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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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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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was lesser (outside
32 analytical error) than the corresponding bottom horizon $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{208}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the organic top horizon in (ii) was unrelated to the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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

49 1. Introduction

50

51 Clair Patterson's finding in the 1960s that more than 90% of the atmospheric Pb in the
52 northern hemisphere at that time was derived from anthropogenic sources such as car-exhaust
53 emissions (in the era of leaded petrol), coal combustion and metal ore smelting (Patterson,
54 1965; Murozumi et al., 1969) has subsequently been supported by many historical studies
55 based on the Pb analysis of cores from ice sheets, peat bogs and lake sediments (e.g. Boutron
56 et al., 1991; Shotyk et al., 1998; Renberg et al., 2001). Such studies have often included Pb
57 isotope analyses, which have provided valuable information on the relative contributions of
58 Pb from sources of differing Pb isotopic composition associated with various human
59 activities over the past few thousand years (e.g. Shirahata et al., 1980; Rosman et al., 1997;
60 Bindler, 2011). Based partly on the isotopic evidence (e.g. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios), it is widely
61 accepted that accumulations of Pb in ice, peat and sediment cores are anthropogenic in origin
62 and that they are the result of long-term and long-range atmospheric deposition (e.g. Steinnes
63 et al., 2005a; Zheng et al., 2007; Steinnes, 2009; Klaminder et al., 2011).

64 In Scotland, there have been numerous studies of the isotopic composition of sources of
65 Pb (Sugden et al., 1993; Farmer et al., 1999, 2000) and of Pb in peat, lake sediments, moss
66 and other terrestrial plants in the rural environment (e.g. Farmer et al., 1996, 1997, 2002,
67 2010, 2015; MacKenzie et al., 1997, 1998; Eades et al., 2002; Weiss et al., 2002; Patrick and
68 Farmer, 2007; Cloy et al., 2008; Kylander et al., 2009). With the exception of a few studies
69 on urban and suburban soils (e.g. Farmer et al., 2011; MacKinnon et al., 2011), most Pb
70 isotopic work on Scottish soils has focussed on the rural environment, in particular at the
71 Glensaugh field station and long-term monitoring site in the rural north east (e.g. Bacon et al.,
72 1992, 1995, 2004, 2006). Data for organic soils at Glensaugh, which is a site distant from any
73 point sources, show typical $^{206}\text{Pb}/^{207}\text{Pb}$ 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 ($^{206}\text{Pb}/^{207}\text{Pb}$ 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 $6\text{-}9\text{ g m}^{-2}$, with
79 $\sim 40\%$ deposited prior to 1900 and a further $\sim 20\%$ 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.

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 HNO₃ (*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 HNO₃ 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 HNO₃ 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 MΩ 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 ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb, 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 ¹⁸⁵Re 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 (± 1 standard deviation (s.d.)) of 42.3 ± 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 (± 1 s.d.) of this test
169 soil over the three years of the NSIS 2 project was 43.2 ± 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 $<25 \mu\text{g L}^{-1}$ with high-purity water
173 ($18.2 \text{ M}\Omega \text{ cm}$) from a Milli-Q water system (Millipore, Watford, UK). Lead isotope ratios
174 ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$) 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 $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ 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 $\pm 0.3\%$. The mean isotope ratios (± 1 s.d.) of $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and
187 $^{208}\text{Pb}/^{206}\text{Pb}$ determined in the in-house ‘Analytical Top Soil’ ($n=12$) as 1.174 ± 0.004 , $2.459 \pm$
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 $^{206}\text{Pb}/^{207}\text{Pb}$,
192 $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$, 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 (≥ 1.44) or unusually low (≤ 1.10) value of the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio*

205

206 Figs. 2a-e present a typical Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio with increasing depth. Of
216 the 169 sites there were only 10 (i.e. 6%) where the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the lowermost soil horizon when it was mineral in nature (cf. Figs. 2a-

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

226

227 Fig. 3 presents histograms of the number of sites with values of $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios*

240 The $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ value ≥ 1.25 (Fig. 3), eight were from NH (four ≥ 1.30), four
246 from NN (one ≥ 1.30), two from NJ and one from each of NM (one ≥ 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 ± 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 ± 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 ± 0.037 (median 1.176).

260 The rock types of stones in the 19 mineral bottom soils which had $^{206}\text{Pb}/^{207}\text{Pb}$ ratios
261 ≥ 1.25 were predominantly granite or schists (e.g. quartz-mica schists). The typically greater
262 values of the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 = 4.47×10^9 years and
265 ^{235}U (half-life = 0.70×10^9 years) present in uraniferous minerals in these soils, in addition to
266 primordial Pb. Values of the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb 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

298 *3.2.2.1 ²⁰⁶Pb/²⁰⁷Pb ratios*

299 The ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb 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

320 *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 ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb ratios

341 The ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$
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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $38 \pm 32 \text{ mg kg}^{-1}$, median 32 mg kg^{-1}) had concentrations $\geq 100 \text{ mg kg}^{-1}$,
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 $133 \pm 99 \text{ mg kg}^{-1}$, 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios*

382 The $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ value was 1.172 ± 0.017 , 1.181 ± 0.019 (or 1.174 ± 0.011 when two values of
385 1.216 and 1.226 were excluded) and 1.171 ± 0.017 for samples with mid-point sample depths
386 of $< 50 \text{ cm}$ (n=9), $50\text{-}79 \text{ cm}$ (n=15) and $\geq 80 \text{ cm}$ (n=12), respectively.

387 On the basis of mean organic bottom soil horizon $^{206}\text{Pb}/^{207}\text{Pb}$ values for individual OS
388 zones, there appeared to be little geographical variation (Fig. 5d, SI Table 5). The mean
389 $^{206}\text{Pb}/^{207}\text{Pb}$ values for the northernmost zones of HU, NB, NC, ND, NF, NG, NH, NJ (n=20)
390 of 1.176 ± 0.022 (median 1.178) (or 1.171 ± 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 ± 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 ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb
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 ²⁰⁶Pb/²⁰⁷Pb ratios and the mean difference between the paired ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁸Pb/²⁰⁷Pb vs. ²⁰⁶Pb/²⁰⁷Pb (Fig. 8). The more recent influence of car-exhaust

420 emissions, containing Pb from leaded petrol (to which Australian Pb of $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and the mean
436 difference between the paired $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio between organic top and organic bottom
446 horizons for these three zonal groupings were very similar at -0.015 ± 0.014 (n=12), $-0.018 \pm$
447 0.017 (n=9) and -0.014 ± 0.023 (n=14), respectively.

448 The plot of $^{208}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ (Fig. 10) again demonstrates the influence of
449 anthropogenic sources of Pb upon the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 ($^{208}\text{Pb}/^{207}\text{Pb} = 1.223 + 1.050 \ ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.939$) is near-identical to that in Fig. 8
452 ($^{208}\text{Pb}/^{207}\text{Pb} = 1.227 + 1.047 \ ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.899$) and differs from the corresponding best-fit
453 line ($^{208}\text{Pb}/^{207}\text{Pb} = 1.436 + 0.883 \ ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.697$) through the mineral bottom data.

454 Fig. 9 also shows quite clearly the lack of relationship between the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and the mean difference between the paired
467 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{208}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ (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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $0.000 \pm$
494 0.009 . In profiles with four sampled horizons (n=23), the mean differences between the

495 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for the
500 lowermost mineral horizon: (i) <1.200 , (ii) ≥ 1.200 . In scenario (i) (n=20), the mean
501 differences between the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, which directly influences the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 ($17\text{-}68 \text{ g m}^{-2}$, mean $32 \pm 18 \text{ g m}^{-2}$) where
525 the anthropogenic Pb inventory was $>15 \text{ g m}^{-2}$, 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 $0.6\text{-}2.2 \text{ g m}^{-2}$, with an
528 overall average of $1.5 \pm 1.2 \text{ g m}^{-2}$, 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 $1.2 \pm 0.7 \text{ g m}^{-2}$,
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 $3.3\text{-}6.2 \text{ g m}^{-2}$, with an
533 overall average of $4.5 \pm 3.0 \text{ g m}^{-2}$. 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 $4.2 \pm 0.7 \text{ g m}^{-2}$,
535 respectively. For dated peat cores collected in the 21st 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 $2.1\text{-}3.6 \text{ g m}^{-2}$
537 (post-1800 AD) for Flanders Moss (NS), $2.5\text{-}4.3 \text{ g m}^{-2}$ (post-1800 AD) for the Red Moss of
538 Balerno (NT) and $2.7\text{-}5.0 \text{ g m}^{-2}$ (post-1800 AD) for Carsegowan Moss (NX).

539 Considering all sites with mineral top horizons together (n=60, i.e. excluding six sites
540 $>15 \text{ g m}^{-2}$), 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in each soil
543 profile. The mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratio calculated for anthropogenic Pb at such sites in HU-NM

544 and NN-NY was 1.158 ± 0.019 and 1.161 ± 0.014 , respectively, with an overall average
545 value of 1.160 ± 0.016 , in good agreement with the mean value of 1.164 ± 0.012 established
546 for total anthropogenic Pb at sites (excluding one site $>15 \text{ g m}^{-2}$) with organic top horizons.
547 Taking these mineral top and organic top horizon sites together, the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $>15 \text{ g m}^{-2}$), 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of
552 1.159 ± 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 $^{206}\text{Pb}/^{207}\text{Pb}$ profiles*

560 The very high value (1.576) of the organic bottom horizon (Oa2) $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for Uist
561 (NF) (SI Fig. 6a) was probably the result of the inclusion of some mineral dust (of high
562 $^{206}\text{Pb}/^{207}\text{Pb}$ 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) $^{206}\text{Pb}/^{207}\text{Pb}$ 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,

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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$
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, $^{206}\text{Pb}/^{207}\text{Pb}$ 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 ($>15 \text{ g m}^{-2}$) 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 ²¹⁰Pb, 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 ²⁰⁶Pb/²⁰⁷Pb
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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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

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813 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 ($100\text{-}600\text{ mg kg}^{-1}$) 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio
835 by OS zone for (a) mineral bottom, (b) mineral top, (c) organic top and (d) organic bottom
836 horizons.

837

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.

841

842 Figure 7. Plots of Pb concentration (logarithmic scale) and of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, organic
843 bottom horizon vs organic top horizon (for paired samples, n=36)

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845 Figure 8. Plots of $^{208}\text{Pb}/^{207}\text{Pb}$ ratio vs $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{208}\text{Pb}/^{207}\text{Pb} = 1.227 + 1.047 ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.899$; and through the
848 organic bottom data (n=32, i.e. excluding two Lewis (NB) and one Uist (NF) samples) is
849 $^{208}\text{Pb}/^{207}\text{Pb} = 1.274 + 1.010 ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.621$). 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{208}\text{Pb}/^{207}\text{Pb}$ ratio vs $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for organic top (shown on two scales
858 for $^{206}\text{Pb}/^{207}\text{Pb}$ ratio) and mineral bottom horizons (for paired samples, n=67). The best-fit
859 line through the organic top data is $^{208}\text{Pb}/^{207}\text{Pb} = 1.223 + 1.050 ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.939$; and
860 through the mineral bottom data is $^{208}\text{Pb}/^{207}\text{Pb} = 1.436 + 0.883 ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.697$. 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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Figure 11. Plots of Pb concentration (logarithmic scale) and of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, mineral bottom horizon vs mineral top horizon (for paired samples, n=66). Closed circles represent mineral top samples from E and B horizons and open circles from A horizons.

Figure 12. Plots of $^{208}\text{Pb}/^{207}\text{Pb}$ ratio vs $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for mineral top and mineral bottom horizons (for paired samples, n=65, i.e. excluding Torridon (NG)). The best-fit line through the mineral top data is $^{208}\text{Pb}/^{207}\text{Pb} = 1.563 + 0.763 \ ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.523$; and that through the mineral bottom data is $^{208}\text{Pb}/^{207}\text{Pb} = 1.723 + 0.644 \ ^{206}\text{Pb}/^{207}\text{Pb}$, $r^2=0.505$.

Figure 13. Diagrammatic OS National Grid Map of Scotland showing the mean anthropogenic Pb inventory (g m^{-2}) by OS zone.

899 SUPPLEMENTARY INFORMATION (SI)

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901 SI FIGURE LEGENDS

902

903 SI Figure 1. Six selected profiles of Pb concentration (open circle) and $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 Wormsleuch (NT), (f) Balhomish (NO).

912

913 SI Figure 3. Six selected profiles of Pb concentration (open circle) and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio
914 (closed circle) vs soil horizon and depth for organic top to mineral bottom (of high
915 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio) sites (all OS zone NH): (a) Strathbran, (b) Garve, (c) Attadale, (d)
916 Dochfour, (e) North Lochaber, (f) Drumguish.

917

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

927

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