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# Influences upon the Lead Isotopic Composition of Organic and Mineral Horizons in Soil Profiles from the National Soil Inventory of Scotland (2007-09)

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**John G. Farmer[a]\*, Margaret C. Graham[a], Lorna J. Eades[b], Allan Lilly[c], Jeffrey R. Bacon[c]**

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[a]School of GeoSciences, The University of Edinburgh, Crew Building, Alexander Crum Brown Road,  Edinburgh, EH9 3FF, Scotland, UK

[b]School of Chemistry, The University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh EH9 3FJ, Scotland, UK

[c]James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, Scotland, UK

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\*Corresponding author. Tel.: +44-131-6504907; fax: +44-131-6620478

*E-mail address:* J.G.Farmer@ed.ac.uk (J.G. Farmer)

23

24    **Abstract**

25

26    Some 644 individual soil horizons from 169 sites in Scotland were analysed for Pb

27    concentration and isotopic composition. There were three scenarios: (i) 36 sites where both

28    top and bottom (i.e. lowest sampled) soil horizons were classified as organic in nature, (ii) 67

29    with an organic top but mineral bottom soil horizon, and (iii) 66 where both top and bottom

30    soil horizons were mineral. Lead concentrations were greater in the top horizon relative to the

31    bottom horizon in all but a few cases. The top horizon $^{206}Pb/^{207}Pb$ ratio was lesser (outside

32    analytical error) than the corresponding bottom horizon $^{206}Pb/^{207}Pb$ ratio at (i) 64%, (ii) 94%

33    and (iii) 73% of sites, and greater at only (i) 8%, (ii) 3% and (iii) 8% of sites. A plot of

34    $^{208}Pb/^{207}Pb$ vs. $^{208}Pb/^{206}Pb$ ratios showed that the Pb in organic top (i, ii) and bottom (i)

35    horizons was consistent with atmospherically deposited Pb of anthropogenic origin. The

36    $^{206}Pb/^{207}Pb$ ratio of the organic top horizon in (ii) was unrelated to the $^{206}Pb/^{207}Pb$ ratio of the

37    mineral bottom horizon as demonstrated by the geographical variation in the negative shift in

38    the ratio, a result of differences in the mineral horizon values arising from the greater

39    influence of radiogenic Pb in the north. In (iii), the lesser values of the $^{206}Pb/^{207}Pb$ ratio for

40    the mineral top horizon relative to the mineral bottom horizon were consistent with the

41    presence of anthropogenic Pb, in addition to indigenous Pb, in the former. Mean

42    anthropogenic Pb inventories of 1.5 and 4.5 g m$^{-2}$ were obtained for the northern and

43    southern halves of Scotland, respectively, consistent with long-range atmospheric transport of

44    anthropogenic Pb (mean $^{206}Pb/^{207}Pb$ ratio ~1.16). For cultivated agricultural soils (Ap), this

45    corresponded to about half of the total Pb inventory in the top 30 cm of the soil column.

46

47    Keywords: Pb, isotope ratios, organic soil, mineral soil, Scotland

48

**1. Introduction**

Clair Patterson's finding in the 1960s that more than 90% of the atmospheric Pb in the northern hemisphere at that time was derived from anthropogenic sources such as car-exhaust emissions (in the era of leaded petrol), coal combustion and metal ore smelting (Patterson, 1965; Murozumi et al., 1969) has subsequently been supported by many historical studies based on the Pb analysis of cores from ice sheets, peat bogs and lake sediments (e.g. Boutron et al., 1991; Shotyk et al., 1998; Renberg et al., 2001). Such studies have often included Pb isotope analyses, which have provided valuable information on the relative contributions of Pb from sources of differing Pb isotopic composition associated with various human activities over the past few thousand years (e.g. Shirahata et al., 1980; Rosman et al., 1997; Bindler, 2011). Based partly on the isotopic evidence (e.g. $^{206}Pb/^{207}Pb$ ratios), it is widely accepted that accumulations of Pb in ice, peat and sediment cores are anthropogenic in origin and that they are the result of long-term and long-range atmospheric deposition (e.g. Steinnes et al., 2005a; Zheng et al., 2007; Steinnes, 2009; Klaminder et al., 2011).

In Scotland, there have been numerous studies of the isotopic composition of sources of Pb (Sugden et al., 1993; Farmer et al., 1999, 2000) and of Pb in peat, lake sediments, moss and other terrestrial plants in the rural environment (e.g. Farmer et al., 1996, 1997, 2002, 2010, 2015; MacKenzie et al., 1997, 1998; Eades et al., 2002; Weiss et al., 2002; Patrick and Farmer, 2007; Cloy et al., 2008; Kylander et al., 2009). With the exception of a few studies on urban and suburban soils (e.g. Farmer et al., 2011; MacKinnon et al., 2011), most Pb isotopic work on Scottish soils has focussed on the rural environment, in particular at the Glensaugh field station and long-term monitoring site in the rural north east (e.g. Bacon et al., 1992, 1995, 2004, 2006). Data for organic soils at Glensaugh, which is a site distant from any point sources, show typical $^{206}Pb/^{207}Pb$ ratios to be 1.15-1.17 in surface horizons but 1.18-

74  1.20 in deeper horizons (Bacon et al., 1992, 1995, 2004, 2006; Farmer et al., 2005). Long-

75  range atmospheric transport and deposition of Pb has been invoked in explanation, with

76  contributory sources including car-exhaust emissions ($^{206}$Pb/$^{207}$Pb ratio ~1.08), Pb ore

77  smelting (~1.17) and coal combustion (~1.18) (Farmer et al., 1999, 2000, 2010). Hilltop peat

78  cores at Glensaugh have shown anthropogenic Pb inventories in the range 6-9 g m$^{-2}$, with

79  ~40% deposited prior to 1900 and a further ~20% between 1900 and 1930 from ore

80  smelting/coal combustion during the UK industrial era, prior to the introduction of leaded

81  petrol, which was in use in the UK until its total ban in 2000 (Farmer et al., 2005).

82      There is, however, an alternative view that there is little evidence for long-range

83  atmospheric transport of Pb. While conceding the influence of human activities in and around

84  urban centres, a few large-scale soil surveys in both Europe and North America have

85  concluded that soil Pb contamination results principally from local point sources with only

86  minimal influence of long-range atmospheric transport (Reimann et al., 2009, 2011, 2012).

87  One such study provided Pb isotope data for European cultivated agricultural soils (Ap, 0-20

88  cm) that included ~ 50 soils for the whole of Scotland, collected on a 50 km grid (Reimann et

89  al., 2012).

90      The National Soil Inventory of Scotland (NSIS) was recently resampled on a 20 km

91  grid and samples taken from a range of soil horizons and depths. This exercise has provided

92  an ideal opportunity to carry out a much more detailed and systematic survey of the Pb status

93  of Scottish soils, in particular of the Pb isotope composition, to investigate the geographical

94  spread, extent and source of Pb contamination in Scotland. A similar country-wide survey has

95  recently been carried out in The Netherlands, where Walraven et al. (2013a, 2013b)

96  concluded that the Pb isotope composition of the additional Pb in ~350 rural topsoils (A, 0-20

97  cm) differed clearly from lithologically inherited Pb, as observed in the corresponding

98  subsoils (BC, C, 100-120 cm), and argued for an anthropogenic origin.

4

99    The specific objectives of this project were to (i) determine the Pb isotopic composition

100   of soil profiles for which Pb concentrations had been measured as part of the recent NSIS

101   2007-09 Survey,  (ii) establish the baseline Pb isotope composition of mineral soils and the

102   potentially anthropogenically influenced Pb isotope composition of both mineral and organic

103   soil horizons throughout Scotland, (iii) compare the Pb isotope composition of surface soil

104   horizons with that of bottom (i.e. lowest sampled) soil horizons and (iv) assess the causes and

105   extent of any observed variations in Pb isotope composition, including the magnitude of the

106   potential anthropogenic contribution.

107

108   **2.      Materials and Methods**

109

110   *2.1 National Soil Inventory of Scotland (NSIS)*

111

112   The National Soil Inventory of Scotland (NSIS) consists of samples taken on a regular grid

113   pattern in 1978-88 (NSIS 1) and resampled in 2007-09 (NSIS 2). The grid was aligned with

114   the Ordnance Survey (OS) National Grid and 183 soil profiles were sampled between 2007

115   and 2009 at 20 km spacing. Fig. 1 shows the distribution among the OS zones (i.e. 100 km

116   grid squares) of the 169 soil profiles on which this paper was ultimately based.

117

118   *2.2 Sampling*

119

120       At each location a soil pit, rectangular in shape and sufficiently large to allow sampling

121   of each of the major horizons, was dug by spade to a depth of at least 75 cm. This was

122   sufficient to allow the description and sampling of the parent material at each location, where

123   possible. Supplementary Information (SI) Table 1 summarises the main soil groups and the

124 number of soil horizons for the sites in each OS zone. A description of the different soil

125 horizons is given in SI Table 2.

126     Approximately 1-1.5 kg of relatively stone-free soil was collected from each horizon.

127 Samples were generally taken from a 10-cm depth band situated approximately in the middle

128 of the horizon or at depths thought to be appropriate where the thickness of the horizon was

129 judged to warrant more than one sample. In some situations where the horizon thickness was

130 less than 10 cm, the top and bottom sample depths were set to allow a representative and pure

131 sample to be collected from the horizon. Thin transition zones up to 6 cm thick were

132 generally excluded where boundaries were gradual or diffuse.

133     The soil material was loosened and extracted using a trowel or knife, collected in a

134 sampling tray held level with the lower boundary of the sample depth, and placed in a low

135 density polyethylene bag. In general, soils were sampled sequentially beginning with the

136 lowest horizon.

137

138 *2.3 Sample preparation and analysis*

139

140 *2.3.1 Acid digestion*

141 Soil samples were air-dried at 30°C and sieved (<2 mm). Ground soil samples (<2 mm, 0.25-

142 5 g) were initially moistened with ~0.5-1 mL of deionised (UHP) water and then digested in a

143 mixture of HCl and $HNO_3$ (*aqua regia*, 3:1) under reflux for 2 h (ISO 11466, 1995). If the

144 samples contained >0.5 g organic C, an additional 1 mL $HNO_3$ was added before digestion

145 for every 0.1 g C above 0.5 g until the reaction stopped and all organic C had been oxidised.

146 In addition, organic samples were left to pre-digest prior to the reflux digestion, typically for

147 16-20 h.

148       The digest was allowed to cool, filtered and made up to a known volume with 0.5 M

149      HNO$_3$ for analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

150

151      *2.3.2 Pb concentration by ICP-MS (James Hutton Institute)*

152      Lead concentrations were determined by ICP-MS using the pulse count mode of an Agilent

153      7500ce instrument with octopole reaction system and nickel cones (Agilent Technologies,

154      Stockport, UK). The RF forward power was 1500 W, with argon gas flows of 0.9 and 0.1 L

155      min$^{-1}$ for carrier and makeup flows, respectively. All sample solutions were diluted with

156      high-purity water (18.2 M$\Omega$ cm) from a Milli-Q water system (Millipore, Watford, UK) in

157      line using the Agilent ISIS system with a ratio of 1:10 and subsequently nebulised using a

158      Babington nebuliser. The spectrum analysis acquisition mode was used, with three points per

159      unit mass and integration times of 1 s per point for each of $^{206}$Pb, $^{207}$Pb and $^{208}$Pb, and three

160      replicate runs per sample. Quantification of Pb was based on summation of counts per second

161      from all three measured isotopes for sample and Pb standard solutions, with $^{185}$Re employed

162      as the internal standard during instrumental analysis. Quality Control solutions were run at a

163      frequency of every 20 samples to evaluate instrument performance, with digest test soils

164      regularly analysed within sample sets to ensure digest quality.

165      An in-house test sample of a mineral soil ('Analytical Top Soil') with indicative Pb

166      concentration ($\pm$ 1 standard deviation (s.d.)) of 42.3 $\pm$ 3.0 mg kg$^{-1}$ (n=1430) was included in

167      each batch of samples and put through the complete analytical procedure including *aqua*

168      *regia* extraction and ICP-MS analysis. The measured Pb concentration ($\pm$ 1 s.d.) of this test

169      soil over the three years of the NSIS 2 project was 43.2 $\pm$ 2.7 mg kg$^{-1}$ (n=197).

170

171      *2.3.3 Pb isotope ratios by ICP-MS (University of Edinburgh)*

172  Soil digest solutions were diluted to a Pb concentration of <25 µg L$^{-1}$ with high-purity water

173  (18.2 MΩ cm) from a Milli-Q water system (Millipore, Watford, UK). Lead isotope ratios

174  ($^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{207}$Pb and $^{208}$Pb/$^{206}$Pb) were then determined by quadrupole ICP-MS using

175  the pulse count mode of an Agilent 7500ce instrument with octopole reaction system and

176  nickel cones (Agilent Technologies, Stockport, UK). The RF forward power was 1540 W and

177  the reflected power 1 W. The argon gas flows were 0.82 and 0.20 L min$^{-1}$ for carrier and

178  makeup flows, respectively, and the peristaltic pumping rates into the Mira mist nebuliser 0.2

179  or 1.2 L min$^{-1}$, respectively. The isotope analysis acquisition mode was used, with three

180  points per unit mass and integration times of 0.3 s per point for each of $^{206}$Pb, $^{207}$Pb and $^{208}$Pb,

181  and six replicate runs per sample. A Pb isotopic reference material from the National Institute

182  of Standards and Technology (NIST), SRM 981, was used for mass bias correction.

183      Mean analytical errors (1 s.d.) on $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{207}$Pb and $^{208}$Pb/$^{206}$Pb ratios in the

184  soil samples (n=674) were ± 0.004, ± 0.008 and ± 0.007, respectively. Overall mean

185  analytical precision for Pb isotope ratio determination in duplicate soil sample solutions

186  (n=63) averaged ± 0.3%. The mean isotope ratios (± 1 s.d.) of $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{207}$Pb and

187  $^{208}$Pb/$^{206}$Pb determined in the in-house 'Analytical Top Soil' (n=12) as 1.174 ± 0.004, 2.459 ±

188  0.005 and 2.095 ± 0.007, respectively, were in good agreement with previously established

189  values of 1.175 ± 0.001, 2.451 ± 0.001 and 2.087 ± 0.002. For NIST SRM 1643e Water

190  Reference Material (n=49), used to check the consistency of inter-batch analytical runs, mean

191  values of 1.167 ± 0.003, 2.450 ± 0.005 and 2.099 ± 0.004 were obtained for $^{206}$Pb/$^{207}$Pb,

192  $^{208}$Pb/$^{207}$Pb and $^{208}$Pb/$^{206}$Pb, respectively.

193

194  **3. Results and Discussion**
195
196

197    Of the 183 sites of NSIS 2, there were 175 for which material from at least two different soil

198    horizons was available and for which both Pb concentration and Pb isotope ratios were

199    obtained. Of these 175 sites, six were considered anomalous by virtue of an unusually high

200    ($\geq$1.44) or unusually low ($\leq$1.10) value of the $^{206}$Pb/$^{207}$Pb ratio determined in the lowest

201    sampled horizon of the soil profile.  Consequently, they are considered separately, leaving

202    169 sites for the bulk of this study (Fig. 1).

203

204    *3.1 Soil Profiles of Pb concentration and $^{206}$Pb/$^{207}$Pb ratio*

205

206    Figs. 2a-e present a typical Pb concentration and $^{206}$Pb/$^{207}$Pb ratio profile for each of five

207    different categories of soil horizon sequences (cf. SI Table 2 for soil horizon descriptions)

208    based upon the nature of the uppermost and lowermost sampled soil horizon. The categories

209    were: (i) organic-organic (36 sites) (Fig. 2a), (ii) organic-mineral (67 sites) (Fig. 2b), (iii)

210    organic-mineral for OS zone NH, where the $^{206}$Pb/$^{207}$Pb ratio for the lowermost mineral

211    horizon was often high (up to 1.35) (Fig. 2c), (iv) mineral (Ap)-mineral (42 sites) (Fig. 2d)

212    and (v) mineral (non-Ap)-mineral (24 sites) (Fig. 2e). There were 66 mineral-mineral sites in

213    total. The predominant trends at the 169 sites of all five categories were of (i) decreasing Pb

214    concentration (usually from the top soil horizon but occasionally (~15%) from the second top

215    horizon) with increasing depth and (ii) increasing $^{206}$Pb/$^{207}$Pb ratio with increasing depth. Of

216    the 169 sites there were only 10 (i.e. 6%) where the $^{206}$Pb/$^{207}$Pb ratio of the top soil horizon

217    was greater (outside 1 s.d. analytical error) than that of the corresponding bottom horizon,

218    compared with 134 (i.e. 79%) where it was lesser. The extent of the difference in individual

219    cases, however, depended upon which combination of organic or mineral uppermost and

220    lowermost soil horizons pertained and, indeed, upon factors such as geographical variation in

221    the $^{206}$Pb/$^{207}$Pb ratio of the lowermost soil horizon when it was mineral in nature (cf. Figs. 2a-

9

222    e). The SI Figs. 1-6 provide six examples of each case including the six anomalous sites, an

223    example of which is shown in Fig. 2f.

224

225    *3.2 $^{206}Pb/^{207}Pb$ ratios and Pb concentrations in top and bottom soil horizons*

226

227    Fig. 3 presents histograms of the number of sites with values of $^{206}Pb/^{207}Pb$ ratios, ranging by

228    0.01 increment from 1.10 to 1.36, corresponding to the three scenarios of top and bottom soil

229    horizon being organic and organic (Fig. 3a), organic and mineral (Fig. 3b) and mineral and

230    mineral (Fig. 3c). Fig. 4 displays separate histograms of Pb concentrations for organic top,

231    organic bottom, mineral top and mineral bottom soil horizons at all sites as appropriate.

232    Individual horizons are considered in turn below.

233

234    *3.2.1 Mineral bottom soil horizon*

235    Of the 169 sites, there were 133 where the bottom soil horizon was classified as mineral (A-1,

236    E-3, B-22, BC-35, C-72). The mean mineral bottom horizon depth range was 56-78 cm, with

237    a mean sample depth range of 65-75 cm.

238

239    *3.2.1.1 $^{206}Pb/^{207}Pb$ ratios*

240    The $^{206}Pb/^{207}Pb$ ratio ranged from 1.132 to 1.348 (Figs. 3b,c) with a mean value of 1.208

241    (median 1.196). The different main mineral bottom soil horizons (B, BC, C) exhibited similar

242    mean and median values of the $^{206}Pb/^{207}Pb$ ratio (Table 1).

243        There was, however, considerable geographical variation across Scotland, as shown by

244    consideration of values in each of the OS zones (SI Table 3). For example, of the 19 sites

245    with a mineral bottom $^{206}Pb/^{207}Pb$ value $\geq 1.25$ (Fig. 3), eight were from NH (four $\geq 1.30$), four

246    from NN (one $\geq 1.30$), two from NJ and one from each of NM (one $\geq 1.30$) and NR.

247 Excluding the Orkney and Shetland Islands (n=3), there appeared to be two main areas

248 (n=117), consisting of contiguous zonal groupings. In the first of these, comprising the six

249 zones NG, NH, NJ, NM, NN, NR (Fig. 1), where the mean values for the mineral bottom soil

250 horizons of the individual zones ranged from 1.201 (NM) to 1.257 (NH) (Fig. 5a, SI Table 3),

251 the overall mean value for the sites in the group (n=64) was $1.227 \pm 0.048$ (median 1.225). In

252 the second grouping, comprising the five zones NO, NS, NT, NX, NY (Fig. 1), where the

253 mean values for the mineral bottom soil horizons of the individual zones ranged from 1.180

254 (NY) to 1.196 (NT) (Fig. 5a, SI Table 3), the overall mean value for the sites in the group

255 (n=53) was $1.189 \pm 0.018$ (median 1.187). A third grouping comprised the rest of the zones in

256 the north and lay on the fringes of the first main grouping, i.e. NF, NB, NC, ND, NK (Fig. 1).

257 The mean values for the mineral bottom soil horizons of the individual zones in this third

258 grouping ranged from 1.177 (NC) to 1.211 (ND) (Fig. 5a, SI Table 3), with an overall mean

259 value (n=13) of $1.188 \pm 0.037$ (median 1.176).

260 The rock types of stones in the 19 mineral bottom soils which had $^{206}Pb/^{207}Pb$ ratios

261 $\geq 1.25$ were predominantly granite or schists (e.g. quartz-mica schists). The typically greater

262 values of the $^{206}Pb/^{207}Pb$ ratio for the bottom mineral soils of the NG, NH, NJ, NM, NN, NR

263 group compared with the rest of Scotland are attributable to the accumulation of radiogenic

264 Pb in these soils resulting from the radioactive decay of $^{238}U$ (half-life = 4.47 x $10^9$ years and

265 $^{235}U$ (half-life = 0.70 x $10^9$ years) present in uraniferous minerals in these soils, in addition to

266 primordial Pb. Values of the $^{206}Pb/^{207}Pb$ ratio as high as 1.35-1.39 have been found in bottom

267 sediments of freshwater lakes in the granitic terrain of the Cairngorm and Grampian

268 Mountains (Yang et al., 2007; Farmer et al., 2015), which are located primarily in OS zones

269 NH, NJ, NN and upper NO.

270

271 *3.2.1.2 Pb concentrations*

272     The mean Pb concentration (range 1.3-133 mg kg$^{-1}$, n=133) for the mineral bottom soil

273     horizon (Fig. 4d) was 13 (median 9.1) mg kg$^{-1}$, with similar mean and median values for the

274     different main mineral bottom soil horizons (Table 1).

275         In contrast to the $^{206}$Pb/$^{207}$Pb results, there did not appear to be much geographical

276     variation in Pb concentration across Scotland as demonstrated by mean and median values for

277     individual OS zones with n≥10 (Fig. 6a, SI Table 4). Furthermore, of the 15 sites with a

278     mineral bottom Pb concentration ≥20 mg kg$^{-1}$ (Fig. 4), one was from NC, two from ND, one

279     from NH, one from NK (one ≥100 mg kg$^{-1}$), one from NM, two from NN, two from NO (one

280     ≥100 mg kg$^{-1}$), one from NR, one from NS and three from NT. In the first grouping (NG,

281     NH, NJ, NM, NN, NR, n=64), established above as having an elevated mean $^{206}$Pb/$^{207}$Pb ratio

282     of 1.227 (median 1.225), the mean Pb concentration was 9.9 (median 7.9) mg kg$^{-1}$. In the

283     second grouping (NO, NS, NT, NX, NY, n=53), for which the mean $^{206}$Pb/$^{207}$Pb ratio was

284     1.189 (median 1.187), the mean Pb concentration was 14 (median 10) mg kg$^{-1}$ [12 (median

285     10) mg kg$^{-1}$ when one value of 121 was excluded]. In the third grouping comprising the rest

286     (NF, NB, NC, ND, NK, n=13), but excluding the Orkney and Shetland Islands, the mean Pb

287     concentration was 23 (median 8.9) mg kg$^{-1}$ [14 (median 8.5) mg kg$^{-1}$ when one value of 133

288     was excluded].

289

290     *3.2.2 Mineral top soil horizon*

291     Of the 169 sites, there were 66 where the uppermost soil horizon was classified as mineral

292     (Ap-42, uncultivated A-21, E-1, B-2). The mean mineral uppermost soil horizon depth range

293     for all A (n=63) was 0-25 cm with a mean sample depth range of 6.2-15.8 cm. For cultivated

294     Ap horizons, the corresponding mean ranges were 0-29 cm and 6.9-16.9 cm; for other A, they

295     were 1-18 cm and 4.7-13.6 cm; and, overall (n=66), the mean ranges were 1-26 cm and 6.9-

296     16.6 cm.

297

### 3.2.2.1 $^{206}Pb/^{207}Pb$ ratios

299  The $^{206}Pb/^{207}Pb$ ratio ranged from 1.153 to 1.236 (Fig. 3c) with a mean value of 1.176

300  (median 1.174), with similar corresponding mean values for all A uppermost horizon samples

301  (n=63) and their sub-sets Ap (n=42) and other A (n=21) (Table 1).

302  There appeared to be some geographical variation, as shown by consideration of values

303  for the OS zones (Fig. 5b, SI Table 3). For example, of the eight sites with a mineral

304  uppermost horizon $^{206}Pb/^{207}Pb$ value ≥1.19 (Fig. 3), five were from NJ (two ≥1.20), one from

305  HY (one ≥ 1.20), one from ND and one from NH. Excluding the Orkney and Shetland Islands

306  (n=2) and combining the two most northerly contiguous zones established for the mineral

307  bottom soil horizon, i.e. NF, NB, NC, ND, NK (n=3) and NG, NH, NJ, NM, NN, NR (n=23),

308  where the mean values for the mineral top soil horizons of the individual zones ranged from

309  1.169 (NK) to 1.195 (ND) (Fig. 5b, SI Table 3), the overall mean value for the group (n=26)

310  was 1.183 ± 0.018 (median 1.179). In the second grouping, the most southerly contiguous

311  zones established for the mineral bottom soil horizon, i.e. the five zones NO, NS, NT, NX,

312  NY (n=38), where the mean and median values for the mineral top soil horizons of individual

313  zones ranged from 1.165 (NS) to 1.175 (NT) (Fig. 5b, SI Table 3), the overall mean value for

314  the group (n=38) was 1.171 ± 0.007 (median 1.172). Alternatively, taking the northernmost

315  zones as HU, HY, NB, NC, ND, NF, NG, NH, NJ, NK, the mean $^{206}Pb/^{207}Pb$ value (n=19)

316  was 1.188 ± 0.017 (median 1.184) (mean sample mid-point depth = 11.8 cm) compared with

317  a mean value (n=47) of 1.172 ± 0.010 (median 1.172) for the southernmost zones NM, NN,

318  NO, NR, NS, NT, NX, NY (mean sample mid-point depth = 11.7 cm).

319

### 3.2.2.2 Pb concentrations

321    The mean Pb concentration (range 3.5-329 mg kg$^{-1}$, n=66) for the mineral top soil horizon

322    (Fig. 4c) was 41 (median 27) mg kg$^{-1}$, with similar mean and median values for the different

323    main mineral top soil horizons of all A, Ap and other A (Table 1).

324        As with the $^{206}$Pb/$^{207}$Pb results, there appeared to be some geographical variation, as

325    shown by consideration of values for the OS zones (Fig. 6b, SI Table 4). Only 11% (2/19) of

326    samples from the northernmost OS zones of HU, HY, NB, NC, ND, NF, NG, NH, NJ, NK

327    (mean 39 ± 74  mg kg$^{-1}$ [or 22 ± 23 mg kg$^{-1}$ when one value of 329 mg kg$^{-1}$ was excluded],

328    median 17 mg kg$^{-1}$) had Pb concentration ≥ 50 mg kg$^{-1}$, compared with 28% (13/47) for the

329    southernmost zones NM, NN, NO, NR, NS, NT, NX, NY (mean 42 ± 34 mg kg$^{-1}$, median 30

330    mg kg$^{-1}$).

331

332    *3.2.3 Organic top soil horizon*

333    Of the 169 sites, there were 103 where the uppermost soil horizon was classified as organic

334    (LF, F, LFH, FH - 24 in all; H-10; O-69).  The mean organic top soil horizon depth range was

335    0-6 cm for LF, F, LFH, FH, 3-11 cm for H and 2-19 cm for O, with corresponding mean

336    sample depth ranges of 0.9-5.7 cm, 3.8-9.7 cm and 5.6-14.5 cm, respectively. Overall, the

337    mean organic top horizon soil depth range was 1.4-15.3 cm, with a mean organic top soil

338    sample depth range of 4.3-12.0 cm.

339

340    *3.2.3.1 $^{206}$Pb/$^{207}$Pb ratios*

341    The $^{206}$Pb/$^{207}$Pb ratio ranged from 1.105 to 1.202 (Figs. 3a,b) with a mean value of 1.156

342    (median 1.159) and mean values for the different organic top soil horizons of 1.135 (median

343    1.136) for LF, F, LFH, FH, 1.154 (median 1.154) for H and 1.163 (median 1.164) for O

344    (Table 1). With respect to O top samples from different depths, the mean $^{206}$Pb/$^{207}$Pb value

345    where the mid-point of sample depth was ≤4 cm (n=8) was 1.147 ± 0.013; ≤10 cm (n=47)

346    1.161 ± 0.013; >10 cm (n=22) 1.167 ± 0.006; ≥18 cm (n=7) 1.170 ± 0.006.

347         Although at first glance there appeared to be some geographical variation across

348    Scotland, on the basis of mean organic top soil horizon $^{206}Pb/^{207}Pb$ values for the OS zones,

349    ranging from 1.130 (NK) and 1.139 (NO) to 1.164 (ND) and 1.171 (NS) (Fig. 5c, SI Table 5),

350    this was largely explicable on the basis of the nature of the organic top soil horizon sampled

351    and the mean sample depth. For example, 83% of NO samples were LF-H (i.e. non-O) and

352    the mean sample depth (n=6) was 4.6 cm. The zones with the next lowest mean $^{206}Pb/^{207}Pb$

353    values (1.142-1.160) were NJ, NH, NN, NT and NM, with mean sample depths of 7.1, 5.6,

354    6.2, 6.4 and 5.3 cm, respectively, and to which LF-H horizons contributed 75, 44, 41, 56 and

355    33% of samples, respectively. In contrast, 0% of NS samples (mean 1.171) were LF-H and

356    the mean sample depth (n=5) was 16.2 cm. The zones (excluding HY and HU for Orkney and

357    Shetland)  with the next highest mean $^{206}Pb/^{207}Pb$ values (1.163-1.164) were ND, NR, NX,

358    NB and NC, with mean sample depths of 12.8, 9.9, 16.3, 9.1 and 11.1 cm, respectively, and

359    to which LF-H horizons contributed 0, 25, 25, 0 and 0% of samples, respectively. The zone

360    with the lowest mean $^{206}Pb/^{207}Pb$ value, NK (1.130) had a mean sample depth (O horizon) of

361    just 2.5 cm.

362

363    *3.2.3.2 Pb concentrations*

364    The mean Pb concentration (range 4.3-580 mg kg$^{-1}$, n=103) for the organic top soil horizon

365    (Fig. 4a) was 77 (median 43) mg kg$^{-1}$ (Table 1), with mean values (mg kg$^{-1}$) for the different

366    organic top soil horizons of 57 (median 43) for LF, F, LFH, FH, 102 (median 52) for H and

367    80 (median 42) for O (Table 1).

368         In contrast to the $^{206}Pb/^{207}Pb$ results, there did appear to be considerable systematic

369    geographical variation, north to south, in the Pb concentration data (Fig. 6c, SI Table 4). Only

370   5.5% (3/55) of samples from the northernmost OS zones of HU, HY, NB, NC, ND, NF, NG,

371   NH, NJ, NK (mean $38 \pm 32$ mg kg$^{-1}$, median 32 mg kg$^{-1}$) had concentrations $\geq 100$ mg kg$^{-1}$,

372   compared with 27% (7/26) from the more centrally located zones NM, NN, NO (mean $113 \pm$

373   135 mg kg$^{-1}$, median 63 mg kg$^{-1}$) and 50% (11/22) from the southernmost zones NR, NS, NT,

374   NX (mean $133 \pm 99$ mg kg$^{-1}$, median 109 mg kg$^{-1}$).

375

376   *3.2.4 Organic bottom horizon*

377   Of the 169 sites, there were 36 where the bottom soil horizon was classified as organic (O-

378   36).  The mean organic bottom soil horizon depth range was 43-90 cm with a corresponding

379   mean sample depth range of 61-72 cm.

380

381   *3.2.4.1 $^{206}Pb/^{207}Pb$ ratios*

382   The $^{206}$Pb/$^{207}$Pb ratio ranged from 1.135 to 1.226 (Fig. 3a), with a mean value of 1.175

383   (median 1.177) (Table 1). For samples taken from profiles with O bottom horizons, the mean

384   $^{206}$Pb/$^{207}$Pb value was $1.172 \pm 0.017$, $1.181 \pm 0.019$ (or $1.174 \pm 0.011$ when two values of

385   1.216 and 1.226 were excluded) and $1.171 \pm 0.017$ for samples with mid-point sample depths

386   of <50 cm (n=9), 50-79 cm (n=15) and $\geq$80 cm (n=12), respectively.

387   On the basis of mean organic bottom soil horizon $^{206}$Pb/$^{207}$Pb values for individual OS

388   zones, there appeared to be little geographical variation (Fig. 5d, SI Table 5). The mean

389   $^{206}$Pb/$^{207}$Pb values for the northernmost zones of HU, NB, NC, ND, NF, NG, NH, NJ (n=20)

390   of $1.176 \pm 0.022$ (median 1.178) (or $1.171 \pm 0.016$ (median 1.176) when two values of 1.216

391   and 1.226 were excluded) were comparable with the mean value of $1.174 \pm 0.012$ (median

392   1.177) for the southernmost zones of NM, NN, NO, NR, NS, NT, NX (n=16).

393

394   *3.2.4.2 Pb concentrations*

395 The mean Pb concentration (range 1.4-36 mg kg$^{-1}$, n=36) for the organic bottom soil horizon

396 (Fig. 4b) was 7.5 (median 4.3) mg kg$^{-1}$ (Table 1). In contrast to the $^{206}$Pb/$^{207}$Pb results, there

397 did appear to be considerable systematic geographical variation, north to south, in the Pb

398 concentration data (Fig. 6d, SI Table 4). None (0/20) of the samples from the northernmost

399 OS zones of HU, NB, NC, ND, NF, NG, NH, NJ (mean 3.8 ± 1.8 mg kg$^{-1}$, median 3.25 mg

400 kg$^{-1}$) had concentrations > 8 mg kg$^{-1}$, compared with 50% (8/16) from the southernmost

401 zones of NM, NN, NO, NR, NS, NT, NX (mean 12 ± 10 mg kg$^{-1}$, median 7.6 mg kg$^{-1}$).

402

403 *3.3 Comparison of top and bottom soil horizon $^{206}$Pb/$^{207}$Pb ratios*

404

405 *3.3.1 Organic top and organic bottom soil horizons*

406 Of the 36 sites with an organic top and organic bottom soil horizon, the Pb concentration was

407 always greater in the former (Fig. 7). There were 23 sites (i.e. 64%) where the top $^{206}$Pb/$^{207}$Pb

408 ratio was lesser (outside 1 s.d. analytical error) than that of the bottom horizon and only three

409 (i.e. 8%) where the latter was lesser (outside 1 s.d.) than the former, the other 10 (i.e. 28%)

410 having top and bottom horizon values within 1 s.d. of each other (Fig. 7). This is also

411 reflected in Table 2, which shows the mean values by OS zone of corresponding top and

412 bottom $^{206}$Pb/$^{207}$Pb ratios and the mean difference between the paired $^{206}$Pb/$^{207}$Pb ratios of the

413 two horizons. The overall mean difference (top minus bottom) for the 36 sites was -0.014

414 (Table 2).

415 　　The finding of increasing $^{206}$Pb/$^{207}$Pb ratios with increasing depth in organic soils such

416 as peat is in line with established trends in cores from ombrotrophic peat bogs from around

417 Scotland (Farmer et al. 1997; MacKenzie et al. 1997, 1998; Cloy et al., 2008) and reflects

418 temporal changes in sources of anthropogenic Pb deposited from the atmosphere, as shown in

419 the plot of $^{208}$Pb/$^{207}$Pb vs. $^{206}$Pb/$^{207}$Pb (Fig. 8). The more recent influence of car-exhaust

420 emissions, containing Pb from leaded petrol (to which Australian Pb of $^{206}$Pb/$^{207}$Pb ratio

421 ~1.04 was a major contributor), relative to Pb from Scottish ore mining/smelting and coal

422 burning can be clearly seen in the organic top horizon. The best-fit lines through the organic

423 top and organic bottom data, however, are of similar gradient, 1.047 and 1.010, respectively

424 (Fig. 8).

425

426 *3.3.2 Organic top and mineral bottom soil horizons*

427 Of the 67 sites with an organic top and mineral bottom soil horizon, the Pb concentration was

428 greater in the former in all but five (two outside analytical error) cases (Fig. 9), although the

429 direct comparison of concentrations is of rather limited value in view of the approximately

430 order of magnitude difference in dry bulk density between these two horizons. There were 63

431 sites (i.e. 94%) where the top horizon $^{206}$Pb/$^{207}$Pb ratio was lesser (outside 1 s.d. analytical

432 error) than the bottom horizon value and only two (i.e. 3%) where the latter was lesser

433 (outside 1 s.d.) than the former, the other two (i.e. 3%) having top and bottom horizon values

434 within 1 s.d. of each other (Fig. 9). This is also reflected in Table 3, which shows the mean

435 values by OS zone of corresponding top and bottom $^{206}$Pb/$^{207}$Pb ratios and the mean

436 difference between the paired $^{206}$Pb/$^{207}$Pb ratios of the two horizons. The overall mean

437 difference for the 67 sites was -0.066 (Table 3), but the magnitude varied noticeably with OS

438 zone. Those with the greatest mean $^{206}$Pb/$^{207}$Pb ratio for the mineral bottom horizon, e.g. NG,

439 NH, NJ, NN and NR (Fig. 5a, SI Table 3), had the largest mean differences of -0.064, -0.109,

440 -0.080, -0.077 and -0.089, respectively, between the paired $^{206}$Pb/$^{207}$Pb ratios for the organic

441 top and mineral bottom horizon (Table 3). Indeed, when the mean differences were computed

442 for the three distinct OS zone groupings established in 3.2.1.1, the -0.084 ± 0.052 for NG,

443 NH NJ, NM, NN and NR (n=41) was much greater than the -0.045 ± 0.023 for NO, NS, NT,

444 NX and NY (n=15) and -0.028 ± 0.040 for NF, NB, NC, ND, NK (n=10). In contrast, the

445    corresponding mean differences in $^{206}Pb/^{207}Pb$ ratio between organic top and organic bottom

446    horizons for these three zonal groupings were very similar at -0.015 ± 0.014 (n=12), -0.018 ±

447    0.017 (n=9) and -0.014 ± 0.023 (n=14), respectively.

448         The plot of $^{208}Pb/^{207}Pb$ vs. $^{206}Pb/^{207}Pb$ (Fig. 10) again demonstrates the influence of

449    anthropogenic sources of Pb upon the $^{206}Pb/^{207}Pb$ ratio of the organic top horizon Pb (cf. Fig.

450    8). Indeed the equation for the best-fit line through the organic top horizon data in Fig. 10

451    ($^{208}Pb/^{207}Pb = 1.223 + 1.050\ ^{206}Pb/^{207}Pb$, $r^2=0.939$) is near-identical to that in Fig. 8

452    ($^{208}Pb/^{207}Pb = 1.227 + 1.047\ ^{206}Pb/^{207}Pb$, $r^2=0.899$) and differs from the corresponding best-fit

453    line ($^{208}Pb/^{207}Pb = 1.436 + 0.883\ ^{206}Pb/^{207}Pb$, $r^2=0.697$) through the mineral bottom data.

454         Fig. 9 also shows quite clearly the lack of relationship between the $^{206}Pb/^{207}Pb$ ratios of

455    organic top and mineral bottom horizons, although there is a tendency for some of the values

456    to be closer in magnitude when the mineral bottom horizon is A, E or B, i.e. perhaps in

457    receipt of some downwardly transported anthropogenic Pb (cf. 3.3.4).

458

459    *3.3.3 Mineral top and mineral bottom soil horizons*

460    Of the 66 sites with a mineral top and mineral bottom soil horizon, the Pb concentration was

461    greater in the former in all but five (two outside analytical error) cases (Fig. 11). There were

462    48 (i.e. 73%) where the top $^{206}Pb/^{207}Pb$ ratio was lesser (outside 1 s.d. analytical error) than

463    the bottom value and only five (i.e. 8%) where the latter was lesser (outside 1 s.d.) than the

464    former, the other 13 (i.e. 20%) having top and bottom horizon values within 1 s.d. of each

465    other (Fig. 11). This is reflected in Table 4, which shows the mean values by OS zone of

466    corresponding top and bottom $^{206}Pb/^{207}Pb$ ratios and the mean difference between the paired

467    $^{206}Pb/^{207}Pb$ ratios of the two horizons. The overall mean difference for the 66 sites was -

468    0.021, but the magnitude varied noticeably with OS zone (Table 4). Those with the highest

469    mean $^{206}Pb/^{207}Pb$ ratio for the mineral bottom horizon, e.g. NG, NH, NJ and NM (cf. Fig. 5a,

470    SI Table 3), had the largest mean differences of -0.033, -0.050, -0.029 and -0.040,

471    respectively, between the paired $^{206}$Pb/$^{207}$Pb ratios for the mineral top and mineral bottom

472    horizon (Table 4). Indeed, when the mean differences were computed for the three distinct

473    OS zone groupings established in 3.2.1.1, the -0.029 ± 0.031 for NG, NH, NJ, NM, NN and

474    NR (n=23) was greater than the -0.015 ± 0.012 for NO, NS, NT, NX and NY (n=38) and -

475    0.007 ± 0.022 for NF, NB, NC, ND, NK (n=3), although much less than the corresponding

476    differences for the sites with organic top and mineral bottom soil horizons (cf. 3.3.2). This

477    can be attributed to (i) the presence in the mineral top horizon of some indigenous Pb in the

478    mineral lattice of greater $^{206}$Pb/$^{207}$Pb ratio than the anthropogenic Pb deposited from the

479    atmosphere which constitutes the Pb in the organic horizons and (ii) the preponderance of

480    samples from NO, NS, NT, NX and NY (38/66, i.e. 58%), which have a lesser mean mineral

481    bottom $^{206}$Pb/$^{207}$Pb ratio (cf. Table 4),  in the mineral top and mineral bottom scenario than is

482    the case  in the organic top and mineral bottom scenario where samples from NG, NH, NJ,

483    NM, NN and NR (41/66, i.e. 62%) predominate (cf. Table 3).

484        The plot of $^{208}$Pb/$^{207}$Pb vs. $^{206}$Pb/$^{207}$Pb (Fig. 12) shows the influence of anthropogenic

485    Pb upon the gradient (0.763) in the mineral top horizon when compared with the gradient

486    (0.644) for the mineral bottom horizon data.

487

488    *3.3.4 Intermediate horizons*

489    For those sites where the A horizon was above only two other soil horizons (n=29), the mean

490    difference between the $^{206}$Pb/$^{207}$Pb ratios of the A and middle horizon was -0.020 ± 0.015,

491    with the A value lesser (outside 1 s.d. analytical error) in 83% of cases. In contrast, the value

492    for the middle horizon was within 1 s.d. of the value for the bottom horizon in 69% of cases,

493    with only a further 14% lesser and 17% greater and an overall mean difference of 0.000 ±

494    0.009. In profiles with four sampled horizons (n=23), the mean differences between the

20

495 $^{206}Pb/^{207}Pb$ ratios for A-second, second-third and third-bottom horizons were -0.017 ± 0.019,

496 -0.002 ± 0.017 and -0.001 ± 0.008, respectively.

497       For comparison, the sites where there was an organic horizon (not necessarily the

498 uppermost organic horizon) directly above at least three mineral horizons (n=42) were

499 divided into two groups based upon the range of values of the $^{206}Pb/^{207}Pb$ ratio for the

500 lowermost mineral horizon: (i) <1.200, (ii) ≥1.200. In scenario (i) (n=20), the mean

501 differences between the $^{206}Pb/^{207}Pb$ ratios for organic-second, second-third and third-bottom

502 horizons were -0.017 ± 0.016, -0.007 ± 0.011  and -0.001 ± 0.007, respectively. In scenario

503 (ii) (n=22), the corresponding mean differences were -0.043 ± 0.020, -0.018 ± 0.022 and -

504 0.008 ± 0.015, respectively. The larger differences in scenario (ii) reflect the greater bottom

505 $^{206}Pb/^{207}Pb$ ratio, which directly influences the $^{206}Pb/^{207}Pb$ ratios of the second and third (both

506 mineral) horizons and makes it easier to discern some downward transport of anthropogenic

507 Pb (of much lower $^{206}Pb/^{207}Pb$ ratio) from the organic and second (predominantly E, eluvial)

508 horizons to the third (B) horizon (cf. 3.3.2, Fig. 9). Transport of anthropogenic Pb from

509 organic soil horizons to mineral soil horizons has been well documented elsewhere. This may

510 be substantial, as reported for forest floors in the north-eastern USA (Miller and Friedland,

511 1994; Kaste et al., 2003; Richardson et al., 2014) and Scandinavia (Brännvall et al., 2001;

512 Steinnes and Friedland, 2005; Steinnes et al., 2005b), less so for Mediterranean (Teutsch et

513 al., 2001) and Dutch (Walraven et al., 2014) roadside soils and to only a very limited extent

514 in the peaty topsoils of the intensively studied small organic-rich upland catchment at

515 Glensaugh, Scotland (Vinogradoff et al., 2005; Bacon et al., 2006; Graham et al., 2006).

516

517 *3.4 Anthropogenic Pb inventories*

518

519    Anthropogenic Pb inventories were calculated for each site. Each sample Pb concentration

520    was extrapolated to the whole of the appropriate horizon and the depth interval and dry bulk

521    density used to convert concentration (mg kg$^{-1}$) to inventory (g m$^{-2}$). All Pb in the organic

522    horizons (L, F, H, O) was taken to be anthropogenic. For mineral horizons, a correction to the

523    measured concentration was made for 'baseline' Pb, taken to be the Pb concentration in the

524    lowermost mineral horizon. Excluding seven sites (17-68 g m$^{-2}$, mean 32 ± 18 g m$^{-2}$) where

525    the anthropogenic Pb inventory was >15 g m$^{-2}$, the mean value for each OS zone is listed in

526    SI Table 6 and displayed in Fig. 13.

527         The range of mean values for each OS zone from HU to NM was 0.6-2.2 g m$^{-2}$, with an

528    overall average of 1.5 ± 1.2 g m$^{-2}$, sites with organic (n=58), Ap (n=13) and A (n=8) top

529    horizons exhibiting comparable mean values of 1.5 ± 1.2, 1.7 ± 1.7 and 1.2 ± 0.7 g m$^{-2}$,

530    respectively. Cloy et al. (2008) reported 1.2 g m$^{-2}$ (post-1800 AD) for a dated peat core

531    collected in 2004 from Turclossie Moss (OS zone NJ).

532         For the remaining zones, NN-NY, the range of mean values was 3.3-6.2 g m$^{-2}$, with an

533    overall average of 4.5 ± 3.0 g m$^{-2}$. The sites with organic (n=44), Ap (n=24) and A (n=15) top

534    horizons were again in good agreement at 4.5 ± 3.3, 4.6 ± 3.0 and 4.2 ± 0.7 g m$^{-2}$,

535    respectively. For dated peat cores collected in the 21$^{st}$ century, Farmer et al. (2015) reported

536    3.70 g m$^{-2}$ (post-1610 AD) for Great Moss (NN), while Cloy et al. (2008) found 2.1-3.6 g m$^{-2}$

537    (post-1800 AD) for Flanders Moss (NS),  2.5-4.3 g m$^{-2}$ (post-1800 AD) for the Red Moss of

538    Balerno (NT) and 2.7-5.0 g m$^{-2}$ (post-1800 AD) for Carsegowan Moss (NX).

539         Considering all sites with mineral top horizons together (n=60, i.e. excluding six sites

540    >15 g m$^{-2}$), the anthropogenic Pb accounted for 43% and 56% of the total Pb inventories for

541    HU-NM and NN-NY, respectively, to the depth of anthropogenic Pb penetration (mean ~30

542    cm) as determined by consideration of Pb concentration and $^{206}$Pb/$^{207}$Pb ratio in each soil

543    profile. The mean $^{206}$Pb/$^{207}$Pb ratio calculated for anthropogenic Pb at such sites in HU-NM

544    and NN-NY was $1.158 \pm 0.019$ and $1.161 \pm 0.014$, respectively, with an overall average

545    value of $1.160 \pm 0.016$, in good agreement with the mean value of $1.164 \pm 0.012$ established

546    for total anthropogenic Pb at sites (excluding one site $>15$ g m$^{-2}$) with organic top horizons.

547    Taking these mineral top and organic top horizon sites together, the $^{206}Pb/^{207}Pb$ ratio of

548    anthropogenic Pb lay between 1.140 and 1.179 at 89% of sites.

549    Similarly, for sites with a specifically Ap mineral top horizon (i.e. excluding six sites

550    $>15$ g m$^{-2}$), the anthropogenic Pb accounted for 36% (HU-NM) and 51% (NN-NY) of the

551    total Pb inventories to a mean depth of ~30 cm and had a calculated mean $^{206}Pb/^{207}Pb$ ratio of

552    $1.159 \pm 0.018$. So far as Scotland is concerned, therefore, these findings are contrary to the

553    conclusion of Reimann et al. (2012) that the atmospheric Pb contamination of the northern

554    hemisphere as demonstrated using ice cores, lake sediments or peat bogs contributes little to

555    the total Pb inventory of European agricultural soils.

556

557    *3.5 Anomalous sites*

558

559    *3.5.1 Unusual $^{206}Pb/^{207}Pb$ profiles*

560    The very high value (1.576) of the organic bottom horizon (Oa2) $^{206}Pb/^{207}Pb$ ratio for Uist

561    (NF) (SI Fig. 6a) was probably the result of the inclusion of some mineral dust (of high

562    $^{206}Pb/^{207}Pb$ ratio) in the bottom horizon, as the value of the dry bulk density was 0.813 g cm$^{-3}$,

563    some 4-5 times greater than the corresponding values for the three overlying horizons, Os1,

564    Os2 and Oa1.

565    The very high value (1.441) of the mineral bottom horizon (Bh) $^{206}Pb/^{207}Pb$ ratio for

566    South Culblean Hill (NJ) (SI Fig. 6b), which is in the eastern Grampian Mountains where the

567    underlying rock is granite, almost certainly resulted from the presence of radiogenic Pb

568    elevated in $^{206}Pb$ relative to $^{207}Pb$, as found elsewhere in the north in this study (cf. Figs. 3c,

23

569    5, SI Fig. 3), a view supported by the high, but less extreme, value of 1.342 for the overlying

570    E(h) horizon (SI Fig. 6b).

571        At the other four sites – Lewis (NB), Skye (NG), Lochan na Bearta (NH) and Mull

572    (NM) (SI Figs. 6c-f) – the $^{206}Pb/^{207}Pb$ ratio uncharacteristically declined from top to bottom

573    horizon, to values of 1.077 (Oa2), 1.050 (BCg), 1.100 (BC) and 1.043 (Ah), respectively.

574    These sites are in NW Scotland and, although not characteristic in general of $^{206}Pb/^{207}Pb$

575    profiles there, could perhaps be indicative of local effects of mineralisation or contamination.

576        That such apparently anomalous values as those above can occur is supported by the

577    findings of a recent regional-scale geochemical survey of soil O and C horizon samples in

578    Nord-Trondelag, Central Norway (Reimann et al., 2015). There, $^{206}Pb/^{207}Pb$ ratios in the O

579    horizon as low as 1.0399, compared with a median value of 1.1512 for O horizon samples

580    and with minimum and maximum values for C horizon samples of 1.0658 and 1.9630,

581    respectively, were reported.

582

583    *3.5.2 Large anthropogenic Pb inventories*

584    The large estimated anthropogenic Pb inventories (>15 g m$^{-2}$) not included in the calculation

585    of mean inventories for individual OS zones (Fig. 13, SI Table 6) related, with one exception

586    (NN, Bruach Burn, Oa, 24.2 g m$^{-2}$),  to sites with uppermost Ap horizons, i.e. Rhum (NG,

587    18.3 g m$^{-2}$), Kincardine (NJ, 67.6), Arbirlot (NO, 21.8), Pappert (NS, 42.9), Borrowstoun

588    (NT, 29.8) and Heathhall 85 (NY, 17.3). The average anthropogenic $^{206}Pb/^{207}Pb$ ratio for

589    these Ap sites was 1.169 ± 0.007. Apart from Bruach Burn, the organic sites with the largest

590    estimated anthropogenic Pb inventories were Meluncart (NO, 10.6 g m$^{-2}$), Stobieside (NS,

591    13.9), Caddonhead (NT, 10.7), Forest of Ae (NT, 10.1) and Wood of Auchleand (NX, 14.0).

592    The site vegetation included from *Sphagnum* moss peat bogs to heather moors and coniferous

593    woodlands. The average anthropogenic $^{206}Pb/^{207}Pb$ ratio for these six sites was 1.166 ± 0.012

594    (1.170 ± 0.006, excluding Caddonhead), very similar to the six Ap sites of elevated

595    anthropogenic Pb inventory. Meluncart (NO, 10.6 g m$^{-2}$) is very close to the long-term

596    monitoring station at Glensaugh (NO), for which a mean value of 7.4 ± 1.5 g m$^{-2}$ (range 6-9 g

597    m$^{-2}$) was recorded for four hilltop peat cores (Farmer et al., 2005). On the basis of the

598    inventory of naturally occurring radioactive $^{210}$Pb, it has been suggested that this could be an

599    area of enhanced deposition of Pb as a result of occult deposition at altitude. Elsewhere,

600    factors such as enhanced trapping, e.g. by the leaves of trees, and subsequent leaf fall could

601    contribute to elevated inventories of Pb in forests. More generally, variations in deposition

602    efficiency might also be expected as a result of site topography relative to prevailing wind

603    direction.

604

605    **4. Conclusions**

606

607    The measurement of Pb isotopic composition in 644 samples from individual horizons of 169

608    soil profiles for which Pb concentrations had previously been determined as part of the

609    National Soil Inventory of Scotland (2007-09) established the following:

610    (i)    the Pb isotope composition of mineral bottom soils (i.e. the lowest sampled mineral

611           horizons) varied geographically and was especially influenced by the presence, in more

612           northerly soils on granitic rocks, of radiogenic Pb that resulted in greater $^{206}$Pb/$^{207}$Pb

613           ratios of up to 1.35 compared with typical values of 1.17-1.20 in more southerly soils;

614    (ii)   the Pb isotope composition of both organic top soil horizons and organic bottom soil

615           horizons (i.e. the lowest sampled organic horizons) was consistent with past

616           atmospheric deposition of Pb from a range of anthropogenic emission sources;

617    (iii)   the lesser $^{206}Pb/^{207}Pb$ ratios and greater Pb concentrations of organic top soil horizons

618            bore no relation to those of underlying mineral bottom soil horizons (i.e. the lowest

619            sampled mineral horizons);

620    (iv)   the lesser $^{206}Pb/^{207}Pb$ ratios but greater Pb concentrations of mineral top soil horizons

621            relative to mineral bottom soil horizons (i.e. the lowest sampled mineral horizons) were

622            consistent with the presence of additional anthropogenic Pb;

623    (v)    based on calculations using measured Pb concentrations and $^{206}Pb/^{207}Pb$ ratios for the

624            soil profiles, the estimated anthropogenic Pb soil inventory was found to vary

625            geographically from an average of 4.5 g m$^{-2}$ in the south to 1.5 g m$^{-2}$ in the north,

626            comparable to values previously determined for ombrotrophic peat bogs and freshwater

627            lake sediments and indicative of long-range atmospheric transport;

628    (vi)   anthropogenic Pb accounted for ~50% of the total Pb inventory to a depth of ~30 cm in

629            cultivated agricultural soils (Ap).

630

631    **Acknowledgements**

632

640

641    **References**

642

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FIGURE LEGENDS

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815 Figure 1. Map of Scotland with the Ordnance Survey (OS) National Grid imposed and the

816 corresponding diagrammatic version showing the distribution among individual OS zones of

817 the 169 soil profile sites considered in this study.

818

819 Figure 2. Six selected profiles of Pb concentration (open circle) and $^{206}$Pb/$^{207}$Pb ratio (closed

820 circle) vs soil horizon and depth: (a) Forest of Ae (OS zone NT), organic top to organic

821 bottom; (b) Balhomish (NO), organic top to mineral bottom; (c) Drumguish (NH), organic

822 top to mineral bottom (of high $^{206}$Pb/$^{207}$Pb ratio); (d) Balcalk (NO), Ap mineral top to mineral

823 bottom; (e) Chanlock (NS), A mineral top to mineral bottom; (f) Mull (NM), organic top to

824 mineral bottom (anomalous site).

825

826 Figure 3. Histograms of number of samples with $^{206}$Pb/$^{207}$Pb ratios in 0.01 intervals from

827 1.10-1.36 for three scenarios: (a) organic top horizon with organic bottom horizon; (b)

828 organic top with mineral bottom; (c) mineral top with mineral bottom.

829

830 Figure 4. Histograms of number of samples with Pb concentrations in 10 mg kg$^{-1}$ intervals (0-

831 90 mg kg$^{-1}$) and 100 mg kg$^{-1}$ intervals (100-600 mg kg$^{-1}$) for (a) organic top, (b) organic

832 bottom, (c) mineral top  and (d) mineral bottom horizons.

833

834 Figure 5. Diagrammatic OS National Grid Maps of Scotland showing mean $^{206}$Pb/$^{207}$Pb ratio

835 by OS zone for (a) mineral bottom, (b) mineral top, (c) organic top and (d) organic bottom

836 horizons.

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838    Figure 6. Diagrammatic OS National Grid Maps of Scotland showing mean Pb concentration

839    by OS zone for (a) mineral bottom, (b) mineral top, (c) organic top and (d) organic bottom

840    horizons.

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842    Figure 7. Plots of Pb concentration (logarithmic scale) and of $^{206}$Pb/$^{207}$Pb ratio, organic

843    bottom horizon vs organic top horizon (for paired samples, n=36)

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845    Figure 8. Plots of $^{208}$Pb/$^{207}$Pb ratio vs $^{206}$Pb/$^{207}$Pb ratio for organic top and organic bottom

846    horizons (for paired samples, n=35, i.e. excluding Aisir (NC)). The best-fit line through the

847    organic top data (n=35) is $^{208}$Pb/$^{207}$Pb = 1.227 + 1.047 $^{206}$Pb/$^{207}$Pb, r$^2$=0.899; and through the

848    organic bottom data (n=32, i.e. excluding two Lewis (NB) and one Uist (NF) samples) is

849    $^{208}$Pb/$^{207}$Pb = 1.274 + 1.010 $^{206}$Pb/$^{207}$Pb, r$^2$=0.621). Mean isotopic ratio values, with 1 s.d.

850    error bars, are shown for leaded petrol (circle), Wanlockhead Pb (inverted triangle) ore and

851    UK coal (square) (cf. Farmer et al., 1999, 2000).

852

853    Figure 9. Plots of Pb concentration (logarithmic scale) and of $^{206}$Pb/$^{207}$Pb ratio, mineral

854    bottom horizon vs organic top horizon (for paired samples, n=67). Closed circles represent

855    mineral bottom samples from A, E and B horizons and open circles from BC and C horizons.

856

857    Figure 10. Plots of $^{208}$Pb/$^{207}$Pb ratio vs $^{206}$Pb/$^{207}$Pb ratio for organic top (shown on two scales

858    for $^{206}$Pb/$^{207}$Pb ratio) and mineral bottom horizons (for paired samples, n=67). The best-fit

859    line through the organic top data is $^{208}$Pb/$^{207}$Pb = 1.223 + 1.050 $^{206}$Pb/$^{207}$Pb, r$^2$=0.939; and

860    through the mineral bottom data is $^{208}$Pb/$^{207}$Pb = 1.436 + 0.883 $^{206}$Pb/$^{207}$Pb, r$^2$=0.697. Mean

861    isotopic ratio values, with 1 s.d. error bars, are shown for leaded petrol (circle), Wanlockhead

862    Pb ore (inverted triangle) and UK coal (square) (cf. Farmer et al., 1999, 2000).

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864    Figure 11. Plots of Pb concentration (logarithmic scale) and of $^{206}$Pb/$^{207}$Pb ratio, mineral

865    bottom horizon vs mineral top horizon (for paired samples, n=66). Closed circles represent

866    mineral top samples from E and B horizons and open circles from A horizons.

867

868    Figure 12. Plots of $^{208}$Pb/$^{207}$Pb ratio vs $^{206}$Pb/$^{207}$Pb ratio for mineral top and mineral bottom

869    horizons (for paired samples, n=65, i.e. excluding Torridon (NG)). The best-fit line through

870    the mineral top data is $^{208}$Pb/$^{207}$Pb = 1.563 + 0.763 $^{206}$Pb/$^{207}$Pb, r$^2$=0.523; and that through the

871    mineral bottom data is $^{208}$Pb/$^{207}$Pb = 1.723 + 0.644 $^{206}$Pb/$^{207}$Pb, r$^2$=0.505.

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873    Figure 13. Diagrammatic OS National Grid Map of Scotland showing the mean

874    anthropogenic Pb inventory (g m$^{-2}$) by OS zone.

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899    SUPPLEMENTARY INFORMATION (SI)

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901    SI FIGURE LEGENDS

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903    SI Figure 1. Six selected profiles of Pb concentration (open circle) and $^{206}$Pb/$^{207}$Pb ratio

904    (closed circle) vs soil horizon and depth for organic top to organic bottom sites: (a) Sallachy

905    (OS zone NC), (b) Dalganachan (ND), (c) Strathrusdale (NH), (d) Fealar Lodge (NO), (e)

906    Loch Lyon (NN), (f) Forest of Ae (NT).

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908    SI Figure 2. Six selected profiles of Pb concentration (open circle) and $^{206}$Pb/$^{207}$Pb ratio

909    (closed circle) vs soil horizon and depth for organic top to mineral bottom sites: (a) Langwell

910    Ullapool (OS zone NC), (b) Kintessack (NJ), (c) Mid-Lorn (NN), (d) Edradour (NO), (e)

911    Wormscleuch (NT), (f) Balhomish (NO).

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913    SI Figure 3. Six selected profiles of Pb concentration (open circle) and $^{206}$Pb/$^{207}$Pb ratio

914    (closed circle) vs soil horizon and depth for organic top to mineral bottom (of high

915    $^{206}$Pb/$^{207}$Pb ratio) sites (all OS zone NH): (a) Strathbran, (b) Garve, (c) Attadale, (d)

916    Dochfour, (e) North Lochaber, (f) Drumguish.

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918    SI Figure 4. Six selected profiles of Pb concentration (open circle) and $^{206}$Pb/$^{207}$Pb ratio

919    (closed circle) vs soil horizon and depth for Ap mineral top to mineral bottom sites: (a)

920    Findon (OS zone NH), (b) Kincardine (NJ), (c) Westpark (NS), (d) Balcalk (NO), (e)

921    Silverburn (NT), (f) Shawhill (NY).

922

923 SI Figure 5. Six selected profiles of Pb concentration (open circle) and $^{206}$Pb/$^{207}$Pb ratio

924 (closed circle) vs soil horizon and depth for A mineral top to mineral bottom sites: (a)

925 Bohally Wood (OS zone NN), (b) Keig (NJ), (c) Chanlock (NS), (d) Langhope (NT), (e)

926 Glenlee (NX), (f) Craigton Row (NX).

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928 SI Figure 6. Six selected profiles of Pb concentration (open circle) and $^{206}$Pb/$^{207}$Pb ratio

929 (closed circle) vs soil horizon and depth for six anomalous sites, all with organic top: (a) Uist

930 (OS zone NF), organic bottom; (b) S. Culblean Hill (NJ), (c) Lewis (NB), (d) Skye (NG), (e)

931 Mull (NM), (f) Lochan na Bearta (NH).

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