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## **The Effects of Lead Sources on Oral Bioaccessibility in Soil and Implications for Contaminated Land Risk Management**

Palmer, S., McIlwaine, R., Ofterdinger, U., Cox, S. F., McKinley, J. M., Doherty, R., Wragg, J., & Cave, M. (2015). The Effects of Lead Sources on Oral Bioaccessibility in Soil and Implications for Contaminated Land Risk Management. *Environmental Pollution*, 198, 161-171. Advance online publication. <https://doi.org/10.1016/j.envpol.2015.01.004>

**Published in:**  
Environmental Pollution

**Document Version:**  
Peer reviewed version

**Queen's University Belfast - Research Portal:**  
[Link to publication record in Queen's University Belfast Research Portal](#)

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

3  
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13

14 Abstract

15  
16 Lead (Pb) is a non-threshold toxin capable of inducing toxic effects at any blood level but availability  
17 of soil screening criteria for assessing potential health risks is limited. The oral bioaccessibility of Pb  
18 in 163 soil samples was attributed to sources through solubility estimation and domain identification.  
19 Samples were extracted following the Unified BARGE Method. Urban, mineralisation, peat and  
20 granite domains accounted for elevated Pb concentrations compared to rural samples. High Pb  
21 solubility explained moderate-high gastric (G) bioaccessible fractions throughout the study area.  
22 Higher maximum G concentrations were measured in urban (97.6mg kg<sup>-1</sup>) and mineralisation  
23 (199.8mg kg<sup>-1</sup>) domains. Higher average G concentrations occurred in mineralisation (36.4mg kg<sup>-1</sup>)  
24 and granite (36.0mg kg<sup>-1</sup>) domains. Findings suggest diffuse anthropogenic and widespread geogenic  
25 contamination could be capable of presenting health risks, having implications for land management  
26 decisions in jurisdictions where guidance advises these forms of pollution should not be regarded as  
27 contaminated land.  
28

29  
30  
31 Keywords: anthropogenic pollution, geogenic contamination, oral bioaccessibility, human health risk  
32 assessment, soil  
33

34 Capsule: Diffuse and widespread Pb sources displayed high oral bioaccessibility, providing  
35 implications for contaminated land risk assessment guidance that excludes these forms of pollution.  
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## 44 1. Introduction

45

46 Lead (Pb) is a toxic trace element that has been the subject of extensive human health research. Its  
47 neurotoxic effects from the oral exposure pathway, particularly in children, are well documented  
48 (EFSA, 2010; ATSDR, 2007; Ryan *et al.*, 2004; CCME, 1999; Rosen, 1995). Some studies also  
49 suggest Pb exposure may be associated with increased incidences of violent crime (Meilke & Zahran,  
50 2012; Nevin, 2007; Nevin, 2000). Whilst many known toxins have quantifiable threshold exposure  
51 levels above which toxic health effects could occur, Pb is currently regarded by the global scientific  
52 community as a non-threshold toxin. Non-threshold toxicity indicates that laboratory studies have not  
53 identified a minimal risk level (MRL) or a no observed adverse effect level (NOAEL). Adverse  
54 health effects could potentially occur at any blood Pb level (EA, 2009; ATSDR, 2007; USEPA, 1988).  
55 Therefore, it is arguable that no amount of Pb exposure can be regarded as safe based on available  
56 research to date.

57

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

73

74 Due to the global variability in Pb NBCs and also with regards to its non-threshold toxicity,  
75 identifying a starting point for contaminated land assessment in a human health context is challenging.  
76 The CCME provides a soil quality guideline of 140 mg kg<sup>-1</sup> in a residential land use setting (CCME,  
77 1999). Following its non-threshold toxicity classification, the generic Pb soil guideline value (SGV)  
78 (DEFRA & EA, 2002a) was withdrawn in the UK. Whilst a selection of provisional Category 4  
79 screening levels (pC4SL) for Pb were recently published (Harries *et al.*, 2013), final C4SLs have not

80 been issued for any soil contaminant. A C4SL denotes a lower tolerable limit for a contaminant in  
81 soil, beneath which human health risk is unlikely to be present.

82

83 Although Pb concentrations in the wider environment have declined since its removal from petrol in  
84 the last century, its ubiquitous anthropogenic presence still persists in soils, particularly around urban  
85 centres (Harries *et al.*, 2013; Appleton *et al.*, 2012a). Previous research worldwide has highlighted  
86 areas of elevated soil Pb concentrations outside of areas where geogenic associations are known to  
87 exist, including within the Republic of Ireland (ROI) and NI (Barsby *et al.*, 2012; Bourennane *et al.*,  
88 2010; Jordan *et al.*, 2007; Ljung *et al.*, 2006; Zhang, 2006). Such findings demonstrate how  
89 anthropogenic pollution sources substantially contribute to elevated soil Pb concentrations. In NI Pb  
90 is found in highest total and extractable concentrations around the Belfast urban area and in soils  
91 overlying mineral deposits, with high soluble Pb measured in peaty upland areas (Jordan *et al.*, 2001).  
92 This latter observation may be accounted for by atmospheric deposition of anthropogenic Pb through  
93 rainfall, as precipitation is the primary moisture source in upland peat soils.

94

95 The large surface area and number of acidic functional groups that are common to peat make it an  
96 ideal substrate to bind trace elements either as sedimentary, deposited, particulate matter or as sorbed  
97 or complexed metal ions (Brown *et al.*, 2000). The major sources of metals in the peat mass of  
98 ombrotrophic peat bogs has been shown to come from atmospheric precipitation (Steinnes &  
99 Friedland, 2006) which has been specifically illustrated in Ireland (Coggins *et al.*, 2006). Whilst the  
100 ability of peat to accumulate trace metals has been well documented, there is little previous data on  
101 the bioaccessibility of trace elements such as Pb in peat rich soils.

102

103 Four Pb source domains were previously identified in NI accounting for elevated soil Pb  
104 concentrations (McIlwaine *et al.*, 2014). A domain is an area where a distinguishable factor is  
105 recognised as controlling the concentration of an element. Urban, peat, granite and mineralisation Pb  
106 source domains were related to elevated concentrations of Pb, with typical threshold values (TTV)  
107 higher than the TTV calculated for the remaining rural domain. TTVs aim to identify the threshold  
108 between diffuse and point source anthropogenic contamination, thereby giving an indication of typical  
109 concentrations within defined geographical areas. Urban Pb source domains are likely to be directly  
110 attributable to anthropogenic activity. Some anthropogenic pollution sources are potentially more  
111 soluble in the environment and resultantly more bioavailable (Ljung *et al.*, 2007; Appleton *et al.*,  
112 2012b), in turn posing a greater risk to human health.

113

114 Not all toxins that are rendered bioaccessible will be bioavailable, but *in vitro* bioaccessibility tests  
115 can better refine the contaminated land risk assessment process by reducing reliance on total soil  
116 contaminant concentrations. Such reliance may overestimate health risks (CIEH, 2009; Scheckel *et*

117 *al.*, 2009; Nathanail & Smith, 2007; Nathanail, 2006; Ruby *et al.*, 1999). The Unified BARGE  
118 (Bioaccessibility Research Group of Europe) Method (UBM) is therefore a useful extraction method  
119 to employ in risk assessment scenarios where oral contaminant exposure is expected to contribute to  
120 toxic health effects. The UBM is a robust soil extraction technique that measures *in vitro* the oral  
121 bioaccessibility of contaminants by mimicking the conditions of the human stomach and upper  
122 intestine (BARGE/INERIS, 2010). The method has been validated for Pb, arsenic and cadmium using  
123 *in vivo* swine data (Denys *et al.*, 2012; Caboche, 2009) and has also been subjected to global inter-  
124 laboratory trials (Wragg *et al.*, 2011). Data obtained from UBM extractions provide an indication of  
125 what fraction of a contaminant may be solubilised in the gastro-intestinal (GI) tract (the bioaccessible  
126 portion) and therefore potentially available for absorption resulting in toxic health effects (the  
127 bioavailable portion).

128

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

## 136 2. Methodology and Study Area

### 137 2.1 Study Area

138

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

149

150 Soil types present in the study area include peats, humic and sand rankers, brown earths, podzols,  
151 mineral gleys and alluviums. Soil pH falls within a narrow acidic range of approximately 5.0 to 6.0

152 (Jordan *et al.*, 2001), with the NI Tellus geochemical survey more recently recording an average pH  
153 of 4.7. This decrease in pH over time suggests acidification of soils may be increasing in the study  
154 area. The climate is temperate and average annual rainfall ranges from a low of 800 mm in the  
155 eastern region to a high of over 1900 mm in the west. The Antrim Glens in the northeast, the Sperrin  
156 Mts. in the west and the granitic Mourne Mts. in the southeast intercept much of the precipitation  
157 borne by air currents which have travelled over the Atlantic Ocean, although the western half of the  
158 study area is most significantly affected by these Atlantic weather patterns (Met Office, 2012).

## 160 2.2 Geochemistry Data Analysis

161  
162 Total and extractable Pb concentration data from the NI Tellus and Tellus Border geochemical  
163 surveys were provided by the Geological Survey of Northern Ireland (GSNI) and by the Geological  
164 Survey of Ireland (GSI), respectively. Rural NI Tellus Survey soil samples were collected on a 2 km<sup>2</sup>  
165 grid at depths of 5 – 20 cm ('A') and 35 – 50 cm ('S'). 'A' samples were analysed for total Pb  
166 concentrations by x-ray fluorescence spectrometry (XRFS) and for extractable concentrations by  
167 inductively coupled plasma mass spectrometry (ICP-MS) following an *aqua regia* digest. 'S' NI  
168 Tellus Survey soil samples were also digested by *aqua regia* and analysed by ICP-MS. Tellus Border  
169 'A' samples were collected on a 4 km<sup>2</sup> grid and analysed by ICP-MS following an *aqua regia* digest  
170 to yield extractable concentration data. Full analytical and field methods employed by these  
171 comprehensive regional geochemical surveys can be found in Smyth (2007) and Knights and Glennon  
172 (2013).

173  
174 As part of this research, additional XRFS analysis was conducted at the British Geological Survey  
175 (BGS) Analytical Geochemistry Facility on a sub-set of 18 Tellus Border 'A' samples in Co.  
176 Monaghan according to the same methods described in the NI Tellus Survey methodology (Smyth,  
177 2007). The additional XRFS data was required for solubility estimation and for calculation of UBM  
178 bioaccessible fractions (BAF) in Co. Monaghan. Geochemistry data were handled in SPSS v.19.0, R  
179 (R Core Team, 2013) and MS Excel 2010.

## 181 2.3 Geostatistical Analysis and Interpolation

182  
183 Geostatistics and semi-variogram parameters were calculated in R with additional interpolation by  
184 ordinary kriging (OK) (Matheron, 1965) and inverse distance weighting (IDW) conducted in ArcMap  
185 10.0 (ESRI, 2010) for illustrative purposes. The OK model yielding a mean prediction error closest to  
186 zero was selected as the final model for generating interpolated surfaces (Lloyd, 2010). Geostatistical  
187 outputs can be influenced by a nonparametric data distribution (Lloyd, 2010; Clarke, 2001; Einax &

188 Soldt, 1999). Pb concentration data were therefore log-transformed prior to interpolation. OK models  
189 were checked for robustness using cross validation statistics and a visual assessment of the best fit  
190 semi-variogram using a maximum search neighbourhood of 12 nearest sample locations. A single Pb  
191 elemental component map is used to visually illustrate the initial data distribution. These maps are  
192 produced with awareness that, due to the compositional nature of geochemical data, single component  
193 maps represent only relative information that is inextricably linked to the relationship between one  
194 elemental component and other co-occurring elements (Pawlowsky-Glahn & Buccianti, 2011;  
195 Aitchison, 1986).

196

197 Semi-variogram parameters give an indication of the spatial structure that exists within a data set.  
198 This in turn can help explain geochemical or environmental processes that affect the spatial  
199 distributions of elements (Goulard & Voltz, 1992; McBratney *et al.*, 1982). The semi-variogram sill  
200 ( $C_1$ ) is synonymous with the sample variance and represents the maximum variance that exists  
201 between measured sample values within the range of spatial correlation ( $a$ ). Beyond the distance  $a$ ,  
202 samples are no longer spatially correlated (Clarke, 2001; Gringarten & Deutsch, 2001). The nugget  
203 variance ( $C_0$ ) is attributed to micro-scale variance outside of sampling resolutions. Although the  
204 nugget effect is commonly regarded as an indication of measurement error or random semi-variogram  
205 behaviour, micro-scale processes which control element distributions may also be accounted for by  
206 the nugget variance. For example, Imrie *et al.* (2008) found that factors attributed to anthropogenic  
207 land use patterns were accounted for by a nugget effect. Dobermann *et al.* (1995) concluded buffalo  
208 excrement influenced soil chemistry over a range that occurred within the nugget variance. Functions  
209 with a high proportion of total variance ( $C_0 + C_1$ ) accounted for by the nugget variance may therefore  
210 be indicative of anthropogenic processes or land use behaviours which have significantly affected  
211 element distributions over shorter spatial scales than were detectable by the primary range ( $a$ ) of the  
212 function.

213

214 OK yields results which increase in accuracy in line with increasing sample numbers (Einax & Soldt,  
215 1999). Due to fewer sample locations in the bioaccessibility data set than were available for  
216 extractable Pb concentration data, bioaccessible Pb concentrations were interpolated using IDW with  
217 a maximum search neighbourhood of five neighbouring sample locations. IDW is an exact  
218 interpolator (Lloyd, 2010) and this method therefore yielded a more accurate range of Pb  
219 bioaccessible concentration values across the interpolated surface.

220

## 221 2.4 Pb Solubility Estimation

222

223 A method for estimating element solubility in soil at a regional scale was applied to the NI Tellus and  
224 Tellus Border XRFS and ICP-MS data, similar to approaches used previously in Finland (Jarva *et al.*,  
225 2009) and Cyprus (Cohen *et al.*, 2012). XRFS measures total element concentrations in soils whereas  
226 ICP concentrations rely on the antecedent *aqua regia* acid extraction. Although *aqua regia* acid is  
227 said to effectively leach many metals (Gill, 1997), the solubility of elements will affect how easily  
228 they are leached from the soil (Delgado *et al.*, 2011). Therefore, by comparing the concentrations  
229 measured by the two methods, element solubility at a regional scale can be estimated. Elements  
230 which are more soluble in the environment generally exhibit higher oral bioaccessibility (Finžgar *et*  
231 *al.*, 2007).

232  
233 ICP extractable concentrations were plotted against XRFS total concentrations using the R statistical  
234 software package (R Core Team, 2013) to explore the relationship between the two analytical  
235 methods. The ratio of XRFS/ICP Pb concentrations was mapped by OK to illustrate geographical  
236 trends in Pb solubility. The classes on the map were defined by the boxplot classes method  
237 (McIlwaine *et al.*, 2014) with an additional class added where the ratio was equal to one (where Pb  
238 concentrations measured by the two analytical methods were equal). Boxplot classifications retained  
239 the appropriate amount of detail to allow a direct comparison with the mapped bioaccessibility results.  
240

## 241 2.5 Pb Domain Identification

242  
243 Domains were previously identified for Pb in NI as described in McIlwaine *et al.* (2014). Total XRFS  
244 concentrations in shallow soils were mapped using empirical cumulative distribution function (ECDF)  
245 classes and compared to the main factors identified as controlling element concentrations—bedrock  
246 geology, superficial geology, land use classification and mineralisation. Elevated concentrations of  
247 Pb were attributed to urban, granite, mineralisation and peat source domains in NI with the remaining  
248 rural domain hosting lower Pb concentrations.

249  
250 Additional Co. Monaghan data were included to identify Pb domains across the extent of the study  
251 area for this research. Bedrock geology data were obtained from the GSI 1:500,000 Bedrock Geology  
252 map (GSI, 2005). Superficial peat cover was identified using the Irish Environmental Protection  
253 Agency Soils and Subsoils Mapping Project data completed by Teagasc (Fealy & Green, 2009). The  
254 Corine land cover data (European Environment Agency, 2012) was used to identify urban and rural  
255 land use within the study area. Areas of known or suspected mineralisation in Co. Monaghan are  
256 identified in the Tellus Border prospectivity map (Coulter & Stinson, 2013).

257



258 Data used for identifying the mineralisation source domain in NI and Co. Monaghan relied upon  
259 prospectivity maps (Coulter & Stinson, 2013; Lusty *et al.*, 2012) and not the locations of working or  
260 historic mines. The mineralisation domain and associated soil Pb is therefore regarded as geogenic  
261 and naturally occurring for the purposes of this research.  
262

## 263 2.6 Oral In Vitro Bioaccessibility Testing

264

265 UBM extractions were carried out in 2009 (Barsby *et al.*, 2012) and 2013 at the BGS Analytical  
266 Geochemistry Facility following the published method (BARGE/INERIS, 2010). The 2009 and 2013  
267 data sets were joined to create a UBM data set of 163 samples for this research. Soil samples (< 2  
268 mm fraction) were selected from the NI Tellus Survey and Tellus Border soil archives to cover a wide  
269 range of soil and underlying bedrock types present in the study area.  
270

271 Standard BGS internal laboratory procedures were followed during UBM extraction and analysis  
272 according to UK Accreditation Service national laboratory requirements. Reagents were sourced by  
273 BGS from Merck, Sigma, Baker and Carl Roth. Saliva, gastric, duodenal and bile solutions were  
274 prepared one day prior to soil extractions to permit stabilisation. Solution pH was adjusted as  
275 required according to UBM specifications using either 37% HCl or 1M HNO<sub>3</sub> (Table 1). Soils not  
276 adhering to pH specifications (pH < 1.5) after one hour of gastric extraction were discarded and re-  
277 extracted at a later date.  
278

279 Extracts were analysed by an Agilent 7500cx series ICP-MS employing an octopole reaction system  
280 in combination with a CETAC autosampler. The instrument was calibrated at the beginning of every  
281 analytical run using a minimum of three standards and one blank for each trace element. Multi-  
282 element quality control check standards were analysed at the start and end of each run and after every  
283 25 samples at minimum.  
284

285 One blank, one duplicate and one certified BGS102 reference soil (Wragg, 2009) were included in the  
286 extraction run for each of seven soils extracted. The BGS102 certificate of analysis provides certified  
287 UBM values for acceptable ranges of gastric (G) Pb concentrations. Average measured G Pb in  
288 reference soils was within one standard deviation of the certified BGS102 value. The mean relative  
289 per cent difference (RPD) for gastric Pb in study area soil samples was 8%. In the intestinal phase  
290 RPD was 14%. In line with the available BGS 102 certified reference value for G Pb, G data are  
291 presented in the following results as it is common practice to report the results yielding the highest  
292 bioaccessibility to ensure health risks are not underestimated. This approach also adheres to the  
293 precautionary principle advocated by UK contaminated land legislation and guidance (DEFRA,

294 2012). Details of quality control for 2009 extractions are similar to the above and are described in  
295 detail in Barsby *et al.* (2012).

### 296 3. Results

#### 297 3.1 Lead Soil Concentrations

298

299 The highest extractable Pb concentrations are found in soils along the northeast coast near the Antrim  
300 Glens, extending south into the Belfast metropolitan area and Ards Peninsula, with the occurrence of  
301 elevated Pb concentrations continuing along the southeast NI-Co. Monaghan border (Fig. 1, Fig. 2A).  
302 Peat soils overlying the Sperrin Mts. in the northwest also host elevated concentrations of Pb. It is  
303 this part of the study area that receives the most precipitation borne from Atlantic Ocean air currents  
304 (Met Office, 2012). The maximum measured extractable Pb concentration occurs near the Belfast  
305 metropolitan area ( $> 3000 \text{ mg kg}^{-1}$ ).

306

307 Although no SGV is currently available for Pb in the UK, Table 2 provides an overview of how Pb  
308 concentrations compare against historic withdrawn and current provisional soil screening criteria.  
309 Fig. 2B illustrates where extractable Pb concentrations exceed the lowest published pC4SL of  $30 \text{ mg}$   
310  $\text{kg}^{-1}$  by at least 10%. This criterion is applicable for a female child in an allotment setting (Harries *et*  
311 *al.*, 2013). Pb concentrations were flagged as exceeding the pC4SL only where the concentration met  
312 or exceeded  $33 \text{ mg kg}^{-1}$  to ensure the measured Pb concentration was sufficiently above the pC4SL.  
313 Extractable Pb concentrations exceed the pC4SL at over 2,208 of 7,234 NI Tellus and Tellus Border  
314 soil sample locations in the study area (Fig. 2B). When total XRFS Pb concentrations are compared  
315 with the pC4SL, the number of occurrences where the screening criterion is exceeded increases to  
316 2,629 (not illustrated).

317

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

324

325 XRFS Pb concentrations were mapped previously by Barsby *et al.* (2012) and exhibit similar spatial  
326 patterns to extractable Pb concentrations. Extractable Pb concentrations are controlled by a spatial  
327 function with a moderate range ( $a$ ) of 22.8 km. Short to medium range spatial functions are  
328 sometimes associated with processes that have a higher frequency of variation over short distances.

329 Such functions can be the result of smaller scale processes such as anthropogenic interactions with the  
330 environment, while long range functions capture the effects of larger scale geologic forming processes  
331 (Imrie *et al.*, 2008; Dobermann *et al.*, 1995). Pb exhibits a spatial structure in the study area that  
332 varies over a short scale in terms of its range relative to trace elements of known geogenic origin such  
333 as nickel or chromium which are controlled by longer range functions (> 70 km; McIlwaine *et al.*,  
334 2014; Barsby *et al.*, 2012). The high proportion of nugget variance (63%) for Pb spatial distributions  
335 (Table 3) also suggests a high degree of micro-scale variation or spatial variability not detected by the  
336 primary range of the Pb function.

337

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

342

### 343 3.2 Lead Solubility and Domain Identification

344

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

349

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

357

358 Fig. 5 illustrates the geographic variability in XRFS/ICP concentrations ratios. Higher levels of Pb  
359 solubility occur in the darker areas of the map, where the ratio is less than one. Where the map  
360 becomes lighter Pb is less soluble. Higher levels of solubility are observed along the central and  
361 western NI-ROI border and throughout the eastern coast. One area of higher solubility strongly aligns  
362 with an identified mineralisation source domain (Fig. 6A). Higher proportions of insoluble Pb occur  
363 in the southeast and northwest near the Mourne and Sperrin Mts., respectively. The Mourne Mts.  
364 comprise the granite source domain and the Sperrin Mts. aligning with the peat source domains.

365 Rural, peat and urban domains host moderately soluble portions of Pb. Although an elevated peat  
366 source domain was also identified in Fig. 6A, Pb solubility trends in Fig. 5 do not clearly align  
367 spatially with patterns illustrated for the peat source domain. Instead Pb solubility in peat is  
368 comparable to the intermediate solubility observed within urban source domains.

369

### 370 3.3 Lead Bioaccessibility

371

372 The results of UBM extractions are summarised in Table 4. G bioaccessibility was higher than GI  
373 bioaccessibility due to the lower pH of the G digestion which increases Pb mobility in solution  
374 (Denys *et al.*, 2012; Farmer *et al.*, 2011; Denys *et al.*, 2007). The maximum G bioaccessible  
375 concentration was 199.8 mg kg<sup>-1</sup>, accounting for 68.6% of total Pb. The median G ICP-BAF was  
376 40.3%, decreasing to 15.6% of extractable Pb concentrations in the GI phase. XRFS-BAF values did  
377 not differ greatly from ICP-BAFs as a result of most Pb in soils in the study area being detectable by  
378 ICP-MS (Fig. 4). Pb gastric bioaccessibility exceeded 50% of total concentrations at 13 different soil  
379 locations across the study area (Fig. 6A).

380

381 Fig. 6A and Table 5 compare elevated Pb source domains with measured gastric oral bioaccessibility.  
382 Across the five source domains (inclusive of the rural domain), the mean ICP-BAF range was 35.6% -  
383 46.4%. The highest maximum BAFs and the highest mean and maximum bioaccessible  
384 concentrations occurred in the mineralisation domain. Despite insoluble portions of Pb observed near  
385 the granite domain (Fig. 5), the highest average BAFs were measured in soils overlying this domain.  
386 Rural areas had the lowest mean and minimum bioaccessible Pb concentrations and the lowest  
387 average BAFs (Table 5). Urban domains accounted for the second highest maximum bioaccessible  
388 Pb concentrations, although peat and urban domains each hosted intermediate levels of bioaccessible  
389 Pb in general when compared to the other source domains (Table 5). Where small urban domains  
390 overlapped with the extent of the mineralisation domain, it was assumed mineralisation acted as the  
391 primary Pb source and samples were assigned to the mineralisation domain.

392

393 Despite the lower solubility of Pb in soils overlying the Sperrin Mts. (Fig. 5), Pb from the peat source  
394 domain present in this area is still moderately bioaccessible (Fig. 6A, Table 5). Similarities in Pb  
395 bioaccessibility between the peat and urban domains may suggest that bioaccessible Pb in these  
396 domains arises from similar sources, such as atmospheric deposition from urban or industrial  
397 emissions. Alternatively, this observation in peat may be coincidental and instead governed by the  
398 presence of dissolved organic matter, low pH and reducing conditions in peat soils that are conducive  
399 to higher levels of trace element mobility and bioaccessibility (Appleton *et al.*, 2013; Palmer *et al.*,  
400 2013; Yang *et al.*, 2003).

401

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

#### 413 4. Discussion

414

415 Part IIA of the 1990 Environmental Protection Act (EPA 1990) outlines the statutory obligations in  
416 England, Wales and Scotland for risk assessing and, if required, remediating potentially contaminated  
417 areas of land. At the time of writing no cohesive contaminated land legislative framework has been  
418 officially adopted in NI or ROI for assessing potential risks to human health from existing land  
419 contamination. Instead, mitigation of potential risks is addressed during the planning and  
420 development process if permission is sought to change land use. Guidance on the NI Environment  
421 Agency (NIEA) web site directs users to English Environment Agency (EA) publications for use  
422 during the planning process as official adoption and enforcement locally of Part 3 of the enacted  
423 Waste and Contaminated Land Order (NI) 1997 has yet to occur (NIEA, 2010). The Irish  
424 Environmental Protection Agency (EPA) has recently put in place a framework for managing  
425 contaminated land at EPA licensed facilities (EPA, 2012), but has not yet developed a specific  
426 contaminated land legislative framework.

427

428 Toxic elements from some types of anthropogenic pollution may be more bioaccessible than those  
429 associated with geogenic sources due to the more soluble phases in which they exist in soil (Appleton  
430 *et al.*, 2012b; Cave *et al.* 2007; Ljung *et al.*, 2007; Cave *et al.* 2003), although this study also found  
431 that Pb attributed to geogenic sources displayed higher average BAFs than Pb from other source  
432 domains. Despite the knowledge that soluble and anthropogenic forms of pollution in the  
433 environment may be more likely to cause harm due to their increased bioavailability and  
434 bioaccessibility, sections 3.21 - 3.26 of the 2012 DEFRA guidance for Part IIA of EPA 1990 state that  
435 soils hosting widespread geogenic contamination or diffuse anthropogenic pollution should not be

436 regarded as contaminated land. The exception is where strong scientific evidence concludes that  
437 significant health risks are being caused or are likely to occur (DEFRA, 2012). This approach is not  
438 unique to the UK. For example, a similar regime is in place in Finland, where the 2007 Government  
439 Decree on the Assessment of Soil Contamination and Remediation Needs (Ministry of the  
440 Environment Finland, 2007) states that the assessment process shall regard natural geological  
441 concentrations and diffuse anthropogenic pollution as contributing to background concentrations  
442 (Jarva *et al.*, 2010). However, such guidance may be misaligned with our knowledge concerning the  
443 health effects from oral Pb exposure in soil, particularly with regard to its non-threshold toxicity  
444 (ASTDR, 2007; USEPA, 1988). Gathering more evidence on other risk pathways for Pb exposure  
445 such as inhalation or edible crop uptake would help underpin with more certainty the potential health  
446 effects from exposure to low level diffuse anthropogenic pollution or widespread geogenic  
447 contamination.

448

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

458

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

## 464 5. Conclusion

465

466 Combining existing knowledge surrounding non-threshold toxicity with the findings that Pb in the  
467 study area displays moderate to high solubility and oral bioaccessibility warrants more detailed risk  
468 evaluation for Pb in soil. The findings of this study should be taken into account during the future  
469 development of final Pb soil screening levels and the adoption of an Irish or Northern Irish  
470 contaminated land regime.

471

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

#### 477 Acknowledgements

478 2013 UBM testing was supported by the EU INTERREG IVA-funded Tellus Border project. Tellus  
479 Border is a € million cross-border project to map the environment and natural resources in the border  
480 region of Ireland and continue the analysis of data in the border counties of Northern Ireland. It is a  
481 joint initiative between the Geological Survey of Northern Ireland, the Geological Survey of Ireland,  
482 Queen's University Belfast and Dundalk Institute of Technology. The views and opinions expressed  
483 in this report do not necessarily reflect those of the European Commission or the SEUPB.

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

487 Special thanks to staff at the Analytical Geochemistry Facility at the BGS Kingsley Dunham Centre,  
488 especially Mr. Tom Barlow and Mr. Elliott Hamilton for their invaluable technical and analytical  
489 support.

490

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