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1 **Comparison of methods used to calculate typical threshold values for potentially toxic elements in soil**

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3 Rebekka McIlwaine^{1*}, Siobhan F. Cox¹, Rory Doherty¹, Sherry Palmer¹, Ulrich Offerdinger¹, Jennifer M.
4 McKinley²

5

6 ¹Environmental Engineering Research Centre, School of Planning, Architecture and Civil Engineering, Queen's
7 University Belfast, Belfast, BT9 5AG, UK

8 ²School of Geography, Archaeology and Palaeoecology, Queen's University Belfast, Belfast, BT9 5AG, UK

9

10

11 *Address correspondence to Rebekka McIlwaine, Environmental Engineering Research Centre, School of
12 Planning, Architecture and Civil Engineering, Queen's University Belfast, Belfast, BT9 5AG, E-
13 mail:rmcilwaine05@qub.ac.uk

14 **1 Abstract**

15 The environmental quality of land can be assessed by calculating relevant threshold values which differentiate
16 between concentrations of elements resulting from geogenic and diffuse anthropogenic sources and
17 concentrations generated by point sources of elements. A simple process allowing the calculation of these
18 typical threshold values (TTVs) was applied across a region of highly complex geology (Northern Ireland) to six
19 elements of interest; arsenic, chromium, copper, lead, nickel and vanadium. Three methods for identifying
20 domains (areas where a readily identifiable factor can be shown to control the concentration of an element),
21 were used: k-means cluster analysis, boxplots and empirical cumulative distribution functions (ECDF). The
22 ECDF method was most efficient at determining areas of both elevated and reduced concentrations and was
23 used to identify domains in this investigation. Two statistical methods for calculating Normal Background
24 Concentrations (NBCs) and Upper Limits of Geochemical Baselines Variations (ULBLs), currently used in
25 conjunction with legislative regimes in the UK and Finland respectively, were applied within each domain. The
26 NBC methodology was constructed to run within a specific legislative framework, and its use on this soil
27 geochemical data set was influenced by the presence of skewed distributions and outliers. In contrast, the
28 ULBL methodology was found to calculate more appropriate TTVs that were generally more conservative than
29 the NBCs. TTVs indicate what a “typical” concentration of an element would be within a defined geographical
30 area and should be considered alongside the risk that each of the elements pose in these areas to determine
31 potential risk to receptors.

32 **2 Suggested Keywords**

33 Background; contaminated land; domain identification; threshold; NBC; ULBL

34 **3 Introduction**

35 Geochemical surveys are carried out for various different reasons. Initially, they were used to define the extent
36 of mineralised areas in prospectivity studies (Hawkes and Webb 1962) and often urban areas would have been
37 avoided in these surveys (Johnson and Ander 2008). However, with developments in the understanding of the
38 effects potentially toxic elements (PTEs) have on the environment and human health, geochemical surveys are
39 increasingly being used in investigations to determine land quality and contamination (Salminen and Tarvainen
40 1997). A fundamental aim of geochemical surveys is often to define PTE concentrations that provide relevant
41 thresholds within spatial element distributions. Originally used as a prospecting tool (Sinclair 1974), threshold
42 values are increasingly employed as a method by which to discriminate “contaminated land” (Rodrigues et al.
43 2009). In this respect, the threshold is often set to differentiate between concentrations of the element that
44 naturally occur in the soil and concentrations that result from diffuse anthropogenic sources, or even to
45 differentiate between diffuse and point anthropogenic sources. However, there remains little consensus on what
46 the aim of calculating these values is, and how values should be calculated.

47 Many terms are used in the literature to describe concentrations of elements in the soil, often with conflicting or
48 overlapping definitions. In order to distinguish between geogenic and anthropogenic contamination Matschullat
49 et al. (2000) define the geochemical background as a “relative measure to distinguish between natural element
50 or compound concentrations and anthropogenically influenced concentrations”, which is similar to Hawkes and

51 Webbs' (1962) definition of background as “the normal abundance of an element in barren earth material”.
52 However British Standards (BS19258) state that the background content of a substance in soil results from both
53 geogenic sources and diffuse source inputs and that the background values should be a “statistical characteristic
54 of the background content” (British Standards 2011) which is therefore similar to Salminen and Tarvainen's
55 (1997) definition of a geochemical baseline as an element's average concentration in the Earth's crust regardless
56 of the source. A discussion by Reimann and Garrett (2005) examines in detail the various terms used to
57 describe these values, including background, threshold, natural background and baseline and the many
58 definitions that exist for these terms.

59 Salminen and Tarvainen (1997) suggest that baseline values are of “essential importance in environmental
60 legislation” to define limits of PTEs in contaminated land and recent changes in contaminated land legislation in
61 England and Wales have recognised this by stating that “normal levels of contaminants in soil should not be
62 considered to cause land to qualify as contaminated land, unless there is a particular reason to consider
63 otherwise” (Defra 2012). Similarly, a recent Government Decree in Finland on the Assessment of Soil
64 Contamination and Remediation Needs (Ministry of the Environment Finland 2007) requires the input of
65 geochemical baseline concentrations in Finnish soils during the assessment process. An investigation of arsenic
66 concentrations at a site of specific interest in southern Italy, led to the development of a statistical methodology
67 for determining the difference between natural and anthropogenic concentrations of metals and metalloids in
68 soils (APAT-ISS 2006). This methodology was retained by the Italian government as it was considered to be
69 not only applicable to this particular site, but also to all other sites of national interest where the same problem
70 was occurring.

71 Within the research described in this paper, the term TTV is used to refer to a value which gives a characteristic
72 concentration for an element within a defined geographical area known as a domain. Previous work by Ander et
73 al (2013a) and Ander et al (2013b) has seen the development of a methodology to determine NBCs of
74 contaminants in English soils, supporting the recent changes to the statutory guidance (Defra 2012). Within this
75 methodology, a domain was defined as an area in which a readily distinguishable factor could be identified as
76 controlling the concentration of the element. This approach has been maintained within this investigation,
77 remembering that these areas need to be defined on an element by element basis using initial assessments of the
78 distribution of the elements within the study area. It is important that the methods used to identify domains take
79 all the relevant factors affecting soil element concentrations into account; geogenic factors, diffuse source
80 anthropogenic inputs and point source contamination. In order to be most relevant and useful for environmental
81 legislation, the typical threshold values calculated should define concentrations of PTEs that are typical of the
82 threshold between geogenic and diffuse anthropogenic source contributions to soil and concentrations that are
83 associated with point sources. If point sources of anthropogenic contamination can be identified, they can be
84 more readily assessed to determine if they pose any risk to the surrounding environment. A number of different
85 industries can make use of definite concentrations which achieve this differentiation. In particular,
86 contaminated land professionals can more easily determine sites that possibly require further investigations
87 because the TTVs are exceeded. In addition, the agricultural industry may be interested in depleted
88 concentrations of these elements where they are also considered to be essential to animal and plant life e.g.
89 copper.

90 Commonly investigated PTEs include arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr),
91 iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) (Ajmone-Marsan
92 et al. 2008; Kelepertsis et al. 2006; Palmer et al. 2013; Paterson et al. 2003; Ramos-Miras et al. 2011).
93 Concentrations of PTEs are assessed for a variety of reasons; As, Hg and Pb are examples of elements
94 commonly investigated in urban areas (Chirenje et al. 2003, 2004; Rodrigues et al. 2006; Wong et al. 2006),
95 while Cr, Ni, V and Zn have previously been investigated as geogenically controlled PTEs within Northern
96 Ireland (Cox et al. 2013; Palmer et al. 2013). Previous research has identified concentrations of As, Cd, Cr, Cu,
97 Ni, Pb, V and Zn in Northern Irish soils that exceed relevant Generic Assessment Criteria (GAC)/Soil Guideline
98 Values (SGVs) (Barsby et al. 2012; Martin et al. 2009a; Martin et al. 2009b; Nathanail et al. 2009). Six PTEs
99 have been selected for investigation in this research; As, Cr, Cu, Ni, Pb and V. These elements are expected to
100 be governed by a mixture of geogenic and anthropogenic sources, a necessary factor in order to complete the
101 aims of this study.

102 The rationale behind this research is to investigate soil geochemical data for Northern Irish soils by 1) using a
103 variety of techniques to identify the principal controls on the spatial variation of the PTEs and determining
104 which technique is most appropriate for the available data set; 2) identifying domains i.e. areas of elevated and
105 reduced PTE concentrations; 3) using previously developed statistical methodologies to calculate TTVs of PTEs
106 within the aforementioned areas and 4) critically comparing the values calculated to determine which statistical
107 method is most appropriate for use in differentiating between diffuse and point source element concentrations.
108 It is worth noting that the TTVs do not assess risk, but instead provide an indication of PTE concentrations that
109 are typical at a site.

110 **4 Materials and Methods**

111 **4.1 Study area**

112 Northern Ireland is part of the United Kingdom which sits in the north east of the island of Ireland (Figure 1a)
113 and is home to over 1.8 million people. Despite being less than 14,000 km² in area, the bedrock in Northern
114 Ireland (Figure 1b) ranges from Mesoproterozoic to Palaeogene in age and as a result is said to present an
115 “opportunity to study an almost unparalleled variety of geology in such a small area” (Mitchell 2004). The
116 bedrock is often simplified into a series of Caledonian terranes and part of a Palaeogene igneous province with
117 distinct geological characteristics. The psammites in the northwest of Northern Ireland are of Neoproterozoic
118 age. The south eastern terrane is Lower Palaeozoic in age and also contains younger igneous intrusions. These
119 Palaeogene igneous intrusions consist of three central complexes; the Mourne Mountains, Slieve Gullion and
120 Carlingford. The southwest comprises of a mixture of sandstones, mudstones and limestones, which are mainly
121 Upper Palaeozoic in age with a distinct Lower Palaeozoic inlier. The north east is dominated by a large area of
122 extrusive Palaeogene basalts. In terms of superficial geology, peatlands cover 12% of land area (Davies and
123 Walker 2013) as shown on Figure 1c. Two main urban areas exist within the country; Belfast and Londonderry,
124 with populations of approximately 280,000 and 108,000 respectively (NI Statistics & Research Agency 2013),
125 with other smaller urban centres including towns and villages (Figure 1c).

126 4.2 Soil geochemical data

127 The Tellus project, managed by the Geological Survey of Northern Ireland (GSNI), comprised both geophysical
128 and geochemical surveys. The geochemical survey saw the collection of nearly 30,000 soil, stream-sediment
129 and stream-water samples across Northern Ireland between 2004 and 2006. Urban and regional soil samples
130 were collected at densities of 4 per km² and 1 per 2 km² respectively. Two depths were sampled at each
131 location; a shallow sample taken between 5 and 20 cm and a deeper sample taken between 35 and 50cm. The
132 sample taken at each location was a composite of auger flights collected at the four corners and the centre of a
133 20 by 20m square. Samples were air-dried at the field-base before transport to the sample store where they were
134 oven dried at 30°C for approximately two to three days. The shallow samples were shipped to British
135 Geological Survey (BGS) laboratories in Keyworth, Nottingham for preparation and analysis via x-ray
136 fluorescence (XRF). Sample preparation entailed sieving to a <2mm fraction, from which a sub-sample was
137 produced for milling and pressed pellet production.

138 A number of quality control methods were employed during the XRF analysis. Two duplicate and two replicate
139 samples were analysed per batch of 100 samples. Three secondary reference materials that were collected in
140 Northern Ireland specifically for the Tellus survey, and one material from BGS's Geochemical Baselines
141 Survey of the Environment (G-BASE) program, were routinely analysed at a rate of two insertions per batch.
142 Certified reference materials were also analysed before and after each batch. Further details of quality control
143 methods are provided by Smyth (2007).

144 4.3 Domain Identification

145 **Fig. 1** Maps showing **a** location **b** simplified bedrock geology and **c** areas of peat substrate (superficial geology),
146 rural and urban areas across Northern Ireland (Bedrock and superficial geology derived from data provided by
147 GSNI (Crown Copyright))

148 4.3.1 Known controls over PTEs

149 In order to calculate TTVs, domains were identified for each element. Domains were selected based on
150 knowledge of the factors shown in Figure 1 which were identified as the main controls over element
151 concentrations in soils.

152 Studies have shown that the majority of glacial till in Northern Ireland is found within only a few kilometres of
153 its origin suggesting that soils usually reflect the character of the underlying geology (Cruickshank 1997; Jordan
154 2001). Therefore bedrock geology is expected to provide a strong control over element concentrations in soil.
155 Geochemically, it is likely that the extrusive and intrusive (in particular, the Antrim Basalt formation and
156 Mourne Mountain Complex) igneous rocks of Northern Ireland will be of most interest, as previous studies
157 have shown that they contain reduced and elevated concentrations of a number of elements (Barrat and Nesbitt
158 1996; Green et al. 2010; Hill et al. 2001; Smith and McAlister 1995; Smyth 2007). Previous studies have
159 demonstrated that soils from the basalt area are more homogeneous in their geochemical content than soils from
160 areas of other rock types, suggesting that the basalts are acting as the soil parent material and the main control
161 over geochemistry in that area (Zhang et al. 2007). A simplified representation of bedrock geology in Northern
162 Ireland derived from GSNI's 1:250000 bedrock geology map is shown in Figure 1b, grouping bedrock types of
163 similar composition and age.

164 Existing literature suggests that areas of peat substrate within Northern Ireland have a control over the
165 distribution of a number of elements (Palmer et al. 2013). Peat bogs that are fed solely by atmospheric
166 deposition (ombrotrophic), can be used as archives of many types of atmospheric constituents (Shotyk 1996),
167 including contamination in the form of PTEs. Topographically elevated areas of peat are more likely to be
168 affected in this way, as increased precipitation is usually associated with elevation (Goodale et al. 1998). Areas
169 of peat were defined using data derived from the GSNI's 1:250000 superficial geology map and are shown on
170 Figure 1c.

171 Urban and rural areas were defined using a revised version of the Corine Land Cover 2006 seamless vector data
172 (European Environment Agency 2012). This approach is different to that taken in the NBC methodology, where
173 the Generalised Land Use Database Statistics for England 2005 (Communities and Local Government 2007)
174 were used. The Corine Land Cover data set covers all of Europe and defines 44 land use classes based on the
175 interpretation of satellite images (European Environment Agency 2012). This has been simplified in Figure 1c
176 to show urban and rural areas in Northern Ireland. The majority of the land use classes were easily defined as
177 either rural or urban, with a few others defined on a site by site basis.

178 In the NBC methodology, metalliferous mineralisation and mining maps, were used to define mineralisation
179 domains throughout the study (Ander et al. 2011). As this information is not available for Northern Ireland, a
180 different approach was taken in using mineral occurrence locations provided by GSNI, alongside relevant
181 literature (Lusty et al. 2009, 2012; Parnell et al. 2000) to aid in mineralised domain identification.

182 **4.3.2 Method used for domain identification**

183 It is important that the methods used to define domains be robust to non-normality and the presence of outliers
184 that are common in geochemical data. Three methods to aid in the domain identification process were
185 compared in this study; k-means cluster analysis (Ander et al. 2011), boxplot mapping (Reimann et al. 2008)
186 and Empirical Cumulative Distribution Function (ECDF) mapping (Reimann 2005). All statistical analysis of
187 data was completed in the R statistical software package (R Core Team 2013), and all geographical analysis and
188 images were completed using ArcMap 10.0 (ESRI 2009).

189 The k-means cluster method (Figure 2a) was used to define domains by Ander et al. (2011) in the NBC
190 methodology. As k-means cluster analysis is of the partitional variety, the number of clusters must be assigned
191 to the technique at the outset (Jain et al. 1999). The most visually acceptable number of clusters, based on an
192 antecedent visual assessment (Templ et al. 2008), was input into the technique and the data were partitioned into
193 the selected number of clusters by minimising the "average of the squared distances between the observations
194 and their cluster centres" (Reimann et al. 2008). The algorithm constructed by Hartigan and Wong (1979),
195 generally considered to be the most efficient (Ander et al. 2011), was used as the default setting in the R
196 software package (R Core Team 2013). Each data point was classified into a cluster by the technique, allowing
197 the creation of a map of the clusters across Northern Ireland.

198 Tukey boxplots of the log-transformed data (Figure 2b) were also used to define the classes for producing maps
199 of the data distribution. Assumptions regarding normal distribution of the data appear in the boxplot
200 construction when the whisker values are calculated, as their calculation (box extended by 1.5 times the length

201 of the box in both directions) assumes data symmetry (Reimann et al. 2008). Log transformations were applied
202 as geochemical data are often strongly right-skewed, and the log-transformation helps the data distribution to
203 approach symmetry, allowing a better visual demonstration of the data when mapped (Reimann et al. 2008).
204 The boxplot was used to split the element concentrations into five classes for mapping; lower extreme values to
205 lower whisker, lower whisker to lower hinge, lower hinge to upper hinge i.e. the box, upper hinge to upper
206 whisker and upper whisker to upper extreme values.

207 The third method applied to map the distribution of the elements used classes based on the empirical cumulative
208 distribution function (ECDF) (Sinclair 1974). The ECDF graph is a discrete step function which jumps by $1/n$
209 at each of the n data points. As shown in Figure 2c, the ECDF plots have been constructed using the log-
210 transformed concentrations of the element, in this case nickel, in order to make breaks in the distribution more
211 obvious. Breaks in the distribution are demonstrated through changes of gradient in the graph, and are likely to
212 be caused by the presence of different sub-populations within the data set, with different underlying factors
213 controlling the concentrations of elements in these populations (Díez et al. 2007; Reimann et al. 2008; Reimann
214 et al. 2005). Therefore breaks in the distribution can be used to distinguish mapping class boundaries.

215 **4.3.3 Domain Corroboration**

216 In order to corroborate the results of the domain identification process, a geostatistical approach involving the
217 construction of semi-variograms was used to ensure that the controlling factors over element concentrations in
218 soil were correctly identified. The geostatistics were generated using ArcMap 10.0 (ESRI 2009). A semi-
219 variogram is based on the Theory of Regionalised Variables (Matheron 1965), which permits interpolation of
220 values on a surface by assuming that data points closest to each other spatially will have a greater influence over
221 estimated values than would data points further away from each other. Several important pieces of information
222 can be identified from the semi-variogram:

- 223 • Spatial variation at a finer scale than the sample spacing (Deutsch and Journel 1998) and measurement error
224 (Journel and Huijbregts 1978) is represented by the nugget (C_0). Such small scale sources of variance can
225 be an indication that sampling or analytical error is present or, that micro-scale processes are governing
226 geochemistry to a greater degree than was detected by sampling resolutions.
- 227 • The spatially correlated variation is represented by the structured component (C_I) (Lloyd 2007).
- 228 • The sill (C_s), where the semi-variogram levels off, is the distance at which pairs of data points are no longer
229 spatially dependent upon each other.
- 230 • The nugget:sill ratio (C_0/C_s) gives the proportion of random to spatially structured variation at the scale
231 being investigated.
- 232 • Ranges of influence (a) can be statistically inferred from the lag distance at which the sill is reached
233 (McKinley et al. 2004), permitting interpretation of specific environmental factors that may be influencing
234 the mapped element of interest.
- 235 • Depending upon the nature of fitting measured values to a semi-variogram, multiple spatial structures can
236 be identified. This is of particular interest where investigations into multiple environmental factors that
237 may be controlling the element of interest are required.

- 238 • An apparent lack of spatial structure also provides important information, such as giving an indication about
239 the suitability of analytical or sampling methods in accurately detecting total element concentrations which
240 are thoroughly representative of a particular study area.

241 **4.4 Calculation of Typical Threshold Values**

242 In response to the legislative requirements discussed in the introduction, different authors have derived methods
243 by which “background” values can be calculated. The NBC methodology (Ander et al. 2013a; Ander et al.
244 2013b) aims to provide a mechanism for revised legislation that differentiates between levels of contamination
245 from geogenic and diffuse sources and those from point source contamination. In order to take account of
246 spatial variability, domains were defined for each element by comparing the results of a k-means cluster analysis
247 to a soil parent material model, land use classifications and mineralisation and mining geographical mapping.
248 Within the methodology, it is recommended that the domains are based on at least 30 values. The NBC was
249 then calculated for each domain using a statistical methodology that (1) assesses the skewness of the
250 geochemical data by observing a histogram and calculating the skewness and octile skewness of the distribution.
251 Based on the results of that assessment, the method (2) performs either a log transformation or a box-cox
252 transformation on the data if necessary and then (3) computes percentiles using either parametric, robust or
253 empirical methods depending on the results of the transformation applied. The NBC is then taken to be the
254 upper 95% confidence limit (UCL) of the 95th percentile. A detailed explanation of how the methodology was
255 constructed and how it should be applied is given in Cave et al. (2012).

256 Jarva et al. (2010) have developed a methodology to allow the calculation of “baselines” in Finland, which in
257 this instance refer to both the “natural geological background concentrations and the diffuse anthropogenic input
258 of substances at regional scale”. As with the above NBC calculations, Finland was divided into a number of
259 geochemical provinces. A key difference between the two methodologies is the consideration of soil type, with
260 baseline values calculated by soil type within geochemical provinces. The ULBL is based on the upper limit of
261 the upper whisker line of the box and whisker plot. A box and whisker plot identifies any values which fall
262 above the upper whisker line as outliers, which may “represent natural concentrations of an element at the
263 sampling site” (Jarva et al. 2010) but are probably not typical of the geochemical province as a whole.
264 Logarithmic transformed data were not used to plot the box and whisker plots, as the untransformed data led to
265 the highest amount of outliers and therefore was felt to give a more conservative value.

266 A key difference between the NBC and ULBL methodology is the determination of what a “conservative” value
267 is considered to be. The ULBL methodology aims to identify the maximum number of outliers, therefore
268 generating a lower concentration for the ULBL and the possibility that larger areas of land will be identified as
269 exceeding the ULBL. The NBC methodology supports the English contaminated land regime, which aims to
270 identify sites where “if nothing is done, there is a significant possibility of significant harm such as death,
271 disease or serious injury” (Ander et al. 2013a). Therefore, by taking the upper 95% confidence limit of the 95th
272 percentile, the aim seems to be to identify the highest risk sites in order to prioritise further investigation and
273 management of these sites.

274 Within this research, both the NBC and the ULBL methodologies were applied to the shallow XRF data
275 available for all of Northern Ireland. NBC calculations were carried out using the R scripts prepared by Cave et

276 al. (2012) while ULBL calculations were undertaken in R using scripts prepared by the authors. Data from
277 shallow soils were selected for analysis so both anthropogenic and geogenic influences on the element
278 concentrations could be determined. XRF was selected as the most appropriate analytical method as it is said to
279 give total results (Ander et al. 2013a).

280 **5 Results and Discussion**

281 **5.1 Comparison of domain identification methods**

282 **Fig. 2** Domain identification methods completed for Ni concentrations in the shallow soils of Northern Ireland
283 analysed by XRF; **a** completed by a k-means cluster analysis, **b** classes defined by boxplot of log transformed
284 concentrations as shown, and **c** classes defined by ECDF of log transformed concentrations as shown, with
285 inverse distance weighting used to map the results (output cell size of 250m, power of two and a fixed search
286 radius of 1500m)

287 Figure 2 gives a comparison of the three methods used to map the distribution of elements and therefore identify
288 domains using Ni as an example. The k-means map (Figure 2a) highlights only the basalts which overlie
289 northeast Northern Ireland. Both the boxplot map (Figure 2b) and the ECDF map (Figure 2c) show areas of
290 elevated and reduced concentrations. Both show elevated concentrations over the basalts, with the boxplot
291 method mapping the boundary of the basalts most effectively. Reduced concentrations are more easily
292 identified through the ECDF map, and are obviously correlated to the Mourne Mountain complex of south
293 eastern Northern Ireland. By comparing this image with areas of peat substrate (Figure 1c), an association
294 between areas of peat and reduced concentrations was also identified.

295 The k-means technique, used in the NBC methodology, produces useful results in the determination of elevated
296 domains; however, it is more commonly used to compare a number of variables and estimate which variables
297 are similar and dissimilar to each other (Romesburg 2004) and the inability of the method to determine domains
298 of reduced concentrations does limit its applicability in practice. In the case of Ni (Figure 2a), the initial
299 assessment demonstrated that 3 clusters would be most appropriate, however a certain amount of prior
300 knowledge regarding the controls over element concentrations is expected in this assessment.

301 Boxplots allow identification of both elevated and reduced concentrations of the elements, with different
302 sections of the distribution related to separate parts of the boxplot. However, the splits in the distribution are
303 still set at arbitrary values within the dataset, meaning actual controlling factors over the element concentrations
304 could be missed.

305 The ECDF method was superior in terms of spatially identifying both elevated and depleted concentrations of
306 elements as it retains a great deal of information about the distribution of the element in the mapped output. It
307 clearly delineates areas of both elevated and depleted concentrations allowing controls over the PTE
308 concentrations to be determined. However, the method does require a level of interpretation as the individual
309 inspecting the graphs decides where the gradient changes occur. This introduces potential for bias as a level of
310 knowledge of the modelled domains could influence the results. It is however important to remember that the
311 outputs from this process are maps, and therefore even though different individuals will generally produce

312 different results when splitting the ECDF plot by gradient, the same general trends will be obtained. Of each of
313 the 3 methods, the ECDF methodology provides the greatest detail and opens the methodology to applications
314 other than the identification of land contamination.

315 **5.2 PTE Domains**

316 Within this investigation, the maps produced using the ECDF technique were compared to the main factors
317 known to control the distribution of elements across Northern Ireland in order to identify domains. The majority
318 of domains were easily identified and the results correlated well with existing literature describing the
319 distribution of elements in Northern Ireland (Young 2013 In Press).

320 **Fig. 3** Domains identified for **a** arsenic **b** chromium, copper, nickel and vanadium and **c** lead based on the
321 ECDF maps produced

322 Finalised domains are shown in Figure 3 for the elements under investigation: arsenic, chromium, copper, lead,
323 nickel and vanadium. Similar controlling factors were identified for Cr, Cu, Ni and V, with elevated
324 concentrations of these elements observed over areas of basalt bedrock geology creating a basalt domain.
325 Reduced concentrations are seen in the Mourne Mountains Complex, associated with naturally occurring low
326 concentrations of these elements in granites, creating the Mournes domain. Cr, Cu, Ni and V are known to be
327 found at elevated concentrations in the Antrim Basalts (Barrat and Nesbitt 1996; Hill et al. 2001; Smith and
328 McAlister 1995) and at reduced concentrations in granites (Wedepohl et al. 1978).

329 Concentrations of Cr, Cu, Ni and V were generally depleted in peat samples overlying all bedrock geologies
330 except the basalts. Overlying the basalt formation, some areas of peat showed depleted Cr, Cu, Ni and V
331 concentrations, while others (generally at lower topographical elevation) showed higher concentrations of each
332 element in line with the basalt domain. This distribution is probably explained by the type of peatland and the
333 land use activities taking place on it (Joint Nature Conservation Committee 2011). Lowland peats appear to
334 have less of a control over element concentrations, meaning the basalts remain as the primary controlling factor
335 and higher concentrations are observed. Upland peats, however, appear to exert a greater control with reduced
336 concentrations being observed. It is also possible that the differing land use on the peat could be affecting its
337 ability to function efficiently, however this subject would require further exploration. This distribution of Cr,
338 Cu, Ni and V was also observed by Young (2013 In Press) and therefore a peat domain was selected which
339 incorporated all areas of peat that do not overlie the basalts, along with areas of peat overlying the basalts that
340 are associated with reduced concentrations of these elements. Depletion of Cr, Cu, Ni and V in this domain may
341 reflect biogeochemical cycling of PTEs within the peats (Novak et al. 2011) but further research would be
342 required to confirm this.

343 All the domains shown for lead are associated with elevated concentrations of the element. The Mourne
344 Mountains Complex show elevated concentrations of lead (Mournes domain), fitting with known elevations of
345 lead in granites (Krauskopf 1979). Elevated concentrations of lead were also associated with urban areas across
346 Northern Ireland (urban domain). Pb is well known for its correlation with anthropogenic activity, and therefore
347 urban centres (Albanese et al. 2011; Locutura and Bel-lan 2011). Identified sources of lead in urban
348 environments include historical use of leaded fuel and lead in paint (Chirenje et al. 2004; Mielke and Zahran

2012; Mielke et al. 2011). A strong correlation was observed between areas of elevated topography with a covering of peat and elevated lead concentrations, as previously described by Young (2013 In Press). This is not surprising, as peat soils are well known for acting as historical records of atmospheric pollution, with higher heavy metal concentrations common in upper peat layers (Givelet et al. 2004; De Vleeschouwer et al. 2007). Chronologies of Pb deposition have been completed for a raised bog in Ireland (Coggins et al. 2006), showing elevated concentrations within the depth range (5-20cm) of the shallow Tellus samples. These topographically elevated areas of peat were separated out from the full peat dataset to form lead's peat domain.

Fig. 4 Mineral occurrences provided by GSNI shown for **a** lead on a map showing lead's mineralisation domain and **b** zinc, lead, gold and copper on a map showing arsenic's mineralisation domains (Crown Copyright)

Finally, a mineralisation domain was also identified for lead. This area was defined using the elevated concentrations of lead as determined on the ECDF map and the extent of the domain was corroborated by the strong correlation between lead mineral occurrences as provided by GSNI, shown in Figure 4a, areas of high to very high prospectivity potential (Lusty et al. 2012) and the mineralised domain identified for Pb. It is worth noting that lead mineral occurrences were identified by GSNI in the south east of Northern Ireland (Figure 4a), however as significantly elevated Pb concentrations were not recorded in that area a mineralised domain was not created in this region. In contrast, the area of lead mineralisation identified in the north west of Northern Ireland was in an area of elevated Pb concentrations. However, closer inspection of the spatial distribution of areas of elevated concentrations and comparison with peat maps showed that although mineralisation may be contributing to the elevated concentrations, their spatial distribution suggests that peat has a controlling role in accumulating this element, probably from atmospheric deposition.

The domains for arsenic were more difficult to define as there was greater uncertainty regarding the factors controlling the distribution of this element. The Shanmullagh formation, consisting of early Devonian age sandstone and mudstone (Mitchell 2004) contained slightly elevated arsenic concentrations, creating the Shanmullagh domain. Two other areas, thought to be associated with mineralisation, were also shown to contain elevated concentrations. These two mineralisation domains were defined in the same manner as the lead mineralisation domain, using the ECDF map, and were named mineralisation 1 and 2. As there are no shown arsenic occurrences on the mineral occurrences information provided by GSNI, a different approach was used to corroborate the extent of these areas. Arsenic is well known as a pathfinder for gold, and is therefore used in prospectivity investigations along with silver, gold, copper, lead, zinc, bismuth and barium (Lusty et al. 2009). A strong correlation is again shown between the mineralised zones identified in this study and mineral occurrences of Ag, Cu, Pb and Zn (Figure 4b), the only mineral occurrences from the previous list that were available from GSNI. The prospectivity for gold within all the identified As mineralised domains is again shown to be high (Lusty et al. 2009, 2012). An interesting, and possibly unexpected finding is the lack of an urban domain for arsenic. However, this was also the case in the calculation of NBCs for England (Ander et al. 2013a).

5.2.1 Domain Corroboration

Table 1 Experimental semivariogram modelled parameters for Ni, Cr, V, As, Cu and Pb concentrations as measured by XRF in shallow soils of Northern Ireland where C_0 = nugget effect, C_1 and C_2 = structured

387 component, a_1 and a_2 = ranges of influence, Total C_x = sill and C_0 /Total C_x = proportion of variance accounted
388 for by C_0

389 The results of the geostatistical approach employed as corroboration are given in Table 1 for all the PTEs
390 investigated. These show that the extent of Cr, Cu, Ni and V distributions in Northern Ireland are strongly
391 controlled by the presence of basalts in the northeast of the region, with ranges (a) not exceeding the largest
392 spatial extent of this geologic formation of approximately 90 kilometres (Figure 1b). Based on variography and
393 source domain identification, elevated concentrations of these four trace elements in the region are attributable
394 to geogenic sources on a spatial scale that exceeds other potential influences over the distribution of this
395 element. However, approximately 13-35% of total variances in Cr, Cu, Ni and V spatial distributions are
396 accounted for by the nugget variance (C_0) suggesting such proportions of variance may be accounted for by
397 smaller scale processes not detected within the soil sampling resolution of the Tellus Survey (Table 1). Arsenic,
398 by comparison, is controlled by a spatial function covering a smaller spatial extent than elements associated with
399 the basalts, with a nugget effect accounting for approximately half of all variance in spatial distribution (48.1%).
400 Lead exhibits the shortest range spatial function, characteristic of trace elements whose distributions are heavily
401 influenced by small scale processes such as anthropogenic activity in urban areas. This trend is also supported
402 by the large nugget effect for this element.

403 On the whole, these results confirm the main controlling factors identified for the PTEs investigated, especially
404 the identification of a basalt domain for Cr, Cu, Ni and V. While the semi-variogram is very useful for
405 identifying spatial controls over elevated element concentrations, reduced domain concentrations cannot be
406 identified using this method.

407 5.3 Typical Threshold Values

408 5.3.1 Normal Background Concentrations

409 In order to assess what is a typical concentration of elements in Northern Irish soils, both the NBC statistical
410 methodology developed by Cave et al. (2012), and the ULBL statistical methodology (Jarva et al. 2010) were
411 applied to data within the defined domains.

412 **Fig. 5** Outputs derived from NBC methodology using R-scripts developed by Cave et al. (2012) for nickel's
413 basalt domain showing **a** histogram and **b** percentiles and relative uncertainty computed using the empirical,
414 gaussian and robust methods

415 Figure 5 gives a visual example of how the NBC methodology was applied. The distribution of Ni within the
416 basalt domain was assessed using a histogram; the values fell within the parameters set by Cave et al. (2012)
417 (Figure 5a) allowing a Gaussian approach to be adopted for calculating percentiles (Figure 5b). A bootstrapping
418 method was applied to calculate the uncertainty surrounding the percentile values (Figure 5b) and the 50th, 75th
419 and 95th percentiles and their associated uncertainty are plotted in Figure 6.

420 **Fig. 6** 50th, 75th and 95th percentiles of each of the elements' domains along with their respective 95% upper and
421 lower confidence limits (vertical lines shown), ULBL concentrations and SGV/GAC where R = residential, A =

422 allotment and C = commercial. Previous SGVs for Pb have been withdrawn; elsewhere SGVs/GACs that are
423 not given are beyond the scale of the graphs

424 Elevation of Cr, Cu, Ni and V in the basalt domain is obvious from Figure 6, while reduced concentrations of
425 these four elements are seen in the Mournes and peat domains. For Cr, the differences between the domains are
426 maintained throughout the 50th, 75th and 95th percentiles. The upper 95% confidence limits of the 95th
427 percentiles for the basalt, Mournes, peat and principal domains are 460, 84, 150 and 290 mg/kg respectively.
428 The Mournes and peat domain contain substantially lower concentrations than those in the principal domain.

429 Similar results are shown for Cu at the 50th and 75th percentiles, but the 95th percentile shows a slight skew in Cu
430 concentrations in the peat domain, with a higher concentration calculated at the 95th percentile in the peats than
431 in the principal domain. The upper 95% confidence limits of the 95th percentile for the basalt, Mournes, peat
432 and principal domains are 130, 41, 68 and 59 mg/kg. The distribution of Cu in the peat domain is heavily right-
433 skewed, with a large presence of outliers. However, a log-transformation of the data brought it within the
434 skewness limits set by Cave et al. (2012) and the gaussian approach was followed for calculating percentiles.
435 Another possible explanation for this distribution is the existence of another controlling factor, other than solely
436 peat substrate, which is contributing to the concentrations of Cu in this domain.

437 A large degree of uncertainty is associated with the values generated for Ni and V in the Mournes domain. For
438 Ni, the 95th percentile was calculated as 24 mg/kg, with the lower and upper confidence limits calculated as 12
439 and 170 mg/kg respectively. The NBC value calculated for the Ni Mournes domain, of 170 mg/kg would
440 therefore appear to be unrealistic, as the maximum value of Ni encountered in this domain was 37 mg/kg. The
441 Mournes domain for Cu, Cr, Ni and V are based on the same 73 data points, making it the smallest domain, but
442 still exceeding the 30 data points recommended in the NBC methodology (Cave et al. 2012). Reasonably large
443 uncertainty is also calculated for vanadium, with the lower and upper confidence limits of the 95th percentile
444 calculated as 39 and 174 mg/kg respectively. In comparison, much less uncertainty is shown for chromium and
445 copper, where the differences between the upper and lower confidence limits for the 95th percentile are 40 and
446 22 mg/kg respectively. It seems that the distributions of these elements in the Mournes domain are responsible
447 for the degree of uncertainty associated with the percentiles calculated. This may be due to the fact that the
448 Mourne granite complex has several fabrics associated with fractionation of basaltic and crustal rock melts
449 (Meighan et al. 1984; Stevenson and Bennett 2011). For V and Ni, a larger occurrence of outliers means that
450 the Box-cox transformation was applied but higher uncertainties were still recorded for the 95th percentiles using
451 this method. Fewer outliers present for Cr and Cu reduced the uncertainty associated with the percentiles,
452 allowing for the calculation of more realistic NBCs.

453 The existence of outliers in vanadium's peat domain saw the application of a log-transformation in order to
454 bring its distribution closer to normal. However, the outliers have still affected the calculation of the 95th
455 percentile (120 mg/kg) and its confidence limits, while the 50th (27 mg/kg) and 75th (49mg/kg) percentiles
456 appear to remain more representative. Nickel's peat domain contained even more outliers, meaning in this case
457 the Box-cox transformation was required to bring the data within the necessary skewness limits (Cave et al.
458 2012). In this instance, the box-cox transformation appears to be more effective in reducing the effect of the

459 outliers, meaning the 50th, 75th and 95th percentiles (7mg/kg, 14mg/kg and 46 mg/kg) seem to give appropriate
460 concentrations when compared to the mapped outputs (Figure 2).

461 For As, elevated concentrations are seen in the two mineralisation domains and the Shanmullagh domain when
462 compared to the principal domain. If the 95th percentile is used as a comparison, the mineralisation 2 domain
463 result is approximately five times greater than the 95th percentile for the principal domain. However, a large
464 degree of uncertainty is associated with the 95th percentiles in the mineralisation 2 domain, as the lower and
465 upper confidence limits range between 56 and 85 mg/kg respectively. The data for this domain were box-cox
466 transformed and theoretical percentiles calculated based on the mean and standard deviation of the data set after
467 an assessment of its distribution. However, the presence of one extreme outlier which lies over 60 mg/kg away
468 from the remainder of the outliers is likely to be causing the extreme skew seen in the calculation of the 95th
469 percentile. For the other three domains; mineralisation1, principal and Shanmullagh, the assessment of the data
470 distribution led to robust percentiles and uncertainties being calculated. Although outliers are also present in
471 these domains, none of them contain outliers as extreme as the one identified for the mineralisation 2 domain.
472 This causes much smaller differences between the upper and lower 95th confidence limits than those identified
473 for the mineralisation 2 domain.

474 For Pb, elevated concentrations are obvious in the urban domain, followed by the mineralisation, Mournes and
475 peat domains. The lowest concentrations of Pb are found in the principal domain. Within the urban domain,
476 reasonably large differences occur between the upper and lower confidence limits, as they range between 240
477 and 300 mg/kg for the 95th percentile. This is to be expected in the urban domain as anthropogenic sources of
478 Pb increase the amount of outliers present in the data set, which in turn increases the uncertainty associated with
479 the percentiles calculated. Although these values of lead are high compared to the principal domain for
480 Northern Ireland, where the 95th percentile ranges between 71 and 77 mg/kg, they are not as high as those found
481 in some other urban areas. Chirenje et al. (2004) reported a 95th percentile of Pb concentrations in Miami, USA,
482 as 453 mg/kg.

483 Figure 6 shows both the strengths and the weaknesses of the NBC methodology. A large presence of outliers
484 within the data set causes issues in the distribution assessment and ultimately in the uncertainty calculations.
485 This stems from the overall distribution of the data, and the effectiveness of the transformation applied and is
486 particularly obvious in the Mournes domain for Ni and V. It is important to note that the NBC methodology is
487 not meant to be used for reduced concentration domains, which the Mournes domains for Ni and V are examples
488 of. However, even for As and Pb where all the domains contain elevated concentrations, the high degree of
489 uncertainty associated with some of the domains causes unrealistic concentrations at the upper 95% confidence
490 limit of the 95th percentile, which is likely to pose difficulties if attempts are made to use NBCs during risk
491 based assessment of contaminated sites rather than just identifying potentially contaminated land as legally
492 defined in the UK as was originally intended. Also, this raises the question as to whether the UCL of the 95th
493 percentile is an effective means of differentiating between diffuse and point contamination from anthropogenic
494 sources.

495 From Figure 6, it is clear that the values shown for the 50th percentile provide a more realistic representation of
496 the comparison between the domains, i.e. for Ni the 50th percentile shows elevated concentrations in the basalt

497 domain (100 mg/kg), widespread concentrations of 27 mg/kg in the principal domain and reduced
498 concentrations of 4.0 and 7.2 mg/kg in the Mournes and peat domains respectively. However, this median value
499 should not be taken as the typical threshold value as it doesn't fulfil the aim of TTVs as whilst median values
500 are a central value for the domain, they don't allow for a differentiation between diffuse and point source
501 anthropogenic contamination. However considering the 50th percentile may be effective within sectors other
502 than the contaminated land sector, as the 50th percentile values can provide useful information on reduced
503 concentration zones, where a possible depletion of essential elements, such as copper, could have consequences
504 for industries such as agriculture.

505 **5.3.2 Upper Limit of Geochemical Baseline Variation**

506 TTVs calculated using the ULBL methodology are also shown on Figure 6. The NBC value (upper confidence
507 interval on the 95th percentile) calculated for copper's peat domain (68 mg/kg) is higher than the value
508 calculated for the principal domain (59 mg/kg) despite outputs from the ECDF domain identification method in
509 Figure 2 suggesting that the peat is an area of depleted copper concentrations. In comparison, the ULBL
510 method provides a more accurate representation of the values expected in reduced domains, with the peat,
511 Mournes and principal domain containing ULBL concentrations of 47, 27 and 76 mg/kg respectively.

512 At elevated concentrations, both the ULBL and NBC methods appear to calculate similar values, with the ULBL
513 method generally calculating slightly lower values for Pb. With regard to the elevated concentrations in the
514 basalt domain for Cr, Cu, Ni and V, the ULBL method calculates concentrations that are at least 20% higher
515 than the respective NBC. This is probably due to the fact that the distribution of these elements in the basalt
516 domain is relatively homogeneous and therefore closer to a normal distribution. When the boxplot is used to
517 identify outlying values for a more normal distribution, fewer values will be identified and so a higher typical
518 threshold value will be set using this method. Although set methods are used in the NBC methodology
519 depending on the distribution of the data, a major strength of the boxplot is its resistance to different types of
520 distribution.

521 **5.3.3 Comparison with relevant criteria**

522 Figure 6 also provides details of SGVs and GACs where they are available for the elements. SGVs and GACs
523 are used to "represent cautious estimates of levels of contaminants in soil at which there is considered to be no
524 risk to health or, at most, a minimal risk to health" (Defra 2012). Therefore they are based on a different
525 approach than that behind the NBC methodology where the aim is to identify sites where "if nothing is done,
526 there is a significant possibility of significant harm" (Ander et al. 2013a). However, a comparison can still be
527 drawn between the values. Figure 6 highlights certain domains for a number of the elements where the typical
528 threshold values are higher than the reference values for residential, and in some cases allotment end uses.
529 Therefore, depending on the size of the exceedance, surpassing these SGV values could suggest a possible risk
530 to human health. For As, the residential SGV of 32 mg/kg (Martin et al. 2009a) is narrowly exceeded in the
531 mineralisation 2 domain and is therefore unlikely to pose significant risks to human health. GAC for Cr-VI are
532 shown on Figure 6 (Nathanail et al. 2009), with exceedance of these concentrations shown in all domains.
533 However, no distinction was drawn between Cr-III and Cr-VI in the Tellus survey. For Ni, the basalt domain
534 shows a significant exceedance of the residential SGV (130 mg/kg) (Martin et al. 2009b) using both the NBC
535 (200 mg/kg) and the ULBL (250 mg/kg) methods, however recent studies by Barsby et al. (2012), Cox et al.

536 (2013) and Palmer et al. (2013) indicate the oral bioaccessibility of Ni in these soils is relatively low (1% to
537 44%). The NBC for Ni in the Mournes domain, whilst high (170 mg/kg), is not a representative value when
538 compared to mapped outputs (Figure 2) and all values for Cu fall within the GAC (Nathanail et al. 2009)
539 making them unlikely to pose significant risks to human health. The NBC for vanadium in the Mournes
540 domain again is unrepresentatively high, with the ULBL method calculating a value of 46 mg/kg which appears
541 to be more representative of mapped outputs. All vanadium results exceed the allotment GAC with values for
542 the basalt, peat and principal domains also exceeding the residential GAC (Nathanail et al. 2009). However
543 bioaccessibility testing reported in Barsby et al. (2012) and Palmer et al. (2013) suggests that only a small
544 fraction of total V in these areas is bioaccessible (8%).

545 **6 Conclusions**

546 In terms of domain identification, the three methods exhibit specific advantages and disadvantages. The k-
547 means technique provided useful results in the determination of elevated domains but its applicability in practice
548 would be limited as it cannot be used to define reduced concentration domains. The boxplot and ECDF methods
549 both allowed identification of elevated and reduced concentration domains. However, the boxplot method splits
550 the distribution at arbitrary values, whereas changes in gradient linked to different data distributions within the
551 overall data set are used to divide the ECDF graph. Splitting the ECDF graph requires a level of interpretation
552 by the individual completing the work, which introduces potential for bias as a level of knowledge of the
553 modelled domains could influence the results. Of the 3 methods, the ECDF methodology provides the greatest
554 amount of detail and opens the methodology to other practical applications rather than just identification of land
555 contamination. However, choice of method may ultimately lie with the decision maker as whatever method
556 they choose may depend on the original goals behind the use of this methodology.

557 The NBC methodology has been developed to sit within a specific legislative framework. By defining the NBC
558 as the upper 95% confidence limit of the 95th percentile it generates a question as to how conservative the
559 approach taken is. In contrast to this, the ULBL methodology generates the maximum number of outliers by
560 using a boxplot of non-transformed data, in order to generate the lowest ULBL concentration. This is
561 demonstrated in Figure 6, where generally the ULBL values calculated are slightly lower than the NBC
562 concentrations. A notable exception to this is for Cr, Cu, Ni and V in the basalts domain, where on all four
563 occasions the ULBL method calculated higher concentrations than the NBC methodology. The largest
564 difference was for Cu, where the ULBL method calculated a concentration 28% higher than the NBC. As well
565 as this, the distribution of the data within each of the domains seems to have a large control over the amount of
566 uncertainty calculated for the relevant percentiles in the NBC method, particularly where a large amount of
567 outliers are present. The transformations applied mainly account for the skewed distributions, but examples
568 remain where the data transformation does not seem to be fully effective (vanadium's peat domain). It is clear
569 from the previous discussion that both methods have their strengths, however in general the ULBL
570 concentrations provide more realistic concentrations for typical threshold values as defined in this study, across
571 the area and elements shown.

572 An interesting investigation, following on from this work, would be to consider the geographic location of each
573 of the outliers identified using the ULBL method. If specific sources of elements could be identified as causing

574 the elevated concentrations of the outlying values, then clarification of how effectively the method discriminates
575 between anthropogenic diffuse and point source concentrations of elements could be gained.

576 One of the primary aims of this research was to investigate soil geochemical data for Northern Ireland, and
577 determine an output in the form of relevant TTVs which define the boundary between geogenic and diffuse
578 anthropogenic source contributions to soil, and those associated with point sources. In this respect, the
579 following is suggested for use;

- 580 • ECDF mapping method for identifying the main controls over PTE concentration distributions and
581 allowing the identification of domains,
- 582 • Calculation of TTVs using the ULBL method (currently employed in Finland) within each of the
583 defined domains.

584 These values will be of interest to a number of parties, as they indicate what a “typical” concentration of an
585 element would be within a defined geographical area. These values should be considered alongside the risk that
586 each of the PTEs pose in these areas, in order to determine potential risk to receptors.

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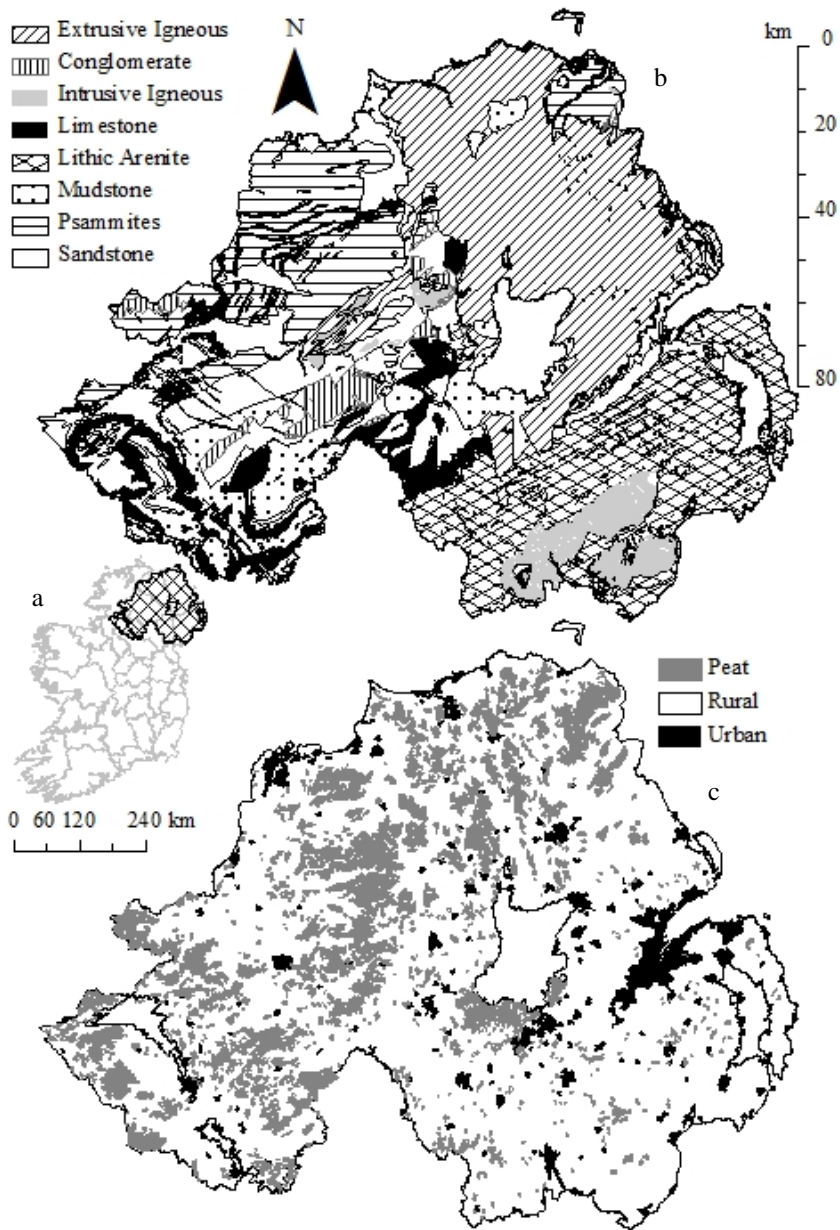
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794 **Figures**

795 **Fig. 1**

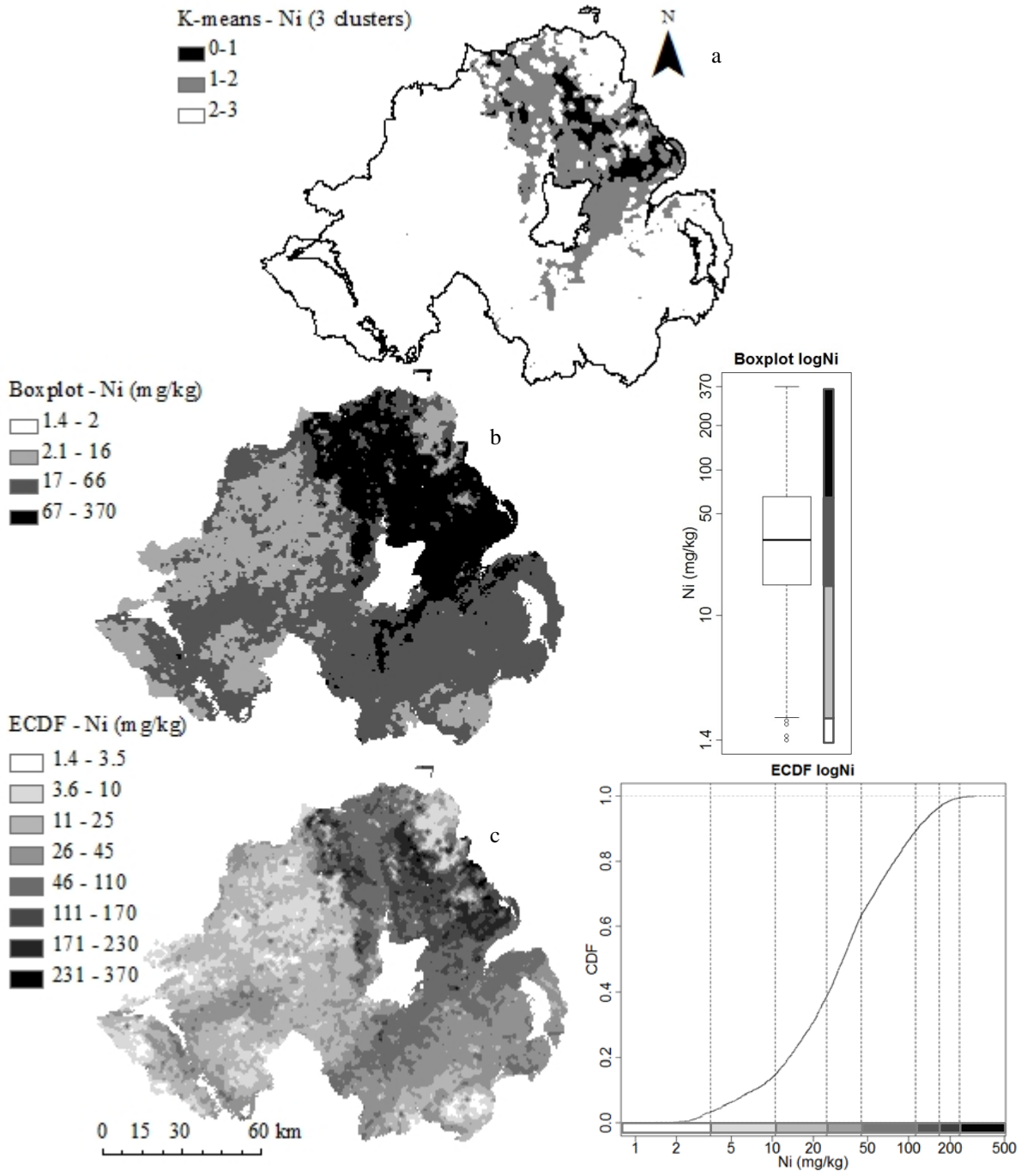


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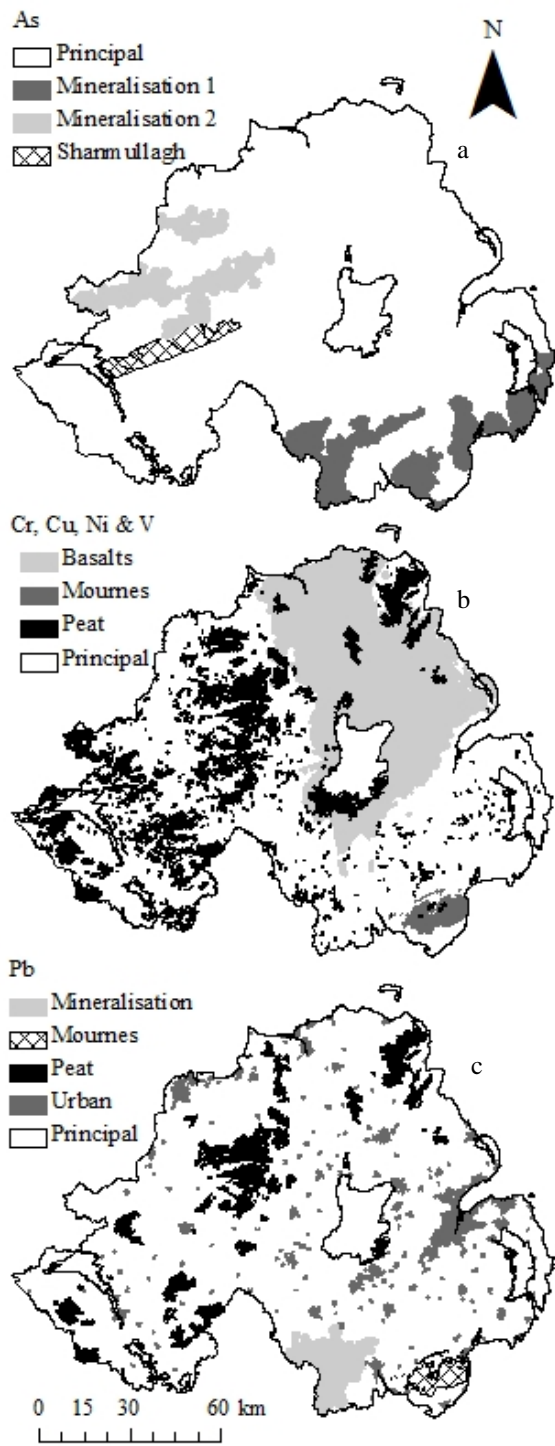
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798 Fig. 2

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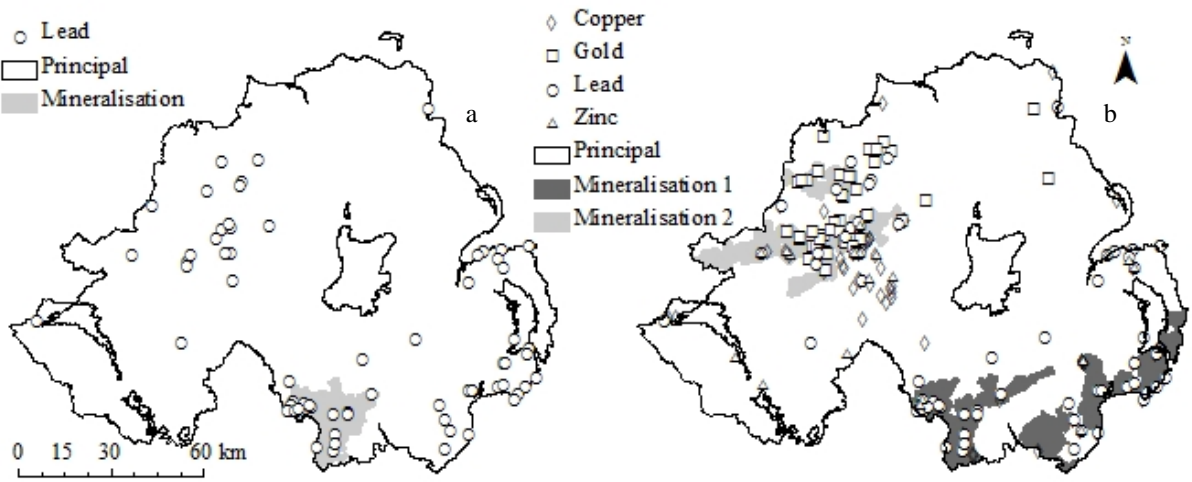
800 Fig. 3



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803 Fig. 4



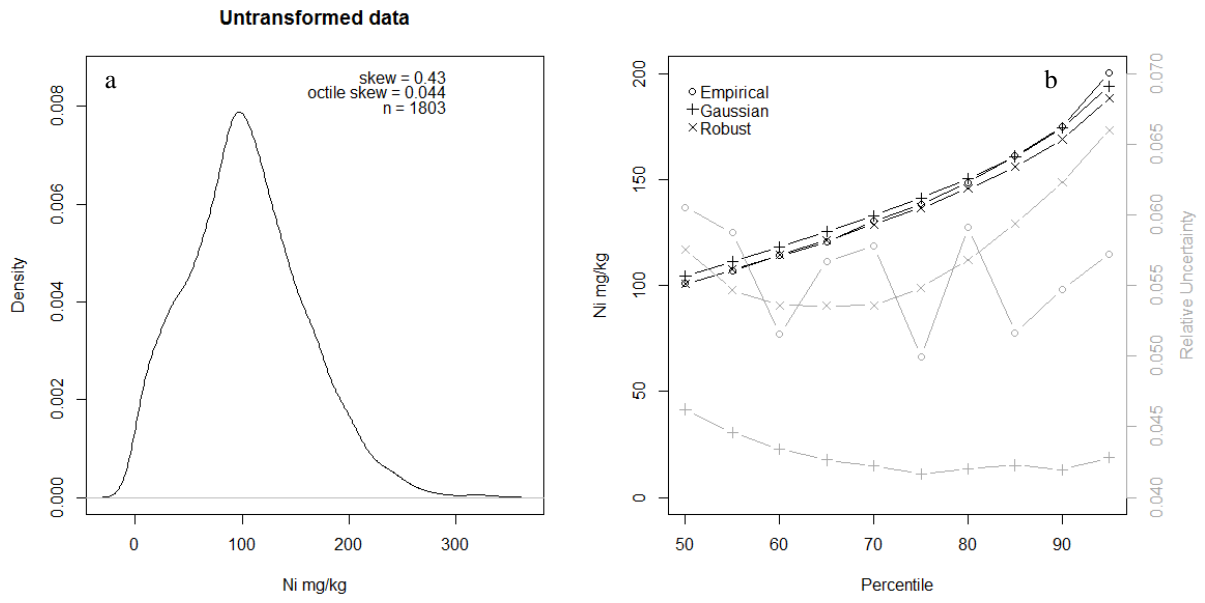
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806 **Table 1**

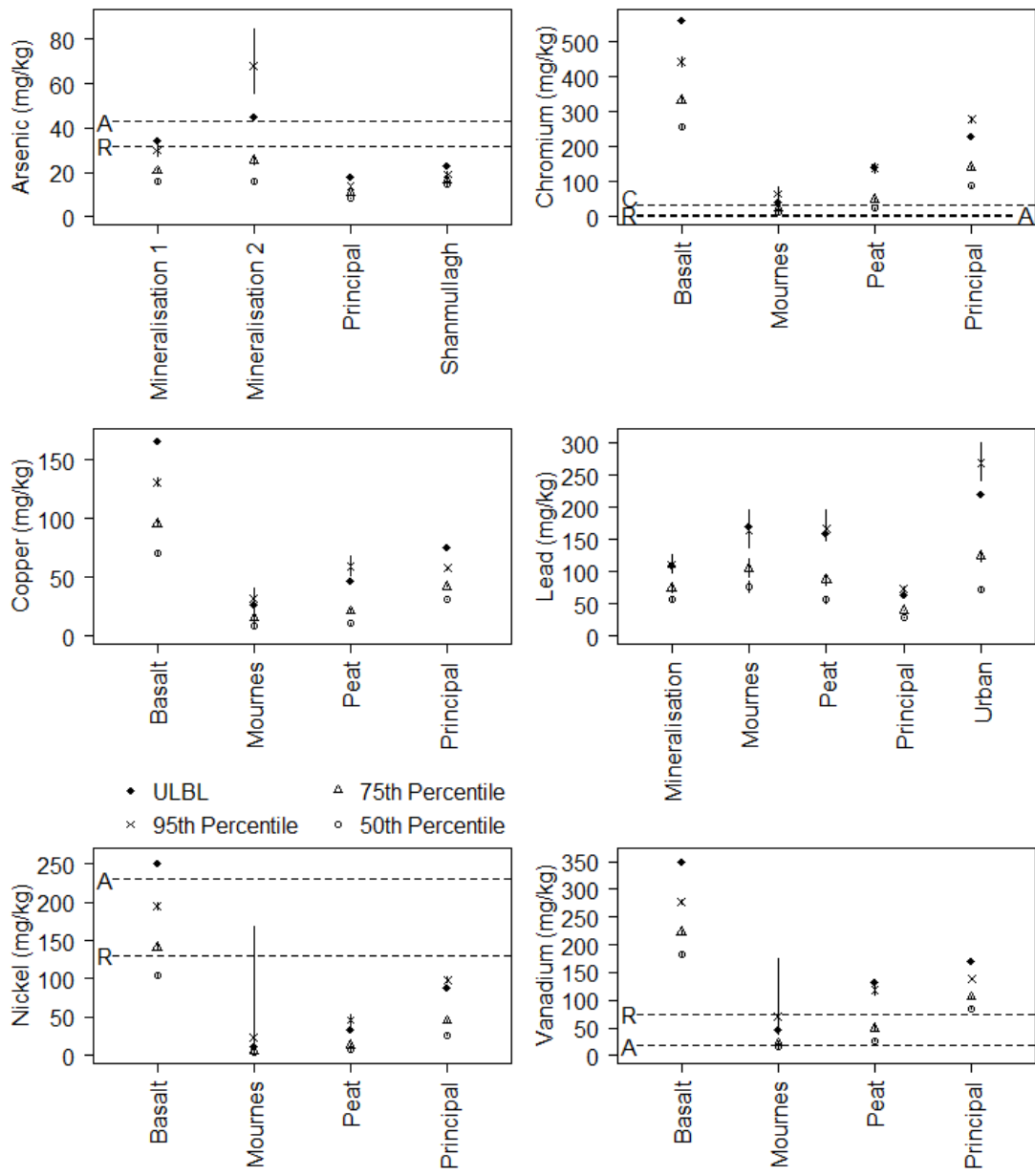
<i>Element</i>	C_0	C_1	C_2	a_1 (m)	a_2 (m)	Total C_x	C_0 /Total C_x (%)
Ni	696.6	207.0	1,948.4	90,093.8	73,881.9	2,852.0	24.4
Cr	2,223.2	11,604.0	3,063.8	86,790.1	7,038.5	16,891.0	13.2
V	697.8	3,014.0	1,257.2	74,193.7	13,816.3	4,969.0	14.0
As	53.5	57.8	--	6,569.9	--	111.3	48.1
Cu	448.4	366.5	462.9	10,882.7	77,709.2	1,277.8	35.1
Pb [†]	55,056.6	12,324.1	--	17,736.0	--	67,380.7	81.7

807 [†](Barsby et al. 2012)



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814 **Supporting Information**

815 **Table S1** 50th, 75th, 95th percentiles and ULBLs for As, Cr, Cu, Pb, Ni and V where n = number of data points in
 816 each domain, LCL = 95% lower confidence limit and UCL = 95% upper confidence limit

Arsenic (mg/kg)	n	50th	50th LCL	50th UCL	75th	75th LCL	75th UCL	95th	95th LCL	95th UCL	ULBL
Mineralisation 1	528	16	16	17	21	20	22	30	28	32	34
Mineralisation 2	351	16	15	17	26	23	28	68	56	85	45
Principal	7015	8.4	8.3	8.5	11	10	11	14	14	14	18
Shanmullagh	133	15	14	15	16	15	17	19	18	21	23

Chromium (mg/kg)	n	50th	50th LCL	50th UCL	75th	75th LCL	75th UCL	95th	95th LCL	95th UCL	ULBL
Basalt	1803	260	250	270	330	320	340	440	430	460	560
Mournes	73	13	11	17	23	19	37	65	43	84	43
Peat	713	24	22	26	50	45	54	140	120	150	140
Principal	5439	89	87	91	140	140	140	280	270	290	230

Copper (mg/kg)	n	50th	50th LCL	50th UCL	75th	75th LCL	75th UCL	95th	95th LCL	95th UCL	ULBL
Basalt	1803	71	69	73	96	93	98	130	130	130	170
Mournes	73	9.3	8.1	11	15	12	18	32	18	41	27
Peat	713	11	9.9	12	22	20	24	59	52	68	47
Principal	5439	32	31	32	42	42	43	58	57	59	76

Lead (mg/kg)	n	50th	50th LCL	50th UCL	75th	75th LCL	75th UCL	95th	95th LCL	95th UCL	ULBL
Mineralisation	208	57	53	60	75	69	81	110	99	130	110
Mournes	75	76	69	85	100	92	120	170	140	200	170
Peat	370	56	50	60	88	80	97	170	150	200	160
Principal	6394	29	28	29	40	39	41	74	71	77	63
Urban	981	73	70	77	130	120	130	270	240	300	220

Nickel (mg/kg)	n	50th	50th LCL	50th UCL	75th	75th LCL	75th UCL	95th	95th LCL	95th UCL	ULBL
Basalt	1803	100	100	110	140	140	140	190	190	200	250
Mournes	73	4.0	3.6	4.5	6.0	5.1	7.4	24	12	170	11
Peat	713	7.2	6.8	7.7	14	12	15	46	40	54	33
Principal	5439	27	26	28	46	45	47	99	96	100	88

Vanadium (mg/kg)	n	50th	50th LCL	50th UCL	75th	75th LCL	75th UCL	95th	95th LCL	95th UCL	ULBL
Basalt	1803	180	180	180	220	220	230	280	270	280	350
Mournes	73	16	14	17	23	19	27	70	39	170	46
Peat	713	27	25	29	49	46	53	120	110	130	130
Principal	5439	84	83	86	110	110	110	140	140	140	170

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