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Long-term spatial and temporal patterns of polycyclic aromatic hydrocarbons (PAHs) in Scottish soils over 20 years, 1990-2009: a national picture.

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1 Long-term spatial and temporal patterns of polycyclic aromatic
2 hydrocarbons (PAHs) in Scottish soils over 20 years
3 (1990-2009): a national picture

4
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19 **Abstract**

20 Long-term spatial and temporal concentrations of polycyclic aromatic hydrocarbons
21 (PAHs) in Scottish soils from four transects were measured in three national-scale
22 surveys conducted between 1990 and 2009. Measured concentrations of 16 priority
23 PAHs ranged from 15690 to 83.7 ng g⁻¹, with an average of 3659±3131 to 727±654 ng
24 g⁻¹, of which the high molecular weight (HMW) PAHs (4~6 rings) accounted for 73.9
25 to 89.6%. Overall, concentrations of PAHs in the soil have decreased over time, but
26 the proportion of carcinogenic Σ PAH₇ has increased. Concentrations of total PAHs
27 correlated significantly with latitude ($R=-0.345$, $p=0.001$). A significant correlation
28 was found between concentrations of PAHs and soil organic carbon (SOC, $R=0.439$,
29 $p=0.000$), which is an important factor, influencing the levels of PAHs in soils. Source
30 apportionment analysis indicated that the emission sources of PAHs have evolved
31 from coal and biomass combustion to more diverse sources during the two decades
32 covered by the surveys. It is likely that this reflects societal development towards a
33 lower carbon economy and less use of biomass burning for domestic space heating.

34 **Keywords:** PAHs, Temporal change, Spatial patterns, Modeling, Soil, Scotland

35

36 **1. Introduction**

37 Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous persistent toxic organic
38 pollutants derived from both natural and anthropogenic emission sources. The United
39 States Environmental Protection Agency (USEPA) and the European Union (EU) have
40 identified 16 PAHs as priority pollutants due to their toxicity and associated risks to
41 human health and the environment (Dimashki et al., 2001; Wang et al., 2011).
42 Therefore, understanding the emission sources, scale effect, environmental behaviour,
43 bioaccumulation and health hazards associated with the spatial-temporal distribution
44 of PAHs has become imperative from an environmental protection and public health
45 perspective (Benfenati et al., 1992; Holmqvist et al., 2006; Holoubek et al., 2009;
46 Villanneau et al., 2011; Villanneau et al., 2013; Cui et al., 2016).
47 Temporal changes in PAHs (concentrations and composition) have been reported in
48 various environment media including sediment cores, soil, and air (Andersson et al.,
49 2014; Garrido et al., 2014; Bandowe et al., 2018). These findings have served to
50 emphasise the need to understand the drivers that result in changes to the PAH profile,
51 especially as these environmental matrices often harbour historic PAH discharges thus
52 the risk of secondary emissions through e.g. transformation need to be understood.
53 Generally, soil plays a significant role in the storage, global cycle, redistribution, and
54 transfer to the food chain of persistent organic pollutants (POPs), with soil organic

55 matter playing an important role in the retention of POPs within the soil matrix
56 (Ockenden et al., 2003; Nadal et al., 2004; Sweetman et al., 2005; Wilcke 2007;
57 Gubler et al., 2015; Ren et al., 2018; Rey-Salgueiro et al., 2018). Numerous studies
58 have reported on the PAH profiles within the UK including emissions inventories,
59 contamination levels, spatial distribution, and source-sink relationships (Wild and
60 Jones 1995; Lohmann et al., 2000; Prevedouros et al., 2004; Smith et al., 2006; Nam
61 et al., 2008; Brown, A. and Brown, R., 2012; Rhind et al., 2013; Brown et al., 2013;
62 Graf et al., 2016). A significant source of PAHs in UK soils and other environmental
63 media has been from combustion of fossil fuels such as coal which was particularly
64 prevalent during the UK industrial revolution of the early 19th Century (Nam et al.,
65 2008). About 90% of the total environmental burden of PAHs in the UK are currently
66 residing in soils, primarily derived from atmospheric deposition (Wild and Jones
67 1995). Given that both emission sources and soil conditions have changed over time,
68 improving our understanding of how concentrations of PAHs have also changed is
69 valuable towards meeting environmental and public health obligations. Therefore,
70 understanding the long-term temporal changes to the concentrations of PAHs in soils
71 at a national scale could help elucidate the main drivers of spacial-temporal evolution
72 and environmental behavior (Zhang et al., 2014).

73 Since the global fractionation and cold condensation for low volatility compounds

74 was reported by Wania and Mackay (1993); analogous fractionations for organic
75 pollutants such as latitudinal fractionation, urban fractionation, longitudinal
76 fractionation, primary and secondary fractionation have all been proposed based on
77 various monitoring and modeling methods (Agrell et al., 1999; Meijer et al., 2002;
78 Meijer et al., 2003; Harner et al., 2004; Gouin et al., 2004; Scheringer et al., 2004;
79 Ren et al., 2007; Li et al., 2010; Lammel and Stemmler 2012; Cai et al., 2014). For
80 example, Nam et al. (2008) found a fractionation phenomenon between the UK and
81 Norway for <4-ring PAHs distribution by long-range atmospheric transport; Wilcke
82 and Amelung (2000) found a fractionation for naphthalene along a climosequence in
83 the North American prairie, but not for other PAHs. All these fractionation phenomena
84 are related to the intensity and pattern of emission sources, physico-chemical
85 properties of chemicals, meteorological conditions and soil properties. In other words,
86 the intensity and diversity of emission sources can be attributed to anthropogenic
87 influence, such as the increasing dominance of low molecular weight PAHs from
88 north to south transect along a 2100 km distance in Argentina (Wilcke et al., 2014).
89 Evidence for these fractionation effects has been reported primarily for
90 polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCHs), and DDTs;
91 which have had almost global-level prohibition for a number of decades. In contrast, it
92 is more challenging to identify fractionation effects for PAHs because they tend to be

93 deposited close to their sources, as well as the fact that emissions are contemporary
94 and on-going e.g. as by-products of incomplete combustion processes.

95 Understanding the environmental processes and variations of organic pollutants can
96 better reflect their sources, distribution and contamination risk in history and current
97 status such as PAHs because they have been continuously emitted. However, little is
98 known about the long-term spatial and temporal changes of PAH concentrations and
99 their environmental behavior on a national scale and how these are affected by
100 environmental parameters including soil properties, land use, and vegetation cover
101 types. Therefore, the objectives of the present study are (1) to determine the long-term
102 (20 years) changes and risk characteristics of contamination levels of PAHs in
103 Scottish soils including the role of soil organic carbon; (2) to understand more fully
104 the spatial-temporal distribution of PAHs in relation to latitude; and (3) to identify
105 changes in the source apportionment of PAHs in soils over 20 years. This is the first
106 study of PAHs conducted in Scottish soils over the long term period (20 years), which
107 provides scientific knowledge of spatial-temporal variations on concentrations,
108 distributions, sources and risk on a national scale. Results from the present study will
109 provide the information that is needed for causing direct and indirect ecological and
110 human health risk by PAHs in the pasture in Scotland.

111

112 **2. Materials and methods**

113 *2.1 Soil samples*

114 Surface soil samples (0-5 cm) were obtained from the National Soils Archive of the
115 James Hutton Institute, Aberdeen, Scotland; the soil types included in this study are
116 presented in Table S1. They comprised batches of 30 samples from each of three soil
117 surveys conducted over a 20-year period: TIPSS (Trends in Pollution in Scottish Soils)
118 in 1990 (TIPSS 1) and 1999 (TIPSS 2) and NSIS 2 (National Soils Inventory in
119 Scotland 2, NSIS 2) in 2007-2009 (Bracewell et al., 1993; Rhind et al., 2013; Zhang
120 et al., 2014). The NSIS 2 samples were collected over 3 years from 2007 to 2009 to a
121 highly specified protocol and are therefore regarded as a single set in the following
122 data analysis and interpretation.

123 Soil samples collected from each of several sites on four transects (**Fig. 1**) were
124 selected: Northern Scotland (8 sites), Central Highlands (8 sites), Central Lowlands (6
125 sites) and Southern Uplands (8 sites). The transect sites selected from the 1990 and
126 1999 surveys were the same as those used in the study of Bracewell et al. (1993).
127 Using a previously published approach (Rhind et al., 2013; Zhang et al., 2014), the
128 2007-2009 samples were represented by soil samples collected from the NSIS2
129 sampling locations that were closest (Euclidian distance 2.5-18.3 km) to the
130 corresponding TIPSS sites.

131 *2.2 Reagents and materials*

132 All the solvents used were of HPLC grade, including methanol, dichloromethane
133 (DCM) and iso-hexane (Rathburn Chemicals, Walkerburn, UK). For each of 16
134 USEPA PAHs including: naphthalene (Nap); acenaphthylene (Acy); acenaphthene
135 (Ace); fluorene (Flu); phenanthrene (Phe); anthracene (Ant); fluoranthene (Fluo);
136 pyrene (Pyr); benz[a]anthracene (BaA); chrysene (Chr); benzo[b]fluoranthene (BbF);
137 benzo[k]fluoranthene (BkF); benzo[a]pyrene (BaP); indeno[1,2,3-cd]pyrene (IcdP);
138 dibenz[a,h]anthracene (DahA); benzo[g,h,i]perylene (BghiP), a stock solution in
139 methanol (approximately 100 µg mL⁻¹ for each component) was produced as well as
140 an internal standard (d-8 Naphthalene, d-10 Acenaphthene, d-10 Fluorene, d-10
141 Phenanthrene, d-10 Anthracene, d-10 Pyrene and d-12 Chrysene: 100 µg mL⁻¹; all
142 supplied by Greyhound, Merseyside, UK). These two standard solutions were stored
143 at 4 °C and diluted in DCM before use. Silica gel (63-200 µm; VWR, Leicestershire,
144 UK) and sodium sulphate (Mallinckrodt Baker, Deventer, Holland) were used for
145 clean-up. They were washed in DCM of Soxhlet-extracted for six hours prior to
146 baking in a muffle furnace at 550 °C overnight (12 hours) before use. Acid-modified
147 silica gel was made at a ratio of 1:2 (98%) sulphuric acid (Analar): silica gel, and then
148 mixed on a roller for one hour and used immediately. All glassware used throughout
149 the analyses was machine-washed and baked at 450 °C for 12 h to eliminate the

150 potential for any organic contamination.

151 *2.3 Sample extraction and instrumental analysis*

152 Soil samples were extracted and analyzed according to the previously published
153 method (Rhind et al., 2013). Briefly, soil samples (approximately 1.0 g) were spiked
154 with 0.3 µg internal standards and 8 mL 1M ethanoic potassium hydroxide added (for
155 the alkaline saponification). The samples were heated to approximately 90 °C for 8
156 hours and allowed to cool before 2 mL of Milli-Q water was added and the analytes
157 extracted into 3×10 mL iso-hexane. The extracts were evaporated to 0.5 mL and
158 loaded onto a 9 g silica, 1 g of acid modified silica and 1 g anhydrous Na₂SO₄ column
159 (22 cm length, i.d. 3 cm, fitted with PTFE taps) that had been pre-conditioned with 40
160 ml iso-hexane. The column was eluted with 10 mL DCM:iso-hexane (1:4) which was
161 discarded, and the PAHs were eluted using 40 mL of 1:4 DCM:iso-hexane. The PAH
162 eluant was concentrated by rotary evaporation before analysis by GC-MS.

163 An Agilent 5975C Mass Spectrometer Detector (MSD) linked to 7890A GC with an
164 autosampler (7683B), was used for PAH analyses with selected ion mode. The
165 capillary column used was ZB-5MS (30 m x 0.25 mm i.d. x 0.25 µm film thickness,
166 Phenomenex, Macclesfield, UK). The oven programme was: 70 °C (3 min) ramped to
167 250 °C at 5 °C min⁻¹ and held for 1 min, then ramped to 300 °C at 6 °C min⁻¹ and held
168 for 6 min and finally ramped to 325 °C at 10 °C min⁻¹ and held for 5 min. The carrier

169 gas was helium. The injector and mass spectrometer were held at 250 °C and 200 °C
170 respectively. The electron impact energy was set 70 eV for mass spectrometer.

171 *2.4 Quality control*

172 Before sample analysis, relevant standards were analyzed to check instrumental
173 performance, peak height and resolution. With each set of samples to be analyzed,
174 reference standard mixtures, quality control samples, and procedural blanks were run
175 in sequence to check for contamination, instrumental performance, peak identification
176 and quantification. Compounds were identified mainly by selected ion and by their
177 retention times. For most of the target compounds, the procedural blanks were less
178 than method limits of detection. Reproducibility of the method was monitored by
179 repeated analysis of spiked quality control (QC) samples (one spiked QC per batch of
180 8 samples). Briefly, these QC samples were unpolluted soil samples which were from
181 Hartwood, Scotland (Rowanhill Association, non-calcareous clay with loamy topsoil
182 and average organic matter). In parallel with every batch of 8 samples, one QC soil
183 (approximately 1.0 g) spiked with target PAHs were analyzed. These were used,
184 together with un-spiked QC soil for background subtraction, to determine the
185 efficiency of recovery. The main recoveries were 80-114% for PAHs (with
186 reproducibility of RSD: 8-28%, Rhind et al., 2013). Limits of detection (LOD) for
187 PAHs were from 1 to 5 ng g⁻¹. All results were expressed on a dry weight basis in ng

188 g⁻¹ DW (dry weight). SOC content was estimated by loss on ignition at 450 °C (Heiri
189 et al., 2010).

190 *2.5 Statistical analysis*

191 Statistical analysis used in this study including Spearman correlation analysis,
192 one-way analysis of variance (ANOVA), multivariate linear regression (MLR) and
193 source apportionment (diagnostic ratio). The statistical software used was SPSS 20.0.
194 The correlation between variables was assessed by the Spearman correlation
195 coefficient with the both-sided hypothesis test. The significant differences between
196 variables were adopted by one-way ANOVA with Dunnett's T3 post hoc test.
197 Statistical significance was considered to be $p < 0.05$. A multivariate analysis was
198 carried out for exploring the influence factors on spatial patterns of PAHs (Section
199 3.2).

200

201 **3. Results and discussion**

202 *3.1 Temporal changes*

203 *3.1.1 PAHs levels*

204 PAHs were measured in soil samples across Scotland in the three separate years
205 between 1990 and 2009 and the concentrations of the 16 individual PAHs are
206 presented in Table S2. The average concentrations of $\sum\text{PAH}_{16}$ were 3659 ± 3131 for

207 1990, 1644 ± 1247 for 1999, and 727 ± 654 for 2009, respectively. Overall PAH levels
208 declined during this period and ranged about three orders of magnitude from 83.7 to
209 15690 ng/g for ΣPAH_{16} and from 49.2 to 9920 ng/g for ΣPAH_7 , respectively (Table
210 S2).

211 The average concentrations of ΣPAH_{16} from transect 4 (low latitude) to transect 1
212 (high latitude) were 5214 ± 2664 , 5099 ± 5536 , 2997 ± 1387 and $1686 \pm 455 \text{ ng/g}$ in
213 1990, 2394 ± 1394 , 1998 ± 1803 , 1443 ± 758 and $831 \pm 220 \text{ ng/g}$ in 1999, and $1227 \pm$
214 966 , 547 ± 148 , 713 ± 581 and $374 \pm 169 \text{ ng/g}$ in 2009, respectively (**Fig. 2**). The
215 one-way ANOVA with Dunnett's T3 post hoc test confirmed the significant difference
216 between transect 4 and transect 1 in 1990, but not in 1999 and 2009. For individual
217 PAHs, the mean concentrations of the five- and six-ring PAHs were significantly
218 higher at transect 4 than at transect 1 in 1990. The same pattern was observed for the
219 four-ring PAHs in 1999, but not in 2009. These temporal changes to PAH composition
220 suggested that the five and six-ring PAHs and four-ring were the major factor
221 affecting change along transects in 1990 and 1999, respectively. Overall, there is an
222 indisputable fact that the concentrations of ΣPAH_{16} declined from 3659 to 727 ng/g
223 between 1990 and 2009 (**Fig. 2**). The one-way ANOVA with Dunnett's T3 post hoc
224 test has also confirmed the decreasing trend of PAHs concentrations at a temporal
225 scale ($p < 0.01$).

226 Measured concentrations of total HMW PAHs with 4~6 rings were higher than total
227 LMW PAHs with 2~3 rings, and the HMW PAHs accounted for 73.9 to 89.6% of all
228 PAHs in these Scottish soils. Human activities can strongly influence concentrations
229 and distribution of PAHs in the environment. Levels of PAHs in most soils, especially
230 those located in remote areas, are governed by deposition processes following
231 anthropogenic PAH emissions (Edwards, 1983; Wilcke, 2007). Becker et al. (2006)
232 revealed that concentrations of PAHs in the Arctic atmosphere have declined between
233 1992 and 2000, which correlates with reduced emissions in the northern hemisphere
234 due to industrial change/decline. In addition, temperature is an important regulating
235 factor on gas-particle partitioning and degradation in the environment. Therefore,
236 degradation rate of PAH's in soils is likely to be influenced strongly by climatic
237 change (Cai et al., 2014), but the degradation of PAHs is a relative slow process
238 especially for the high molecular weight compounds.

239 The $\sum\text{PAH}_{16}$ concentrations in the three separate years in Scottish soils (Table S2)
240 were comparable to contemporary arable, grassland and background soils from Poland
241 (Maliszewska-Kordybach, 1996; Maliszewska-Kordybach, 2000;
242 Maliszewska-Kordybach et al., 2008), UK (Cousins et al., 1997; Nam et al., 2008),
243 Norway (Nam et al., 2008) and China (Wang et al., 2010; Ma et al., 2013) (Table 1).
244 However, concentrations of PAHs in this study were much lower than urban soils in

245 Glasgow (Scotland, UK), Ljubljana (Slovenia), and Torino (Italy), respectively
 246 (Morillo, et al., 2007). Meanwhile, the range of soil PAH concentrations in Scotland is
 247 similar to those measured along an 80 km urban-rural transect in the Greater Toronto
 248 Area (Canada) (Table 1). The changes in concentrations of PAHs in Scottish soils at
 249 spatial-temporal scale may be driven by a comprehensive influence of emission
 250 source, population, climate change (temperature), latitude, SOC and land use type.
 251 Generally, the concentrations of PAHs in soils are related to land use type and their
 252 levels in arable soils tend to be lower compared to other land uses such as grassland or
 253 forest soils. It is suggested that agricultural production and management practices
 254 result in dilution effects for many pollutants (Maliszewska-Kordybach, et al. 2008).

255 **Table 1** PAH concentrations in soils compared to other studies (ng/g)

sites	Number of PAHs	Range	Median/mean	Reference
The UK	12	20-7400	460/1100	Cousins, et al. (1997)
Glasgow, UK	15	1487-51822	8337/11930	Morillo, et al. (2007)
Ljubljana, Slovenia	15	218-4488	791/989	Morillo, et al. (2007)
Torino, Italy	15	148-3410	702/857	Morillo, et al. (2007)
The UK	15	42-11200	641	Nam, et al. (2008)
Norway	15	8.6-1100	154	Nam, et al. (2008)
Poland	16	28-2447	264	Maliszewska-Kordybach (1996)
Poland	13	75-11391	294/520	Maliszewska-Kordybach (2000)
Poland	16	80-7264	395/616	Maliszewska-Kordybach, et al. (2008)
Toronto, Canada	15	58-3200		Wong, et al. (2009)
Beijing-Tianjin, China	16	31.6-1475	336.4	Wang, et al. (2010)
Heilongjiang, China	15	30.1-870	154/209	Ma, et al. (2013)

256 *3.1.2 Risk characteristics*

257 Over three quarters (77%) of soil samples analysed in this study were obtained from
258 grazing land. There is therefore the potential for PAHs in the soil to move through the
259 foodchain via the herbage, to grazing animals, and eventually through to human
260 exposure via milk and meat consumption. The soil contamination classification
261 system based on 16 PAHs was suggested by Maliszewska-Kordybach (1996) as a risk
262 screening method. According to this classification system, *heavily contaminated soil*
263 (>1000 ng/g) reduced from 96.7% to 13.3% and *non-contaminated soil* (<200 ng/g)
264 increased from 0.0% to 10.0% between 1990 and 2009, respectively (**Fig. 3**).
265 However, it is important to note that the ratio of the important carcinogenic $\sum\text{PAH}_7$ to
266 $\sum\text{PAH}_{16}$ increased from 59.1% to 68.4% between 1990 and 2009, although the
267 contents of total 16 PAHs decreased. This is expected because the carcinogenic
268 $\sum\text{PAH}_7$ are primarily HMW PAHs with 4~6 rings, that tend to have relatively high
269 K_{ow} (octanol-water partition coefficient). This means that they are more likely to be
270 retained in the soil, while the lighter 3 ring PAHs (that make up the majority of the
271 remaining $\sum\text{PAH}_{16}$) are more likely to dissipate over time.

272 3.2 Spatial patterns

273 Within the soil, PAHs will tend to bind to the SOM (Mackay, 2001; Ockenden et al.,
274 2003). A significant correlation was found between concentrations of $\sum\text{PAH}_{16}$ and
275 SOC ($R=0.436$, $p<0.001$) and it was also found between SOC and PAH fractions

276 based on molecular weight (Table S3). This indicates that SOC could be the important
277 factor affecting the spatial patterns of PAHs in Scottish soils. The result being
278 different from the findings of Heywood et al. (2006) who investigated PAHs in British
279 soils showed that no correlation was found between PAHs and soil organic matter
280 (SOM). Lohmann et al. (2000) reported that other factors including proximity to
281 sources, land use type, wet deposition etc. could be stronger influences on the spatial
282 distribution of PAHs in soils compared to SOC due to the fact that the primary route
283 of PAH to soil is via atmospheric dispersion. This difference in findings might be due
284 to the fact that Scottish soils have elevated levels of SOM compared to the UK as the
285 whole. It is also the case that many of the sampling locations in this study are now
286 very remote and many of the emission sources are historic, thus increasing the
287 importance of SOM in PAH distribution, i.e. once retained in the soil the PAHs have
288 potential to be stored for significant time periods because the HMW PAHs do not
289 easily dissipate.

290 The total concentrations of PAHs in soils declined with increasing latitude between
291 1990 and 2009. While there was a significant negative correlation between
292 concentrations of PAH and latitude ($R=-0.345$, $p<0.01$), it was difficult to de-couple
293 this from the effect of transect. In general, concentrations of PAHs in soils tend to be
294 more elevated closer to source regions, especially for HMW PAHs. According to the

295 National Records of Scotland, around 70% of Scotland's population live in the Central
296 Low lands (relative low latitude) i.e. mainly concentrated between transect 4 and 3 in
297 this study (**Fig. 1**), and thus the population patterns may influence the distribution of
298 PAHs. The development of industry and other urban developments are closely
299 associated with population density, with the most elevated concentrations of PAHs in
300 British soils found close to industrial/urban centers (Heywood et al., 2006). B[a]A and
301 B[b]f can be assumed representative of source characteristics due to their relatively
302 low volatility and close association with particles thus they cannot exhibit long-range
303 atmospheric transport, although could be in association with aerosols (Wang et al.,
304 2006). In this study, concentrations of B[a]A and B[b]f were significantly negatively
305 correlated with latitude ($R = -0.673 \sim -0.461$, $p < 0.01$ for B[a]A; $R = -0.627 \sim -0.372$,
306 $p < 0.05$ for B[b]f).

307 From our findings SOC, latitude, population density and ambient temperature could
308 all be important factors controlling the occurrence of PAHs in soils. To investigate this
309 further, these factors were included in a multiple linear regression model:

$$310 \quad \log(C) = b_0 + b_1 \log(L) + b_2 \log(T) + b_3 \log(P) + b_4 SOC \quad (10)$$

311 where b_0 is the intercept and b_1 , b_2 , b_3 , and b_4 are fitting coefficients reflecting the
312 change of PAH concentrations (C) as a function of latitude (L), ambient temperature
313 (T), population (P) and SOC.

314 The results of the stepwise regression model for total PAHs and 2-6 rings PAH are
315 shown in Table S4. The indicator for population was not significant, despite there
316 being an apparent gradient in population from south to north. However, we found that
317 SOC is an important factor, influencing levels of 2- to 6-rings PAHs and total PAHs,
318 and latitude is another significant factor for PAHs except 2-rings PAH (Table S4).

319 The ratio of more volatile LMW PAHs to HMW PAHs may be used to identify the
320 spatial distribution and transport ability of PAHs. Although this positive correlation
321 between latitude and the ratio of LMW/HMW PAHs ($R=0.298$, $p<0.01$) was weak, it
322 does indicate that LMW PAHs become relatively more abundant with increasing
323 latitude. This might be due to the propensity of LMW PAHs to travel further from
324 emission sources via atmospheric transport compared to HMW PAHs. In fact, the
325 LMW PAHs with lower K_{ow} values (e.g. naphthalene) could be volatilized and more
326 readily reach the most remote areas. On the contrary, the HMW PAHs with higher K_{ow}
327 values are more likely to become associated with SOC and therefore remain in closer
328 proximity to sources (Nam et al., 2008).

329 As described above, the concentrations of PAHs in Scottish soils during the period of
330 two decades decreased with increasing latitude, which exhibited the general
331 characteristics of the latitude fractionation effect. This could be related to fundamental
332 changes in PAH emission sources, long-range atmospheric transport and climatic

333 conditions. In addition, temperature and SOC content are important factors that affect
334 soil-air exchange and secondary emissions for organic pollutants according to concept
335 of secondary fractionation (Li et al., 2010). Therefore, degradation of organic soils
336 leading to the re-volatilization of PAHs as secondary emission sources seems
337 plausible, especially for 2- to 4- ring PAHs. In addition, the structure of PAH emission
338 sources has undergone significant change during 1990 to 2006 in UK, especially the
339 emissions of transport sources have increased from 29.9% to 62.0% and metal
340 production has decreased from 44.8% to 0.3% (**Fig. S1**). In addition, it has been
341 estimated that local emission sources and atmospheric advective transport account for
342 ~75% and ~25% of the total PAHs in the atmosphere, respectively (Lohmann et al.,
343 2000). All these could result in the changes to the spatial distribution of PAHs found
344 in this study.

345 *3.3 PAH source apportionment*

346 The diagnostic ratios of PAHs have been widely used as a useful tool for source
347 identification to distinguish different sources in multimedia (Yunker et al., 2002; Yang
348 et al., 2013). However, post-emission transformation and degradation of PAHs
349 especially during long-range transport have usually be neglected (Wang et al., 2017).
350 Interpretation of these ratios is therefore problematic, especially for more volatile
351 PAHs. Due to their relative stability in the environment, the ratios of Fluo:Fluo+Pyr

352 and IcdP:IcdP+BghiP, have been adopted as the most suitable indicators to infer
353 petroleum or combustion sources especially in remote areas (Ding et al., 2007). In this
354 study, the majority of Fluo/(Fluo+Pyr) values were greater than 0.5, and all ratios of
355 IcdP/(IcdP+BghiP) were greater than 0.2 with 80% greater than 0.5 in 1990 (**Fig. 4**),
356 indicating that coal and biomass combustion are the major contributor to levels of
357 PAHs in the soil. Similarly, most of Fluo/(Fluo+Pyr) values were greater than 0.5, and
358 70% of IcdP/(IcdP+BghiP) values were greater than 0.5 in 1999 (**Fig. 4**), suggesting
359 the PAHs might be derived from coal and biomass combustion, and also liquid fossil
360 fuel combustion (vehicle exhaust). In 2009, all Fluo/(Fluo+Pyr) values were greater
361 than 0.5, while values of IcdP/(IcdP+BghiP) had reduced to only 63.3% greater
362 than 0.5, 30.0% between 0.2~0.5 and 6.7% less than 0.2 (**Fig. 4**), indicating that
363 sources of PAHs have become more diverse.

364 **4. Conclusions**

365 Long-term spatial and temporal variations of PAHs in Scottish soils over 20 years, as
366 well as accompanying process with contamination levels, risk characteristics,
367 fractionation and source apportionment were studied in this paper. The results showed
368 that HMW PAHs accounted for 73.9 to 89.6% in Scottish soils (these figures are in
369 agreement with the background of global change, energy structure optimization and
370 pollution control management). Concentrations of PAHs have significantly decreased

371 over time, as well as showing fractionation from low to high latitude. While
372 concentrations of PAHs in the soil have decreased significantly during the period of
373 two decades, the proportion of carcinogenic \sum PAH₇ has increased. Statistical analysis
374 indicated that SOC and latitude are the most important factors associated with the
375 spatial distribution of PAHs found in this study. The results of general diagnostic
376 ratios of PAHs suggested that sources have become more diverse over time, and this
377 may be attributed to changes in emission source structure and human activities in
378 Scotland.

379 **Conflict of interest**

380 The authors declare no conflict of interest.

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388

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Supplementary Information

Long-term spatial and temporal patterns of polycyclic aromatic
hydrocarbons (PAHs) in Scottish soils over 20 years (1990-2009): a
national picture

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Table S1 Soil type of sampling sites

Sampling site	Transect number	Land use
Corrie nan Arr	1/1	Grazing
Glen Docherty	1/2	Grazing
Strath Vaich	1/3	Grazing
Croick	1/4	Grazing
Loch Buidhe	1/5	Grazing
Kinbrace	1/6	Grazing
Rumster	1/7	Peatland
Canisbay	1/8	Peatland
Loch Creran	2/1	Grazing
Glencoe	2/2	Grazing
Loch Rannoch	2/3	Grazing
Drumochter Pass	2/4	Grazing
Glen Feshie	2/5	Grazing
Lecht	2/6	Grazing
Home Farm	2/7	Grazing
Blackhills	2/8	Peatland
Queenside Loch	3/1	Peatland
Thief's Hill	3/2	Grazing
Earl's Hill	3/3	Grazing
Kaimknowe	3/4	Grazing
Blacklaw Hill	3/5	Grazing
Bonnyton	3/6	Arable
Pinwherry Hill	4/1	Grazing
Eldrick Hill	4/2	Grazing
Afton Reservoir	4/3	Grazing
Hawkwood	4/4	Grazing
Wylie's Hill	4/5	Grazing
Peat Law	4/6	Grazing
Dogden Moss	4/7	Peatland
Laverlock Law	4/8	Peatland

Table S2 PAH concentrations in Scottish soils in three separate years (1990, 1999 and 2009) (n = 30, ng/g)

	1990						1999						2007-9					
	A.M. ± St.d.	G.M.	Min.	Median	Max.	%	A.M. ± St.d.	G.M.	Min.	Median	Max.	%	A.M. ± St.d.	G.M.	Min.	Median	Max.	%
Nap	222.3±130.6	184.9	49.7	204.2	49.7	6.1	97.1±54.3	83.0	25.2	81.9	211.8	5.9	25.5±16.7	21.0	7.7	21.3	77.7	3.4
Acy	20.3±18.5	14.2	2.8	14.9	2.8	0.5	12.7±11.6	8.6	2.3	7.8	42.8	0.7	7.4±6.1	5.7	1.8	5.5	22.7	0.6
Ace	16.3±17.3	11.2	4.0	8.7	4.0	0.3	10.1±6.2	8.8	4.0	8.5	27.0	0.4	6.9±8.2	4.7	2.8	3.3	21.6	0.2
Flu	21.2±14.9	17.0	4.6	16.3	4.6	0.6	7.8±3.3	7.2	2.7	7.6	15.9	0.4	13.2±24.9	6.9	3.3	5.7	103.3	1.0
Phe	243.3±209.6	188.2	61.7	194.2	61.7	6.6	88.8±51.9	75.2	15.5	84.9	216.4	5.4	38.2±28.9	29.6	7.0	30.4	121.6	4.6
Ant	21.5±26.7	14.0	4.8	13.6	4.8	0.5	16.2±16.2	12.1	5.0	9.8	65.5	0.7	12.6±5.3	11.4	5.5	16.1	17.5	0.5
Fluo	393.8±508.2	237.4	48.5	201.1	48.5	10.8	236.7±377.4	120.7	14.0	123.7	1962.4	14.4	54.6±49.2	37.2	6.3	43.3	198.8	7.5
Pyr	210.8±275.0	124.3	19.4	109.8	19.4	5.8	97.2±112.8	63.4	12.6	75.6	589.2	5.9	35.5±36.8	23.1	3.7	25.7	154.7	4.9
BaA	104.6±136.1	58.4	5.3	53.5	5.3	2.9	46.9±46.5	31.4	1.2	36.0	202.0	2.9	21.1±23.4	13.6	2.6	13.7	97.9	2.8
Chr	308.2±307.9	219.5	28.4	222.3	28.4	8.4	130.7±100.5	96.8	12.0	105.4	381.8	8.0	81.3±78.9	53.5	10.7	53.0	358.6	11.2
BbF	950.4±798.7	694.4	98.6	628.8	98.6	26.0	393.6±356.4	273.7	35.6	333.0	1503.5	23.9	146.8±173.0	87.7	8.6	100.3	915.5	20.2
BkF	194.1±169.1	143.4	19.1	127.6	19.1	5.3	101.5±80.8	75.8	8.1	79.7	329.3	6.2	47.5±54.7	29.7	3.9	33.2	277.2	6.5
BaP	89.6±109.3	49.9	2.9	54.9	2.9	2.4	45.3±43.8	28.9	2.7	28.2	171.6	2.8	106.0±118.4	61.5	5.0	60.2	488.6	14.6
IcdP	408.9±414.4	253.9	11.8	259.1	11.8	11.2	170.3±163.5	108.7	14.6	112.6	756.3	10.4	75.8±107.5	38.0	1.1	43.4	559.9	10.4
DahA	106.1±96.5	71.6	5.7	65.7	5.7	2.9	54.0±46.3	38.6	4.5	38.4	189.0	3.3	19.7±23.8	11.9	1.4	14.8	124.8	2.6
BghiP	354.7±355.3	228.0	13.1	244.9	13.1	9.7	146.8±140.0	95.0	14.3	118.2	666.6	8.9	66.3±70.8	42.2	6.0	50.4	342.5	9.1
∑PAH _{2-ring}	222.3±130.6	184.9	49.7	204.2	560.8	6.1	97.1±54.3	83.0	25.2	81.9	211.8	5.9	25.5±16.7	21.0	7.7	21.3	77.7	3.4
∑PAH _{3-ring}	315.7±270.5	242.3	85.5	242.3	1260.6	8.6	123.9±73.9	104.7	18.3	108.8	323.1	7.5	50.5±50.8	34.1	5.4	35.3	212.0	6.7
∑PAH _{4-ring}	254.3±347.5	139.4	5.3	149.0	2043.7	27.8	511.6±581.2	335.6	52.2	375.1	3069.3	31.1	191.8±177.5	132.5	23.2	145.6	809.7	26.4
∑PAH _{5-ring}	1234.0±1057.0	905.9	120.5	858.8	5291.4	33.7	540.3±458.7	390.4	57.3	457.1	1857.6	32.9	300.4±274.5	213.6	28.1	202.2	1274.2	41.3
∑PAH _{6-ring}	869.7±852.1	561.9	30.7	560.0	4021.9	23.8	371.2±339.0	251.0	41.1	248.4	1588.8	22.6	161.1±199.3	99.7	16.4	92.3	1027.2	22.2
∑PAH ₁₆	3659.1±3130.5	2782.6	414.1	2270.5	15690.1	-	1644.1±1246.9	1264.4	196.1	1362.4	5283.2	-	726.7±653.7	540.5	83.7	523.2	3294.5	-
∑PAH ₇	2161.9±2153.5	1953.5	171.7	1425.7	9920.3	59.1	942.4±762.2	691.4	100.1	759.0	3362.9	57.3	496.9±478.6	352.3	49.2	347.1	2415.4	68.4

Table S3 Pearson correlation coefficients for the relationship between SOC and different rings PAHs

	SOC	2-ring PAH	3-ring PAH	4-ring PAH	5-ring PAH	6-ring PAH
SOC	1					
2-ring PAH	.501**	1				
3-ring PAH	.342**	.684**	1			
4-ring PAH	.255*	.394**	.839**	1		
5-ring PAH	.346**	.505**	.794**	.858**	1	
6-ring PAH	.342**	.410**	.627**	.742**	.916**	1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Table S4 The unstandardized coefficients (B) and standardized coefficients (Beta) for the multiple linear regression for Scottish soil samples (n=90).

(1) Dependent Variable: total PAHs

Model ($R=0.689, p<0.001$)		Unstandardized Coefficients		Standardized Coefficients	Sig.
		B	Std. Error	Beta	
Included Variables	Intercept	35.149	7.872		0.000
	<i>SOC</i>	0.007	0.001	0.484	0.000
	Log (<i>T</i>)	1.258	0.451	0.233	0.007
	Log (<i>L</i>)	-19.360	4.698	-0.361	0.000

Note: The model was run in the stepwise mode to include significant parameters and to remove any insignificant variables.

Excluded Variables: *P*

(2) Dependent Variable: 2-ring PAH

Model ($R=0.765, p<0.001$)		Unstandardized Coefficients		Standardized Coefficients	Sig.
		B	Std. Error	Beta	
Included Variables	Intercept	0.167	8.085		0.984
	<i>SOC</i>	0.009	0.001	0.561	0.000
	Log (<i>T</i>)	2.406	0.463	0.385	0.000

Excluded Variables: *L* and *P*

(3) Dependent Variable: 3-ring PAH

Model ($R=0.746, p<0.001$)		Unstandardized Coefficients		Standardized Coefficients	Sig.
		B	Std. Error	Beta	
Included Variables	Intercept	32.454	8.507		0.000
	<i>SOC</i>	0.007	0.001	0.451	0.000
	Log (<i>T</i>)	2.557	0.488	0.402	0.000
	Log (<i>L</i>)	-19.263	5.077	-0.305	0.000
Excluded Variables: <i>P</i>					

(4) Dependent Variable: 4-ring PAH

Model ($R=0.672, p<0.001$)		Unstandardized Coefficients		Standardized Coefficients	Sig.
		B	Std. Error	Beta	
Included Variables	Intercept	45.875	8.865		0.000
	<i>SOC</i>	0.006	0.001	0.383	0.000
	Log (<i>T</i>)	1.390	0.508	0.233	0.008
	Log (<i>L</i>)	-25.485	5.291	-0.431	0.000
Excluded Variables: <i>P</i>					

(5) Dependent Variable: 5-ring PAH

Model ($R=0.631, p<0.001$)		Unstandardized Coefficients		Standardized Coefficients	Sig.
		B	Std. Error	Beta	
Included Variables	Intercept	32.006	8.816		0.000
	<i>SOC</i>	0.006	0.001	0.459	0.000
	Log (<i>L</i>)	-17.741	5.262	-0.326	0.001
Excluded Variables: <i>P</i> and <i>T</i>					

(6) Dependent Variable: 6-ring PAH

Model ($R=0.672, p<0.001$)		Unstandardized Coefficients		Standardized Coefficients	Sig.
		B	Std. Error	Beta	
Included Variables	Intercept	39.486	10.016		0.000
	<i>SOC</i>	0.007	0.001	0.427	0.000
	Log (<i>T</i>)	1.457	.574	0.226	0.013
	Log (<i>L</i>)	-22.633	5.977	-0.355	0.000
Excluded Variables: <i>P</i>					

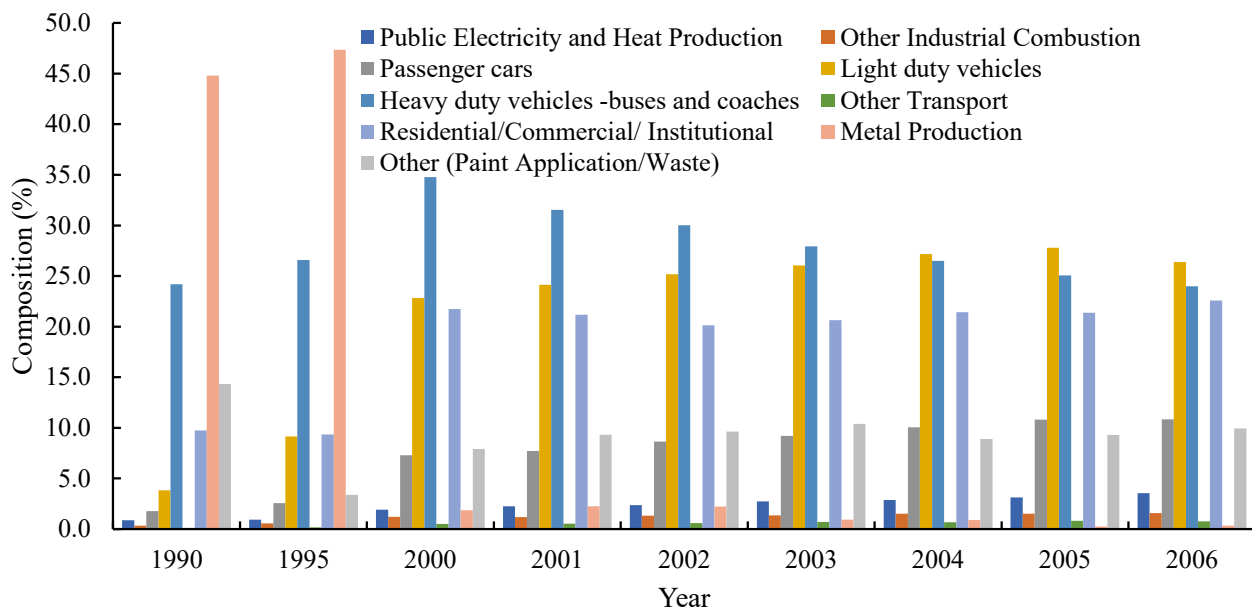


Fig. S1 Composition of emitted 16 PAHs by aggregated UN/ECE (United Nations Economic Commission for Europe) source category in UK

References:

Team, U. E. I., Dore, C. J., Watterson, J. D., Murrells, T. P., Passant, N. R., Hobson, M. M., & Li, Y. (2008). UK emissions for air pollutants 1970 to 2006. Department for Environment Food and Rural Affairs, UK.

Figures

Fig. 1 Transect location map (with sample sites indicated) of Scottish soil sampling

Fig. 2 Concentrations of total PAHs in Scottish soils along four transects (ref to the appropriate figure) in the three separate years

Fig. 3 Contamination risk in Scottish soils between 1990 and 2009

Fig. 4 Cross plot for the ratios of $\text{Fluo}/(\text{Fluo}+\text{Pyr})$ versus $\text{IcdP}/(\text{IcdP}+\text{BghiP})$ in the three separate years in Scottish soils.

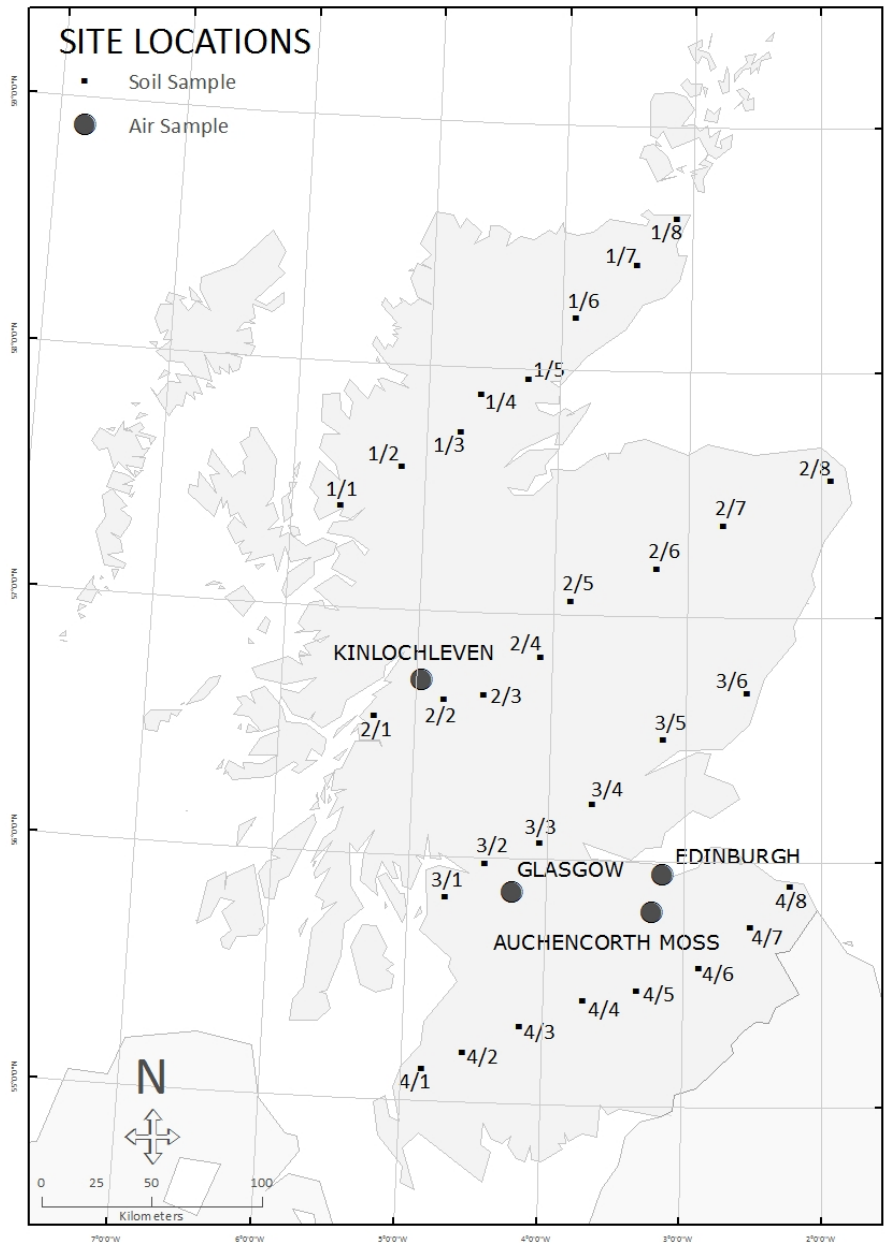


Fig. 1 Transect location map (with sample sites indicated) of Scottish soil sampling

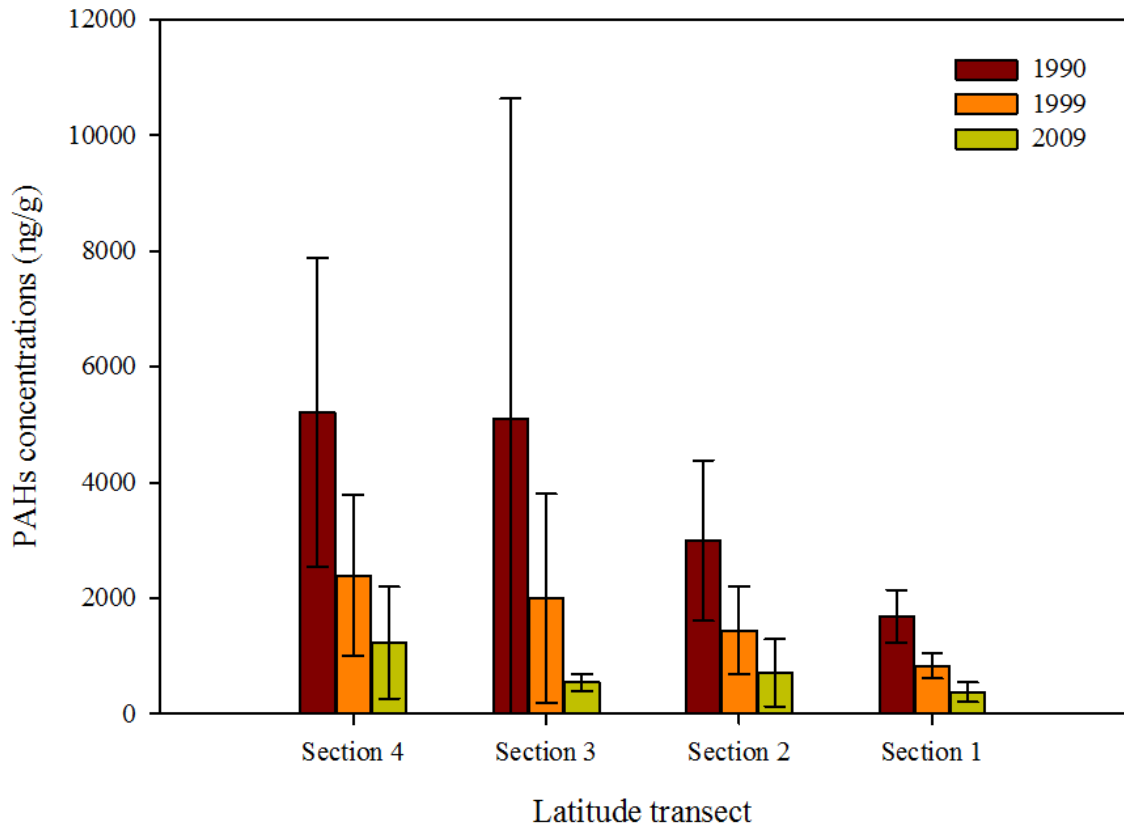


Fig. 2 Average concentrations of total PAHs in Scottish soils along four transects (ref to the appropriate figure) in the three separate years

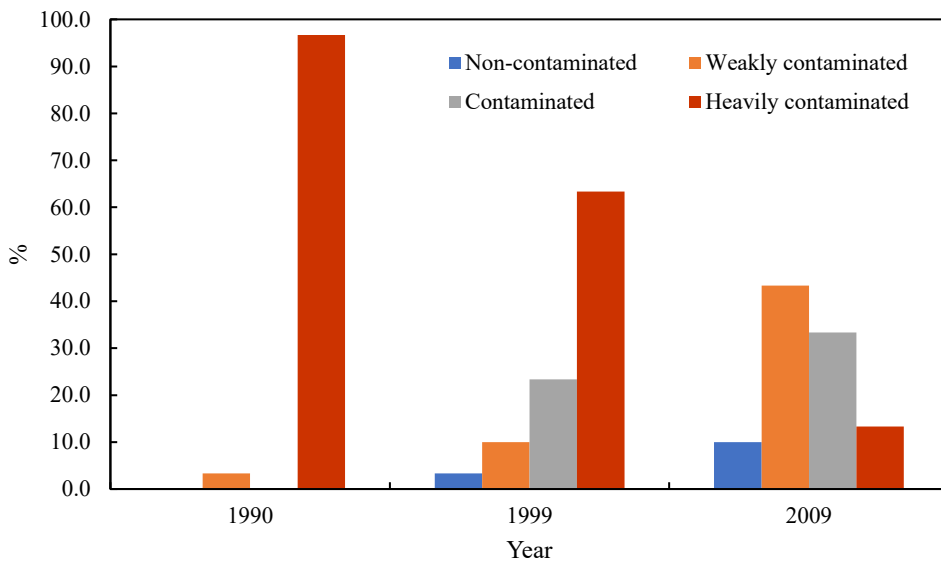
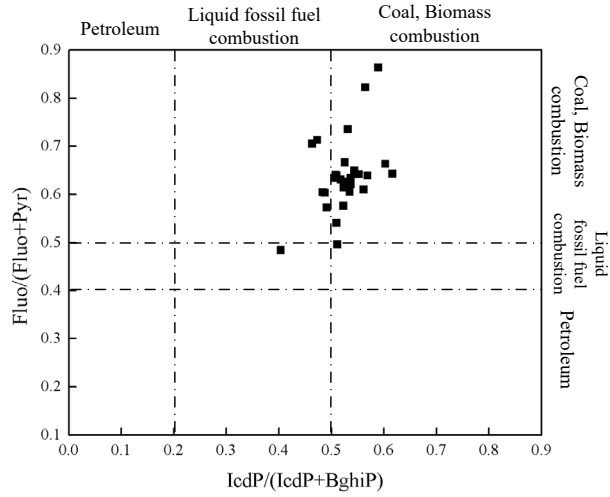
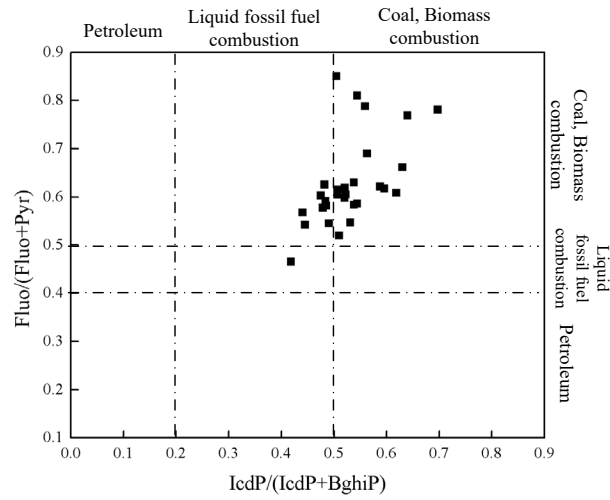


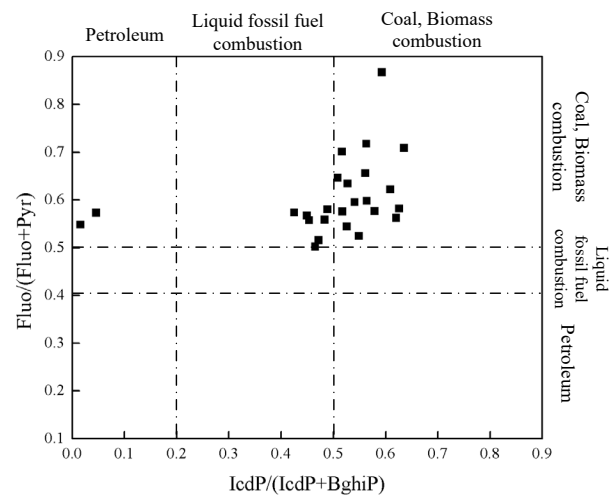
Fig. 3 Contamination risk in Scottish soils between 1990 and 2009



1990



1999



2009

Fig. 4 Cross plot for the ratios of $\text{Fluo}/(\text{Fluo}+\text{Pyr})$ versus $\text{IcdP}/(\text{IcdP}+\text{BghiP})$ in the three separate years in Scottish soils.