Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK

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A R T I C L E   I N F O

A B S T R A C T

Surface soils from a 19 km² area in east London, UK were analysed for polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) ($n = 76$). $\sum^{16}$ PAH ranged from 4 to 67 mg/kg (mean, 18 mg/kg) and $\sum^{50}$ PAH ranged from 6 to 88 mg/kg (mean, 25 mg/kg). $\sum^{7}$ PCB ranged from 1 to 750 µg/kg (mean, 22 µg/kg) and $\sum^{tri-hepta}$ PCB ranged 9 to 2600 µg/kg (mean, 120 µg/kg). Compared to other international cities concentrations were similar for PAH but higher for PCB. Normal background concentrations (NBC) were calculated and compared to risk-based human health generic assessment criteria (GAC). Benzo[*a*]pyrene NBC for urban (6.9 mg/kg), semi-urban (4.4 mg/kg) and urban + semi urban (6 mg/kg) domains exceed residential (1 mg/kg) and allotment (2.2 mg/kg) LQM/CIEH GAC (at 6% SOM) and the Indeno[*1,2,3-cd*]pyrene NBC for urban (6.8 mg/kg) and urban + semi-urban (5.2 mg/kg) domains exceed the residential (4.2 mg/kg) LQM/CIEH GAC (at 6% SOM).

Capsule Abstract: Normal background concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls are elevated in east London soils and in some cases exceed regulatory assessment criteria.

1. Introduction

London is Europe's largest city by population and one of the top five richest by GDP in the world. The capital has a long industrial history which has contributed to sources of organic pollutants in soil such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB). These compounds are strongly hydrophobic and lipophilic as well as having a propensity to accumulate in plant and animal tissues. PAH are present in soil as a result of natural and anthropogenic processes which produce both point source and diffuse emissions. PCB are not found naturally in the environment and are mainly present in soils due to point source releases (Creaser et al., 2007a). However, studies have also reported that PCB are prone to long-range atmospheric transport and deposition, controlled by temperature induced volatilisation (Jones and De Voogt, 1998; United Nations – Economic Commission for Europe, 1994). PAH and PCB tend to remain in soil for extended periods of time due to their comparatively long half-life, which can range from years to decades (Jones and De Voogt, 1998; Environment

Agency, 2008). These characteristics are important since both PAH and PCB have been implicated in adverse effects on human and environmental health (Environment Agency, 2009a; Nathanail et al., 2009; ATSDR, 2011).

Previous studies published by the Environment Agency for England and Wales reported elevated concentrations of PAH and PCB in UK urban soil (Creaser et al., 2007a, 2007b). PAH sources were thought to be mixed and predominantly include those from traffic and domestic combustion, while PCBs were likely to have arisen from atmospheric deposition as a consequence of original point source releases. Similar findings have been reported for cities such as: Glasgow, Scotland (Morillo et al., 2007); Birmingham, England (Smith et al., 1995); Boston, US (Bradley et al., 1994); and Xiamen in China (Xing et al., 2005). In addition, many geo-environmental site investigations take place each year for regulatory purposes that give rise to a large volume of soil contamination information that is not published in peer reviewed journals. Notwithstanding, there is paucity of comprehensive background data on soil PAH and PCB concentrations for London. Our study bridges this knowledge gap by systematically sampling an area of 19 km² in the Greater London Authority (GLA) ($n = 76$) (Fig. 1). Moreover, this study recognises that the source of PAH and PCB is especially important were concentrations are elevated, which is why where

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possible, relevant methods and explanations for each compound group are presented.

Analyses of each sample comprised 33 PAH (parent and alkylated), 7 PCB congeners, 5 PCB homologous series and total organic carbon (TOC). TOC was selected as a soil property that is known to affect soil-compound sorption interactions (Reid et al., 2000). PAH and PCB concentrations are evaluated statistically, including the use of a recently proposed method for deriving normal background concentrations (NBC) of contaminants in soil (Ander et al., 2013). Concentration data are compared to those recorded in similar urban areas to identify whether there are any obvious differences for London. A discussion of the potential sources of soil PAH is presented to characterise the likely contribution of point and diffuse emissions. The PCB congener profile is also discussed along with findings from other studies. NBCs are calculated for 16 parent PAH, $\sum^{16}$ PAH, $\sum^{50}$ PAH, 7 PCB congeners, $\sum^7$ PCB, 5 homologous PCB series and $\sum^{\text{tri-hepta}}$ PCB. This study also compares NBCs with selected human health generic assessment criteria (GAC) to put them in a of risk-based land management context.

2. Materials and methods

2.1. Soil sampling

Surface soil samples ($n = 76$) were collected between 4th and 18th April 2009 from a 19 km^2 area covering Abbey Wood, Thamesmead, Erith, Belvedere and Jenningtree Point in the GLA of London, UK (Fig. 1). Four sites were selected every kilometre square and the position of each location recorded using a handheld Garmin GPS device (accuracy ±5 m). At each site soil samples were recovered from four corners and the centre of a 20 m by 20 m square grid at a depth of 5–20 cm using a hand-held Dutch auger. The samples were combined, sealed in a Rilsan bag, stored at ∼4 °C for 1–3 h and then frozen at −18 °C. Sampling locations covered the following eleven land-use types: commercial and residential, domestic garden, golf course, industrial, park, playground, road verge, rough grazing, school, urban open space and water treatment works.

2.2. Laboratory analysis

All soils were freeze-dried, disaggregated and passed through a brass sieve with an aperture of 2 mm before being agate ball milled (Vane et al., 2007b). This method was chosen as a statistically robust method for high precision and accuracy PAH quantification (Beriro et al., 2014).

2.2.1. Polycyclic aromatic hydrocarbons

Soils ∼1 g were spiked with: naphthalene-d$_8$, biphenyl-d$_{10}$, phenanthrene-d$_{10}$, pyrene-d$_{10}$, benzo[a]athracene-d$_{10}$, benzo[a]-pyrene-d$_{12}$ and benzo[g,h,i]perylene-d$_{12}$ of between 267 and 4000 ng/g dry/wt and extracted with hexane/acetone 1:1v/v. Extracts were dried, reduced to ∼0.25 mL and transferred to an SPE cartridge (Varian, Bond Elute). The first fraction was eluted with pentane (0.5 + 1 mL), the second with 6 mL hexane/iso-propanol (97:3 v/v) and spiked with: methylnaphthalene-d$_{10}$ (107 ng/g) and chrysene-d$_{12}$ (729 ng/g) and reduced to 0.5–1.0 mL. Concentrations of PAH were measured using a Varian 3800 gas chromatograph (GC) coupled to a Varian 1200L triple quadropole mass spectrometer operating in full scan mode (ionisation energy 70 eV, mass range 47–500 amu) (GC/MS).

2.2.2. Polychlorinated biphenyls

Soils (∼10 g) were spiked with PCB 34, 62, 119, 131 and 173 (9.0–9.7 ng/g) and PCB 19 and 147 (7.9–10.1 ng/g) and extracted

with hexane/acetone 1:1 v/v followed by addition of concentrated H$_2$SO$_4$ (5 mL) (Vane et al., 2011a). The hexane extract was reduced and cleaned using the same SPE method as for PAH and spiked with PCB 29 and 157 (3.1–3.3 ng/g) and reduced.

Concentrations of PCB were measured using GC/MS. The MS was operated in selected ion mode (m/z 71, 220, 256, 258, 292, 326, 328, 360, 362, 394, 396) with a scan time of 0.5 s. Congener profile distributions for tri to hepta-chlorinated biphenyls were determined using 5 separate individual relative response factors for each congener group. A standard consisting of 2×5 individual PCBs based on first and last eluting congener was used to define the 'retention time window' for each group. The sum of these 5 groups is $\sum^{\text{tri-hepta}}$ PCB and $\sum^7$PCB comprised congeners 28, 52, 101, 118, 153, 138, 180.

2.2.3. Total organic carbon

Total organic carbon (TOC) content was determined using an Elementar VarioMax C, N analyser after acidification with HCl (50% v/v) to remove carbonate. The limits of quantification for a typical 300 mg sample were 0.18%. Details of this method have been described previously (Vane et al., 2007a).

2.3. Data evaluation

The data were grouped into urban and semi-urban domains. The urban domain ($n = 42$) was defined by land-use, i.e. developed land and the semi-urban domain ($n = 34$), i.e. undeveloped land were assigned using information presented in 1953-present Ordnance Survey maps. Differences in PAH and PCB concentrations between the two domains were tested using Levene's and Bartlett's test for homogeneity of variance followed by a Student's t-test to decide which domains should be used to derive NBC and compare with GAC.

An NBC is the upper confidence limit of the 95th percentile, providing a conservative estimate of the background concentration over a given area accounting for geogenic and diffuse sources of pollution (Cave et al., 2012; Ander et al., 2013). NBCs have recently been introduced into the contaminated land regime in England and Wales under Part 2a of the Environmental Protection Act 1990 (EPA) (as amended) by secondary statutory guidance in each country (DEFRA, 2012). The regime supports the derivation of normal levels of contaminants as a way of identifying concentrations that represent low rather than unacceptably high levels of risk. NBCs should not be used in support of the National Planning Policy Framework (NPPF), which states that the developer or site owner needs to ensure the land is safe for its intended use. (Paragraph 121: CLG, 2012). The data underpinning the NBCs could contribute to one of many lines of evidence that may be used to assist with risk-based land management under these and other regimes (Environment Agency, 2004).

GAC are scientific risk-based conservative estimates of chemical concentrations in soil, below which the level of risk posed under specific exposure scenarios to people may be negligible or minimal (Environment Agency, 2009d). A GAC is the concentration of contaminant that would give rise to an estimated Average Daily Exposure that is equal to the Health Criteria Value for that contaminant (Environment Agency, 2009c). Far from representing thresholds of unacceptable risk GAC indicate concentrations below which the risk is negligible or minimal and whose exceedance should trigger a detailed quantitative risk assessment. The level of unacceptable risk varies among different legal regimes. For Part 2a of the EPA it is the significant possibility of significant harm (SPOSH) such as death, life threatening diseases, other diseases likely to have serious impacts on health, serious injury, birth defects and impairment of reproductive function (DEFRA, 2012). The NPPF states that unacceptable risks should be prevented by ensuring land is
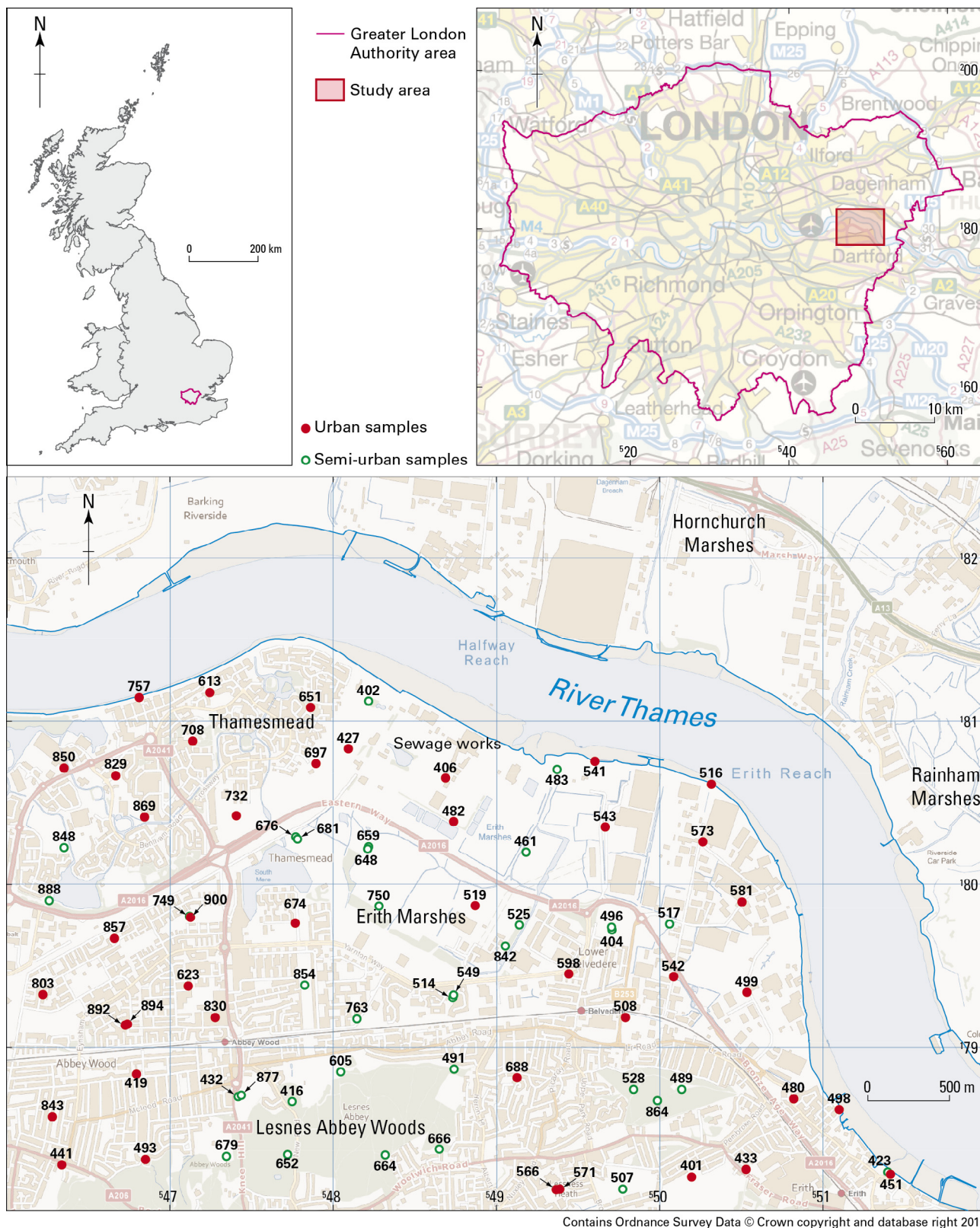
Fig. 1. Map of east London showing the sample locations and reference numbers.

appropriate for its location, it is safe and after remediation not capable of being defined as Contaminated Land under Part 2a of the EPA (CLG, 2012). LQM/CIEH GAC have been published for 16 PAH for three land-use types (residential with plant uptake, allotment and commercial) and three soil organic matter (SOM) contents (1%, 2.5% and 6%) (Nathanail et al., 2009). There is an Environment Agency derived GAC, called a soil guideline value (SGV), for dioxin like PCB (Environment Agency, 2009b). For this study the calculated NBCs are compared with published LQM/CIEH GAC for 16 PAH and the SGV for PCB.

3. Results and discussion

3.1. Polycyclic aromatic hydrocarbons

3.1.1. Data summary

The spatial distribution of $\sum^{16}$ PAH across the study area is summarised in Fig. 2. $\sum^{16}$ PAH concentrations ranged from 4 to 66 mg/kg with a mean of 18 mg/kg and a median of 14 mg/kg. The highest $\sum^{16}$ PAH concentrations were at Abbey Wood Park (Sample ref: 749; 66 mg/kg), A206 roadside verge (Sample ref: 433; 65 mg/kg), Jenningtree Point industrial park (Sample ref: 516; 58 mg/kg), Abbey Wood (Sample ref: 843; 54 mg/kg), Bostall Woods (Sample ref: 493; 51 mg/kg) and Riverside golf course (Sample ref: 697; 41 mg/kg) (see Fig. 1 for sample locations and Fig. 2 for sample concentrations). Relative contributions made by parent and alkylated PAH for all samples are presented in boxplots (Fig. 3). Descriptive statistics are presented in the Supporting information (SI: Table 1).

3.1.2. Comparison of data with other urban areas

Other studies of PAH in urban soils report similar concentrations to those presented in this research. A UK study reported $\sum^{22}$ PAH concentrations in the range of <1 to 55 mg/kg ($n = 366$) (Creaser et al., 2007c). Similarly, Glasgow has soils with $\sum^{15}$ PAH concentrations in the range of 1–52 mg/kg ($n = 15$) (Morillo et al., 2007; Vane et al., 2011). In contrast, lower amounts of PAH have been observed in urban soils from Wales and the Midlands/Birmingham (Butler et al., 1984; Smith et al., 2001; Wild and Jones, 1995). Comparable amounts of PAH have also been recorded outside the UK: e.g. New Orleans, USA (<1 to 41 mg/kg; mean 6 mg/kg), Boston, US (highest conc. 360 mg/kg; mean 19 mg/kg),

Moscow, Russia (<1 to 1 mg/kg), Torino, Italy (1–24 mg/kg; mean 2 mg/kg), Switzerland (highest conc. 8 mg/kg) (Bradley et al., 1994; Desaules et al., 2008; Morillo et al., 2007; Wang et al., 2004; Wilcke et al., 2005). The PAH data in this study are far lower than those encountered for soils which have suffered specific point sources releases of pollution. For example, a former tar works site in Newcastle upon-Tyne, UK, yielded surface soil PAH concentrations ranging from 66 to 1400 mg/kg (Lorenzi et al., 2010). This suggests that the study data presented herein for an area of London represents diffuse pollution sources.

3.1.3. Source apportionment of PAH

PAH distribution data for all samples showed minor contributions of low molecular weight PAH (2–3 ring) such as naphthalene, methylnaphthalenes and acenapthylene (Fig. 3). This may be due to their increased susceptibility to weathering by oxidation and increased losses due their higher aqueous solubility (Marynowski et al., 2011). In contrast, major contributions from higher molecular weight PAH (4–6 ring) including fluoranthene, pyrene and benzo[a]pyrene were observed (Fig. 3), although it is acknowledged that high molecular weight compounds may also experience losses due to weathering. The sole exception to this finding is phenanthrene, the most thermodynamically stable of the three-ringed parent PAH, which was also present at relatively high amounts in all London soils. Overall, the soils were dominated by 4–6 ring PAH which generally signifies PAH from mainly fossil fuel combustion (McCready et al., 2000; Vane et al., 2007a). This notion was corroborated by high concentrations of other pyrolytic PAHs namely, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene (Fig. 3). However,
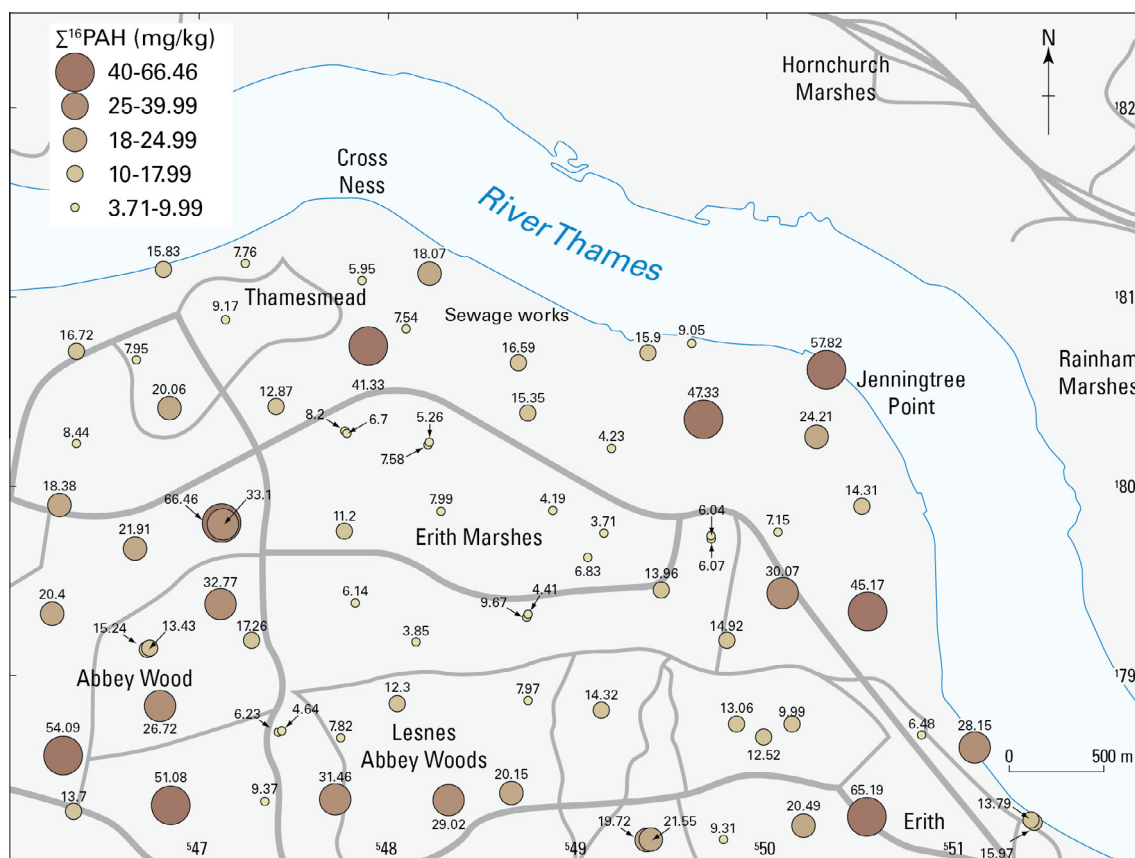

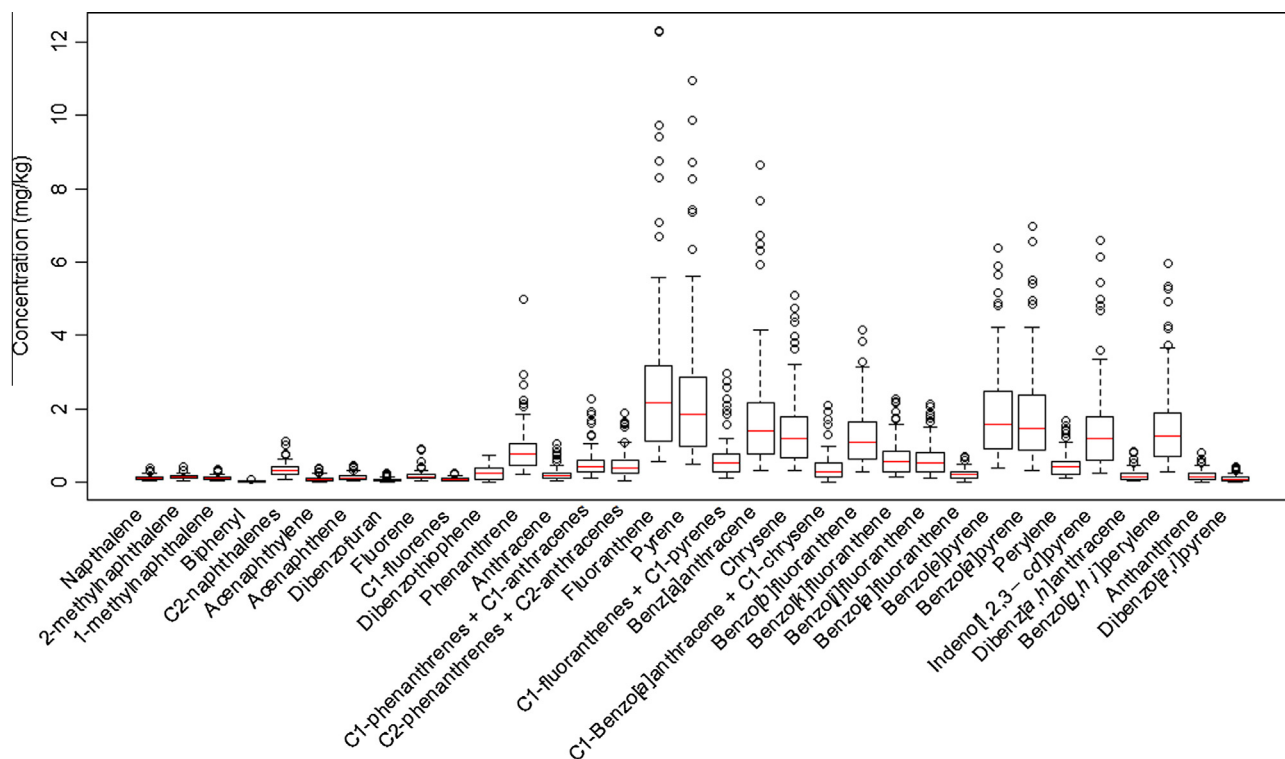**Fig. 2.** Map of $\sum^{16}$ PAH concentrations across the survey area.

Fig. 3. PAH concentrations for all samples displaying outliers (circle markers), highest and lowest non-outliers (upper and lower whisker limits), upper and lower quartiles (upper and lower box limits) and median values (horizontal red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

it should be borne in mind that weathering processes such as leaching (solubilisation), evaporation/volatilisation and biodegradation can modify PAH distribution (Wilcke, 2000). For example, it has been shown that parent PAH and low molecular weight PAH are more susceptible to microbial degradation than alkylated PAH and high molecular weight compounds (Douglas et al., 1996). On balance, the distribution of parent PAH suggests an environmentally modified pyrolytic source.

Alkylated PAH compounds e.g. 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN) are important constituents of diesel fuels and are also found in wood smoke, burnt peatlands and unburnt coal in minor amounts (Conde et al., 2005; Yang and Lu, 2005; Achten and Hofmann, 2009; Vane et al., 2013). The low concentrations of 1-MN and 2-MN relative to other PAH suggests that non-combusted petroleum sources (e.g. fugitive diesel spills) are an unlikely source. The ratio of parent to alkylated PAH has been widely utilised as a simple yet diagnostic tool in environmental source apportionment studies (Ou et al., 2004; White et al., 2005; Stout and Emsbo-Mattingly, 2008). These have shown that petrogenic sources produce greater amounts of alkylated PAH relative to parent PAH, whereas pyrogenic sources yield parent PAH in greater abundance than their alkylated counterparts. Accordingly, crude oil and coal show parent/alkyl PAH values of approximately 0.2 whereas those from coal tar and creosote are about 3. The ratios of the C1-benzo[a]antracene + C1-chrysene/ benzo[a]antracene + chrysene showed a mean of 0.11 which is commensurate with pyrogenic sources.

A complementary approach to characterising PAH source (petrogenic vs. pyrolitic) in soil and sediments is to use PAH isomeric ratios: phenanthrene/anthracene (Phen/Anth) compared with fluroanthene/pyrene (Fanth/Pyr) (Budzinski et al., 1997), benzo[a]anthracene/(benzo[a]anthracene + chrysene) (BaA/(BaA + Chrys)) compared with fluoranthene/(fluoranthene + pyrene) (Fl/(Fl + Pyr)) (Yunker et al., 2002) (Figs. 4 and 5). Isomer ratios,

are to a certain extent, able to distinguish PAH from petrogenic as compared to incomplete combustion/pyrolitic sources because phenanthrene and fluoranthene are more thermodynamically stable than anthracene and pyrene isomeric counterparts (Vane et al., 2013). Consequently, PAH formed at low temperature (e.g. slow thermal maturation of organic matter in petroleum) produce Phen/Anth ratios of >10 and Fanth/Pyr of <1 whereas PAH formed at higher temperatures (e.g. partial combustion of fossil fuels) provide Phen/Anth ratios of <10 and Fanth/Pyr of > 1. Inspection of the
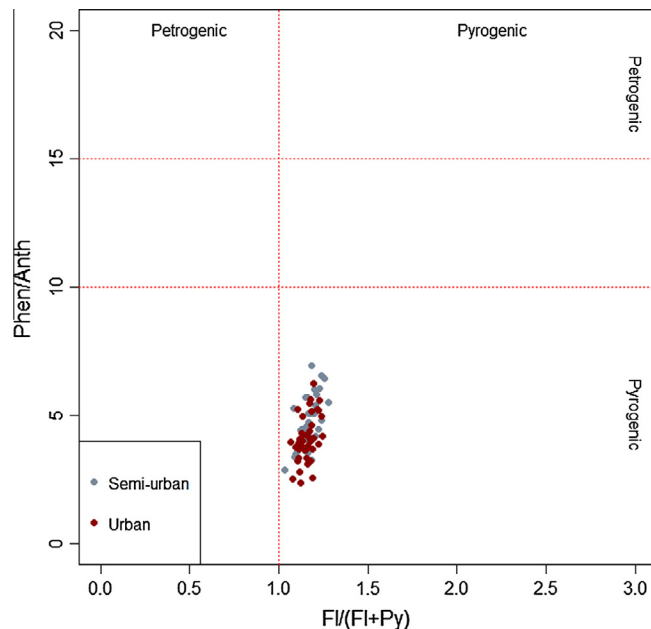

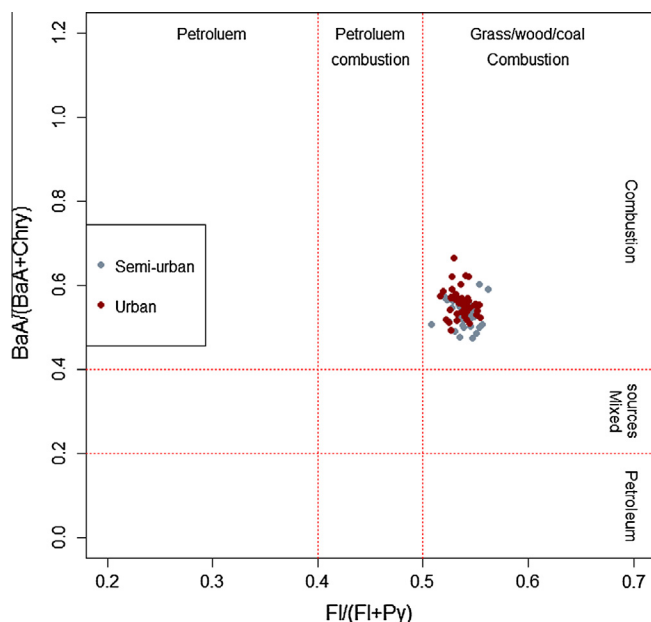**Fig. 4.** Isomeric ratio plot of Phen/Anth and Fanth/Pyr.

Fig. 5. Bi-plot of BaA/BaA + Chrys and Fanth/Fanth + Pyr for London soils.

Phen/Anth to Fanth/Pyr isomeric plot shows that all of the soils plot within the pyrolytic quadrant, supporting the assertion that the PAH were mainly derived from organic matter that has been subject to high temperature processes (Fig. 4). The second plot using BaA/BaA + Chrys and Fanth/Fanth + Pyr also suggests that PAH are from pyrogenic sources such as petroleum, grass, wood and coal combustion (Fig. 5). Atmospheric PAH ratios measured in London between 1991 and 2008 show BaA/BaA + Chrys to be much lower and Fanth/Fanth + Pyr to be consistent with our findings (Katsoyiannis et al., 2011). These results suggest that soil PAH is a mixed source comprising atmospheric pyrogenic PAH as well as additional direct pyrogenic inputs from other sources.

Traffic exhaust can be a major source of pyrolytic PAH producing a relatively high concentration of benzo[g,h,i]perylene (BghiP) compared to benzo[a]pyrene. Accordingly, it has been reported that traffic sources can be inferred when the ratio of BghiP to BaP exceeds 3.14 (Creaser et al., 2007b). It has recently been shown that estuarine sediments deposited in close proximity to major carriageways can yielded BghiP/BaP values of >9, demonstrating that traffic sourced PAH are conserved in the sedimentary record (Creaser et al., 2007c; Vane et al., 2011). For the current study none of the soils gave values greater than 3.14, and the range of values found (0.6–1.1, with a mean of 0.8) were rather invariant – perhaps supporting a more recent study that questions the validity of these ratios (Katsoyiannis et al., 2011). Overall, the ratios suggest mixed pyrolytic sources that cannot be solely ascribed to traffic sources. Other potential sources include combustion in power stations, combustion by industry or possibly domestic and or natural fires (Wilcke, 2000, 2007). An explanation for the dominance of high molecular weight combustion derived PAH could be that they originated from the now decommissioned Belvedere oil burning power station which operated from 1962 to mid-1980s near Jenningtree Point (Fig. 2). However, inspection of total PAH concentrations for the study area revealed no obvious evidence of a PAH pollution plume gradient as would be expected from a single dominant point source (Fig. 2).

As has been shown, isomeric ratio plots can be useful in providing possible explanations of the processes that result in the formation of PAH present in the study samples. However, the method alone is not definitive and has even been reported to be a source of uncertainty (Katsoyiannis et al., 2011, 2007). Alternative exploratory data analysis methods may be used as additional lines-of-evidence, e.g. Principal Components Analysis (PCA) (Hu et al., 2013; Carlon et al., 2001; Dahle et al., 2003; Stout et al., 2001; Wang and Fingas, 2003; Thavamani et al., 2012) and regression analysis (Schauer et al., 1996, 2007). Moreover, analytical methods such as compound specific isotope analysis are reported to be reliable determinants of the source of PAH (McRae et al., 2000; Snape et al., 2001; Górka et al., 2014).

The relationship between TOC and $\sum^{16}$ PAH was examined using Pearson's correlation coefficient. Results show a weak

Table 1
The upper confidence limit of 95th percentile (NBC) for 16 parent PAH, $\sum^{16}$ PAH and $\sum^{50}$ PAH for each domain compared with residential, allotment and commercial land-use scenarios 6% SOM LQM/CIEH GAC.

Parent PAH (US EPA 16)	Calculated NBC (mg/kg)			Published LQM/CIEH GAC for 16 parent PAH (Nathanail et al., 2009) (mg/kg)		
	Urban (n = 42)	Semi-urban (n = 34)	Urban + semi-urban (n = 76)	Residential land-use	Allotment land-use	Commercial land-use
Naphthalene	**0.34**[b]	**0.23**[b]	**0.29**[b]	8.7	23	1100 (432)[sol]
Acenaphthylene	**0.41**[b]	**0.19**[b]	**0.32**[b]	850	160	100,000
Acenaphthene	**0.44**[b]	**0.28**[b]	**0.38**[b]	1000	200	100,000
Fluorene	**0.66**[b]	**0.88**[c]	**0.54**[b]	780	160	71,000
Phenanthrene	**2.9**[b]	**1.8**[b]	**2.80**[b]	380	90	23,000
Anthracene	**1**[b]	**0.6**[b]	**0.81**[b]	9200	2200	540,000
Fluoranthene	**12**[b]	**5.3**[b]	**9.70**[b]	780	290	23,000
Pyrene	**11**[b]	**5**[b]	**8.4**[b]	1600	620	54,000
Benz[a]anthracene	**8.7**[b]	**4.6**[b]	**7.0**[b]	5.9	10	97
Chrysene	**5.6**[b]	**3.7**[b]	**4.7**[b]	9.3	12	140
Benzo[b]fluoranthene	**4.4**[b]	**3.1**[b]	**3.8**[b]	7	13	100
Benzo[k]fluoranthene	**2.5**[b]	**2.1**[c]	**2.1**[b]	10	23	140
Benzo[a]pyrene	**6.9**[b]	**4.4**[b]	**6.0**[b]	1[a]	2.1[a]	14
Indeno[1,2,3-cd]pyrene	**6.8**[b]	**3.7**[b]	**5.2**[b]	4.2[a]	7.1	62
Dibenz[a,h]anthracene	**0.91**[b]	**0.48**[b]	**0.73**[b]	0.9	2.3	13
Benzo[g,h,i]perylene	**6.2**	**3.6**[b]	**5.2**[b]	47	160	660
$\sum^{16}$ PAH	**68**	**41**[b]	**56**[b]	na	na	na
$\sum^{50}$ PAH	**91**	**45**[b]	**75**[b]	na	na	na

Notes: na GAC not applicable.
 [a] GAC exceeded by one or more NBC.
 [b] NBC calculated using log-transformed data.
 [c] NBC calculated using box-cox transformed data.

positive relationship (0.02) whereas in sediments correlations are typically stronger (Vane et al., 2009). Weak correlations between TOC and PAH are common in soils (Bucheli et al., 2004; Heywood et al., 2006; Ribes et al., 2003), though on occasions some statistically significant relationships have been encountered (Cousins et al., 1997). Weak correlations have been ascribed to the operation of a non-equilibrium situation (Bucheli et al., 2004). When PAH from combustion processes are released to the atmosphere they do so in association with soot particles. Once in the air the more volatile, low molecular weight PAH i.e. the 2-ringed PAHs (naphthalene, 2-methylnaphthalene) and the 3-ringed PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene), partition from the soot particles more rapidly into the vapour phase than do the less volatile high molecular weight PAH i.e. the 4-ringed PAH (fluoranthene, pyrene, benz[a]anthracene, chrysene), the 5-ringed PAH (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene) and the 6-ringed PAH (benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene), which tend to remain sorbed to the particulate phase (Bucheli et al., 2004). Upon deposition to the soil, the low molecular weight PAHs, being in the vapour phase, are free to partition into, and equilibrate more readily with, the soil TOC than the more strongly particle bound high molecular weight PAH. Accordingly, for the London soils, where high molecular weight PAH predominate, a lack of correlation of TOC with total PAH concentration may be anticipated. This finding is indicative of a diffuse source of pollution, further substantiating the likelihood that the concentrations recorded are typical of background concentrations rather than a dominant single source.

3.1.4. Comparison of normal background concentrations with generic assessment criteria

$\sum^{16}$ PAH concentrations are generally lower for the semi-urban domain than the urban domain (Fig. 2). $\sum^{16}$ PAH data were applied to Levenne's and Barlett's test for homogeneity of variance. The null hypothesis of was accepted for Bartlett's test ($p > 0.05$), suggesting the data are of equal variance. Results of a Student's t-test showed that the null hypothesis should be rejected ($p \leqslant 0.01$), suggesting there is a significant difference between the mean $\sum^{16}$ PAH concentrations for the urban and semi-urban domains. NBCs were calculated for 16 parent PAH, $\sum^{16}$ PAH and $\sum^{50}$ PAH for urban, semi-urban and urban + semi-urban domains (Table 1). The 16 parent PAH selected are those defined by the United States Environmental Protection Agency (USEPA) as "Consent Decree" priority pollutants (USEPA, 1987). NBCs for the urban domain are higher than the semi-urban domain. NBCs for the urban + semi-domain (all data) account for these differences by representing an approximate average of the two domains. The urban + semi-urban NBCs are proposed as suitably representative of the whole study area given the mostly urban setting of this part of London.

NBCs for 16 parent PAH were compared with published residential, allotment and commercial land-use LQM/CIEH GACs (6% SOM) (Nathanail et al., 2009) (Table 1). The 6% SOM GACs were chosen on the basis of the TOC data. TOC was recorded between 3% and 21% with a mean of 7%. Using a SOM conversion factor of 1.74 (Pribyl, 2010), calculated conservative values ranging from 5% to 37% with a mean of 12%. The benzo[a]pyrene NBC for all domains exceeds the LQM/CIEH GAC for residential and allotment land-uses (Table 1). The Indeno[1,2,3-cd]pyrene NBC for the urban domain exceeds the residential LQM/CIEH GAC (Table 1). Fig. 6 shows the relationship between the benzo[a]pyrene NBC and LQM/CIEH GAC for each domain. These results suggest that if data were to be reviewed in the context of the regulatory requirements of the NPPF for proposed residential development, further investigation would probably be needed to show that sites are safe and suitable
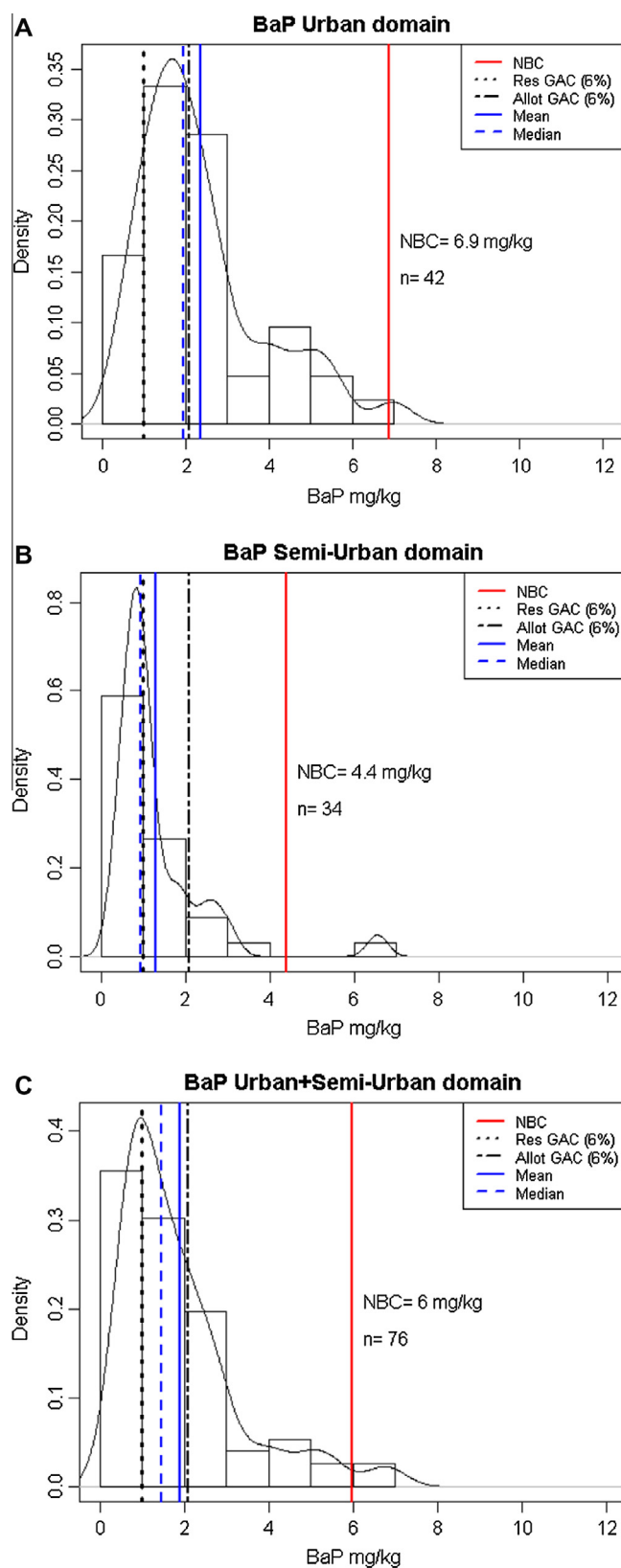

Fig. 6. Summary of consolidated for benzo[a]pyrene annotated with the calculated NBC and published GAC for the urban, semi-urban and urban + semi-urban domains.

for use. Similarly, if sites within the study area were to be examined by the local authority in the context of Part 2a of the EPA then further investigation may also be necessary.
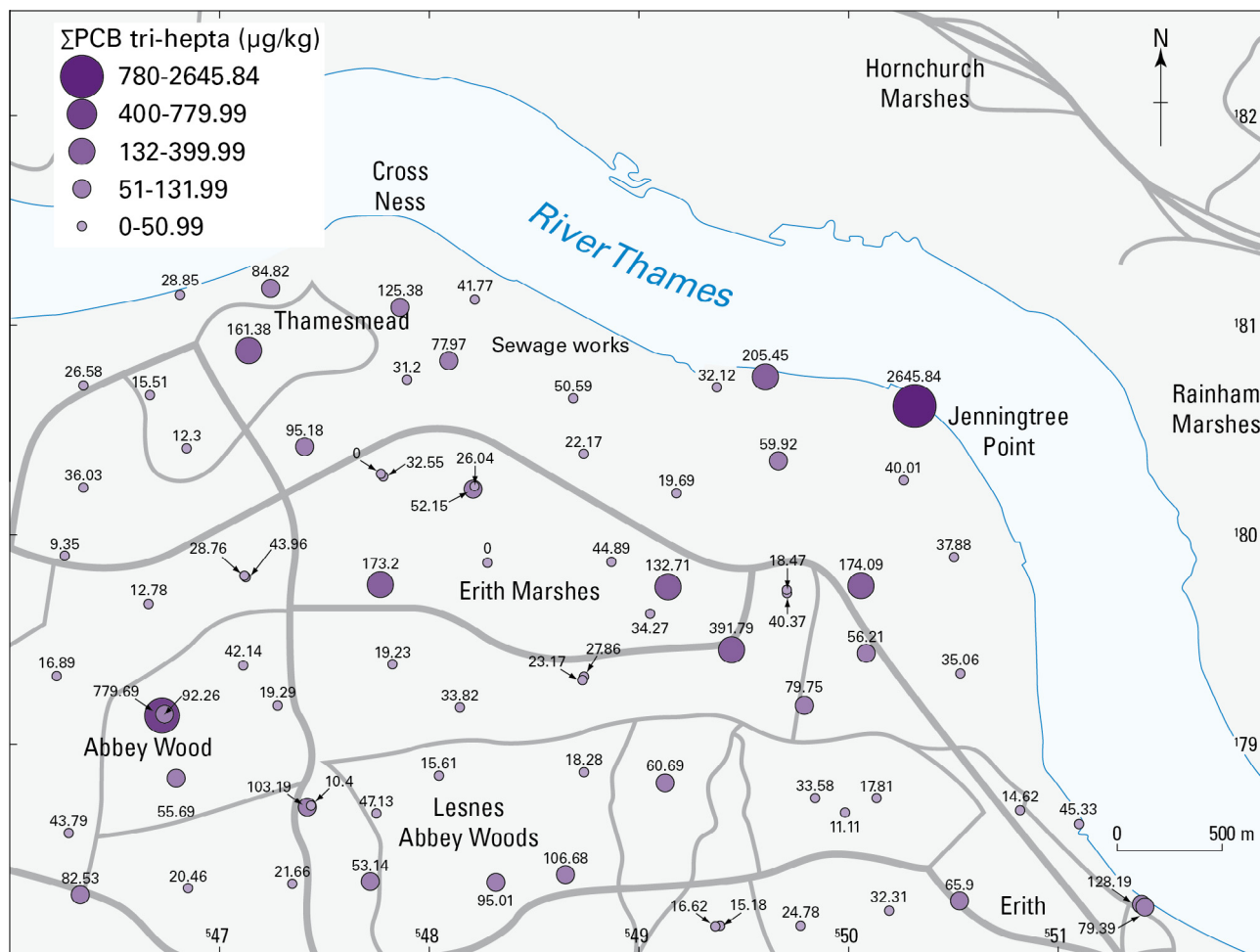
Fig. 7. Map showing spatial distribution of Total PCB across the survey area where larger circles indicate higher concentrations.

3.2. Polychlorinated biphenyl concentrations

3.2.1. Data summary

PCB analyses comprised 7 congeners (PCB 28, PCB 52, PCB 101, PBB 118, PCB 138, PCB 153, PCB 180), 5 homologous series (tri, tetra, penta, hexa, hepta) and $\sum^{\text{tri-hepta}}$ PCB. Quality control procedure resulted in removing 2 samples from the dataset, leaving 74 samples for evaluation. The individual congeners selected are the ICES-7 defined during the International Conference of the Environment of the Sea based on their prominence and persistence (Environment Agency, 2003). The spatial distribution of $\sum^{\text{tri-hepta}}$ PCB across the study area is summarised in a diagram (Fig. 7). $\sum^{\text{tri-hepta}}$ PCB concentrations ranged from 9 to 2642 μg/kg with a mean of 123 μg/kg. The highest recorded concentrations (>500 μg/kg) were at industrial/commercial sites at Erith Reach (Sample ref: 516; 2642 μg/kg), Abbey Wood (Sample ref: 892; 780 μg/kg), Erith Marshes (Sample ref: 750; 764 μg/kg), Thamesmead (Sample ref: 676; 542 μg/kg) and Erith Marshes (Sample ref: 541; 567 μg/kg). The relative contributions made by the ICES-7 congeners and the homologous series for all samples are presented as boxplots (Fig. 8 and Fig. 9). Descriptive statistics for all PCB data are presented in the Supporting Information (SI: Table 2).

3.2.2. Comparison of data with other urban areas

Comparing recorded PCB concentrations with other studies is generally complicated by differences between the selected congeners and associated statistics. However, ICES-7 PCB data for urban and suburban soils in the UK, Russia and France show that median values are higher than another UK study (1.77 μg/kg) (2007a) (Table 2). Mean values for $\sum$7 ICES-7 PCB for this study (21.4 μg/kg) are comparable with suburban data for France (21.5 μg/kg) (Motelay-Massei et al., 2004) but slightly higher than data recorded in Moscow (9.9 μg/kg) (Wilcke et al., 2006) (Table 2). A review of 12 studies were not comparable because of differences between congeners analysed (Table 3). As expected, the concentrations recorded in this study are considerably lower than point source releases associated with the manufacture and industrial uses of PCB. For example, a former telecommunications manufacturing site in south west England showed mean concentrations of 120,000 μg/kg for $\sum$7 PCB (Norris et al., 1999) and a PCB manufacturing facility in Sauget, US showed concentrations ranging from 150 to 27,000 μg/kg total PCB (congener types not identified) distributed within a 1500 m radius of the site (Stratton, 1976).

3.2.3. PCB congener distribution

A summary of both individual congeners and homologous series concentrations shows that London soil samples are enriched in penta-, hexa-, and hepta- chlorobiphenyls (CB) (87% in mass) (Figs. 8 and 9). This finding agrees with previous reports of 85% (which included mono-, di-, and octa-CB) in urban soils from Cedar Rapids, USA (Martinez et al., 2012). Similar profiles have also been identified in Glasgow, Scotland in urban soils where a higher proportion of penta-CB was also observed (Cachada et al., 2009). However,
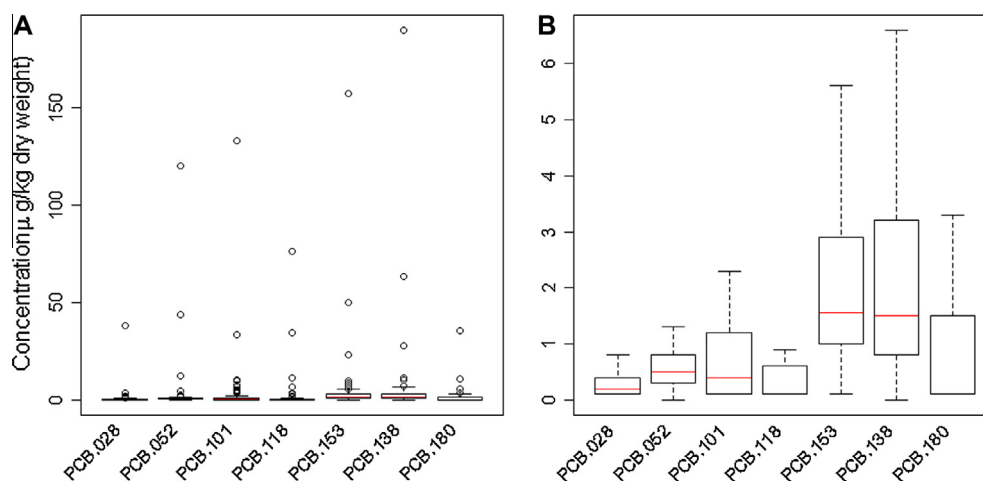
Fig. 8. PCB congener concentrations for all samples with outliers (circle markers) (A), without outliers (B), highest and lowest non-outliers (upper and lower whisker limits), upper and lower quartiles (upper and lower box limits) and median values (horizontal red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

significant contribution of tri-CB reported in the Tianjin region of China was attributed to the recent localised production of this congener group (Li et al., 2010). Losses of tri- and tetra-CB congeners (via volatilisation) and the relative dominance of the heavier chlorinated biphenyls over time (25 years) have also been reported (Lead et al., 1997). Temporal change is the likely explanation of

the congener pattern in our study where tri-CB constitutes a minor component (Fig. 9). This is probably because a large proportion of these congeners are lost via volatilisation whilst in-situ (Harrad et al., 1994; Johnson et al., 2006). Similarly, the depletion of lighter PCB may be associated with urban soils in comparison with rural sites, as observed in France (Motelay-Massei et al., 2004). Using a
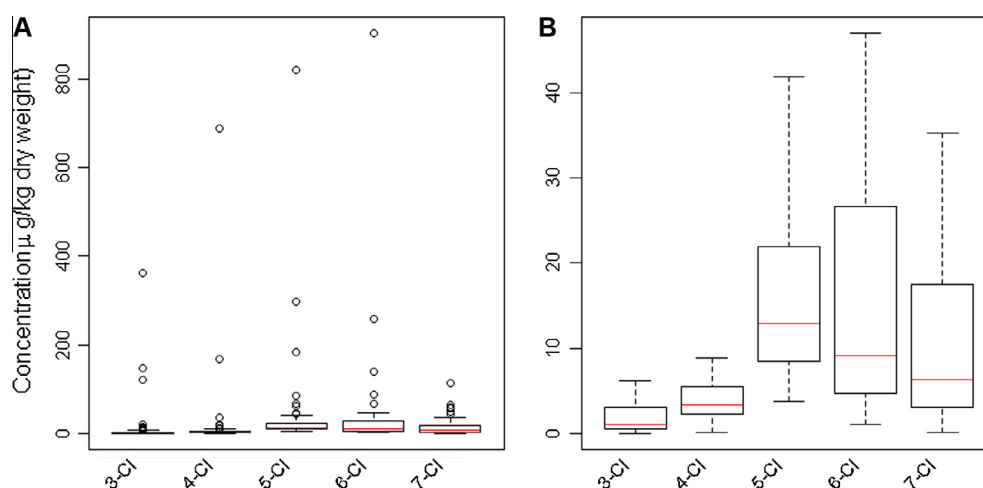

Fig. 9. PCB homologous series concentrations for all samples with outliers (circle markers) (A), without outliers (B), highest and lowest non-outliers (upper and lower whisker limits), upper and lower quartiles (upper and lower box limits) and median values (horizontal red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Summary of PCB data in urban and suburban soils in the UK, Russia and France.

Author	Location	Parameter	n	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	$\sum$PCB $_7$
This study	London, urban	Mean	76	0.8 (±4.4)[*]	3.0 (±14.6)	3.3 (±15.7)	2.1 (±9.6)	5.1 (±18.8)	5.9 (±22.8)	1.4 (±4.4)	21.4 (±89.3)
		Median		0.2	0.5	0.4	<0.2	1.6	1.6	0.1	4.9
		Range		0.2–38	0.2–120	0.2–133	0.2–76	0.2–157	0.2–190	0.1–36	0.6–751
		% of $\sum$PCB		2%	7%	8%	5%	13%	15%	3%	53%
Creaser et al. (2007a)	England, urban	Median		–	–	–	–	–	–	–	1.77
Wilcke et al. (2006)	Moscow, urban	Mean; median	11	0.6;	1.8;	3.7;	5.4;	4.3;	6.1;	0.9;	13.9; 9.9
Motelay-Massei et al. (2004)	France, suburban	Mean	5	–	3.58	1.92	3.34	5.15	1.48	6.05	21.5

[*] Value in parentheses is the standard deviation of mean $\sum$PCB within each study.

Table 3
Summary of summed PCB congener data in urban and suburban soils in UK, European cities, Spain, France, Germany, Romania, United States and Russia.

Author	Location	Land-use	n	Number of PCB congeners quantified	∑PCB (µg/kg)		
					Mean[a]	Median	Range
This study	London	Urban	76	∑PCB	103 (±313)	40.2	9.3–2646
Alcock et al. (1993)	NW England, UK	Urban and rural	39	45	–	30	14–670
Cachada et al. (2009)	Glasgow, UK	Urban[1]	20	19	–	22	4.5–78
Creaser et al. (2007a)	England, UK	Urban	42	26	4.41 (±6.07)	2.52	0.76–39
Creaser et al. (2007b)	UK	Urban	87	26	3.04 (±1.68)	1.86	0.98–39
Cachada et al. (2009)	5 European cities	Urban[1]	100	19	–	7.9	0.62–73
García et al. (2003)	Madrid	Urban–suburban	12	20	–	32	9.0–66
Motelay-Massei et al. (2004)	Harfleur, France	Suburban	5	22	40.1	–	–
Krauss and Wilcke (2003)	Bayreuth, Germany	Urban	49	12	–	13.0	0.82–158
Covaci et al. (2001)	Romania	Urban	13	19	57.3 (±41.0)	–	–
Martinez et al. (2012)	Cedar Rapids, USA	Urban	64	164	56.0 (±160)	20.0	3.0–1200
Wilcke et al. (2006)	Moscow	Urban and peri-urban	11	17	13.9	9.9	3.1–42

[a] All values in parentheses are standard deviations of the mean ∑PCB within each study; Urban[1]–urban public spaces, away from known contamination.

ratio of PCB 28 to total PCB as a simple indicator confirms that the average PCB 28 contribution in rural soils is 7%, while in urban soils it is 2.5%, the current study agrees where PCB 28 = 2% (Creaser et al., 2007a) (Table 2). The congener distribution of both lighter and heavier molecules is therefore reasonably consistent with finding made in previous studies.

3.2.4. Comparison of normal background concentrations with soil guideline values

The $\sum^{tri-penta}$ PCB concentrations in 4 samples are greater by at least an order of magnitude than other samples (Samples 26: 2640 µg/kg, 31: 570 µg/kg, 39: 400 µg/kg and 74: 780 µg/kg) (Fig. 8). The land-use ascribed to each sample is either industrial or commercial which together with the concentrations suggests point source releases. Prior to calculating PCB NBCs, these 4 samples were filtered out of the dataset to reduce bias. It is suggested that point sources are commonly due to leakages from sealed and open systems, disposal and accidental spills and leaks (Breivik et al., 2002). Such sources are likely to be the main contributor to atmospheric PCB and therefore an important contributor to diffuse pollution sources (Creaser et al., 2007a).

Concentrations of $\sum^{tri-penta}$ PCB are similar between the urban domain and semi-urban domain (Fig. 7). Data were applied to Levenne's and Bartlett's test for homogeneity of variance ($p \geqslant 0.05$). The null hypothesis was accepted for Levene's test, suggesting the data are of equal variance. The data were then applied to the Student's t-test. Results suggest there is no difference between

Table 4
Calculated upper confidence limit of 95th percentile (NBC) for individual ICES-7 PCB and summed tetra, penta, hexa and hepta PCB homologues for each domain.

PCB congener/summed set of congeners	Filtered urban + semi-urban domain NBC (µg/kg) (n = 70)
PCB 28	1.8
PCB 52	2.9
PCB 101	7.8
PCB 118[a]	4.4
PCB 138	10.5
PCB 153	9
PCB 180	4.7
$\sum^7$	180
$\sum^{3-Cl}$	22
$\sum^{4-Cl}$	20
$\sum^{5-Cl}$	48
$\sum^{6-Cl}$	66
$\sum^{7-Cl}$	73
$\sum^{tri-hepta}$	170

na Not applicable because SGV or GAC do not exist for congener or homologous series.
[a] Dioxin-like mono-ortho PCB.

the mean concentrations of $\sum^{tri-penta}$ PCB for the two domains ($p \geqslant 0.01$). Only PCB concentrations for the urban + semi-urban domain ($n = 71$) were used to calculate NBCs for individual congeners and homologous series (Table 4).

A comparison of the calculated NBCs with the SGV for dioxins, furans and dioxin-like PCBs in soil is limited to PCB 118 only. This is because the SGV is designed to be compared with the sum of dioxins, furans and dioxin-like PCBs in soil. For this study, PCB 118 was the only dioxin-like PCB analysed (PCB 118). The calculated NBC of 4.4 µg/kg for the filtered urban + semi-urban domain does not exceed the residential and allotment SGV (8 µg/kg) or the commercial SGV (240 µg/kg) (Environment Agency, 2009b). The PCB data alone would probably not immediately call for regulatory measures. However, there are many persistent compounds covered by the SGV for dioxins, furans and dioxin-like PCBs that were not quantified as part of this study.

4. Conclusions

This study reports the concentrations of PAH and PCB in soil samples taken from a 19 km² area in the east of London, UK. Key quantitative findings include: (1) $\sum^{16}$ PAH ranged from 4 to 67 mg/kg with a mean of 18 mg/kg; (2) $\sum^{50}$ PAH ranged from 6 to 88 mg/kg with a mean of 25 mg/kg; (3) $\sum^7$ PCB ranged from 1 to 750 µg/kg with a mean of 22 µg/kg; (4) $\sum^{tri-hepta}$ PCB concentrations ranged 9–2600 µg/kg with a mean of 120 µg/kg. PAH concentrations were comparable with other cities, whereas PCB concentrations were higher. Isomeric PAH ratios suggest multiple pyrogenic sources, inferred to be representative of diffuse pollution. PCB congener profiles were generally dominated by ⩾penta-CB congeners. Selected NBCs were compared to human health GACs. The benzo[a]pyrene NBC for the urban (6.9 mg/kg), semi-urban (4.4 mg/kg) and urban + semi urban (6 mg/kg) domains exceeded the residential (1 mg/kg) and allotment (2.2 mg/kg) LQM/CIEH GAC (at 6% SOM) and that the Indeno[1,2,3-cd]pyrene NBC for urban (6.8 mg/kg) and urban + semi-urban (5.2 mg/kg) domains exceeded the residential (4.2 mg/kg) LQM/CIEH GAC (at 6% SOM). The NBC for benzo[a]pyrene and Indeno[1,2,3-cd]pyrene suggest that further investigation would be required for future risk-based land management under Part 2a of the EPA for residential or allotment land-use within the study area. Although not directly relevant, NBC exceedances of the GAC suggest these substances should be considered where a change in land-use is being considered. The PCB 118 NBC (a dioxin-like PCB) did not exceed the SGV, however, further monitoring of dioxins, furans and other dioxin-like PCB within the study area would be prudent to inform ongoing risk-based land management decision-making.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014.09.013.

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