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## The relationship between historical development and potentially toxic element concentrations in urban soils

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1 Title: The relationship between historical development and potentially toxic element  
2 concentrations in urban soils

3

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20 Abstract

21 Increasing urbanisation has a direct impact on soil quality, resulting in elevated  
22 concentrations of potentially toxic elements (PTEs) in soils. This research aims to assess  
23 if soil PTE concentrations can be used as an 'urbanisation tracer' by investigating  
24 geogenic and anthropogenic source contributions and controls, and considering PTE  
25 enrichment across historical urban development zones. The UK cities of Belfast and  
26 Sheffield are chosen as study areas, where available shallow and deep concentrations of  
27 PTEs in soil are compared to identify geogenic and anthropogenic contributions to  
28 PTEs. Cluster analysis and principal component analysis are used to elucidate the main  
29 controls over PTE concentrations. Pollution indices indicate that different periods of  
30 historical development are linked to enrichment of different PTEs. Urban subdomains  
31 are identified and background values calculated using various methodologies and  
32 compared to generic site assessment criteria. Exceedances for a number of the PTEs  
33 considered suggest a potential human health risk could be posed across subdomains of

34 both Belfast and Sheffield. This research suggests that airborne diffuse contamination  
35 from often historical sources such as traffic, domestic combustion and industrial  
36 processes contribute greatly to soil contamination within urban environments. The  
37 relationship between historical development and differing PTEs is a novel finding,  
38 suggesting that PTEs have the potential for use as ‘urbanisation tracers’. The  
39 investigative methodology employed has potential applications for decision makers,  
40 urban planners, regulators and developers of urban areas.

41

42 Capsule

43 Potentially toxic elements have the potential for use as ‘urbanisation tracers’ due to their  
44 association with different historical anthropogenic sources.

45

## 46 **1 Introduction**

47 Globally, more people now live in urban areas than in rural areas; in 2014 54% of the world’s population  
48 lived in urban areas. This has rapidly increased from just 30% in 1950 and is projected to reach 66% by  
49 2050 (UN 2014). The demand put on these geographically limited urban environments will intensify as  
50 population density increases, with a direct impact on soil quality.

51 Sources of potentially toxic elements (PTEs) in urban areas are often both geogenic and anthropogenic  
52 (Argyrazi & Kelepertzis 2014; Rodrigues et al. 2009), with both point and diffuse anthropogenic sources  
53 common (Marchant et al. 2011). Typical anthropogenic sources such as industry, traffic (leaded fuel,  
54 brake pads and tire wear (Argyrazi & Kelepertzis 2014; Dao et al. 2014)) and waste disposal are known to  
55 contribute to PTE concentrations in soil (Ajmone-Marsan & Biasioli 2010). Domestic outputs in urban  
56 environments, in the form of fuel burning and waste, can also be large contributors to soil PTE  
57 concentrations (Biasioli et al. 2006; Glennon et al. 2014).

58 As urban areas continue to grow, a factor that must be considered is how human health can be affected  
59 by PTEs in soil. Can development be appropriately and sustainably managed considering previous land  
60 uses and soil PTE concentrations? The economic importance of urban soils must be balanced with  
61 ensuring potentially contaminated urban sites are safe for redevelopment.

62 Numerous urban geochemical investigations have been completed across the world (Biasioli et al. 2006;  
63 Argyrazi & Kelepertzis 2014; Glennon et al. 2014; Kelepertzis & Argyrazi 2015; Golden et al. 2015;

64 Johnson et al. 2011; Thorton 2009; Mielke 1999) and it is by building upon this library of research that we  
65 can fully understand how urban PTE sources vary geographically. The study areas used in this research  
66 have diverse bedrock and rich industrial histories, making them the ideal locations for investigating  
67 combined geogenic and anthropogenic contributions to soil PTE concentrations.

68 This research aims to understand if PTE concentrations in soil can be used as a tracer for urbanisation by;  
69 (1) investigating geogenic and anthropogenic contributions to PTE concentrations in soil, (2) identifying  
70 groups of PTEs controlled by similar sources, (3) understanding how historical city development may  
71 have influenced soil quality by considering PTE enrichment across city development zones and (4)  
72 calculating typical threshold values for the anthropogenic PTEs from similar sources. A novel  
73 investigative methodology will be employed utilising depth ratios, a range of multivariate statistical  
74 techniques and pollution indices. The objective is to generate a methodology for use in other urban  
75 areas, for a range of potential pollutants, to inform on city areas most likely to be contaminated.

76 Eleven PTEs are considered; arsenic (As), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo),  
77 nickel (Ni), lead (Pb), antimony (Sb), tin (Sn), vanadium (V) and zinc (Zn). These elements are expected  
78 to be related to different geogenic and anthropogenic sources within the study areas; in particular they  
79 are likely to represent contamination from a variety of historical industrial processes. Elements such as  
80 As, Cr, Cu, Ni, Pb and Zn commonly feature in urban geochemical studies due to their anticipated  
81 anthropogenic sources (Johnson & Ander 2008) while Carrero et al. (2013) demonstrate a relationship  
82 between a variety of the chosen PTEs, including Mo, Sb and Sn, and soils heavily impacted by traffic.  
83 Previous research in one of the study areas (McIlwaine et al. 2014; McIlwaine et al. 2015; Cox et al. 2013;  
84 Barsby et al. 2012; Palmer et al. 2015) has demonstrated concentrations of various PTEs to be controlled  
85 by geogenic sources in the form of bedrock geology.

86

## 87 **2 Methodology**

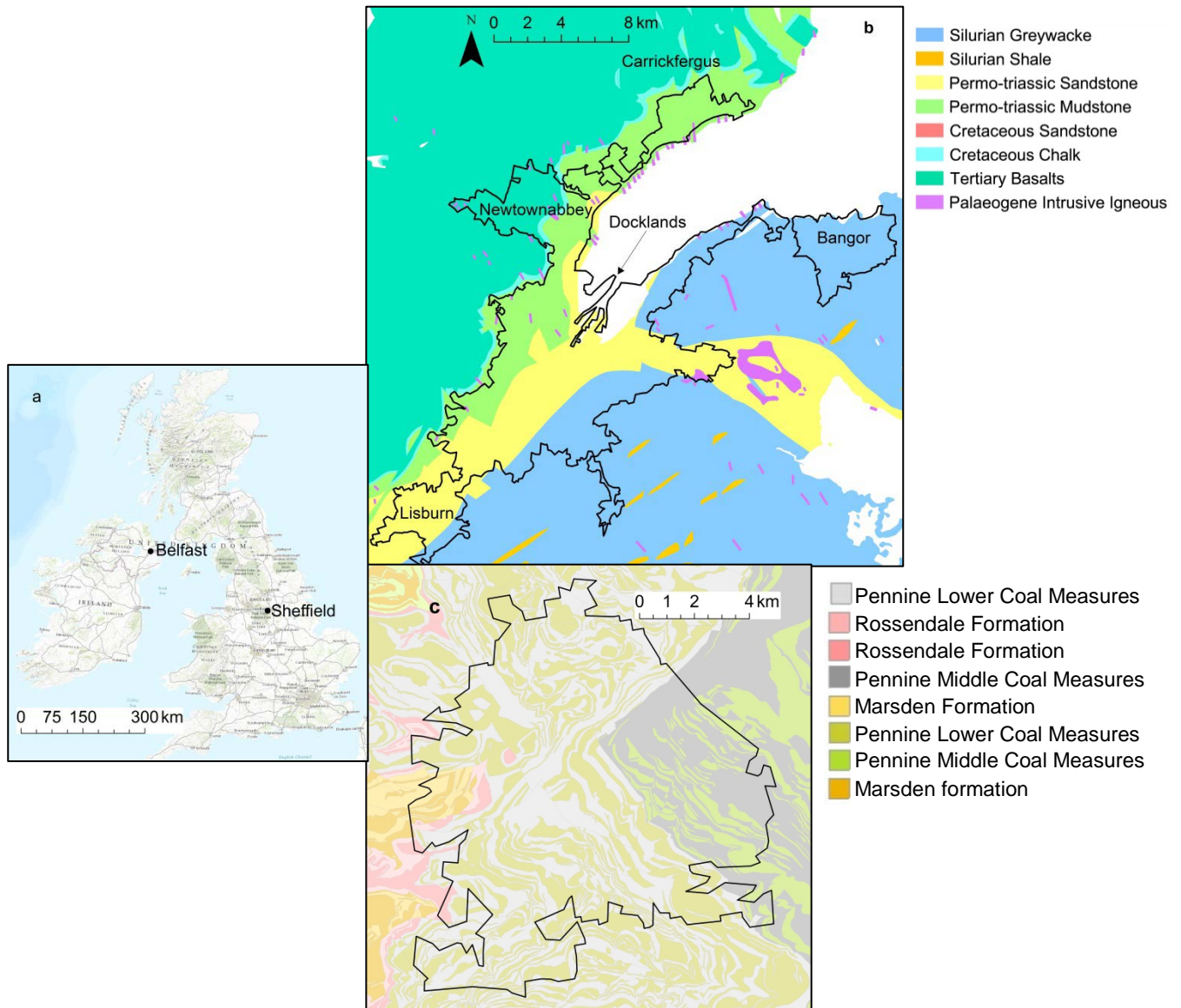
88

### 89 **2.1 Study areas**

90 Two cities within the United Kingdom have been chosen as study areas for this research. Belfast,  
91 Northern Ireland's capital and largest city has been compared with Sheffield, a city in South Yorkshire,  
92 England. These cities were selected due to their similar industrial heritage in heavy engineering  
93 (although Sheffield's is slightly greater and more varied than Belfast) and their similar geology.

94 The Corine land cover data (European Environment Agency 2012) was utilised to define both the Belfast  
95 and Sheffield study area boundaries (Figure 1). This data is split into 44 different land uses based on the

96 interpretation of satellite images. The majority of land uses were simplified into either urban or rural;  
 97 areas of urban fabric and industrial units were obviously urban while areas of pasture and forest were  
 98 clearly rural. Where any inconclusive land uses were identified, the surrounding land use was utilised as  
 99 an indicator of land use type on a site by site basis. Within Sheffield, the Corine boundary was slightly  
 100 reduced due to the spatial extent of the geochemical data available.



101  
 102 *Figure 1 Maps showing a) location of Belfast and Sheffield within the UK, b) simplified bedrock geology in Belfast*  
 103 *(bedrock geology derived from data provided by Geological Survey Northern Ireland (GSNI) (Crown Copyright))*  
 104 *and c) bedrock geology in Sheffield (taken from BGS GeoIndex)*

105 **2.1.1 Belfast**

106 A simplified representation of the highly diverse bedrock geology in Belfast, from GSNI's 1:250000 map,  
 107 is produced in Figure 1. Silurian greywacke and Silurian shale are the two oldest rock formations,  
 108 forming part of the Southern Uplands-Down-Longford Terrane, followed by the Permo-triassic  
 109 sandstones and mudstones. This is covered in the west of the city by Cretaceous sandstone and chalk

110 and finally by the most recent Tertiary basalts which run along the north west boundary of city (Mitchell  
111 2004). A number of Palaeogene intrusions occur within the study area. Geology has previously been  
112 identified as a control over element concentrations in Northern Irish soil (McIlwaine et al. 2014), with  
113 areas of basalt and sandstone identified as containing elevated concentrations of different PTEs. This  
114 study area is therefore of interest due to the expected geogenic controls within an urban environment.

115 Superficial geology within Belfast (Supplementary Information 5) has been reproduced from a GSNI map  
116 showing the geology of Belfast and District (Bazley et al. 1984). It is found in the form of till, glacial sands  
117 and gravels, and alluvium within the vicinity of the River Lagan.

118 Historical maps of Belfast (Land and Property Services 1858; Land and Property Services 1901; Land and  
119 Property Services 1919) have been used to produce historical study area boundaries for 1858, 1901 and  
120 1919-1939. Historical development of surrounding towns that are now incorporated in the greater Belfast  
121 area (Carrickfergus and Bangor on Figure 1) has not been included.

122 Belfast is historically recognised for both linen production and ship-building; the early 18th century saw  
123 the introduction of the linen industry involving bleaching, weaving and spinning processes while ship-  
124 building was introduced later in the 18th century (Beckett & Glasscock 1967; Crawford 1986). The city  
125 was an important manufacturing centre during the industrial revolution with other common businesses  
126 including rope works, bleachers, glass manufacturers, tobacco factories and distilleries (Royle 2007).  
127 Present-day Belfast is much more reliant on service provision related occupations (82% in Northern  
128 Ireland in the 2013 Census of Employment (NISRA 2014)) than the historical industrial and  
129 manufacturing employment.

### 130 **2.1.2 Sheffield**

131 Sheffield is underlain by Carboniferous deposits of Westphalian and Namurian age (Freestone et al.  
132 2004). The rocks are highly faulted and folded creating many discontinuous outcrops (Figure 1). The  
133 Middle Coal Measures Formation outcrops to the east of the city centre; it is Westphalian in age and  
134 composed of sandstone. The Lower Coal Measures Formation, also composed of sandstone and  
135 Westphalian in age, underlies most of the city centre. The Rossendale and Marsden Formations are  
136 present to the west of the study area comprising of mudstone and siltstones.

137 Quaternary deposits cover approximately 10% of Sheffield (Supplementary Information 5); silt alluvium  
138 is located in the river valleys around and in the city of Sheffield while some river terrace deposits in the  
139 form of sand and gravel also infill these valleys (Freestone et al. 2004).

140 Historical maps (OS Six Inch England and Wales 1851; Bartholomew's "Half Inch Maps" of England and  
141 Wales 1904; Bartholomew's Revised "Half Inch Maps" 1920; 1:25000 maps of Great Britain 1953) of

142 Sheffield have also been used to produce historical study area boundaries for 1850-1851, 1904, 1920 and  
143 1938-1951.

144 Sheffield is located in South Yorkshire in England and is believed to have been originally founded in the  
145 8<sup>th</sup> century. Coal has played an important role in the city's history, being mined and burnt for "space  
146 heating and industrial purposes in Sheffield since Roman times" (Rawlins et al. 2005). By the 1750s, more  
147 than 150 firms were dedicated to steel manufacture within the city. High quality cutlery, an export for  
148 which Sheffield is recognised, has been produced in the city since that time (Gilbertson et al. 1997).  
149 Industrial expansion continued until the late 1960s, when British Steel opened their Tinsley Park Works  
150 in the north east of the city. The steel and cutlery industry in Sheffield began to decline in the late 1970s  
151 and 1980s when cheaper alternatives were being produced in other areas of the world. This also affected  
152 the coal used to fuel industry in Sheffield, with coal use declining dramatically from the mid-1980s  
153 (Gilbertson et al. 1997).

154

## 155 **2.2 Geochemical data**

156 The Tellus project, managed by GSNI, was completed across Northern Ireland between 2004 and 2007,  
157 comprising both geophysical and geochemical surveys. In total, 781 Tellus soil sample locations (4  
158 samples per km<sup>2</sup>) fall within the defined Belfast boundary (<200 km<sup>2</sup>). Geochemical measurements are  
159 available via a variety of different analytical techniques. Total concentrations determined by X-ray  
160 fluorescence (XRF) were available for the shallow (5-20 cm) soil samples. Aqua regia extractable data are  
161 available for the shallow and deep (35-50 cm) samples, with the PTEs investigated within this study  
162 analysed by a mixture of Inductively Coupled Plasma (ICP) Optical Emission Spectrometry (OES) and  
163 ICP Mass Spectrometry (MS).

164 Similar sampling density and analytical techniques were employed during G-BASE sampling of  
165 Sheffield. However, this G-BASE data was solely analysed by XRF and at this stage only the shallow (5-  
166 20cm) soils have been analysed. Some 495 G-BASE soil sample locations fall within the defined Sheffield  
167 boundary. More detailed information on the Tellus datasets including quality assurance and quality  
168 control procedures can be found in Green et al. (2010); Knights (2007) and Smyth (2007) and information  
169 on the Geochemical Baseline Survey of the Environment (G-BASE) protocols followed are provided by  
170 Johnson (2005).

171

### 172 **2.3 Depth comparison**

173 Comparing shallow (5-20cm) and deep (35-50cm) PTE concentrations gives a greater understanding of  
174 anthropogenic and geogenic inputs to PTE concentrations in soil. Generally, if the shallow  
175 concentrations are more elevated this suggests an anthropogenic control over the PTE (Chiprés et al.  
176 2009) while a geogenic control will result in elevated concentrations in the deep samples (Galán et al.  
177 2008). Although this assumption will generally hold true, it is important to note that urban soil is often  
178 replaced or altered due to development, with potential for contaminated soils to be reworked or placed at  
179 depth. Even with relatively undisturbed soils care should be taken as the presence of organic matter may  
180 cause differences between horizons (Reimann & Garrett 2005).

181 Ratio boxplots based on the shallow concentration of the PTE divided by its deep concentration have  
182 been constructed to provide an indication of the general inputs to different PTEs in Belfast. The data  
183 based on the aqua regia extraction, followed by an ICP finish was used for this comparison as it is  
184 available at both depths therefore providing a valid comparison. This comparison could not be  
185 completed for Sheffield where only shallow data is available. The docks area of Belfast (Figure 1) is  
186 developed on reclaimed land so, within that small area (approximately 6.5 km<sup>2</sup>), the assumptions  
187 regarding depth are not likely to hold true, however, there is no particular evidence to suggest this occurs  
188 elsewhere within Belfast. The scale of the data used to complete this comparison and the size of the  
189 study area suggests that this depth comparison will inform on controlling sources.

190

### 191 **2.4 Source identification and relationships between PTEs**

192 Multivariate techniques in the form of cluster analysis and principal component analysis (PCA) have  
193 been used to determine underlying controls over the PTE dataset (Andersson et al. 2010; Candeias et al.  
194 2011; Argyraki & Kelepertzis 2014).

195 Shallow XRF data was used for this analysis; previous research by McIlwaine et al (2015) suggests  
196 elemental form may affect the concentrations determined by ICP-OES/ICP-MS following an aqua regia  
197 digestion. This is of particular importance within urban environments as the source of the PTE is likely  
198 to control its form. Shallow data are of more relevance for this section of the research due to interest in  
199 the anthropogenic controls over the PTEs, and also because shallow/surface soils drive risks to humans  
200 through inhalation of dust, ingestion of soil and dermal contact (Cole & Jeffries 2009; CL:AIRE 2014a;  
201 Nathanail et al. 2015).

202 Geochemical data is compositional in nature, meaning that all the values are relative to each other i.e. all  
203 the elements analysed in a sample sum to a constant value. Therefore, all total element concentrations



204 depend on the concentrations of the other elements in that sample meaning that they should be 'opened'  
205 prior to multivariate statistical analysis (Pawlowsky-Glahn & Egozcue 2006; Reimann et al. 2012;  
206 Aitchison 1982). The centred log-ratio (clr) transformation was found to be an appropriate manner for  
207 'opening' geochemical data prior to multivariate data analysis within this research as it allows retention  
208 of the relationship with the original variables of the dataset. Prior to completion of the cluster analysis  
209 and PCA the data was also scaled to unit variance to ensure differences in scale would not control the  
210 outputs.

211 Cluster analysis has been used as an exploratory data analysis method with the aim of splitting the data  
212 under consideration into a number of groups which are similar in their characteristics or behaviour  
213 (Reimann et al. 2008). The commonly utilised Ward's minimum variance method (Astel et al. 2007;  
214 Frenieu et al. 2013; Ward 1963) was used to form groups of subsets based on their similarity as defined by  
215 specified characteristics and the Euclidean distance.

216 The PCA plots geochemical data in multivariate space, searching for the direction that contains  
217 maximum variability. The resulting loadings describe the relationship between the original variables and  
218 the Principal Components (PCs), while the scores describe the relationship between each of the  
219 observations and the PCs (Reimann et al. 2008). In order to understand the spatial distribution of the  
220 PCs, the score for each observation has been plotted, forming a map of how the PC is distributed. This  
221 allows a comparison between controlling variables and geographical distribution, providing a full  
222 interpretation of the PCA (Reimann et al. 2008). This interpolated map was produced using inverse  
223 distance weighting (output cell size of 200m, power of 2 and a search radius of 500m) which is  
224 recommended for use within spatially dense networks (Dirks et al. 1998).

225

## 226 **2.5 Urban growth**

227 Pollution indices (PIs) have been utilised to gain an understanding of how the PTE concentrations within  
228 the Belfast and Sheffield development zones (based on the historical boundaries discussed in Section 2.1)  
229 show various levels of enrichment. These PIs have been calculated using;

230

$$PI = U_c/R_c$$

231 where  $U_c$  is the median element concentration within the development zone under consideration and  $R_c$  is  
232 the median rural element concentration. A study by Biasioli et al. (2006) used PIs in a similar manner to  
233 estimate the enrichment of a city with certain PTEs. In order to determine the influence of different  
234 urban environments over PTE concentrations through anthropogenic sources the most effective  
235 comparison is with rural environments. Previous research has suggested that there was no obvious

236 agricultural input of anthropogenic PTEs to the rural environment within Northern Ireland (McIlwaine et  
237 al. 2014; McIlwaine et al. 2015). The median rural concentration has been used as the median is more  
238 robust to outlying values than the more commonly used mean (Zhang et al. 2007).

239 The median rural element concentrations were easy to calculate for the Belfast study area, as the Tellus  
240 rural data was available. The median rural element concentrations for the Sheffield study area were  
241 taken from Freestone et al. (2004), which provided the 'median concentrations in regional surface soil  
242 samples overlying Carboniferous Coal Measures, Humber-Trent atlas areas'.

243

## 244 **2.6 Background or typical threshold values**

245 A variety of methods for calculating background concentrations were utilised, and the results contrasted  
246 and compared to gain an understanding of their strengths. The domains (areas where a readily  
247 identifiable factor can be shown to control the concentration of the PTE) were based on the findings of the  
248 PCA and historical analysis, and as such were defined using the historical development zones identified.  
249 As previously suggested for use at a regional scale in Northern Ireland, the typical threshold value (TTV)  
250 (McIlwaine et al. 2014) methodology which utilises the Finnish upper limit of geochemical baseline  
251 variation (ULBL) (Jarva et al. 2010) to define background concentrations was employed. The ULBLs are  
252 based on the upper limit of the upper whisker line of the box and whisker plots, which can be calculated  
253 using:

$$254 \text{ULBL} = P_{75} + 1.5 \times (P_{75} - P_{25})$$

255  $P_{75}$  and  $P_{25}$  are the 75<sup>th</sup> and 25<sup>th</sup> percentiles of the element concentrations respectively (Jarva et al. 2010).  
256 Logarithmic transformed data were not used to plot the box and whisker plots, as the untransformed  
257 data led to the highest amount of outliers and therefore gives a more conservative value. This is a very  
258 straightforward method for calculating background values, solely requiring the calculation of the 75<sup>th</sup>  
259 and 25<sup>th</sup> percentiles.

260 In addition, the Normal Background Concentration (NBC) method employed for use alongside Part 2A of  
261 the Environmental Protection Act in England and Wales was used. Within the NBC methodology, it is  
262 recommended that the domains are based on at least 30 values (Cave et al. 2012). The NBC is calculated  
263 for each domain using a statistical methodology given in (Cave et al. 2012). The NBC is then taken to be  
264 the upper 95% confidence limit of the 95<sup>th</sup> percentile. The project outputs included R code scripts which  
265 can be used to determine NBCs, as discussed by Johnson et al. (2012). These R scripts have been utilised  
266 by the author to calculate NBCs within this research.

267 The median + 2MAD (median absolute deviation) (Reimann et al. 2005) method was also utilised. The  
268 median + 2MAD, boxplot upper whisker and English NBC methods were compared as methods by

269 which to calculate background concentrations in urban environments in a study by Rothwell & Cooke  
 270 (2015). The lack of systematically collected geochemical data (no G-BASE data was available) meant that  
 271 a different approach had to be taken within this study in Gateshead; site investigation data collected  
 272 during the planning process was instead used. The local authority determined that the median + 2MAD  
 273 method provided the preferred NBCs within this study as it consistently gave the most conservative  
 274 values i.e. the lowest NBC (Rothwell & Cooke 2015).

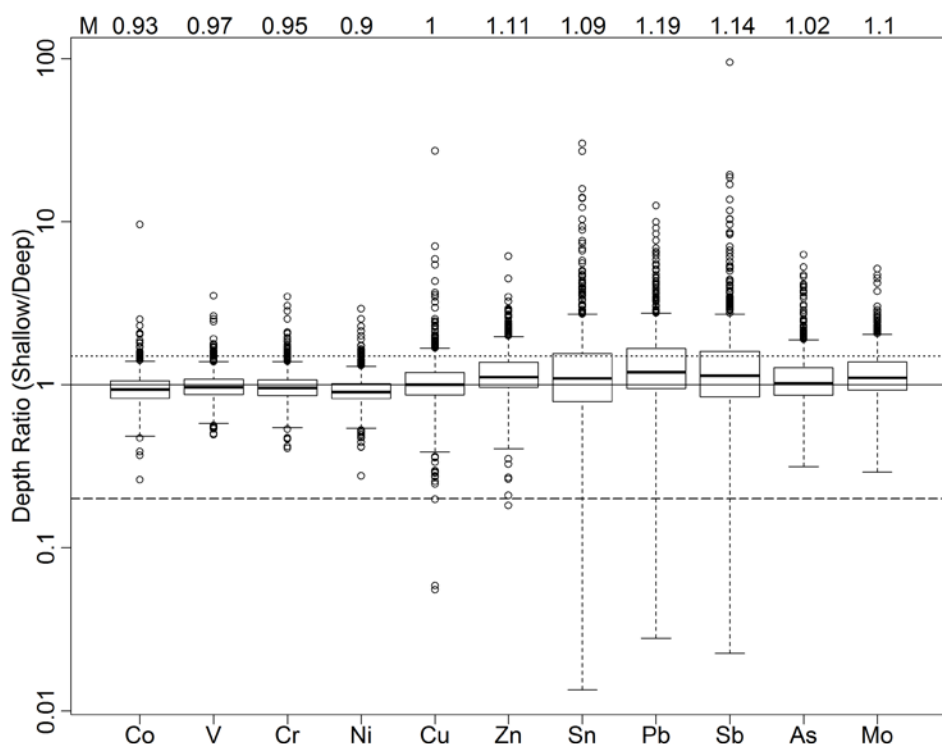
275

## 276 3 Results and discussion

277

### 278 3.1 Depth ratio

279



280 *Figure 2 Boxplots of the shallow/deep PTE concentrations (depth ratio) using ICP following an aqua regia digestion*  
 281 *data for Belfast (solid black line shows where the shallow and deep concentrations are equal, dashed line shows*  
 282 *where the depth ratio is equal to 0.2, dotted line shows where the depth ratio is equal to 1.5 and the M values*  
 283 *represent the median depth ratio)*

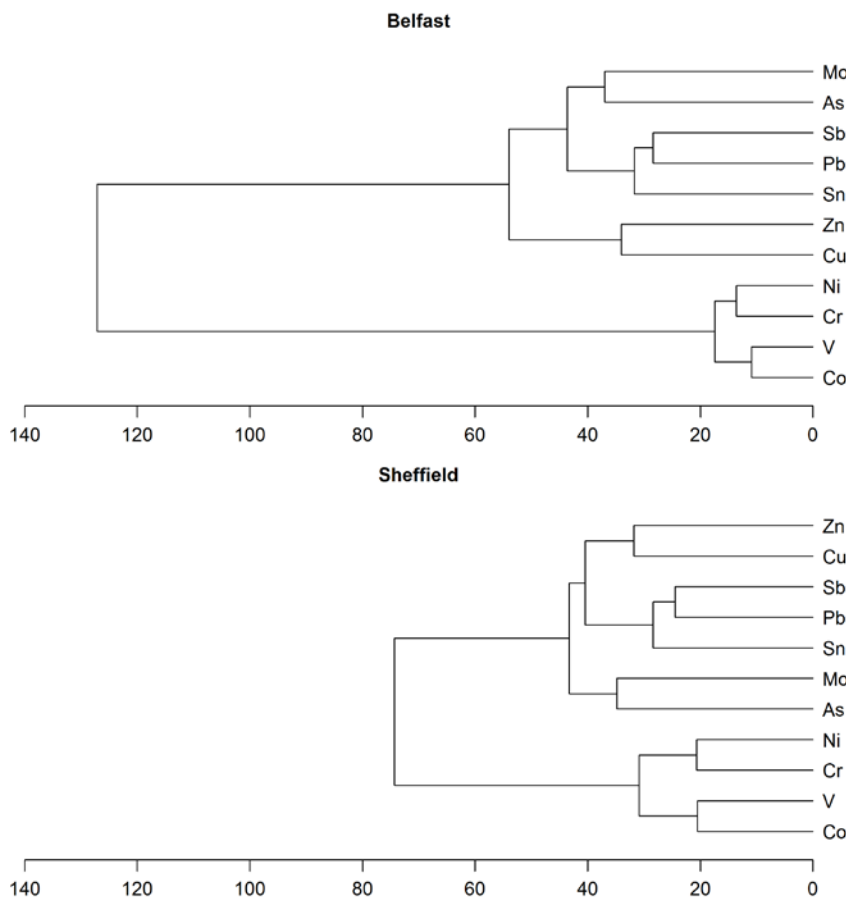
284 From the Belfast depth comparison, similar boxplot characteristics are shown for Co, V, Cr and Ni; the  
 285 majority of the boxplot falls below a ratio of one, representing more elevated concentrations in deep soils.  
 286 A number of lower outliers are identified, related to elevated concentrations at depth, while the upper  
 287 outliers are likely to be related to anthropogenic sources of these PTEs in shallow soils. This pattern  
 288 suggests a predominantly geogenic control over these PTEs within Belfast. The upper outliers may be a  
 289 useful way of spatially assessing anthropogenic point sources of these PTEs in the study area. These

290 outliers show a great deal of consistency across the Co, V, Cr and Ni distributions; the depth ratio falls  
291 above 1.5 (dotted line on Figure 2) for at least 3 of the PTEs at 18 sample locations and for all 4 PTEs at 8  
292 sample locations.

293 Geogenic controls are also exerted over Cu and Zn, however the overall pattern for these PTEs is a little  
294 different. A larger variance of the ratio is obvious, with a wider dispersion of the boxplot's whiskers. A  
295 number of lower outliers may represent the geogenic influence over these PTEs, however the increased  
296 amount of upper outliers suggest a more substantial anthropogenic contribution to Cu and Zn  
297 concentrations. However, it should be noted that copper can complex with organic matter in soils  
298 (Karlsson et al. 2006) which may also explain the degree of variance of the ratio observed. Further work  
299 is needed to define the effects of organic matter on such metal distribution in soils.

300 The remainder of the PTEs appear to be controlled by anthropogenic processes as the medians of the  
301 depth ratio are generally higher than 1 and only upper outliers are present. They can be split into two  
302 groups; As and Mo behave in a similar manner as both show a relatively small variance with only upper  
303 outliers. Although Pb, Sb and Sn also only have upper outliers they demonstrate a much larger variance.  
304 This is related to a small number of samples where the deep concentration is much greater than the  
305 shallow concentration, for example the number of samples where the depth ratio is below 0.2 (dashed  
306 line on Figure 2) is 7, 6 and 15 for Pb, Sb and Sn respectively. Most of these samples are dispersed across  
307 the study area and are potentially related to sites where the deeper soil has been disturbed or replaced  
308 (perhaps with waste materials) during development leading to higher concentrations of these PTEs at  
309 depth. An alternative possible explanation for this pattern is that these PTEs are more easily leached  
310 from shallow to deeper soils at these locations.

311 **3.2 Cluster analysis**



312  
 313 *Figure 3 Dendrograms demonstrating the cluster analysis completed for Belfast and Sheffield, with axis*  
 314 *representing dissimilarity height between variables*

315 The cluster analysis (Figure 3), which considers shallow soils analysed by XRF, groups the PTEs in Belfast  
 316 in a very similar pattern to that previously determined by the depth ratio analysis (Figure 2). The PTEs  
 317 are first split into two main groups which can be explained by controlling geogenic (Co, V, Cr and Ni)  
 318 and anthropogenic (Cu, Zn, Sn, Pb, Sb, As and Mo) factors.

319 Within the geogenic cluster two separate groups of Co and V, and Cr and Ni are present. Previous  
 320 research has shown strong correlations between all these PTEs in a Northern Ireland context (Barsby et  
 321 al. 2012), related to the stark control areas of Tertiary basalt exert over these PTEs. The total  
 322 concentration maps of Co, V, Cr and Ni (Supplementary Information 1) show extremely similar spatial  
 323 distributions. Although the main control over these PTEs in Belfast is the Tertiary basalts, a few  
 324 anthropogenic hot spots are dispersed across Belfast. It could be these point sources, and their influence  
 325 over the PTEs separately, that creates the difference between the Co and V, and Cr and Ni groups.

326 Three smaller groups make up the anthropogenic cluster in Belfast; firstly Cu and Zn, secondly As and  
 327 Mo and finally Sn, Pb and Sb (Pb and Sb are most closely related within this cluster). As highlighted in  
 328 Section 3.1, these separate groupings are related to the different source contributions for these PTEs.

329 Although anthropogenic controls govern these concentrations, Cu and Zn are probably grouped because  
330 they also have geogenic contributions from the Tertiary basalts. From an anthropogenic perspective, the  
331 close grouping of Cu and Zn could also be explained by their role in the production of brass (Herting et  
332 al. 2008). Arsenic and Mo are anthropogenically controlled, but again a possible geogenic influence from  
333 the Silurian greywackes resulting in elevated concentrations of As and Mo in overlying soils (Young &  
334 Donald 2013) could cause them to cluster together within the overall anthropogenic cluster. No geogenic  
335 contributions to Pb, Sb or Sn could be identified within the study area suggesting a sole anthropogenic  
336 control over these PTEs, creating their separate grouping (Figure 3).

337 The results of the cluster analysis for Sheffield (Figure 3) are strikingly similar to those presented for  
338 Belfast. Two main separate groupings are noted; Zn, Cu, Sb, Pb, Sn, Mo and As are grouped separately  
339 from Ni, Cr, V and Co. As demonstrated on the concentration maps (Supplementary Information 1), Ni,  
340 Cr, V and Co show elevated concentrations to the north-east of the study area. Although they are all  
341 affected by the presence of other point sources in Sheffield, the large anthropogenic source to the north-  
342 east is their most obvious characteristic, resulting in them being grouped together.

343 In contrast, the other PTEs all have other factors affecting their concentration distributions. This cluster  
344 analysis suggests similar sources controlling three groups of PTEs, 1) Zn and Cu, 2) Sb, Pb and Sn and 3)  
345 As and Mo. Although these elements are anthropogenically controlled it is difficult to narrow down  
346 their specific sources. As noted for Belfast, Zn and Cu could be grouped together due to their role in the  
347 production of brass. The Pb, Sb and Sn concentrations are again likely to be solely anthropogenic; the  
348 widespread nature of their elevated concentrations might suggest a controlling atmospheric deposition  
349 source.

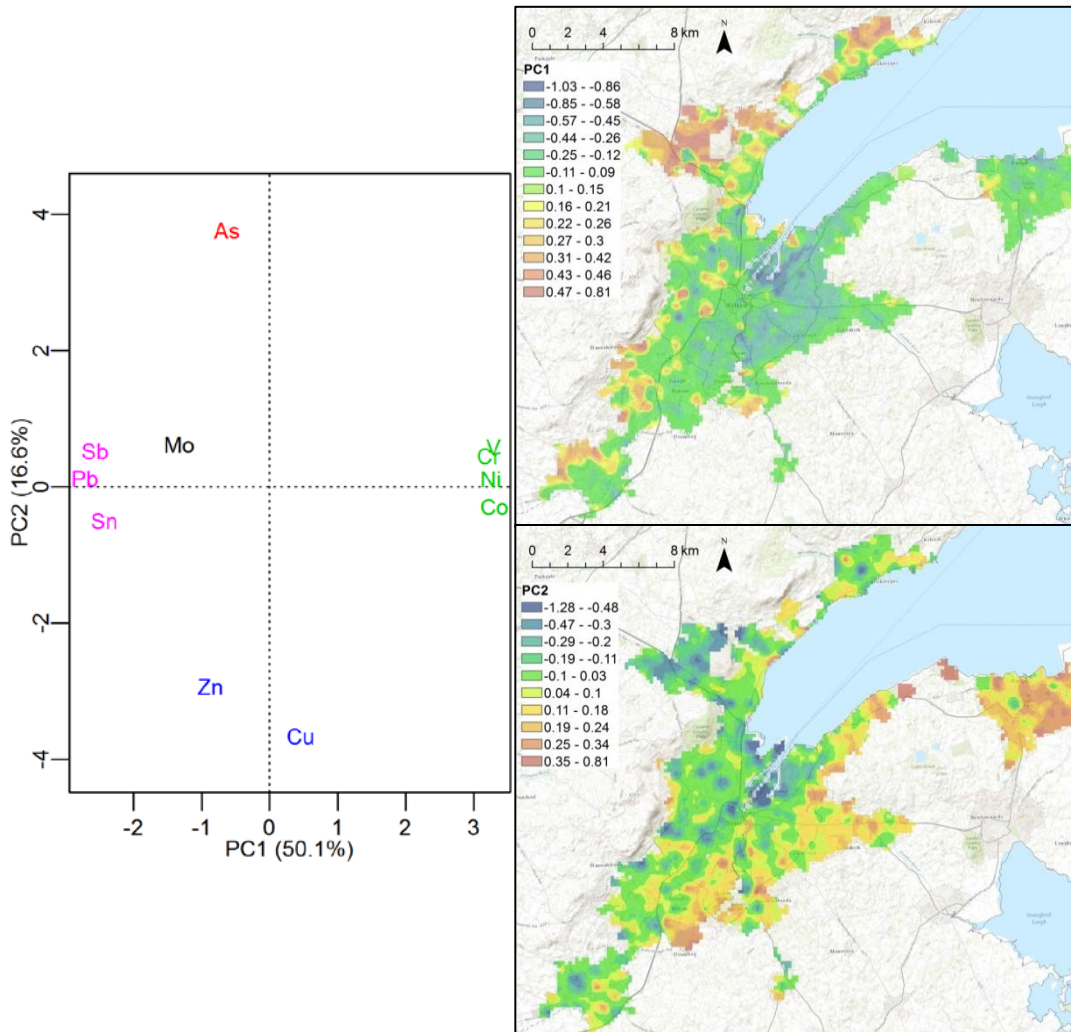
350 The difference in the scale on the cluster analysis from the two cities should be noted. The overall  
351 difference between the two groups, (Ni, Cr, V and Co are grouped separately from Mo, As, Sb, Pb, Sn, Zn  
352 and Cu) is much greater for Belfast than for Sheffield. In addition, the PTEs identified as being of  
353 geogenic origin in Belfast (Ni, Cr, V and Co) have a much smaller difference in height (between the two  
354 groups and the adjacent PTEs), than is noted for these PTEs in Sheffield. This suggests stronger  
355 similarity between these PTEs in Belfast, defending the identification of controlling geogenic and  
356 anthropogenic sources of these PTEs in Belfast and Sheffield respectively.

357 Although the other group of PTEs (Mo, As, Sb, Pb, Sn, Zn and Cu) show similar height differences in  
358 Belfast and Sheffield between most of the groups, the overall difference between the Zn and Cu group,  
359 and the Mo, As, Sb, Pb and Sn group is much greater for Belfast than it is for Sheffield. This could be  
360 explained by the geogenic contributions to Zn and Cu in Belfast compared to the governing  
361 anthropogenic controls over Mo, As, Sb, Pb and Sn.

362 These results are useful for providing preliminary information on links between PTEs; in order to  
363 ascertain the underlying associations between the anthropogenic PTEs more detailed multivariate  
364 analysis is required, along with an understanding of how their sources vary spatially.

365

### 366 3.3 Principal component analysis



367

368 *Figure 4 Results of PCA completed for Belfast using shallow XRF data, with PC1 and PC2 maps*

369 The first two identified PCs explain 67 % of the total variance within the results of the Belfast PCA. PC1  
370 separates the geogenic controls over Co, V, Cr and Ni from the anthropogenic PTEs. Cobalt, V, Cr and Ni  
371 (green on biplot) cluster closely reemphasising their almost identical spatial distributions related to their  
372 similar sources. The strong control exerted by the Tertiary basalts over these PTEs is represented in the  
373 red areas in the PC1 map (Figure 4).

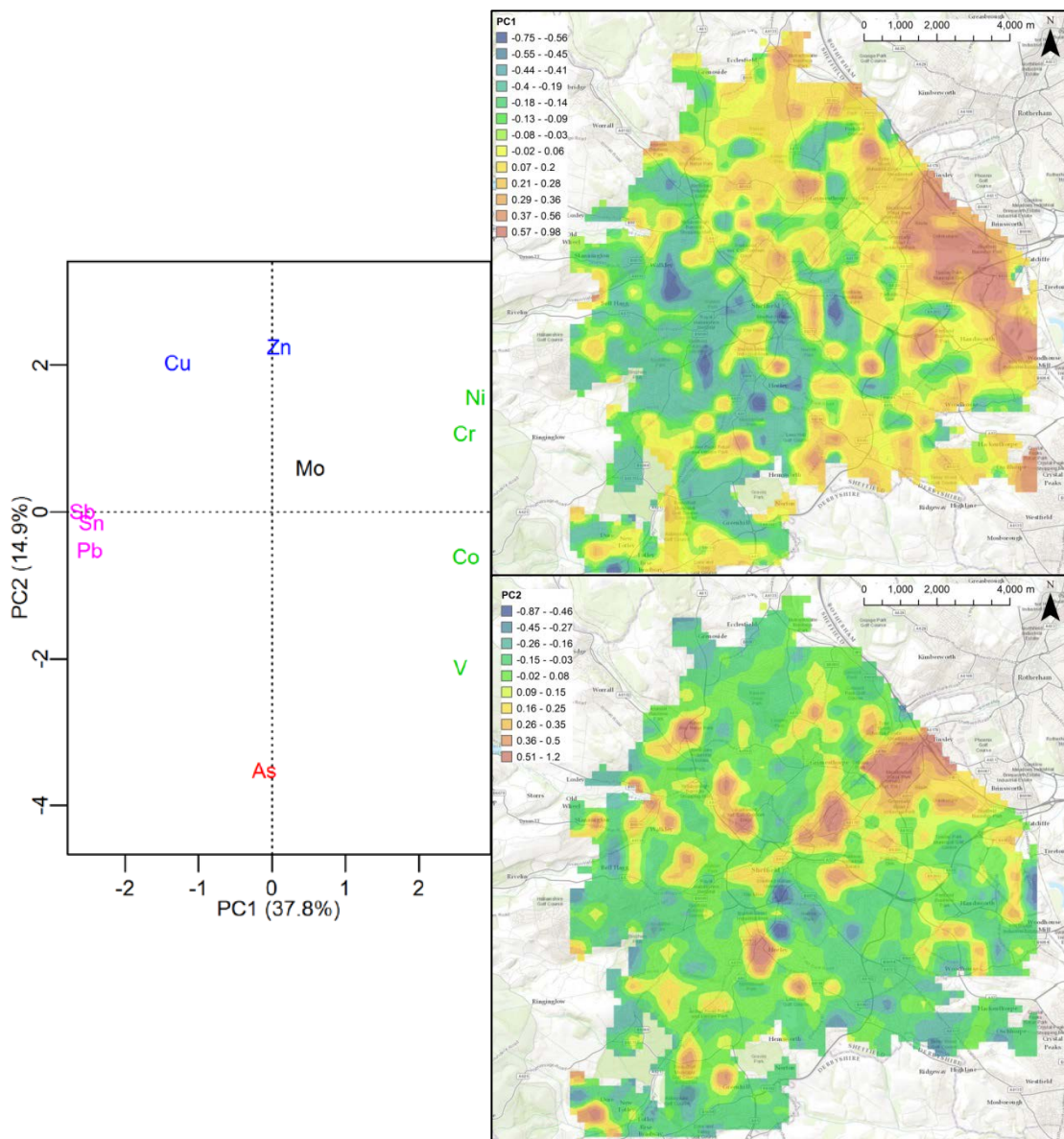
374 The PC1 results distinguish Pb, Sb and Sn (pink on biplot) as the most clearly defined anthropogenic  
375 PTEs. The map of PC1 shows the anthropogenic group to create a halo effect around the oldest part of  
376 the city, with a stronger presence towards the east of the city. The shipbuilding industry has been based

377 within this area of this city for many years, with George Best Belfast City Airport now also located here.  
378 This pattern is particularly obvious from the 1901 zone out to the modern Belfast zone, suggesting a long-  
379 term pattern of contamination within these soils.

380 PC2 appears to be explained by different contaminant sources contributing to As (red on biplot), and Cu  
381 and Zn (blue on biplot). The widespread As contributions suggest a domestic source such as coal  
382 combustion (Duan & Tan 2013), whereas the dark areas related to Cu and Zn suggest point sources across  
383 the city centre and also highlight the area of Tertiary basalts in the west of the city. A geogenic  
384 contribution to As in areas overlying Silurian greywacke is also possible; although the concentrations of  
385 As in this type of bedrock would not be expected to be particularly elevated, we would expect them to be  
386 higher than those found over the Tertiary basalts (Young & Donald 2013).

387 An airborne diffuse source of PTEs aligns well with previous research which demonstrated that  
388 characteristic polycyclic aromatic hydrocarbon (PAH) ratios in soils were from an airborne diffuse source  
389 from a mixture of biomass, solid fuel and fossil fuel combustion (Doherty et al. 2015).





390

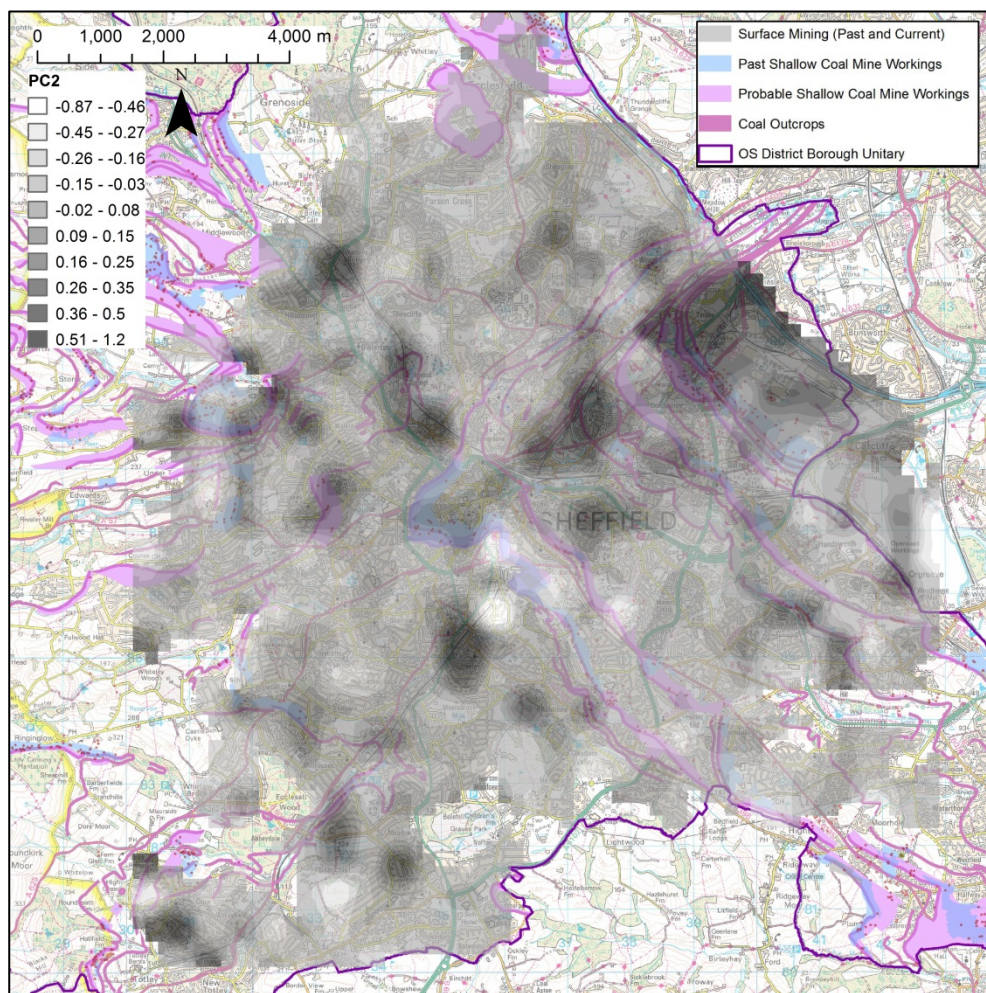
391 *Figure 5 Results of PCA completed for Sheffield using shallow XRF data, with PC1 and PC2 maps*

392 The PCA outputs for Sheffield are similar to those for Belfast (Figure 5). In total PC1 and PC2 account for  
 393 53% of the total variance within the dataset. This is 14% less than the PCA completed for Belfast  
 394 highlighting that there may be additional environmental and geochemical parameters affecting variance,  
 395 for example current land use and activity, in Sheffield.

396 Within PC1 the results again clearly separate Ni, Cr, Co and V (green) from Sb, Pb and Sn (pink). In  
 397 contrast to the Belfast results, Ni, Cr, Co and V are distributed much more widely on the biplot (Figure 5),  
 398 demonstrating that they are still anticipated to be from the same or similar sources, though not as closely  
 399 correlated in Sheffield as in Belfast. The map for PC1 demonstrates that Ni, Cr, Co and V exert the  
 400 greatest control over a large area along the north-east boundary of the study area where many of  
 401 Sheffield's iron and steel works were/are found (as shown in red and orange in the PC1 map (Figure 5)).  
 402 The elevated concentrations could be related to the industrial use (in these various factories) of the coal  
 403 which also occurs naturally in this area.

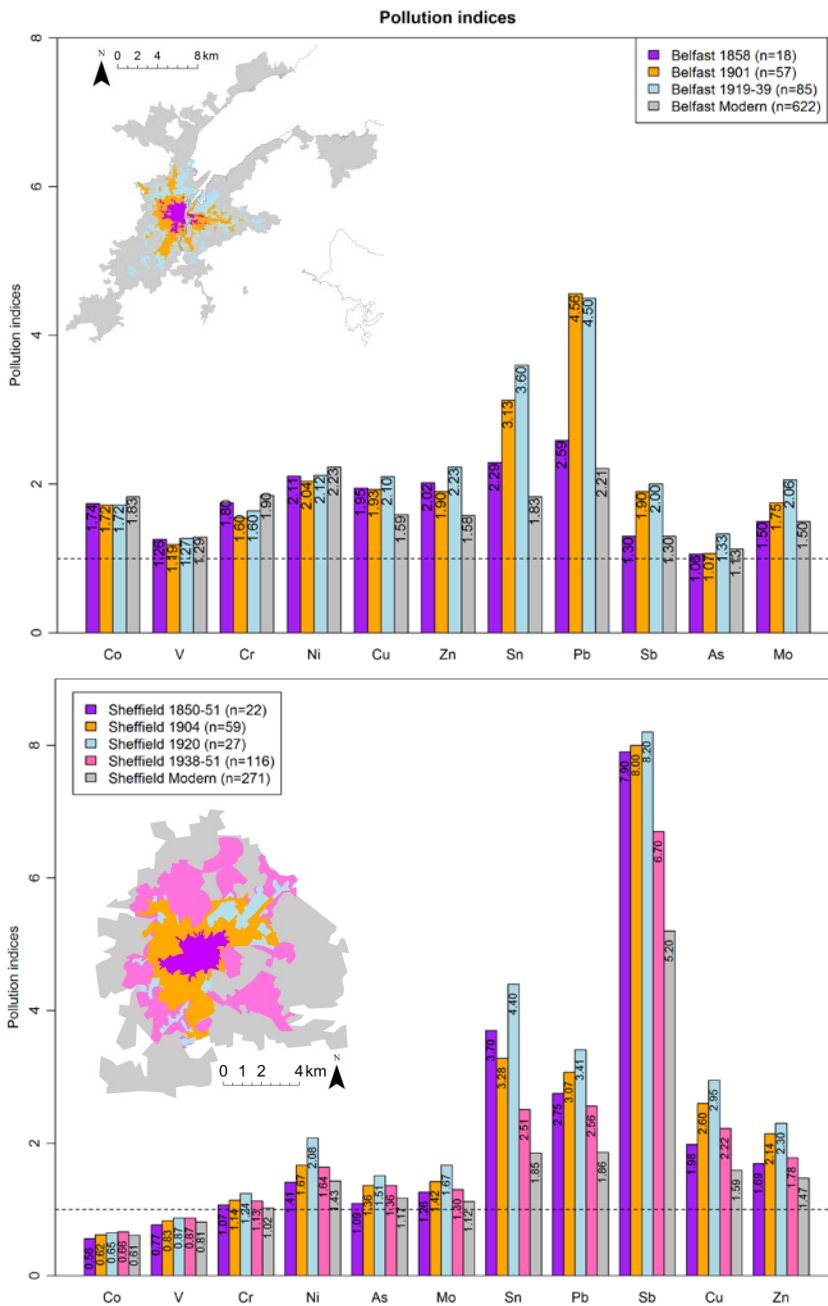
404 The darker blue colours on the PC1 map (Figure 5) represent the areas controlled by Pb, Sb and Sn, and  
405 similarly to Belfast these PTEs are shown to form a halo around the oldest area of the city. The  
406 widespread nature of these PTEs on their total concentration maps (Supplementary Information 1)  
407 suggests an atmospheric deposition anthropogenic source.

408 For Sheffield, PC2 separates As (red), from Cu and Zn (blue). In contrast to the Belfast PCA results, Ni  
409 and Cr also seem to have an influence over PC2, falling towards the same side as Zn and Cu on the  
410 biplot. The blue areas on the PC2 map are related to elevated concentrations of As, suggesting a  
411 particular point source of As in these areas. The red areas are related to Zn, Cu, Ni and Cr and fall in a  
412 similar, though smaller, area to the north-east of the location identified in PC1. As shown in Figure 6,  
413 PC2 seems to be influenced by the geogenic presence of coal with many of the red areas on the map  
414 aligning with coal outcrops in Sheffield. Therefore, PC2 seems to identify a geogenic or mining  
415 contribution to PTE concentrations (Zn, Cu, Ni and Cr) in Sheffield in the form of coal outcrops.



416

417 *Figure 6 Map of PC2 from PCA completed for Sheffield using shallow XRF data compared with the specific coal*  
418 *mining legacy plan for Sheffield created by the Coal Authority (The Coal Authority 2015)*



420

421 Figure 7 Bar chart showing the PI for the PTEs within each of Belfast's and Sheffield's development zones (dashed  
 422 line where PI = 1)

423 Pollution indices are used to assess the enrichment of the PTEs in the different historical development  
 424 zones of both cities. In Belfast, the PIs are calculated using rural median concentrations, thereby  
 425 demonstrating enrichment of these PTEs in the different Belfast zones compared to rural Northern  
 426 Ireland. The PIs suggest that certain groups of PTEs are related to different development zones of Belfast  
 427 (Figure 7).

428 For Co, V, Cr and Ni the highest PI is within the modern Belfast zone, due to the fact that a greater  
 429 proportion of the modern Belfast area overlies basalts, which have a significant control over their

430 concentrations, than in the remainder of the development zones. These PIs are much reduced when the  
431 median concentration of the PTEs in soils overlying areas of Tertiary basalts replaces the rural median  
432 concentration (Supplementary Information 2). For example, the PIs for V, Co, Cr and Ni within the  
433 modern development zone reduce from 1.29, 1.83, 1.85 and 2.23 to 0.59, 0.69, 0.62 and 0.66 respectively.

434 Pb concentrations are at their highest within the 1901 Belfast zone, although the PI is only slightly higher  
435 at 4.56 than that within the 1919-1939 zone (4.50). For Cu, Zn, Sn, Sb, As and Mo the highest PIs are  
436 located within the 1919-1939 zone suggesting this development zone is the most enriched for the  
437 anthropogenically controlled PTEs. However, these PTEs do differ across historical zones: the second  
438 highest PI (Cu and Zn – constituents of brass) falls within the 1858 zone, Sn, Sb and Mo have an elevated  
439 PI within the 1901 zone, and As within the modern Belfast zone. This suggests that rapid growth  
440 associated with development of heavy industry in Belfast between 1901 and 1919-1939 may be  
441 responsible for the elevated concentrations of a number of PTEs. However, contamination from all of  
442 these PTEs is likely to have begun before this period of time.

443 Overall, Pb and Sn have the highest pollution indices suggesting the biggest anthropogenic enrichment of  
444 these PTEs in the study area. These are also two of the oldest and best recognised urban contaminants.  
445 Although Sb and Mo also show anthropogenic enrichment, it is at a much lower level with PIs ranging  
446 between 1.30 and 2.00 for Sb and 1.50 and 2.06 for Mo. Geogenic contributions to As in the form of  
447 natural mineralisation (McIlwaine et al. 2014) in rural areas of Northern Ireland probably results in lower  
448 PIs for As.

449 As opposed to the PIs calculated for Belfast, the PIs for Sheffield are calculated using a rural median  
450 solely from the Carboniferous Coal Measures, rather than the median concentrations from the entire  
451 surrounding rural area. The results therefore tell us about enrichment of these PTEs in the urban area  
452 compared to one type of bedrock geology, rather than enrichment compared to the rural area as a whole.

453 The PIs calculated for Sheffield are consistently highest within the 1920 zone. This suggests that industry  
454 in Sheffield between 1904 and 1920 may be responsible for the most elevated PTE concentrations in soils.  
455 For Sn, Pb and Sb the PIs fall considerably within the 1938-1951 zone, below all three of the previous  
456 historical zones. The PIs are lowest for Cr, Mo, Sn, Pb, Sb, Cu and Zn in the modern zone, and lowest for  
457 Co, V, Ni and As in the 1850-1851 zone.

458 Lead, Sb and Sn show the greatest accumulation in Sheffield's soils (highest PIs), followed by Cu and Zn.  
459 The PIs for Sb are high due to its low median concentration in the Carboniferous Coal Measures (0.5  
460 mg/kg). Cobalt and V are depleted in Sheffield's soils when compared to the rural median, while Cr, Ni,  
461 As and Mo show minimal accumulation.

### 462 3.5 PTE typical threshold values

463 Within the Belfast study area, four PTEs (Co, Cr, Ni and V) have been clearly identified as elements that  
464 are geogenically controlled. The remainder of the PTEs in Belfast (As, Cu, Mo, Pb, Sb, Sn and Zn) are  
465 dominated by anthropogenic inputs. In Sheffield, all the PTEs show an anthropogenic influence. From  
466 these results, different methods for calculating background concentrations have been applied to assess  
467 the concentrations of the anthropogenically controlled PTEs within the city development zones, which  
468 have been shown to act as urban subdomains. These background values indicate what a 'typical' or  
469 background concentration of these PTEs would be within the defined domain; aiming to differentiate  
470 between concentrations related to geogenic and diffuse anthropogenic sources, and concentrations  
471 generated by point sources.

472

473 *Table 1 Summary of background values calculated for the PTEs in Belfast regarded as having some anthropogenic input within the separate development zones via the ULBL,*  
 474 *Median + 2MAD and NBC methods (BC = box-cox transformation, L = log transformation and E = empirical)*

	1858			1901			1919-1939			Modern		
	ULBL	M +2MAD	NBC	ULBL	M +2MAD	NBC	ULBL	M +2MAD	NBC	ULBL	M +2MAD	NBC
As	18	13	-	21	15	BC 37	26	17	E 52	19	14	L 21
Cu	120	95	-	160	100	BC 210	200	120	BC 640	120	80	L 130
Mo	2.8	1.8	-	3.5	2.4	L 4.7	5.1	3.0	E 18	2.7	1.8	L 3.1
Pb	190	140	-	430	280	L 490	620	270	BC 1300	200	120	L 260
Sb	2.7	1.9	-	4.3	3.1	L 10	7.2	3.7	BC 33	3.0	2.1	L 4.3
Sn	16	11	-	20	14	L 33	51	18	BC 1000	14	7.7	BC 24
Zn	240	210	-	310	220	L 470	510	290	BC 2100	240	170	L 290

475

476 Normal background concentrations cannot be calculated for the 1858 Belfast domain as there are only 18  
477 samples available within this area. With the exception of the Median + 2MAD method for Pb, all the  
478 background values calculated are highest within the 1919-1939 zone. This would be expected for all the  
479 PTEs apart from Pb, where the calculated PI is highest within the 1901 zone (Figure 7) suggesting the  
480 greatest enrichment of Pb in this zone. Upon further investigation this was found to be related to the  
481 distribution of the data. As the PI is based on the median of the dataset it is less affected by skew than  
482 the background value calculations via the ULBL and NBC methods; the 1919-1939 Pb data is more highly  
483 skewed than the 1901 Pb data. This suggests a more homogenous source of Pb, such as atmospheric  
484 deposition, within the 1901 zone, whereas the 1919-1939 zone is possibly witnessing atmospheric  
485 deposition as well as more independent point sources of Pb. This is possibly associated with increased  
486 development in the east of the city within this 1919-1939 zone, as identified and discussed within the PC1  
487 results (Section 3.3).

488 *Table 2 Summary of background values calculated for the PTEs in Sheffield regarded as having some anthropogenic input within the separate development zones via the*  
 489 *ULBL, Median + 2MAD and NBC methods (BC = box-cox transformation, L = log transformation, N = no transformation and E = empirical)*

	1850-1851			1904			1920			1938-1951			Modern		
	ULBL	M +2MAD	NBC	ULBL	M +2MAD	NBC	ULBL	M +2MAD	NBC	ULBL	M +2MAD	NBC	ULBL	M +2MAD	NBC
As	62	34	-	70	44	L 77	54	39	-	50	38	L 61	41	31	L 50
Co	31	22	-	29	23	L 40	36	24	-	29	23	E 41	29	23	E 28
Cr	220	130	-	190	130	E 780	270	140	-	190	130	E 600	160	120	E 370
Cu	210	110	-	300	160	L 590	250	150	-	180	120	L 260	120	80	BC 200
Mo	12	7.4	-	12	8.3	L 23	15	8.3	-	9.1	6.7	BC 19	8.3	5.9	L 13
Ni	97	57	-	82	62	BC 240	120	82	-	75	58	BC 140	68	51	L 89
Pb	940	440	-	930	530	L 1400	800	460	-	560	360	L 790	370	250	L 600
Sb	16	8.0	-	14	8.2	L 20	12	6.7	-	11	6.2	BC 22	7.2	4.6	L 9.2
Sn	100	47	-	77	45	L 170	69	48	-	46	28	L 64	33	21	L 46
V	130	110	-	140	110	N 140	130	110	-	140	110	E 150	140	110	L 130
Zn	420	290	-	620	400	L 920	520	380	-	420	280	BC 880	330	230	L 390

490



491 NBCs cannot be calculated for the 1850-1851 or 1920 Sheffield domain as there are only  
492 22 and 27 samples available within these areas respectively. The domains with the most  
493 elevated background values are reasonably consistent across the ULBL and Median +  
494 2MAD calculations. Where these differences occur it is likely to be related to the  
495 distribution of the data, as explained for Pb in the Belfast results.

496 The main differences between the ULBL and Median + 2MAD concentrations are noted  
497 for Pb, Sb and Sn. The highest concentrations via the ULBL method are in the 1850-1851  
498 zone for all three PTEs, whereas via the Median + 2MAD method the highest  
499 concentrations are in the 1904 zone for Pb and Sb and the 1920 zone for Sn. In  
500 conjunction with the spatial distribution previously discussed, the most elevated  
501 concentrations of all of these PTEs seem to form a halo surrounding the oldest part of  
502 the city, suggesting a stronger alignment with the ULBLs than the Median + 2MAD  
503 values.

504 The ULBL method highlights the highest concentrations for Co, Cr, Mo and Ni in the  
505 1920 zone, while the Median + 2MAD method has the highest concentrations for Co, Cr,  
506 Mo, Ni, Sn and V in this zone. The concentrations of V do not vary much across the  
507 development zones for any the methods used to calculate background values,  
508 suggesting this PTE is not influenced by different periods of historical development to  
509 the same extent as the other PTEs.

510 As can be seen in Supplementary Information 3, the most conservative background  
511 concentrations (i.e. the lowest concentrations) are calculated by the Median + 2MAD  
512 method, while the least conservative (i.e. the highest concentrations) are calculated via  
513 the NBC method, for all the PTEs except V. This is true for the majority of the  
514 background concentrations calculated, not just for Sheffield's modern zone.

515 Rothwell & Cooke (2015) suggested the median + 2MAD method for use because it  
516 consistently calculated the most conservative background concentrations in their study  
517 in Gateshead. Although this is a sensible precaution from a risk perspective, it may not  
518 be realistic to state that further investigation may be required at 19% of sampled sites  
519 within Sheffield's modern zone where the concentration of Pb is above the calculated  
520 Median + 2MAD value. The ULBLs provide concentrations between the most  
521 conservative Median + 2MAD concentrations and the least conservative NBCs; they may  
522 therefore be more appropriate values to use in gaining an understanding of background

523 concentrations of different PTEs in these studies. In addition, the NBC methodology is  
524 only applicable to domains with more than 30 samples and so it can't be applied in a  
525 number of the urban subdomains identified.

526 The ULBL methodology has previously been applied on a Northern Ireland regional  
527 scale to generate TTVs (McIlwaine et al. 2014). Although only compared with NBCs at  
528 this regional level, it was still identified as the most appropriate method for calculating  
529 background values.

### 530 **3.5.1 Comparison with generic assessment criteria**

531 Comparisons can be drawn between the recommended background values calculated  
532 via the ULBL method and UK generic assessment criteria such as suitable 4 use levels  
533 (S4ULs) and provisional category 4 screening levels (pC4SLs). These different criteria  
534 vary slightly in their definition, and are available for different PTEs. Suitable 4 use  
535 levels are based on the same level of risk as soil guideline values (SGVs) i.e. minimal or  
536 tolerable risk. However, S4ULs were generated using an updated exposure model and  
537 are available for additional land uses (public open spaces) (Nathanail et al. 2015).  
538 Provisional C4SLs have been created to support Defra's statutory guidance for Part 2A  
539 of the Environmental Protection Act. The guidance stated that where there is no risk  
540 that land poses a significant possibility of significant harm, or the level of risk is low, the  
541 category 4 classification should be used. At the other extreme, category 1 encompasses  
542 areas where the risk of the land posing a significant possibility of significant harm is  
543 unacceptably high (CL:AIRE 2014a). Therefore the key difference between S4ULs and  
544 C4SLs is the level of risk they consider; S4ULs are guidelines considering a level that is  
545 tolerable or posing a minimal risk to human health whereas C4SLs describe a higher  
546 level of risk which can still be considered low enough to allow category 4 land  
547 classification (CL:AIRE 2014a). The available S4ULs and pC4SLs are provided in  
548 Supplementary Information 4.

549 All the calculated background values for As in Belfast fall below the lowest SGV (32  
550 mg/kg), S4UL (37 mg/kg) and pC4SL (37 mg/kg), while all the ULBLs for Sheffield fall  
551 above these values. The highest ULBL for Sheffield (70 mg/kg), calculated for the 1904  
552 zone, is higher than the residential and allotment SGVs, pC4SLs and S4ULs  
553 (Supplementary Information 4). For Cu and Zn all the ULBLs fall below the lowest  
554 available S4ULs (520 mg/kg and 620 mg/kg for Cu and Zn respectively) for both Belfast

555 and Sheffield, with the exception of the 1904 ULBL for Zn which is equal to the  
556 allotment S4UL of 620 mg/kg. The comparison for Cr depends upon its speciation; the  
557 ULBLs calculated within Sheffield are all lower than the most conservative S4UL for  
558 Cr(III), but vast exceedances are obvious across the development zones for Cr(VI). The  
559 ULBLs calculated for Ni in Sheffield are all within the most conservative S4UL for Ni  
560 (130 mg/kg for residential areas). Exceedances of the most conservative S4UL for V (91  
561 mg/kg for allotments) are shown for all the ULBLs calculated for Sheffield.

562 The ULBLs calculated for Pb are high, especially in the 1919-1939 development zone for  
563 Belfast (620 mg/kg) and the 1850-1851 zone for Sheffield (940 mg/kg). This is of concern  
564 as Pb is known to be a non-threshold toxin i.e. no minimal risk level has been identified  
565 (Palmer et al. 2015). The lowest published pC4SL for Pb is 34 mg/kg, identified for  
566 allotment land use (CL:AIRE 2014b). The ULBLs calculated are 5.6, 12.6, 18.2 and 5.9  
567 times greater than this pC4SL within the 1858, 1901, 1919-1939 and modern  
568 development zones respectively in Belfast, and 27.6, 27.4, 23.5, 16.5 and 10.9 times  
569 greater in the 1850-1851, 1904, 1920, 1938-1951 and modern development zones in  
570 Sheffield. These calculated ULBLs are elevated when compared to the pC4SLs for Pb,  
571 and for sample locations where the ULBLs are exceeded in particular, further  
572 investigation may be required to examine the potential risk posed.

## 573 **4 Conclusions**

574 The scale of PTE concentration data available within the study area considered allowed  
575 for a thorough examination of the effects of historical development on soil PTE  
576 concentrations. Clear groups of PTEs were identified within the study area investigated  
577 via depth ratios, a range of multivariate statistical techniques and PIs. In particular,  
578 depth ratios proved to be a useful technique for identifying controlling sources in this  
579 urban environment. The concentrations in shallow soils were found to be controlled to  
580 a greater extent by anthropogenic influences than concentrations in deeper soils, which  
581 remain controlled by principally geogenic processes. Controlling sources and links  
582 between historical development and PTE concentrations were identified, suggesting the  
583 investigative methodology employed within this research may be useful for application  
584 within other urban environments.

585 The depth ratio boxplots suggested the highest levels of anthropogenic input for Pb, Sb  
586 and Sn followed by As and Mo in Belfast. Geogenic inputs were found to control the  
587 concentrations of Ni, Co, Cr and V, while Cu and Zn were influenced by both  
588 anthropogenic and geogenic inputs. The marked similarity in the spatial distributions  
589 of the geogenically controlled PTEs (Co, V, Cr and Ni) clearly demonstrates the control  
590 that the Tertiary basalts have over their concentrations, and suggests similar point  
591 sources of anthropogenic contributions perhaps due to importing of 'clean' topsoil,  
592 which originally overlaid the Antrim basalts, in these areas. PTEs under predominantly  
593 anthropogenic sources in Belfast can be split into three groups; 1) Sn, Pb and Sb, 2) Cu  
594 and Zn and 3) As and Mo. Cu and Zn receive some geogenic contribution to their  
595 concentrations from the Tertiary basalts but similar anthropogenic contributions are also  
596 obvious. Increasing anthropogenic contributions to both As and Mo see them grouped  
597 similarly, with Pb, Sb and Sn noted for the greatest anthropogenic contribution.

598 All of the PTEs investigated were found to be under some anthropogenic influence in  
599 Sheffield. Nickel, Co, Cr and V were found to align well in a large area along the north-  
600 east boundary of Sheffield where they were shown to occur at elevated concentrations.  
601 This pattern is thought to be related to the various industrial land uses located in this  
602 part of the city; many of Sheffield's iron and steel works were/are found here. The  
603 elevated concentrations could be related to the industrial use (in these various factories)  
604 of the coal which also occurs naturally in this area. Similarly to Belfast, Pb, Sb and Sn  
605 were shown to form a halo around the oldest area of the city. The widespread nature of  
606 these PTEs on their total concentration maps suggests anthropogenic atmospheric  
607 source deposition. A geogenic contribution to Zn, Cu, Ni and Cr concentrations was  
608 identified in the form of coal outcrops in Sheffield.

609 The relationship between historical development and differing PTEs is a novel finding  
610 from this research. This suggests that PTEs have the potential for use as 'urbanisation  
611 tracers' as different PTEs have been shown to be associated with different historical  
612 anthropogenic sources.

613 Background values were calculated for the PTEs deemed to have some form of  
614 anthropogenic input (via the PCA) within each of the city's development zones. These  
615 PTEs demonstrated varying historical sources within the development zones which  
616 result in varying background values. The background values for Belfast were generally

617 highest in the 1919-1939 development zone, suggesting that soil contamination was at its  
618 greatest in Belfast between 1901 and 1939. This coincides with when shipbuilding and  
619 its associated industries, such as iron and steel foundries, were at their zenith. The  
620 background values calculated for Sheffield varied more widely across the different  
621 development zones considered. The ULBL method was determined to be the most  
622 appropriate for calculating background values within this research, and the ULBLs were  
623 compared to SGVs, S4ULs and pC4SLs. A number of exceedances of these generic  
624 assessment criteria were noted for various PTEs in various development zones. This  
625 demonstrates that the potential risk associated with PTEs in urban environments may  
626 require further assessment. The development of urban subdomains refines the areas that  
627 need to be considered for additional investigation.

628 Current statutory guidance for Part 2A of the Environmental Protection Act states that  
629 widespread geogenic or diffuse anthropogenic pollution in soil should not be regarded  
630 as contaminated land unless other evidence demonstrates that it poses a risk. These  
631 findings establish that PTE concentrations associated with geogenic and diffuse  
632 anthropogenic contamination are elevated to levels that do have the potential to pose  
633 risk to human health. However, as with anthropogenic point sources, a regional  
634 assessment of PTE bioaccessibility would need to be completed to assess the level of risk  
635 posed. These findings potentially suggest that a relevant legislative regime that ensures  
636 geogenic and diffuse anthropogenic contamination are effectively dealt with may be  
637 required.

638

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652

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