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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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Abstract

Long-term spatial and temporal concentrations of polycyclic aromatic hydrocarbons (PAHs) in Scottish soils from four transects were measured in three national-scale surveys conducted between 1990 and 2009. Measured concentrations of 16 priority PAHs ranged from 15690 to 83.7 ng g^{-1}, with an average of 3659±3131 to 727±654 ng g^{-1}, of which the high molecular weight (HMW) PAHs (4~6 rings) accounted for 73.9 to 89.6%. Overall, concentrations of PAHs in the soil have decreased over time, but the proportion of carcinogenic $\sum PAH_7$ has increased. Concentrations of total PAHs correlated significantly with latitude (R=-0.345, p=0.001). A significant correlation was found between concentrations of PAHs and soil organic carbon (SOC, R=0.439, p=0.000), which is an important factor, influencing the levels of PAHs in soils. Source apportionment analysis indicated that the emission sources of PAHs have evolved from coal and biomass combustion to more diverse sources during the two decades covered by the surveys. It is likely that this reflects societal development towards a lower carbon economy and less use of biomass buring for domestic space heating.

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

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous persistent toxic organic pollutants derived from both natural and anthropogenic emission sources. The United States Environmental Protection Agency (USEPA) and the Europian Union (EU) have identified 16 PAHs as priority pollutants due to their toxicity and associted risks to human health and the environment (Dimashki et al., 2001; Wang et al., 2011). Therefore, understanding the emission sources, scale effect, environmental behaviour, bioaccumulation and health hazards associated with the spatial-temporal distribution of PAHs has become imperative from an environmental protection and public health perspective (Benfenati et al., 1992; Holmqvist et al., 2006; Holoubek et al., 2009; Villanneau et al., 2011; Villanneau et al., 2013; Cui et al., 2016).

Temporal changes in PAHs (concentrations and composition) have been reported in various environment media including sediment cores, soil, and air (Andersson et al., 2014; Garrido et al., 2014; Bandowe et al., 2018). These findings have served to emphasise the need to understand the drivers that result in changes to the PAH profile, especially as these environmental matrices often harbour historic PAH discharges thus the risk of secondary emissions through e.g. transformation need to be understood. Generally, soil plays a significant role in the storage, global cycle, redistribution, and transfer to the food chain of persistent organic pollutants (POPs), with soil organic matter playing an important role in the retention of POPs within the soil matrix (Ockenden et al., 2003; Nadal et al., 2004; Sweetman et al., 2005; Wilcke 2007; Gubler et al., 2015; Ren et al., 2018; Rey-Salgueiro et al., 2018). Numerous studies have reported on the PAH profiles within the UK including emissions inventories, contamination levels, spatial distribution, and source-sink relationships (Wild and Jones 1995; Lohmann et al., 2000; Prevedouros et al., 2004; Smith et al., 2006; Nam et al., 2008; Brown, A. and Brown, R., 2012; Rhind et al., 2013; Brown et al., 2013; Graf et al., 2016). A significant source of PAHs in UK soils and other environmental media has been from combustion of fossil fuels such as coal which was particularly prevalent during the UK industrial revolution of the early 19th Century (Nam et al., 2008). About 90% of the total environmental burden of PAHs in the UK are currently residing in soils, primarily derived from atmospheric deposition (Wild and Jones 1995). Given that both emission sources and soil conditions have changed over time, improving our understanding of how concentrations of PAHs have also changed is valuable towards meeting environmental and public health obligations. Therefore, understanding the long-term temporal changes to the concentrations of PAHs in soils at a national scale could help elucidate the main drivers of spacial-temporal evolution and environmental behavior (Zhang et al., 2014).

Since the global fractionation and cold condensation for low volatility compounds was reported by Wania and Mackay (1993); analogous fractionations for organic pollutants such as latitudinal fractionation, urban fractionation, longitudinal fractionation, primary and secondary fractionation have all been proposed based on various monitoring and modeling methods (Agrell et al., 1999; Meijer et al., 2002; Meijer et al., 2003; Harner et al., 2004; Gouin et al., 2004; Scheringer et al., 2004; Ren et al., 2007; Li et al., 2010; Lammel and Stemmler 2012; Cai et al., 2014). For example, Nam et al. (2008) found a fractionation phenomenon between the UK and Norway for <4-ring PAHs distirbution by long-range atmospheric transport; Wilcke and Amelung (2000) found a fractionation for naphthalene along a climosequence in the North American prairie, but not for other PAHs. All these fractionation phenomena are related to the intensity and pattern of emission sources, physico-chemical properties of chemicals, meteorological conditions and soil properties. In other words, the intensity and diversity of emission sources can be attributed to anthropogenic influence, such as the increasing dominance of low molecular weight PAHs from north to south transect along a 2100 km distance in Argentina (Wilcke et al., 2014). Evidence for these fractionation effects has been reported primarily for polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCHs), and DDTs; which have had almost global-level prohibition for a number of decades. In contrast, it is more challenging to identify fractionation effects for PAHs because they tend to be deposited close to their sources, as well as the fact that emissions are contemporary and on-going e.g. as by-products of incomplete combustion processes.

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

2. Materials and methods

2.1 Soil samples

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

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

2.2 Reagents and materials

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

2.3 Sample extraction and instrumental analysis

Soil samples were extracted and analyzed according to the previously published method (Rhind et al., 2013). Briefly, soil samples (approximately 1.0 g) were spiked with 0.3 µg internal standards and 8 mL 1M ethanoic potassium hydroxide added (for the alkaline saponification). The samples were heated to approximately 90 ºC for 8 hours and allowed to cool before 2 mL of Milli-Q water was added and the analytes extracted into 3×10 mL iso-hexane. The extracts were evaporated to 0.5 mL and loaded onto a 9 g silica, 1 g of acid modified silica and 1 g anhydrous Na_2SO_4 column (22 cm length, i.d. 3 cm, fitted with PTFE taps) that had been pre-conditioned with 40 ml iso-hexane. The column was eluted with 10 mL DCM:iso-hexane (1:4) which was discarded, and the PAHs were eluted using 40 mL of 1:4 DCM:iso-hexane. The PAH eluant was concentrated by rotary evaporation before analysis by GC-MS.

An Agilent 5975C Mass Spectrometer Detector (MSD) linked to 7890A GC with an autosampler (7683B), was used for PAH analyses with selected ion mode. The capillary column used was ZB-5MS (30 m x 0.25 mm i.d. x 0.25 µm film thickness, Phenomenex, Macclesfield, UK). The oven programme was: 70 ºC (3 min) ramped to 250 ºC at 5 ºC min^{-1} and held for 1 min, then ramped to 300 ºC at 6 ºC min^{-1} and held for 6 min and finally ramped to 325 ºC at 10 ºC min^{-1} and held for 5 min. The carrier gas was helium. The injector and mass spectrometer were held at 250 ºC and 200 ºC respectively. The electron impact energy was set 70 eV for mass spectrometer.

2.4 Quality control

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

g^{-1} DW (dry weight). SOC content was estimated by loss on ignition at 450 °C (Heiri et al., 2010).

2.5 Statistical analysis

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

3. Results and discussion

3.1 Temporal changes

3.1.1 PAHs levels

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

1990, 1644±1247 for 1999, and 727±654 for 2009, respectively. Overall PAH levels declined during this period and ranged about three orders of magnitude from 83.7 to 15690 ng/g for $\sum PAH_{16}$ and from 49.2 to 9920 ng/g for $\sum PAH_7$, respectively (Table S2).

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

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

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

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

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)

3.1.2 Risk characteristics

Over three quarters (77%) of soil samples analysed in this study were obtained from grazing land. There is therefore the potential for PAHs in the soil to move through the foodchain via the herbage, to grazing animals, and eventualy through to human exposure via milk and meat consumption. The soil contamination classification system based on 16 PAHs was suggested by Maliszewska-Kordybach (1996) as a risk screening method. According to this classification system, *heavily contaminated soil* (>1000 ng/g) reduced from 96.7% to 13.3% and *non-contaminated soil* (<200 ng/g) increased from 0.0% to 10.0% between 1990 and 2009, respectively (**Fig. 3**). However, it is important to note that the ratio of the important carcinogenic $\sum PAH_7$ to $\sum PAH_{16}$ increased from 59.1% to 68.4% between 1990 and 2009, although the contents of total 16 PAHs decreased. This is expected because the carcinogenic $\sum PAH_7$ are primarily HMW PAHs with 4~6 rings, that tend to have relatively high K_{ow} (octanol-water partition coefficient). This means that they are more likely to be retained in the soil, while the lighter 3 ring PAHs (that make up the majority of the remaining $\sum PAH_{16}$) are more likely to dissipate over time.

3.2 Spatial patterns

Within the soil, PAHs will tend to bind to the SOM (Mackay, 2001; Ockenden et al., 2003). A significant correlation was found between concentrations of $\sum PAH_{16}$ and SOC (R=0.436, p<0.001) and it was also found between SOC and PAH fractions based on molecular weight (Table S3). This indicates that SOC could be the important factor affecting the spatial patterns of PAHs in Scottish soils. The result being different from the findings of Heywood et al. (2006) who investigated PAHs in British soils showed that no correlation was found between PAHs and soil organic matter (SOM). Lohmann et al. (2000) reported that other factors including proximity to sources, land use type, wet deposition etc. could be stronger influences on the spatial distribution of PAHs in soils compared to SOC due to the fact that the primary route of PAH to soil is via atmospheric dispersion. This difference in findings might be due to the fact that Scottish soils have elevated levels of SOM compared to the UK as the whole. It is also the case that many of the sampling locations in this study are now very remote and many of the emission sources are historic, thus increasing the importance of SOM in PAH distribution, i.e. once retained in the soil the PAHs have potential to be stored for significant time periods because the HMW PAHs do not easily dissipate.

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

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

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

$$\log\left(C\right) = b_0 + b_1 \log(L) + b_2 \log(T) + b_3 \log(P) + b_4 SOC \qquad (10)$$

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

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

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

As described above, the concentrations of PAHs in Scottish soils during the period of two decades decreased with increasing latitude, which exhibited the general characteristics of the latitude fractionation effect. This could be related to fundamental changes in PAH emission sources, long-range atmospheric transport and climatic conditions. In addition, temperature and SOC content are important factors that affect soil-air exchange and secondary emissions for organic pollutants according to concept of secondary fractionation (Li et al., 2010). Therefore, degradation of organic soils leading to the re-volatilization of PAHs as secondary emission sources seems plausible, especially for 2- to 4- ring PAHs. In addition, the structure of PAH emission sources has undergone significant change during 1990 to 2006 in UK, especially the emissions of transport sources have increased from 29.9% to 62.0% and metal production has decreased from 44.8% to 0.3% (**Fig. S1**). In addition, it has been estimated that local emission sources and atmospheric advective transport account for ~75% and ~25% of the total PAHs in the atmosphere, respectively (Lohmann et al., 2000). All these could result in the changes to the spatial distribution of PAHs found in this study.

3.3 PAH source apportionment

The diagnostic ratios of PAHs have been widely used as a useful tool for source identification to distinguish different sources in multimedia (Yunker et al., 2002; Yang et al., 2013). However, post-emission transformation and degradation of PAHs especially during long-range transport have usually be neglected (Wang et al., 2017). Interpretation of these ratios is therefore problematic, especially for more volatile PAHs. Due to their relative stability in the environment, the ratios of Fluo:Fluo+Pyr and IcdP:IcdP+BghiP, have been adopted as the most suitable indicators to infer petroleum or combustion sources especially in remote areas (Ding et al., 2007). In this study, the majority of Fluo/(Fluo+Pyr) values were greater than 0.5, and all ratios of IcdP/(IcdP+BghiP) were greater than 0.2 with 80% greater than 0.5 in 1990 (**Fig. 4**), indicating that coal and biomass combustion are the major contributor to levels of PAHs in the soil. Similarly, most of Fluo/(Fluo+Pyr) values were greater than 0.5, and 70% of IcdP/(IcdP+BghiP) values were greater than 0.5 in 1999 (**Fig. 4**), suggesting the PAHs might be derived from coal and biomass combustion, and also liquid fossil fuel combustion (vehicle exhaust). In 2009, all Fluo/(Fluo+Pyr) values were greater than 0.5, while values of IcdP/(IcdP+BghiP) had reduced to only 63.3% greater than 0.5, 30.0% between 0.2~0.5 and 6.7% less than 0.2 (**Fig. 4**), indicating that sources of PAHs have become more diverse.

4. Conclusions

Long-term spatial and temporal variations of PAHs in Scottish soils over 20 years, as well as accompaning process with contamination levels, risk characteristics, fractionation and source appoinment were studied in this paper. The results showed that HMW PAHs accounted for 73.9 to 89.6% in Scottish soils (these figures are in agreement with the background of global change, energy structure optimization and pollution control management). Concentrations of PAHs have significantly decreased over time, as well as showing fractionation from low to high latitude. While concentrations of PAHs in the soil have decreased significantly during the period of two decades, the proportion of carcinogenic $\sum PAH_7$ has increased. Statistical analysis indicated that SOC and latitude are the most important factors associated with the spatial distribution of PAHs found in this study. The results of general diagnostic ratios of PAHs suggested that sources have become more diverse over time, and this may be attributed to changes in emission source structure and human activities in Scotland.

Conflict of interest

The authors declare no conflict of interest.

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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
$\sum PAH_{2\text{-ring}}$	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
$\sum PAH_{3\text{-ring}}$	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
$\sum PAH_{4\text{-ring}}$	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
$\sum PAH_{5\text{-ring}}$	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
$\sum PAH_{6\text{-ring}}$	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
$\sum PAH_{16}$	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	-
$\sum PAH_{7}$	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
	SOC	0.007	0.001	0.484	0.000
	Log (T)	1.258	0.451	0.233	0.007
	Log (L)	-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
	SOC	0.009	0.001	0.561	0.000
	Log (T)	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
	SOC	0.007	0.001	0.451	0.000
	Log (T)	2.557	0.488	0.402	0.000
	Log (L)	-19.263	5.077	-0.305	0.000
Excluded Variables: P					

(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
	SOC	0.006	0.001	0.383	0.000
	Log (T)	1.390	0.508	0.233	0.008
	Log (L)	-25.485	5.291	-0.431	0.000
Excluded Variables: P					

(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
	SOC	0.006	0.001	0.459	0.000
	Log (L)	-17.741	5.262	-0.326	0.001
Excluded Variables: P and T					

(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
	SOC	0.007	0.001	0.427	0.000
	Log (T)	1.457	.574	0.226	0.013
	Log (L)	-22.633	5.977	-0.355	0.000
Excluded Variables: P					

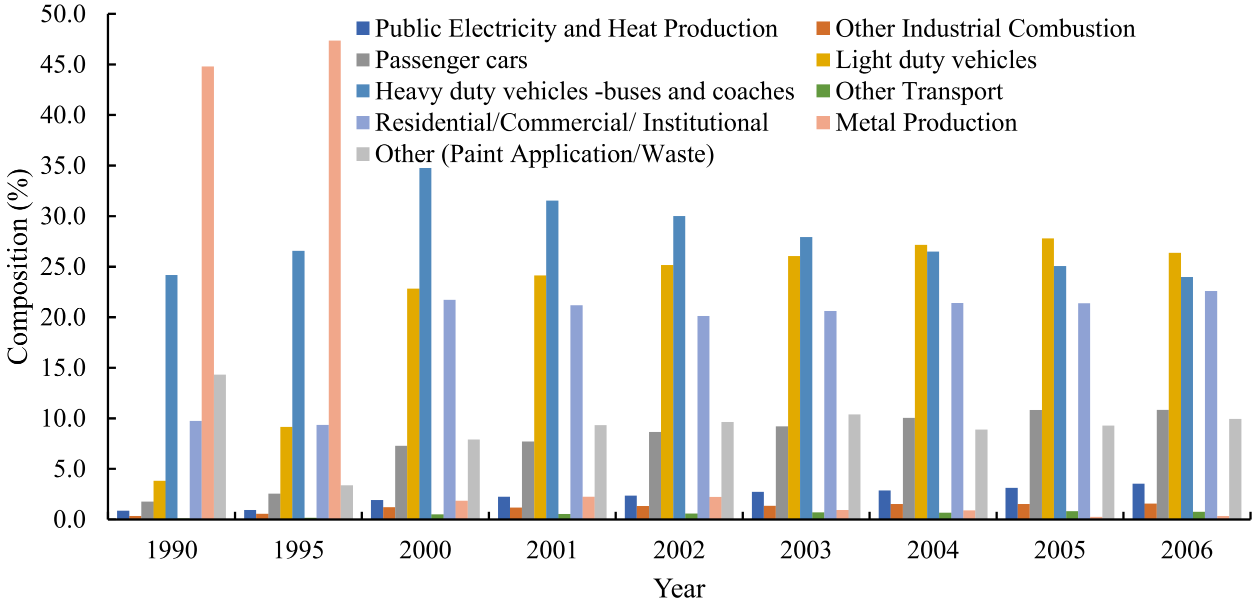


Fig. S1 Composition of emitted 16 PAHs by aggregated UN/ECE (United Nations Economic Commission for Europe) source category in UK

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 Fluo/(Fluo+Pyr) verus IcdP/(IcdP+BghiP) in the three separate years in Scottish soils.

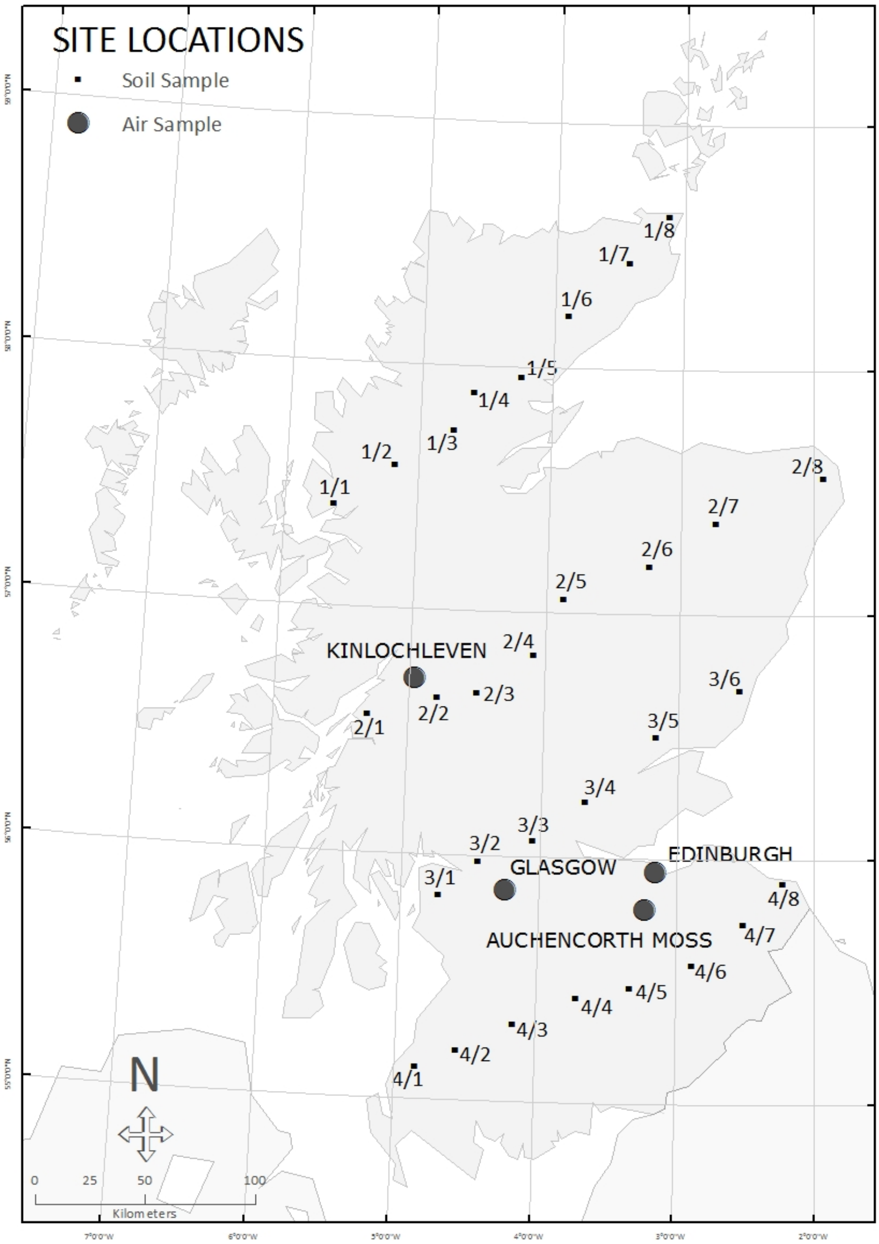


Fig. 1 Transect location map (with sample sites indicated) of Scottish soil sampling

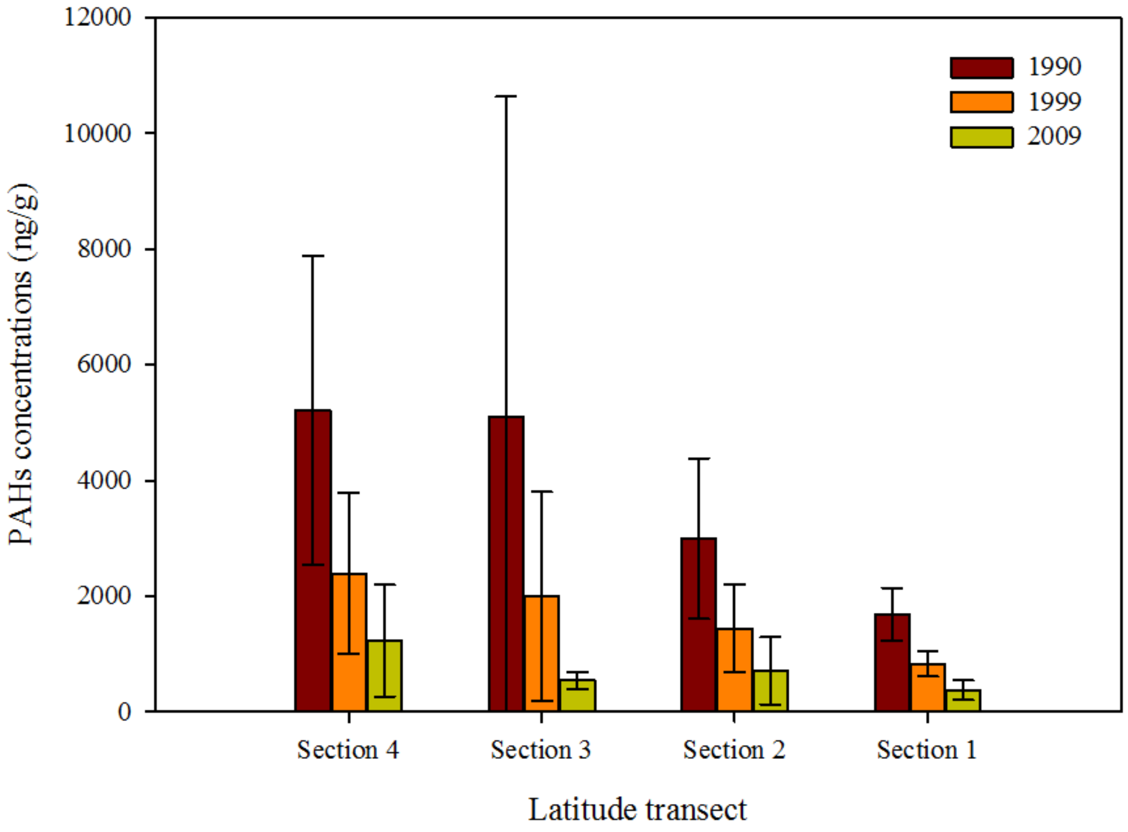


Fig. 2 Average concentrations of total PAHs in Scottish soils along four transects (ref to the appropriate figure) in the three separate years

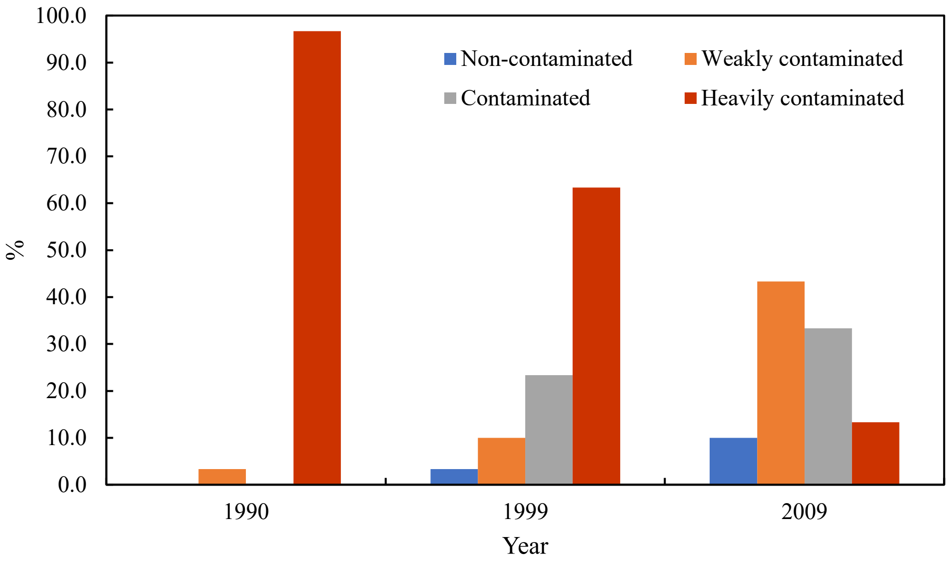
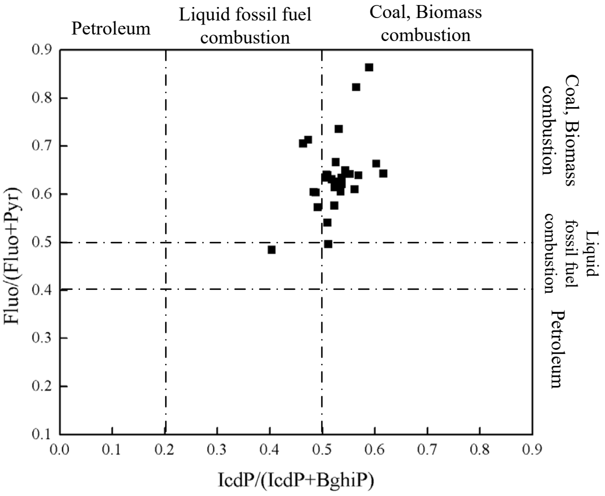
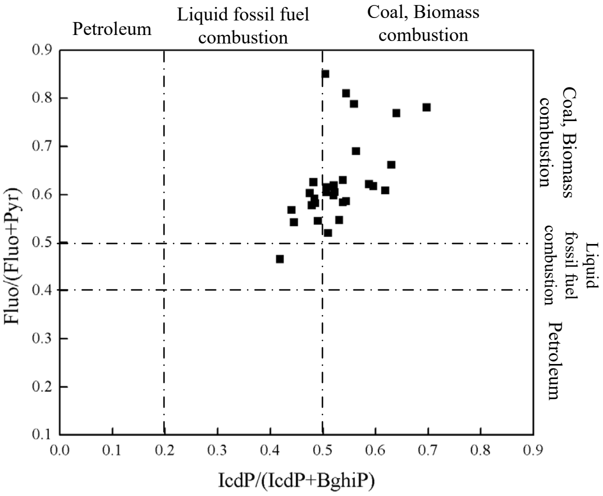


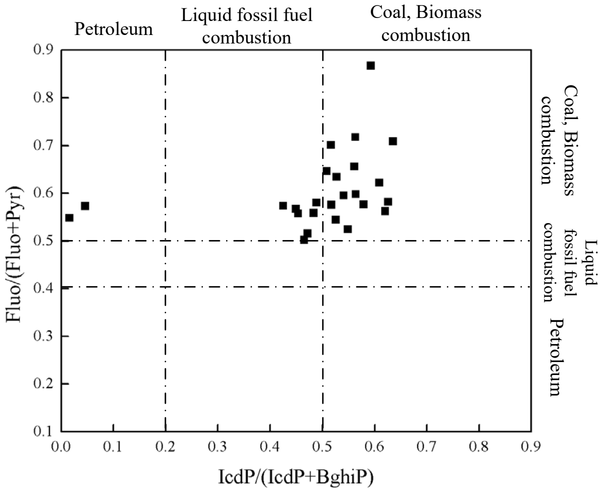
Fig. 3 Contamination risk in Scottish soils between 1990 and 2009



1990



1999



2009

Fig. 4 Cross plot for the ratios of Fluo/(Fluo+Pyr) verus IcdP/(IcdP+BghiP) in the three separate years in Scottish soils.