controlled by a spatial function with a moderate range (a) of 22.8 km. Short to medium range spatial functions are sometimes associated with processes that have a higher frequency of variation over short distances. Such functions can be the result of smaller scale processes such as anthropogenic interactions with the environment,

while long range functions capture the effects of larger scale geologic forming processes (Imrie et al., 2008; Dobermann et al., 1995). Pb exhibits a spatial structure in the study area that varies over a short scale in terms of its range relative to trace elements of known geogenic origin such as nickel or chromium which are controlled by longer range functions (>70 km; McIlwaine et al., 2014; Barsby et al., 2012). The high proportion of nugget variance (63%) for Pb spatial distributions (Table 3) also suggests a high degree of micro-scale variation or spatial variability not detected by the primary range of the Pb function.

Fig. 3 illustrates the difference between Pb extractable concentrations in NI Tellus Survey ‘A’ soils and ‘S’ soils as measured by ICP-MS following an *aqua regia* digest. Pb is present at higher average and maximum concentrations in 'A' soils than 'S' soils. Anthropogenic and atmospheric Pb deposition to soil is expected to be most pronounced at surface level ('A').

3.2 Lead Solubility and Domain Identification

Figs. 4 and 5 illustrate comparative differences in Pb extractable and total concentrations. Such information can provide insight into contaminant sources. For example, geogenic metals are often highly insoluble and exhibit lower bioaccessibility (Cox *et al.*, 2014) whilst other forms of anthropogenic pollution tend to be more soluble and more bioaccessible (Ljung *et al.*, 2006).

Fig. 4 plots the relationship between XRFS and ICP Pb concentrations, with a 1-1 ratio represented by the dashed line shown on the scatterplot. Although soil analysis by XRFS detects an additional insoluble portion of Pb, the cluster of most points around the 1-1 line shows that a significant proportion of total Pb soil concentrations was detectable by ICP, with XRFS concentrations exceeding ICP concentrations by no more than 15%. This suggests the majority of Pb in soil is soluble and not encapsulated by an insoluble mineral matrix. Pb encapsulated by insoluble minerals generally displays decreased bioavailability and bioaccessibility (Ruby *et al.*, 1999).

Fig. 5 illustrates the geographic variability in XRFS/ICP concentrations ratios. Higher levels of Pb solubility occur in the darker areas of the map, where the ratio is less than one. Where the map becomes lighter Pb is less soluble. Higher levels of solubility are observed along the central and western NI-ROI border and throughout the eastern coast. One area of higher solubility strongly aligns with an identified mineralisation source domain (Fig. 6A). Higher proportions of insoluble Pb occur in the southeast and northwest near the Mourne and Sperrin Mts., respectively, with the Mourne Mts. comprising the granite source domain and the Sperrin Mts. and associated geology aligning with the peat source domains. Rural, peat and urban domains host moderately soluble portions of Pb. Although an elevated peat source domain was also identified in Fig. 6A, Pb solubility trends in Fig. 5 do not clearly align spatially with patterns illustrated for the peat source domain. Instead Pb solubility in peat is comparable to the intermediate solubility observed within urban source domains.

3.3 Lead Bioaccessibility

The results of UBM extractions are summarised in Table 4. G bioaccessibility was higher than gastro-intestinal (GI) bioaccessibility due to the lower pH of the G digestion which increases Pb mobility in solution (Denys *et al.*, 2012; Farmer *et al.*, 2011; Denys *et al.*, 2007). The maximum G bioaccessible concentration was 199.8 mg kg^{-1}, accounting for 68.6% of total Pb. The median G ICP-

BAF was 40.3%, decreasing to 15.6% of extractable Pb concentrations in the GI phase. XRFS-BAF values Pb did not differ greatly from ICP-BAFs as a result of most Pb in soils in the study area being detectable by ICP-MS (Fig. 4). Pb gastric bioaccessibility exceeded 50% of total concentrations at 13 different soil locations across the study area (Fig. 6A).

Fig. 6A and Table 5 compare elevated Pb source domains with measured gastric oral bioaccessibility. Across the five source domains (inclusive of the rural domain), the mean ICP-BAF range was 35.6% - 46.4%. The highest maximum BAFs and the highest mean and maximum bioaccessible concentrations occurred in the mineralisation domain. Despite insoluble portions of Pb observed near the granite domain (Fig. 5), the highest average BAFs were measured in soils overlying this domain. Rural areas had the lowest mean and minimum bioaccessible Pb concentrations and the lowest average BAFs (Table 5). Urban domains accounted for the second highest maximum bioaccessible Pb concentrations, although peat and urban domains each hosted intermediate levels of bioaccessible Pb in general when compared to the other source domains (Table 5). Where small urban domains overlapped with the extent of the mineralisation domain, it was assumed mineralisation acted as the primary Pb source and samples were assigned to the mineralisation domain.

Despite the lower solubility of Pb in soils overlying the Sperrin Mts. (Fig. 5), Pb from the peat source domain present in this area is still moderately bioaccessible (Fig. 6A, Table 5). Similarities in Pb bioaccessibility between the peat and urban domains may suggest that bioaccessible Pb in these domains arises from similar sources, such as atmospheric deposition from urban or industrial emissions. Alternatively, this observation in peat may be coincidental and instead governed by the presence of dissolved organic matter, low pH and reducing conditions in peat soils that are conducive to higher levels of trace element mobility and bioaccessibility (Appleton *et al*., 2013; Palmer *et al*., 2013; Yang *et al.*, 2003).

Regional trends in measured gastric bioaccessible Pb concentrations are illustrated by Fig. 6B. Higher levels of gastric bioaccessibility are present around the Belfast metropolitan area, along the extent of the NI-ROI border, and also along the northeast coast. In addition to a peat source domain immediately north of this latter coastal location, mining activity occurs in this area (GSNI, 2014), although a Pb mineralisation domain is not present. Another area where measured bioaccessible Pb concentrations are high is south of Lough Neagh in proximity to an urban source domain. In general, observed spatial patterns in Pb bioaccessibility closely align with those observed for elevated Pb soil concentrations (Fig. 2A), areas of higher Pb solubility (Fig. 5) and also with elevated mineralisation, urban, and peat Pb source domains (Fig. 6A). These findings may suggest that both diffuse anthropogenic and widespread geogenic Pb sources are capable of presenting health risks from the oral exposure pathway.

4. Discussion

Part IIA of the 1990 Environmental Protection Act (EPA 1990) outlines the statutory obligations in England, Wales and Scotland for assessing potentially contaminated areas of land to determine if sites are fit for proposed land use. At the time of writing no cohesive contaminated land legislative framework has been officially adopted in NI or ROI for assessing potential risks to human health. Guidance on the NI Environment Agency (NIEA) web site directs users to English Environment Agency (EA) publications as official adoption and enforcement of Part 3 of the enacted Waste and Contaminated Land Order (NI) 1997 has yet to occur (NIEA, 2010). The Irish Environmental Protection Agency is currently in the process of developing its own framework.

Toxic elements from some types of anthropogenic pollution may be more bioaccessible than those associated with geogenic sources due to the more soluble phases in which they exist in soil (Appleton *et al*., 2012*b;* Cave *et al*. 2007; Ljung *et al*., 2007; Cave *et al*. 2003), although this study also found that Pb attributed to geogenic sources displayed higher average BAFs than Pb from other source domains. Despite the knowledge that soluble and anthropogenic forms of pollution in the environment may be more likely to cause harm due to their increased bioavailability and bioaccessibility, sections 3.21 - 3.26 of the 2012 DEFRA guidance for Part IIA of EPA 1990 state that soils hosting widespread geogenic contamination or diffuse anthropogenic pollution should not be regarded as contaminated land. The exception is where strong scientific evidence concludes that significant health risks are being caused or are likely to occur (DEFRA, 2012). This approach is not unique to the UK. For example, a similar regime is in place in Finland, where a Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) (Ministry of the Environment Finland, 2007) states that the assessment process shall regard natural geological concentrations and diffuse anthropogenic pollution as contributing to background concentrations (Jarva *et al.*, 2010). However, such guidance may be misaligned with our knowledge concerning the health effects from oral Pb exposure in soil, particularly with regard to its non-threshold toxicity (ASTDR, 2007; USEPA, 1988). Gathering more evidence on other risk pathways for Pb exposure such as inhalation would help underpin with more certainty the potential health effects from exposure to low level diffuse anthropogenic pollution or widespread geogenic contamination.

The high solubility of Pb in surface soils and reduced Pb concentrations in deep soils in the study area suggests that a portion of elevated Pb concentrations is from diffuse anthropogenic pollution sources. This finding is supported by the observed spatial trends in Pb soil distributions where elevated concentrations align with urban and peat source domains. Upland peat soils may be intercepting anthropogenic Pb carried in rainfall. The medium range spatial structure observed for extractable Pb concentrations also supports the conclusion that anthropogenic processes may be influencing or have historically influenced Pb soil concentrations. Bioaccessibility in the urban domain was higher than that observed in the remaining rural domain, demonstrating the anthropogenic effects of industrial activity and higher population densities over Pb distributions and associated possible health effects.

From an oral risk exposure standpoint, the region identified as a mineralisation domain hosted the highest concentrations of bioaccessible Pb. Although the granite domain accounted for lower maximum levels of bioaccessibility compared to the other domains, average BAFs were highest in soils overlying the granite domain. These findings suggesting that risk associated with geogenic sources of Pb should also be taken into consideration.

5. Conclusion

Combining existing knowledge surrounding non-threshold toxicity with the findings that Pb in the study area displays moderate to high solubility and oral bioaccessibility and warrants more detailed risk evaluation for Pb in soil. The findings of this study should be taken into account during the development of final Pb soil screening levels and the adoption of an official Irish or Northern Irish contaminated land regime, if or when such measures take place.

Conclusions regarding toxicity risks from oral soil Pb exposure can only be made on a site specific basis taking all exposure pathways and relevant land use scenarios into account. However, the findings of this research suggest that diffuse anthropogenic forms of pollution and the presence of natural geogenic contaminants should be considered more carefully in a health risk context, particularly in the case of a non-threshold toxin such as Pb.

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Figures

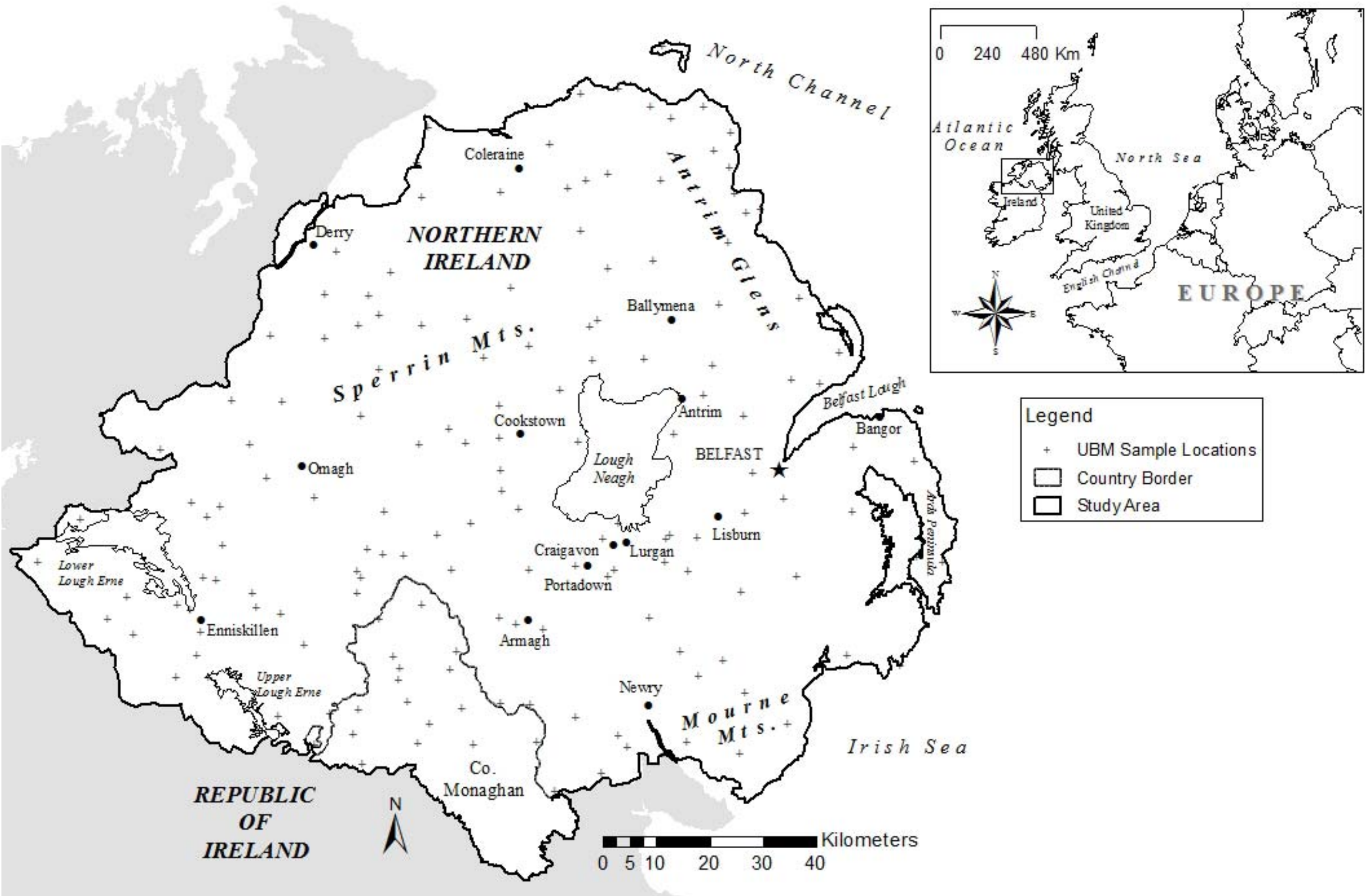

Fig. 1 Study area map showing location in Europe and 163 UBM sample locations across Northern Ireland and Co. Monaghan in the Republic of Ireland (ROI); Northern Ireland images are GSNI Crown Copyright

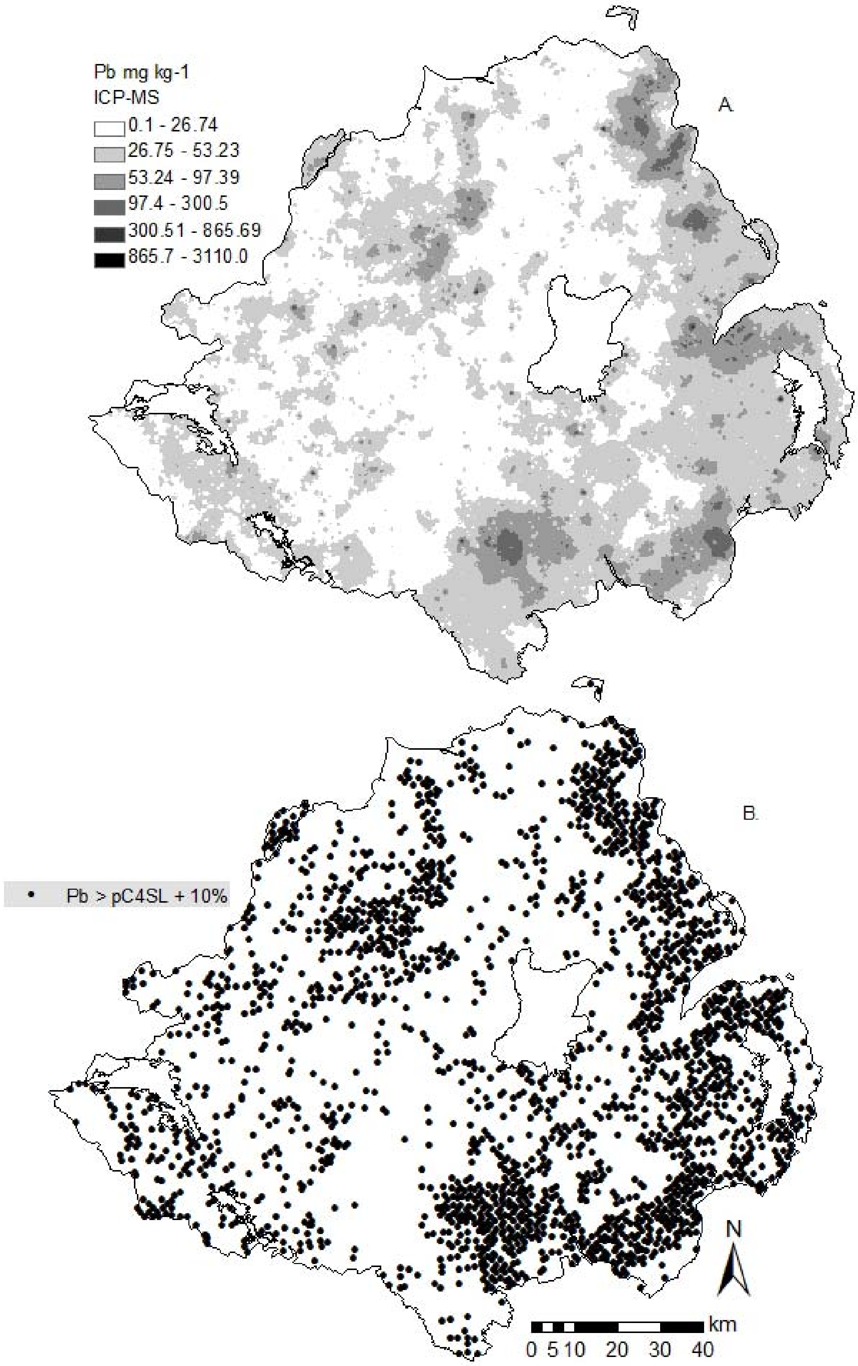

Fig. 2 (A) ICP-MS Pb concentrations (mg kg^{-1}) in 'A' soils across study area and (B) soil sample locations from NI Tellus and Tellus Border geochemical surveys where 'A' soil concentrations exceed the lowest published pC4SL of 30 mg kg^{-1} by 10% or greater (n = 2,208) for a female child receptor in an allotment setting (Harries *et al.*, 2013)

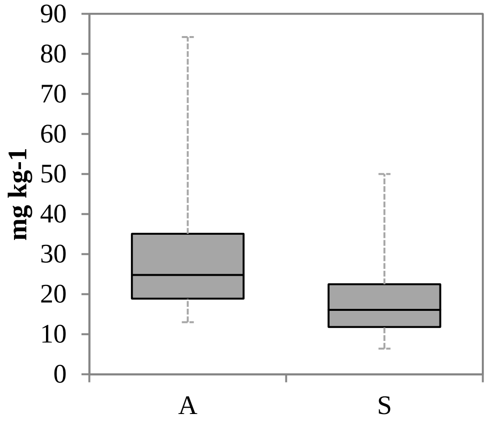

Fig. 3 Surface ('A') Pb extractable concentrations versus beneath-surface ('S') Pb extractable concentrations as measured by ICP-MS following an *aqua regia* digest in Northern Ireland. Lower and upper error bars represent 5^{th} and 95^{th} percentile ranges, respectively.

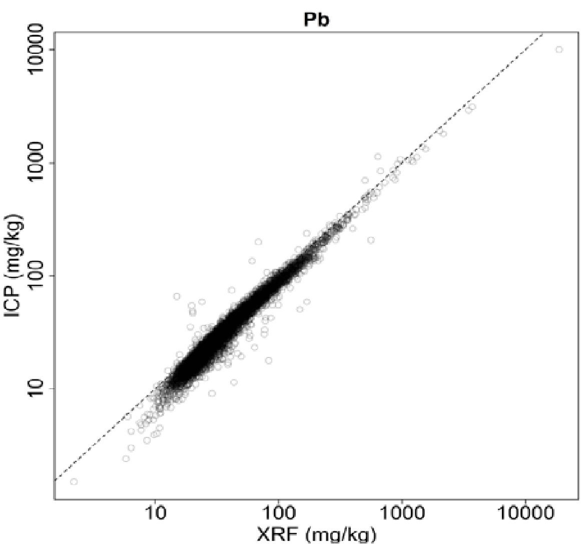

Fig. 4 Pb extractable concentrations in 'A' soils measured by ICP-MS plotted against total Pb XRFS concentrations in NI and Co. Monaghan; dashed line indicates a 1-1 ratio between the two concentrations

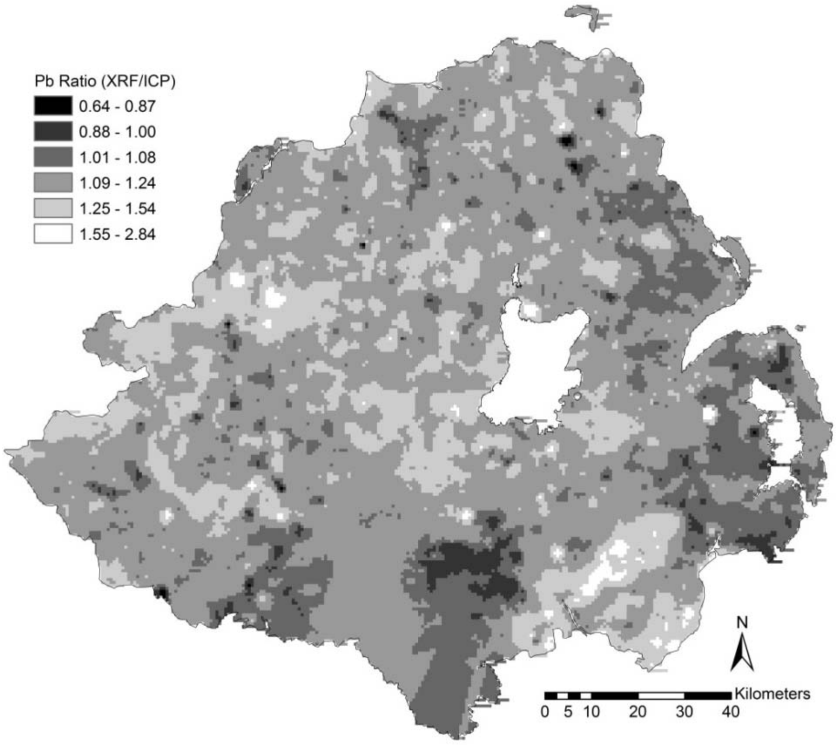

Fig. 5 Map of XRFS total-ICP extractable Pb concentrations; high ratios illustrate areas of lower Pb solubility and low ratios illustrate where high Pb solubility exists

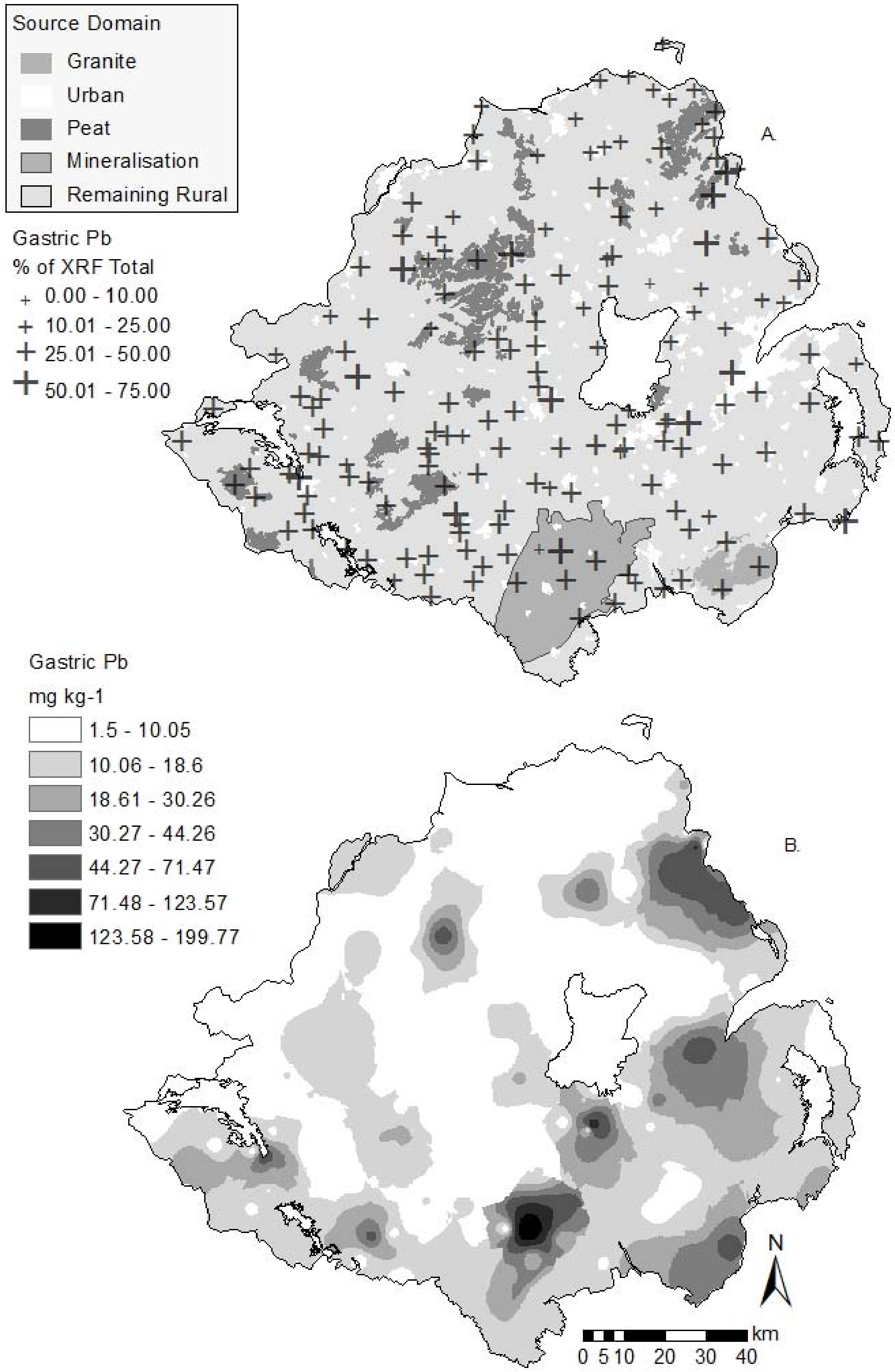

Fig. 6 (A) Elevated Pb source domains within study area identified by ECDF method overlain with measured Pb G BAFs expressed as percentage of total XRFS concentrations and (B) Pb oral bioaccessibility (mg kg^{-1}) interpolated by IDW, 5 nearest neighbours; $n = 163$

Tables

Table 1 pH tolerances for stabilised UBM digestive fluids

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

Table 2 Summary of study area and sample set ‘A’ soil Pb concentrations compared against historic and provisional generic UK soil assessment criteria and study area typical threshold values (TTVs); all values in mg kg^{-1}

Historic UK SGV[a]	pC4SL[b]	Study Area Source Domain TTVs[c]		Pb ‘A’ Soil Concentrations						
					Study Area *n* =7,234[d]			Study Sample Set *n* = 163[e]		
				Method	Mean	Med	Max	Mean	Med	Max
Res/Allot		Mineral	Granite							
450	30-330	110	170	XRFS	41.6	28.8	18,756	39.8	28.7	291.0
		Peat	Urban							
Commercial		160	220							
750	1100-6000	Remaining Rural		ICP-MS	31.5	23.2	3,110	35.4	23.5	268.0
		63								

[a]DEFRA & EA, 2002*a* & 2002*b*
[b]Range of values dependent on different modelled exposure and land use scenarios as presented in Harries *et al.* (2013). Res = residential, allot = allotment.
[c]The unique values calculated for this study incorporating 18 sample locations in Co. Monaghan did not yield different TTV results from McIlwaine *et al.,* 2014. Mineral = mineralisation domain.
[d]Based on NI Tellus and Tellus Border geochemical survey data where 7,234 samples were analysed by ICP-MS in NI and Co. Monaghan. 6,862 were analysed by XRFS in NI with 18 additional samples in Co. Monaghan analysed by XRFS outside of routine Tellus Border survey analyses.
[e]Inclusive of 90 samples from Barsby *et al.*, 2012

Table 3 Pb geostatistical summary showing 98% of total variance in Pb extractable soil distributions is accounted for by a short-range function as modelled in Fig. 2 while total concentrations show Pb concentrations are controlled by a longer range function suggestive of geogenic processes

	Nugget Variance C_o	Function Variance C_1	Range (km) *a*	Total Variance $C = C_0 + C_1$	Unexplained Variance $\% C_o = (C_o/C_1)*100$
Extractable Pb (ICP)	0.004	0.197	1.2	0.201	2%
Total Pb (XRFS)	0.193	0.100	32.9	0.293	66%
XRFS/ICP Ratio	0.004	0.014	3.5	0.018	21%

Table 4 Summary of gastric (G) and gastro-intestinal (GI) Pb bioaccessible concentrations (mg kg^{-1}) and bioaccessible fractions (BAF, %) in study area (*n* = 163)

	mg kg^{-1}			XRFS-BAF			ICP-BAF		
	Med	Max	Min	Med	Max	Min	Med	Max	Min
G Pb	8.6	199.8	1.5	33.9	68.6	8.2	40.3	74.6	9.7
GI Pb	3.8	85.9	0.0	12.8	35.1	0.2	15.6	38.1	0.3

Table 5 Comparison of Pb G bioaccessible concentrations (mg kg^{-1}) and BAF (%) against identified Pb concentrations in 'A' soils overlying five Pb source domains in study area

Domain	G Pb			ICP-BAF			XRFS-BAF		
	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
Mineralisation *n* = 9	36.4	199.8	6.9	42.7	74.6	15.8	37.3	68.6	8.2
Granite *n* = 3	36.0	49.0	16.3	46.4	52.2	37.5	40.2	46.8	34.4
Peat Soil *n* = 18	20.6	74.9	2.6	42.6	66.2	13.4	37.3	64.4	12.3
Urban *n* = 31	19.9	97.6	2.3	41.7	67.1	14.3	36.4	64.0	13.0
Remaining Rural *n* = 102	9.7	51.3	1.5	35.6	65.8	9.7	30.5	58.9	9.8