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Variation in soil chemistry related to different classes and eras of urbanisation in the London area

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ABSTRACT

Systematic mapping of the chemical environment of urban areas from around the world has demonstrated the strong impact of urbanisation on topsoil geochemical distributions originally controlled by the underlying parent material (PM). The variance of some elements including As, Ba, Ca, Cr, Cu, Mo, P, Pb, Sb, Se, Sn and Zn in urban domains appears to be impacted by a mixture of geogenic and anthropogenic controls. This study evaluates how soil chemistry has been influenced by different eras of urbanisation within London and other UK urban areas using (a) the pre-1940 Dudley Stamp First Land Utilisation Survey data and (b) the modern urban domain principally defined by the aggregate classes of the 2007 Land Cover Map. In the London area, calcium, and possibly a substantial proportion of Cu, Pb, Sn and Zn enrichment observed in soils impacted by pre-1940 urbanisation relative to soils impacted only by post-1940 urbanisation, may be partly related to the destruction of buildings during the period 1940–1941 rather than from the disposal or aerial dispersion of coal ash from domestic fires. Some Pb, Cu, Sb, Sb, Sn and Zn contamination appears to be caused by road traffic (leaded petrol and brake dust). The relationships between pre- and post-1940 urbanised areas in London also characterise most of 20 other urban centres in England and Wales for which BGS holds soil chemistry data.

1. Introduction

Whilst parent material (PM) is the primary geogenic control for some chemical elements in urban areas (Appleton and Adlam, 2012; Appleton et al., 2013), the variance of many elements including As, Ba, Ca, Cr, Cu, Mo, P, Pb, Sb, Se, Sn and Zn in urban domains appears to be impacted by a mixture of geogenic and anthropogenic controls which have developed over different eras of urbanisation. Sources of anthropogenic contamination in urban areas include industrial manufacturing and processing, power and waste incineration plants, domestic coal burning including the historic disposal of ash, emissions from vehicles (especially from the use of leaded petrol), fertilizer use, dispersion of Pb and other metals together with cement, concrete and bricks from demolition and construction including the use of building and demolition waste material for land reclamation and the creation of artificial ground (Albanese and Breward, 2011). The highest levels of contamination are to be expected in areas with the longest history of urbanisation.

Preliminary assessments of the topsoil chemistry of the predominantly urban Greater London Authority (GLA) area are available in BGS (2011), Knights and Scheib (2011), Scheib et al. (2011), Ferreira et al. (2017). Lark and Scheib (2013) used model-based analysis, cokriging and Wald statistics to examine how land use recorded at soil sample sites within the Great London Authority (GLA) area accounts for variations in soil Pb concentrations. McIlwaine et al. (2017) reporting on the relationship between potentially toxic element (PTE) concentrations and historical urban development in the soils of Belfast and Sheffield concluded that different PTEs are associated with different periods of development and that soil pollution can be linked to diffuse contamination from road traffic, domestic fuel combustion and industrial processes.

The study reported here focusses on processes causing widespread dispersion of contaminants rather than local sources such as industrial manufacturing or waste incineration plants. In particular, we assess whether the different eras of urbanisation in the UK have resulted in significantly different concentrations of elements in surface soils once the confounding influence of parent material (geology) has been eliminated.

2. Materials and methods

2.1. Geology and soil chemistry data

The Greater London Authority (GLA) urban area is underlain by Cretaceous and Palaeogene sedimentary rocks covered in some areas by

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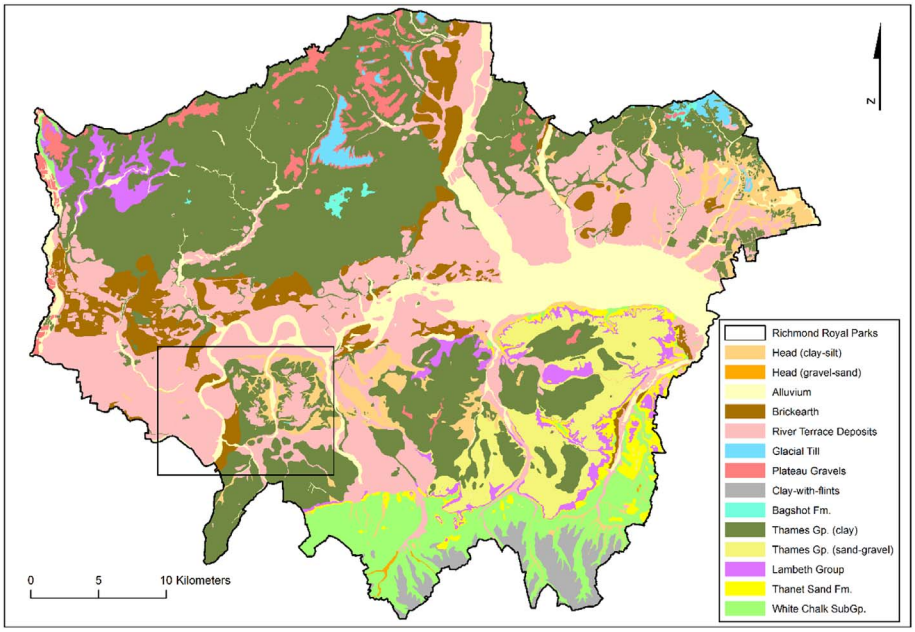

Fig. 1. Simplified soil parent material map of London (box in SW corner indicates extent of Fig. 4).

Quaternary superficial deposits of which the most extensive are alluvium, river terrace deposits and brickearth (Fig. 1; see Appleton et al., 2013; for greater detail). In some sectors of the GLA, topsoil chemistry will reflect a complex Anthropocene history rather than soil parent material (geology). For example, the Victoria Embankment Gardens, located between the Ministry of Defence on Whitehall and the River Thames, are part of a reclamation scheme started in 1864 and completed in 1875 for which the subsoil was derived from the construction of the Metropolitan District Railway and the topsoil from Barking Creek.

BGS urban soil chemistry data are available for 6308 sites within the GLA area. Soil samples were collected from open ground on a 500 m grid with a sample being taken as close as possible to the centre of each 500 m grid square giving a density of approximately 4 samples per km^2 (BGS, 2011; Flight and Scheib, 2011). However, the actual distribution of sample sites did not follow the systematic rule exactly in that the soil samples are, for various reasons, located relatively randomly within the 500 grid squares (Supplementary material, Fig. SM-1). At each site, composite samples, based on 5 sub-samples taken at the centre and four corners of a 20 m square were collected from the topsoil (5–20 cm depth). In addition, 80 samples from the BGS G-BASE (Geochemical Baseline Survey of the Environment) regional topsoil survey located within the GLA were included in the study. These samples were collected at a sampling density of 1 sample per 2 km^2 (Johnson et al., 2005). Forty eight chemical elements were determined in the < 2 mm size fraction of the topsoils using X-ray fluorescence spectrometry (XRFS), together with loss on ignition (LOI at 450 °C) and pH in all the urban samples and 50% of the rural samples. Sample preparation, analytical methods, and quality control procedures are described in Allen et al. (2011) and Johnson (2011) and statistical parameters and detection limits are presented in Ferreira et al. (2017).

2.2. Land use

2.2.1. Pre-1940

The pre-1940 urban and rural domains were defined using the land use data created by scanning and digitising original maps from the Dudley Stamp (DS) Land-Utilisation Survey (Stamp, 1931, 1948; Environment Agency, 2007), the survey work for which was completed in 1941 but mainly carried out between 1931 and 1934 (i.e. pre-1940). In this study, topsoil data were grouped into two general classes: (1) Urban (combining DS Urban and Suburban categories) and (2) Non-Urban (combining DS Arable, Forest and Woodland, Heath and Moorland, Meadow and Grass, and Orchard categories). Previous uses of the DS land use data and some of its limitations are described in Baily et al. (2011); Swetnam, 2007; and Taylor et al., 2010.

2.2.2. Post-1940

A simplified Land Cover (LC) classification (Table 1) developed from the aggregated classes of the Land Cover Map 2007 (LCM2007) vector data set (Morton et al., 2011) was used to define areas currently built-up (BU) and not built-up (NBU). LCM 2007 digital data are derived by automated classification of satellite imagery where each 25 m pixel is assigned to a land cover class based upon its spectral characteristics. At 4% of soil sample sites, there is a discrepancy between the BGS general site land use (LU) class (Supplementary material Table SM-1) and the LCM2007 data. At these sites, the spatially more accurate LU class was used to reclassify the attribution from the LCM 2007 data. As would be expected, concentrations of Pb in soils from small areas of Park, Recreational Ground, Urban open space, and Woodland and Forest located within BU areas are substantially higher than for these classes of Land Use located within NBU areas (Table 2).

Attribution of soil samples with the Dudley Stamp and Land Cover information allowed soil chemistry comparisons to be made between the following domains: (1) Areas built-up pre-1940 (grey in Fig. 2); (2) Areas built up since approximately 1940 (red in Fig. 2); and (3) Areas that have never been urbanised (white in Fig. 2). Data for areas built-up pre-1940, post-1940 and areas that have never been urbanised are coded as OLD, NEW and NURB respectively.

Table 1
Land cover (LC) classification derived from LCM2007 Aggregate land cover classification.

Land Cover (LC) class	No. soil samples	LCM2007 Aggregate land cover class
Built-up (BU)	4051	Built-up areas and gardens
Not built-up (NBU)	2337	Arable; Improved grassland; Mountain, heath, and bog; Semi-natural grassland; Broadleaf and Coniferous woodland

Table 2
Pb in soil summary statistics illustrating relationship between Land Cover (LC) class and BGS site general land use (LU) classes.

Land cover (LC) class	BGS general site land use (LU) class (see Supplementary material Table SM-1 for classification)	No. sites in GLA	GM-Pb (mg/kg)
Built-up (BU)	Cemetery/Crematorium	101	246
	Commercial and Residential	207	227
	Domestic Gardens/Allotments	1615	290
	Golf	15	118
	Industrial	123	215
	Park	355	247
	Pasture	4	342
	Recreational	245	218
	Road verge	590	232
	Rough Grazing	29	139
	Urban open space	943	235
	Woodland and Forest	35	182
Not built-up (NBU)	Arable	292	68
	Park	432	154
	Recreational	291	146
	Urban open space	212	164
	Golf	150	97
	Pasture	157	77
	Rough Grazing	346	85
	Woodland and Forest	246	104

2.3. London bomb site data base

The London bomb site data base compiled by the University of Portsmouth contains the locations of 31,373 sites where bombs landed over the eight month period of the Blitz (October 1940–June 1941) within civil defence region 5 (London) which consisted of the 28 Metropolitan Boroughs in the London County Council. The digital database was compiled from scanned and geo-referenced maps of the London World War II bomb census maps from the National Archive. The bomb site data were used in this study to examine the potential impacts of bombing during the Blitz on soil chemistry.

2.4. Statistical analysis

MINITAB® 15 and R® (R Core Team, 2016) were used for statistical analysis. ANOVA and other statistical analyses assume that population distributions are normal for each group, variances are equal for all groups, and also that observations are randomly and independently representative of the populations (Reimann et al., 2008). However, these requirements are rarely met completely by data from soil chemistry surveys, which have traditionally been designed to achieve a regular sample density. The application of a log-transform in general produces more normal distributions with lower skewness coefficients, especially for elements such as Pb where anthropogenic contamination is a major factor. Medians are generally used as an indicator for the central value of a data distribution (Reimann et al., 2008). In some cases, data were log-transformed (Log_e) when the skewness coefficient exceeded 1.0. Medians and geometric means are very similar. For comparative purposes centred logratio (clr) transformation (Reimann et al., 2008, 2012) based on the major elements, Pb and Zn was used to deal with the compositional nature of geochemical data when examining inter-domain variation of Ca, Pb and Zn. For the data subset (n = 3328) used in Fig. 6, R2 between LnCa and clrCa is 87% and 94% between Ln and clr values for Pb and Zn. Flem et al. (2017) recommend clr or ilr (isometric log-ratio) transformations for bivariate, multivariate and compositional data analysis of chemical element concentrations. However, clr transformations were not adopted routinely in this study principally because the direct link to the element concentrations is lost, for example in relation to soil quality criteria and medians form the main basis of this study together with variation of medians with distance from roads and bomb sites. In this study, Tukey's method provides confidence intervals for pairwise differences between means of clr transformed Ca and Pb data. Enrichment ratios (ratios of domain medians) are used to describe the contrast between pre-1940 (OLD), post-1940 (NEW) urbanised and never urbanised (NURB) domains.

3. Results and discussion

3.1. Enrichment ratios

Surface soil samples from currently built-up areas that were also built up pre-1940 (OLD) have Ca, Cu, Ge, P, Pb, Sb, Sn and Zn concentrations that are 1.2–1.75 times higher than in areas that have been built up (urbanised) since 1940 (NEW; Table 3). Ca, Cu, Pb, Sb, Sn and Zn are 2.2–3.2 times higher in areas built-up pre-1940 (OLD) compared with areas that have never been urbanised (NURB) in the GLA, and 2.1 to 5.2 times higher than in areas not built up outside the GLA but within

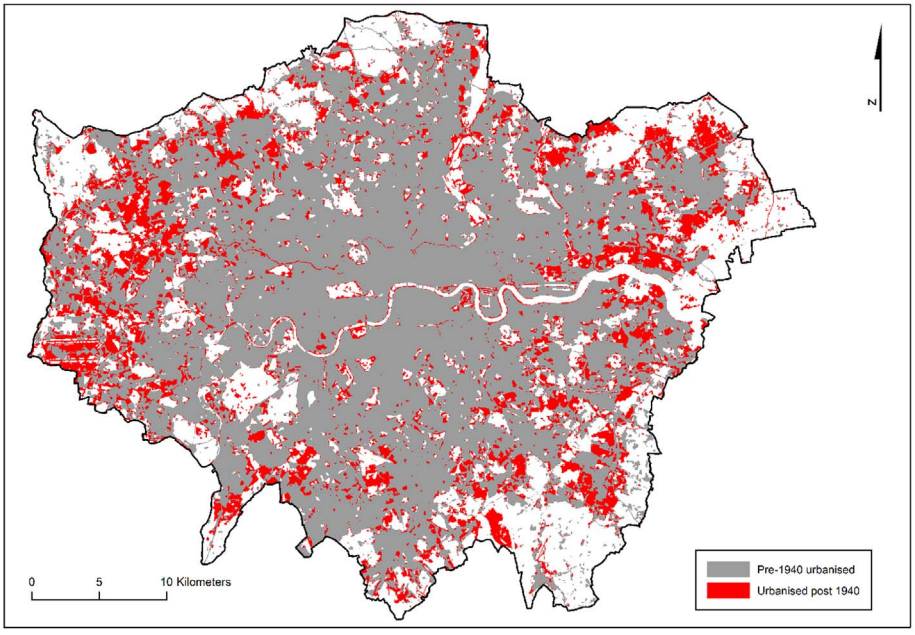

Fig. 2. Areas of London (GLA) urbanised pre- and post-1940 (white areas: never urbanised; based on Dudley Stamp and Land Cover Map 2007 data: © L. Dudley Stamp/Geographical Publications Ltd, Audrey N. Clark, Environment Agency/DEFRA and Great Britain Historical GIS; © NERC (CEH) 2011. © Crown Copyright 2007. Ordnance Survey Licence number 100017572. © third-party licensors).

Table 3
Median topsoil values for post-1940 (NEW) and pre-1940 (OLD) urban domains and the never urbanised (NURB) domain in the GLA compared with Not Built Up domain in Southeast England (SEEN) outside the GLA but within the London Region (Appleton et al., 2013) with corresponding enrichment ratios.

	Domain median concentrations				Enrichment Ratios		
	NEW	OLD	NURB	SEEN	OLD/ NEW	OLD/ NURB	OLD/ SEEN
N	981	3275*	1719**	1469***			
%							
Al	4.28	3.70	4.44	4.39	0.86	0.83	0.84
Ca	0.91	1.21	0.55	0.57	1.32	2.19	2.12
Fe	2.73	2.71	2.61	2.55	0.99	1.04	1.06
K	1.15	1.04	1.20	1.12	0.90	0.86	0.93
Mg	0.48	0.42	0.48	0.48	0.88	0.88	0.88
Mn	0.04	0.04	0.04	0.06	1.02	1.16	0.74
P	0.13	0.16	0.11	0.11	1.23	1.48	1.47
Si	30.31	31.01	30.64	32.69	1.02	1.01	0.95
Ti	0.35	0.31	0.38	0.38	0.91	0.82	0.83
mg/kg							
As	15	17	14	13	1.11	1.20	1.28
Ba	380	398	353	339	1.05	1.13	1.17
Cd	0.6	0.7	0.5	0.5	1.08	1.30	1.30
Ce	51	48	52	56	0.93	0.92	0.85
Co	12	12	11	12	0.97	1.07	0.97
Cr	74	70	77	75	0.95	0.91	0.93
Cu	45	60	27	21	1.33	2.21	2.86
Ga	11	10	11	11	0.93	0.91	0.92
Ge	1.5	1.8	1.2	1.1	1.20	1.50	1.64
La	25	23	26	29	0.92	0.88	0.79
LoI	7.3	7.2	7.5	6.0	0.99	0.97	1.20
Mo	1.5	1.7	1.2	0.9	1.13	1.42	1.89
Ni	26	27	22	21	1.02	1.23	1.28
Pb	158	276	87	53	1.75	3.17	5.21
pH	6.6	6.8	5.6	6.1	1.03	1.21	1.11
Rb	59	52	63	63	0.88	0.82	0.83
Sb	2.8	4.2	1.6	1.1	1.50	2.63	3.82
Se	0.6	0.6	0.6	0.4	1.00	1.00	1.50
Sn	13	20	7	4	1.60	2.70	5.00
Sr	77	82	67	62	1.06	1.22	1.32
Th	6.9	6.3	7.4	7.8	0.91	0.85	0.81
U	2.3	2.1	2.3	2.3	0.94	0.91	0.93
V	80	75	78	71	0.94	0.96	1.06
Y	21	20	21	23	0.95	0.97	0.87
Zn	153	211	87	76	1.38	2.43	2.78
Zr	278	263	309	355	0.95	0.85	0.74
clrCa	−0.009	0.254	−0.442	−0.357			

*n LoI and pH = 3274, **n LoI and pH = 1687, ***n LoI and pH = 1022.

the London Region (defined in Appleton et al., 2013). In all cases, Pb exhibits the highest enrichment ratios followed by Sn and Sb (Table 3).

In order to reduce the impact of element concentration variability related to parent material (Appleton et al., 2013), further comparisons between the two eras of urbanisation are based on data for the parent material units with the highest number of soil samples. These are Thames Group clays, River Terrace Deposits (sands and gravels), Brickearth, Thames Group sands, White Chalk and Alluvium; Supplementary material Table SM-2). For the metallic and metalloid trace elements, all the major parent material domains apart from Alluvium (for reasons discussed below) exhibit very strong enrichment of Pb (53–85%; Fig. 3a) in the pre-1940 urban areas (OLD) with lesser enrichment of Sn (41–59%; Fig. 3b), Ge (13–46%), Sb (26–49%, Zn (27–41%), Cu (5–36%), Cd (up to 14%), Mo (up to 20%) and As (up to 19%) (Supplementary material Table SM-2).

The White Chalk (WCK) has lower pre-1940/post-1940 (OLD/NEW) ratios for the metals-metalloid trace elements, compared with the other parent materials (Supplementary material Table SM-2b), probably because the degree of urbanisation and anthropogenic contamination is less extreme over this PM, which is mainly found at the southern margin of the GLA.

Even higher enrichment ratios are indicated when comparing the

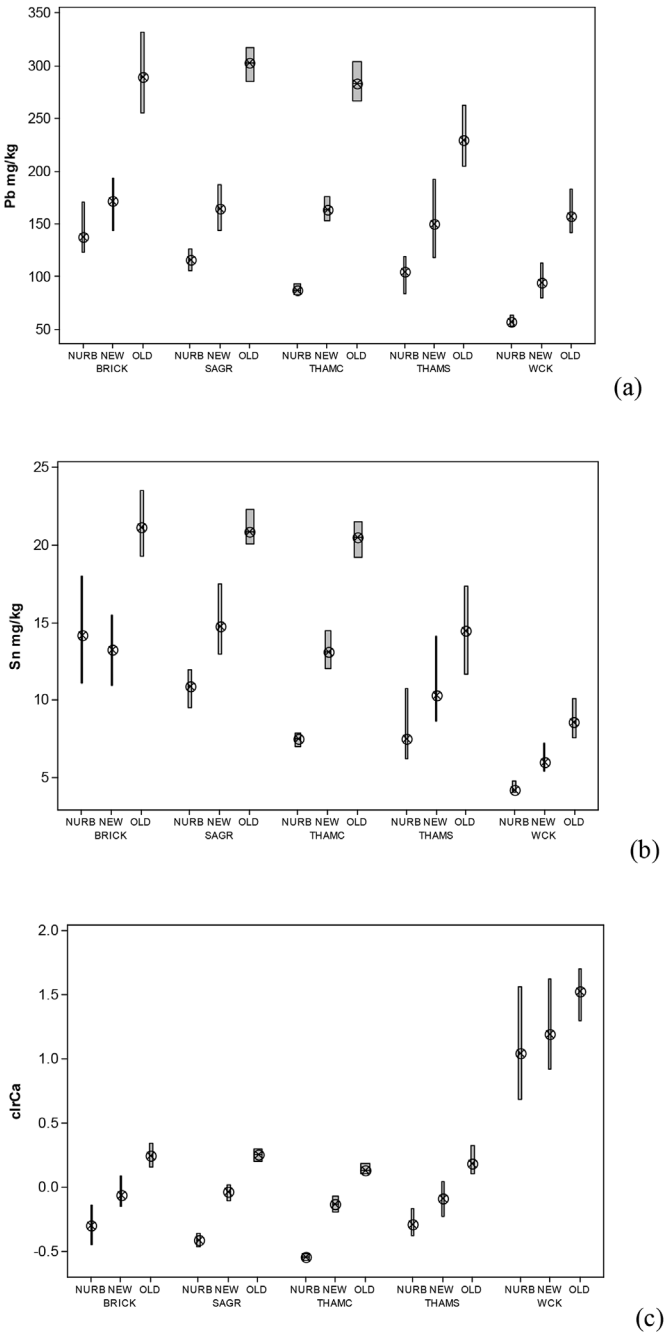

Fig. 3. Boxplots of (a) Pb, (b) Sn and (c) clrCa in soils from five major geological units (BRICK = Brickearth, SAGR = River Terrace Deposits, THAMC = Thames Group clays, THAMS = Thames Group sands, WCK = White Chalk) subdivided into areas never urbanised (NURB) and urbanised pre- (OLD) and post (NEW) 1940 (circle with cross = median, box = median 95% confidence limits, box width proportional to number of samples).

pre-1940 urbanised areas with never urbanised areas (OLD/NURB data in Supplementary material Table SM-2). Pb is 2.6–3.3 times higher in soils underlain by River Terrace Deposits and Thames Group clays with slightly lower enrichment ratios for Sb, Sn and Sn (1.9–2.8).

In areas underlain by Thames Group clays, River Terrace Deposits (sands and gravels), Brickearth, and Thames Group sands, calcium is 36–48% higher in the pre-1940 OLD urban areas compared with those areas that have been built-up since that time (NEW), whilst for the White Chalk (Fig. 1; WCK in Supplementary material Table SM-2b) it is 27% higher. Phosphorus is between 6 and 24% higher in the pre-1940 (OLD) urbanised areas. Higher levels of enrichment are indicated when

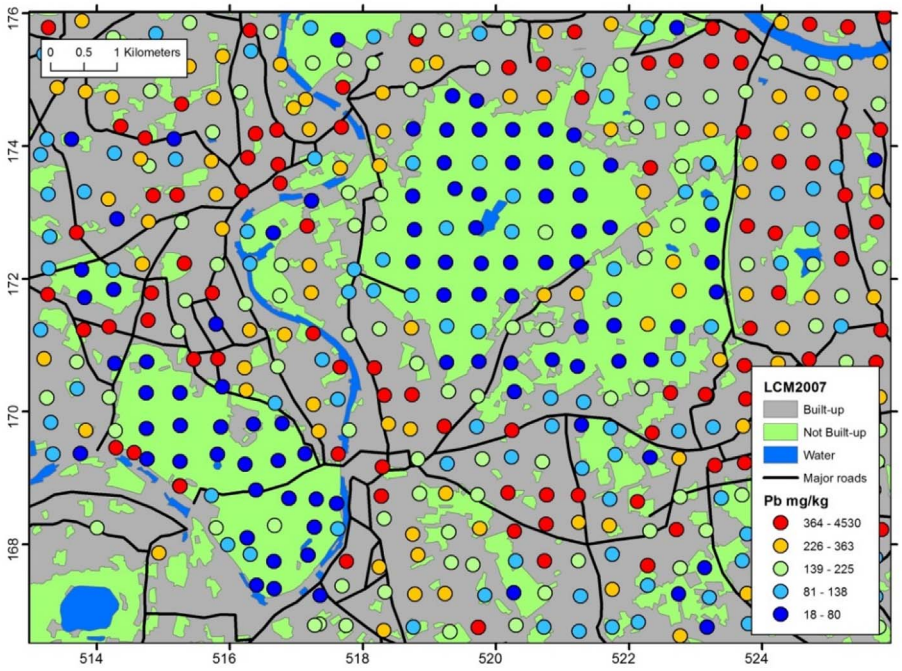

Fig. 4. Pb in topsoils, generalised LCM2007 land cover and major roads in the Richmond Royal Parks area, London (area of this map shown in Fig. 1; LCM2007 Land cover © NERC (CEH) 2011. © Crown Copyright 2007. Ordnance Survey Licence number 100017572. © third-party licensors; Major roads: Ordnance Survey data © Crown Copyright and database rights [2017]).

these pre-1940 urbanised areas are compared with areas within the GLA that have never been urbanised (NURB), being the highest for Ca (2.3 times higher for River Terrace Deposits, Thames Group clays and Thames Group sands, Supplementary material Table SM-2).

Knights and Scheib (2011), and Scheib et al. (2011) observed consistently lower concentrations of metals within the historic Royal Parks, Hampton Court and Wimbledon Common in the Richmond area of south-west London. These parks have not been directly impacted by significant urban development throughout the last 200–300 year history of London. Median concentrations are presented (Table 4) for subsets of top soil samples overlying Thames Group clays and River Terrace Deposits selected from an area of approximately 115 km^2 that includes the parks and surrounding built-up urban areas (Fig. 4). Three other PMs occur within the Richmond area but these have an inadequate number of samples (17–45) for statistical analysis. Ca, Cu, Pb, Sb, Sn and Zn are approximately 2–3 times enriched in the current built-up (BU) domain soils overlying both PMs compared to the not built-up (NBU) domain. Al, Fe, K, Mg, Mn, and P have enrichment ratios of 1.2–1.8, whilst Si is slightly lower in built-up areas (BU/NBU ratios = 0.93–0.98). This will partly reflect the compositional (closed data) characteristics of this type of geochemical data but some of these variations may imply subtle geogenic variations within the two PMs; higher Al, K, Fe, Mg and Mn possibly indicate higher clay and secondary iron oxide contents in the built-up domain (BU) soils. This might also explain why some of the minor elements such as Co, Cr, Ga, and Ni are also higher. Higher LoI and lower pH in the Richmond Royal Parks (NBU) soils probably reflects higher organic material content due to accumulation of decomposing leaves and grass.

Comparison of median soil values for the Richmond Royal Parks with the GLA (Table 4 and Supplementary material Table SM-3) shows that enrichment ratios (BU/NBU) are similar for the major and trace elements with ratios of 1.5 or greater, leading to the conclusion that soils in the Richmond Royal Parks are not substantially different to other areas in the GLA with the same underlying geology that are not built-up.

Soil data for areas classified as built-up using LCM2007 land cover data in 20 other urban centres in England and Wales (Scheib and Nice, 2007; Fordyce et al., 2005; Flight and Scheib, 2011) exhibit similar or stronger enrichment in As, Cd, Cu, Pb, Sn and Zn in pre-1940 urbanised areas (OLD) compared with post-1940 urbanisation (NEW) (Table 5). There is some variation in the OLD/NEW ratios between the urban areas but the ratios are broadly similar for most areas. Ca and other

Table 4
Median topsoil concentrations and enrichment ratios for built-up (BU) and not built-up (NBU) domains defined by the land cover classification (Table 1) for River Terrace Deposits and Thames Group clays in (i) the Richmond Royal Parks area and (ii) the GLA.

Element	River Terrace Deposits (SAGR)						Thames Group Clays (THAMC)					
	Richmond Royal Parks			GLA			Richmond Royal Parks			GLA		
	BU	NBU	BU/NBU	BU	NBU	BU/NBU	BU	NBU	BU/NBU	BU	NBU	BU/NBU
No.	162	86		1174	428		79	46		1499	749	
%												
Ca	0.83	0.36	2.3	1.06	0.54	2.0	0.82	0.29	2.9	1.08	0.54	2.0
P	0.18	0.12	1.5	0.17	0.14	1.2	0.13	0.08	1.6	0.14	0.10	1.5
mg/kg												
Cu	43	20	2.2	58	36	1.6	39	20	2.0	59	30	2.0
Pb	251	83	3.0	277	128	2.2	204	80	2.6	244	94	2.6
Sb	3.3	1.5	2.2	4.1	2.3	1.8	2.9	1.5	1.9	4.0	1.7	2.4
Sn	17	7	2.6	20	12	1.7	13	8	1.8	18	8	2.3
Zn	164	60	2.7	202	102	2.0	134	47	2.9	201	87	2.3

Table 5
Median topsoil concentrations and enrichment ratios for LCM2007 built-up domain subdivided into pre-1940 (OLD) and post-1940 (NEW) urban domains for all and selected urban areas outside London.

	Urban outside London			Coventry			Derby			Sheffield			Swansea		
	NEW	OLD	OLD/NEW	NEW	OLD	OLD/NEW	NEW	OLD	OLD/NEW	NEW	OLD	OLD/NEW	NEW	OLD	OLD/NEW
As	14	17	1.2	9	11	1.2	12	15	1.3	23	21	0.9	43	49	1.1
Cd	0.5	0.7	1.4	0.3	0.3	1.0	1.8	2.1	1.2	0.6	0.7	1.2	1.3	2.3	1.8
Cr	67	70	1.0	65	65	1.0	64	65	1.0	96	88	0.9	64	69	1.1
Cu	31	56	1.8	32	63	2.0	36	49	1.4	71	52	0.7	96	168	1.8
Ni	29	30	1.0	25	27	1.1	28	33	1.2	37	39	1.1	32	42	1.3
Pb	81	180	2.2	66	159	2.4	109	257	2.4	142	227	1.6	149	368	2.5
Sn	6	13	2.2	7	15	2.1	6	8	1.3	12	16	1.3	19	43	2.3
Zn	131	193	1.5	101	169	1.7	137	220	1.6	161	197	1.2	330	568	1.7
No.	1909	2128		126	78		83	105		111	224		105	119	

major element variation is difficult to assess, as there are insufficient soil samples on any one PM.

3.2. Building demolition, construction and land reclamation

The enrichment ratios suggest that one or more events or processes, which affected the pre-1940 urban domain, have caused soils over these PMs to be enriched in Ca and to a lesser extent P, as well as some metals and metalloids. One possibility is that widespread destruction of buildings across large sectors of the London urban domain, especially during the period 1940–41, when more than 1 million houses were destroyed or severely damaged by strategic bombing, may have resulted in Ca-bearing cement and lime dust being incorporated into top soils causing this enrichment. Elevated Pb in the pre-1940 urban areas may be partly derived from paint and/or lead pipes. Lead was the main white pigment in paint used extensively from the 1920's to the early 1960's and less commonly until it was banned in 1992; so many post-1940 houses will also have significant amounts of Pb in the original paint layer. Cu, Sn and Zn are commonly used in buildings (paint, galvanised metal, water pipes etc.). Based on visual estimation, the spatial variation of bomb density is broadly similar to that for Pb in soil whereas the spatial variation of Ca is strongly impacted by parent material chemistry, especially the distribution of the White Chalk (compare Fig. 1 with Supplementary material Fig. SM-2). Using a Brickearth, River Terrace Deposits and Thames Group clays subset of the London soil data with broadly similar Ca and Pb concentrations (Supplementary material Table SM-2), which comprise the major proportion (67%) of the London soil data, it transpires that whilst the variation of bomb density is similar to soil Pb and Ca (Fig. 5), the correlation is not very strong (R^2 (adjusted) = 15% and 13%, respectively for Pb and Ca (Supplementary material Fig. SM-3).

There is a progressive increase in median Ca and clr Ca with proximity to bomb sites in the pre-1940 (OLD) urban domain (Fig. 6). Ca is relatively stable in the post-1940 (NEW) urban domain that should not have been impacted by bomb damage, apart from at its margins where there could have been dispersion of Ca from bomb-damaged buildings in adjacent pre-1940 urbanised areas (Fig. 6). In the never urbanised domain (NURB), there is a slight increase in Ca within 100 m from the nearest bomb site that could also reflect dispersion of dust from bomb damaged buildings in nearby pre-1940 urbanised areas (Fig. 6). It should be noted that there is a relatively high degree of uncertainty for medians for the 0–25 m distance range of the NEW and NURB domains as these are based on < 25 samples. Pb, clrPb, Zn, clr Zn, Cu and Sn vary very little with distance from the nearest bomb site in the post-1940 (NEW) domain (Fig. 6 and Supplementary material Fig. SM-4) whilst all these elements increase gradually with proximity to bomb sites in the pre-1940 (OLD) domain. The distance profiles for Cd and Sb are less consistent but medians for both are low (Supplementary material Fig. SM-4). Profiles for the never urbanised domain (NURB) are generally flat between 100 and 200 m and > 400 m or exhibit slight increases with more erratic variation close to bomb sites (Fig. 6; Supplementary material Fig. SM-4). The progressive increase in Pb, Zn, Sn, Sb and Cu with proximity to bomb sites in the pre-1940 (OLD) domain is suggestive of significant contamination related to the destruction of buildings during the Blitz (1940–41) which would have affected only those sectors of post-1940 urbanisation and never urbanised ground near the margins of the older urbanised areas impacted by bombing. The variations of median chemical element concentrations and clr values for Ca, Pb and Zn in relation to distance from bomb sites are very similar (Fig. 6).

However, the substantial overall enrichment in Ca, Pb, Zn, Cu, Sb, Sn and to a less extent Cd in both the post- and pre-1940 urban domains cannot be due solely to bomb damage. It could reflect widespread dispersed contamination from a combination of construction activities using cement and concrete, leaded paint, coal combustion products including ash as well as contaminants from road traffic.

Ca is not enriched in soils over Alluvium from the pre-1940 compared with the post-1940 urban areas. Pb and Sn are enriched, but only by 15% and 11% respectively, compared with the much higher enrichment of 25–32%, 72–79% and 42–68% for Ca, Pb and Sn in soils derived from Thames Group clays, River Terrace Deposits, Brickearth and Thames Group sands (Supplementary material Table SM-2). Ca enrichment in Alluvium soils from areas built-up since 1940 may be caused by the disposal of millions of tons of debris from bomb-damaged buildings and its use for land reclamation at Hackney, Leyton and Becontree marshes, and for flood prevention in the Lea Valley (Ward, 2015). Twenty-nine percent of Alluvium soil sites are actually located on Artificial ground, predominantly in the valleys of the rivers Thames and Lea. In contrast, Artificial ground underlies only 3% and 7% of soil sites on Thames Group clays and River Terrace deposits, respectively. Ca in soils on Artificial ground is 70%, 40% and 60% higher for ground underlain by Alluvium, River Terrace deposits and Thames Group clays, respectively. However, when the data are grouped also by urbanisation era (i.e. pre- or post-1940), it is apparent that whereas Ca is always higher on Artificial ground, the contrast between sites on bedrock or superficial geology (GEO) and Artificial ground (ART) is always greater for post-1940 urbanised areas (NEW, Fig. 7a). This may reflect the use of debris from bomb-damaged buildings for post-1940 land reclamation. The same relationships are observed for clrCa. The situation is different for Pb, which is slightly higher in soils from Artificial ground in post-1940 urbanised areas but slightly lower on Artificial ground in pre-1940,'s urbanised areas (Fig. 7b). This suggests that demolition or other debris that was used to reclaim land in the pre-1940 urbanised areas (OLD in Fig. 7b) has lowered the median Pb concentrations. Conversely, debris from the pre-1940 urbanised areas (with relatively high Pb) used to reclaim land in the post-1940 urbanised domain has resulted in a slight increase in soil Pb concentrations (ART in Fig. 7b). For sites on River Terrace Deposits and Thames Group clays, this has resulted in the medians for Artificial ground in pre- and post-1940 urbanised areas being closer together than the medians for GEO (bedrock

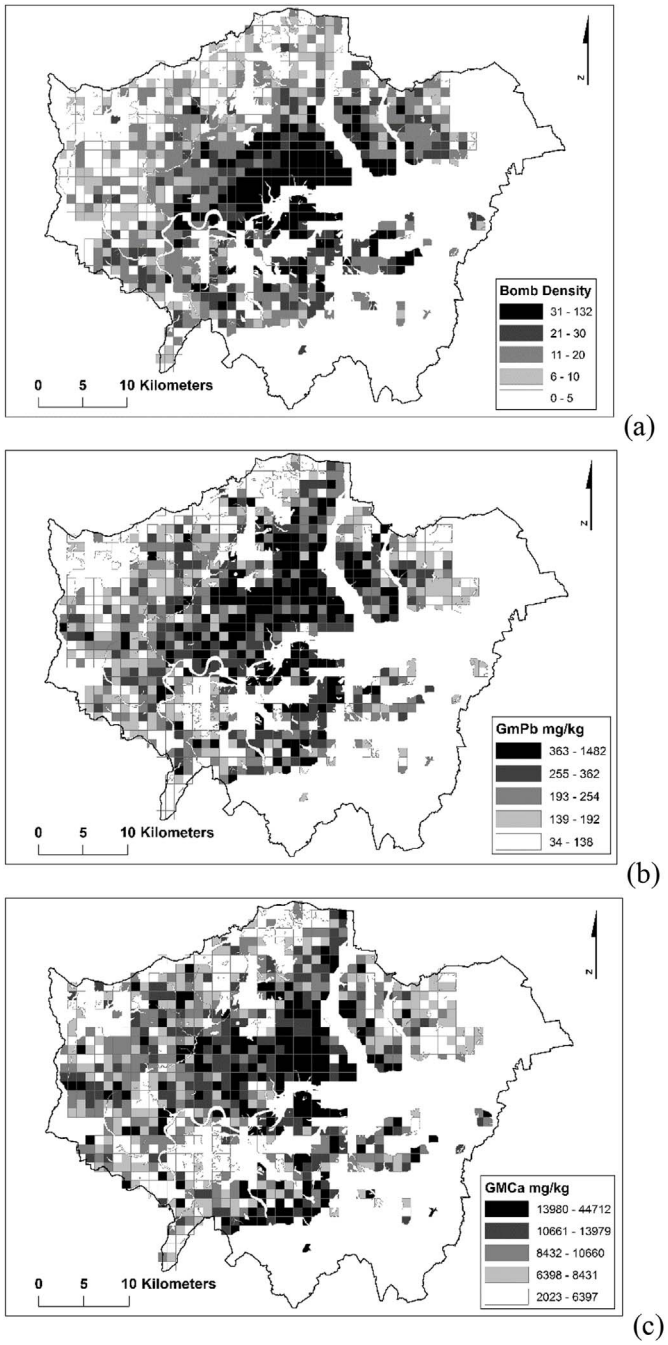

Fig. 5. (a) Number of bomb sites, (b) GM Pb (mg kg^{-1}) and (c) GM Ca (mg kg^{-1}) in 1 km grid squares for sectors of the GLA with both soil chemistry and bomb site data underlain by Brickearth, River Terrace deposits or Thames Group clays (contains Bomb Sight data by University of Portsmouth licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 Unported License).

or superficial geology) sites (Fig. 7b).

3.3. Domestic coal burning and ash disposal

An alternative explanation for the observed enrichment ratios is that ash from coal combustion spread on the soils and deposition of airborne particulates during the period when coal was extensively used for domestic heating and cooking has resulted in higher concentrations of Pb, Ge, Sb, Zn, Cu, Cd, Mo and As. Through most of the 19th and the early half of the 20th centuries, coal was used for heating and this generated large quantities of smoke leading up to the Great Smog of 1952, which killed 4000 people in London. The Clean Air Act 1956 mandated the use of smokeless fuels at a time when most homes used open fires for heating. Contamination of soil through aerial dispersion of coal derived particulates and disposal of coal ash by spreading on domestic garden soils will have led to widespread enrichment in coal related metals and metalloids. Higher concentrations would be expected in the pre-1940 urbanised domains due to the longer time period (about 150 years) over which this type of contamination occurred, compared with the post-1940 domain in which significant contamination will have occurred for up to about 15 years.

Si, Al, Fe, K, and Ca are the major constituents of combustion residues (furnace bottom ash and fly ash) from bituminous coal from the UK Yorkshire Coalfield (Spears and Martinez-Tarrazona, 2004), so these are also likely to be a major constituent of ash derived from domestic burning of coal. Al and Ca are about twice as high in coal combustion ash compared with soils overlying Thames Group clays whilst concentrations of Fe and Mg are about 1.4 time higher and K and Si about 0.8 times lower. If the enrichment of Ca in the pre-1940 urban domain is related to coal ash, then Al would also be expected to be enhanced. However, this is not the case and Al is slightly higher in the never urbanised (NURB) soils from some PMs (Supplementary material Table SM-2). As, Cr, Cu, Mo, Ni, Sr, V, and Y are 3–14 times higher in coal combustion residues (Spears and Martinez-Tarrazona, 2004) compared with never urbanised (NURB) Thames Group clay soils (Supplementary material Table SM-2). The pre-1940 urbanised soils (OLD) are not as enriched in As, Cu and Mo as would be expected if these elements were dominantly from coal combustion residues whilst Ba, Cr, V and Y are almost the same in never urbanised (NURB) and pre-1940 urbanised (OLD) soils overlying Thames Group clays (Spears and Martinez-Tarrazona, 2004; Supplementary material Table SM-2). Higher enrichment ratios would be expected if coal ash were a significant factor. On this evidence the Ca, and possibly also a substantial part of the Cu, Pb, Sn and Zn enrichment is perhaps more likely to be related to destruction of buildings in the period 1940–41 than from the disposal of coal ash from domestic fires, although road traffic contamination is also likely to be a contributory factor.

3.4. Emissions from vehicles (road traffic)

The relationship between Pb and other elements associated with road traffic (Harrison, 1979; Warren and Birch, 1987; Ward, 1990; Leharne et al., 1992; Charlesworth et al., 2003; Robertson et al., 2003; Thornton, 2012) was evaluated in the GLA by examining how these elements vary with proximity to different classes of roads. Ordnance Survey OS Open Roads data was used to calculate distances between soil sample sites and roads (Supplementary material Figure SM-5).

Sites relatively close to major roads (principally high traffic volume A roads but including a few motorways) have higher median Pb concentrations than sites at similar distances from minor (relatively low traffic volume, unclassified) roads (Fig. 8) but this difference is only apparent within 50 m from the roads. Beyond this distance, there is little difference between sites near major and minor roads. The same relationships exist for Cu, Sb and Zn, and to a lesser extent also for Sn, although the enrichment ratios between sites > 400 m and those < 25 m from roads are less than for Pb, probably due to the deposition and accumulation of greater quantities of Pb from leaded petrol compared with Cu, Sb and Zn from brake linings and tyres.

However, the close spatial association of buildings with roads is a potentially confounding factor, especially in the urbanised sectors of London. So part of the contamination close to roads could be related to buildings, including the historical disposal of ash and airborne deposition from domestic coal fires, Pb from paint, Zn from galvanised metal including corrugated iron sheets, tin cans, copper pipes and electrical wire, as well as Cd and P from fertilizer. It has also been demonstrated above that some of this metal contamination could be derived from debris from buildings destroyed during the Second World

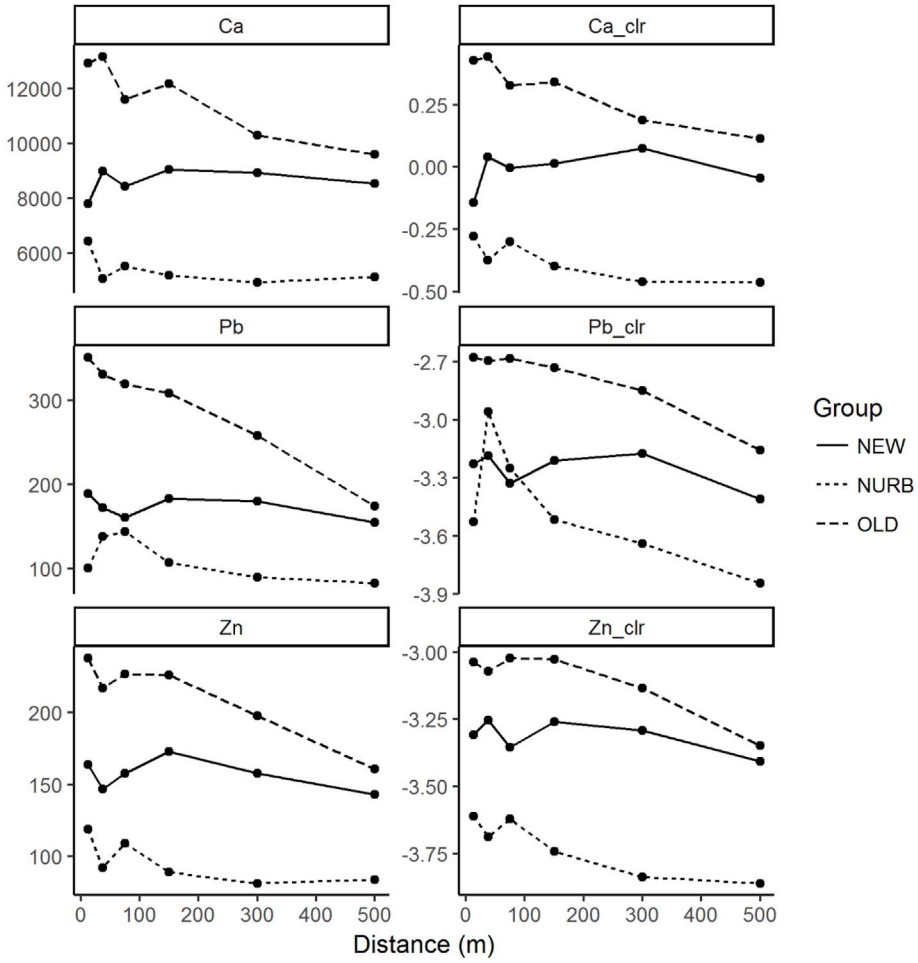

Fig. 6. Variation of median topsoil Ca, clr Ca, Pb, clrPb, Zn and clrZn with distance from the nearest bomb site grouped by urbanisation domain (OLD = pre-1940, NEW = post 1940, NURB = never urbanised). Based on soils overlying Thames Group clays and Terrace Gravel Deposits in areas with bomb site data. Data grouped into 0-25-50-100-200-400 and > 400 m intervals plotted at group centre distance or at 500 m for > 400 m group; n = 3328 (contains Bomb Sight data by University of Portsmouth licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 Unported License).

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Trends in Ca related to building demolition will be affected by the confounding factor of parent material composition. Taking just the data for Thames Group clays and River Terrace deposits which both have similar median Ca concentrations (0.5%) in never urbanised (NURB) soils, the increase in Ca with proximity to roads, and probably in general and coincidentally with density of buildings, is confirmed (Fig. 9 and Supplementary material Figs. SM 6–7). Over the range 0–24 m to 100–199 m when all groups have 10 or more samples (Supplementary material Table SM-4) the enrichment ratios (median 0–24 m/median 100–199 m) for pre-1940 urbanised areas (OLD) are 1.8–1.9 for Ca, Pb and Zn and 1.4 to 1.6 for Cd, Cu, Sb and Sn.

Lower median 0–24 m/median 100–199 m ratios characterise the areas urbanised since 1940 (NEW; Pb 1.5, Sb 1.4, Ca, Cd, P and Sn 1.2) and the never urbanised (NURB) domain, when the ratios are 1.2 for Ca, Cu, Sb and Zn but only 1.1 for Pb. Higher enrichment ratios of up to 3.5 for Pb occur over the 0–24 m to > 200 m range in the urbanised areas and 1.8 over the range 0–24 m to > 400 m in the never urbanised domain, although the uncertainty of these ratios must be relatively high due to the small number of samples > 200 m from roads (Supplementary material Table SM-4).

A two way analysis of variance was used to look at the effect of distance to roads (categorised into 0–25 m, 25–50 m, 50–100 m, 100–200 m, 200–400 m) and the three categories of urbanisation (OLD, NEW, NURB) on clr transformed Ca and Pb using the Thames Group clays and River Terrace deposits data (n = 3599). For both elements, the ANOVA identified significant differences between the distance to roads categories and the three urbanisation categories but the interaction between the distance to roads and urbanisation was not significant. For clrPb, the Tukey honest significant difference pairwise test showed that all the distance to road categories were significantly different from each other ($p < .016$) and that all urbanisation groups were significantly different ($p < .0017$). For clrCa, the Tukey honest significant difference pairwise test showed that all the distance categories were different from each other ($p < .019$) apart from a non-significant difference between the 50–100 m and the 100–200 m, the 50–100 m and the 200–400 m, and the 100–200 m and the 200–400 m categories. For the urbanisation categories and clrCa, the Tukey honest significance difference pairwise test showed a significant difference ($p < .0001$) between all OLD and NEW categories and the NURB and OLD categories but not between the NURB and NEW categories ($p = .1$).

Thorpe and Harrison (2008), Pant and Harrison (2013) and Wang et al. (2017) summarise the sources of elements associated with road traffic (Cu, Zn, Pb, Cd, Cr, Co, Ni, As, Ba, Sb, Mn, V, Pt, and Rh) of which the most dominant historically is reported to be Pb from leaded petrol/gasoline. Subsidiary amounts of Ba, Cu, Fe, Sb, Zn, Cd, Co, and Cr come from brake linings (of which Cu is the most abundant) and tyres (only Zn significantly exceeds crustal abundance; Thorpe and Harrison, 2008). Previous studies (detailed in Wang et al., 2017) show that concentrations of Pb and Cd increase with traffic volume while concentrations of Cu, Zn, Cd and Pb decreased with distance from the roads. Wang et al. (2017) in their study of trace elements in soils adjacent to highways found that only Cu, Zn, Pb and Cd were above local background concentrations. Cu:Sb ratios have been proposed as being characteristic of brake wear particles with a ratio of 9:1 reported for London (Gietl et al., 2010).

Crosby et al. (2014) concluded that correlations between Fe with Zn, Mn, Cu and Ti suggest anthropogenic combustion processes were

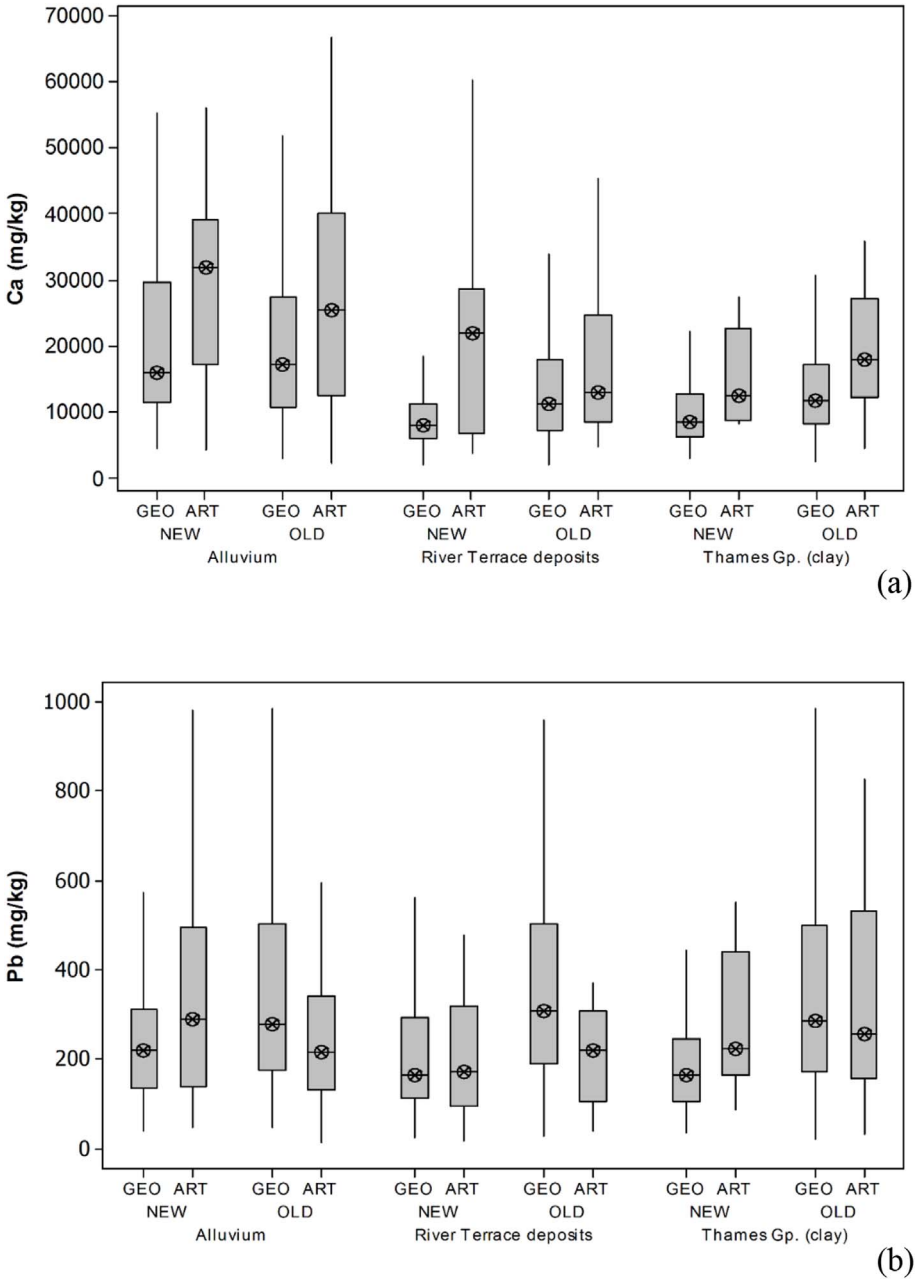

Fig. 7. Boxplot of (a) Ca and (b) Pb in soils from Alluvium, River Terrace Deposits and Thames Group clays subdivided into areas urbanised post-1940 (NEW) and pre-1940 (OLD) and sites located on either bedrock or superficial geology (GEO) or artificial ground (ART) [circle with cross = median, box = interquartile range, whiskers extend to the lowest or highest value within the lower or upper limit, where Lower limit = Q1- 1.5 (Q3 - Q1) and Upper limit = Q3 + 1.5 (Q3 - Q1)].

the main sources of these metals in urban road sediment in central London. Deposition of Fe particles occurs when pulling away and due to increased brake wear when stopping, together with deposition of Cu and Zn from brake linings and tyre wear. Crosby et al. (2014) reported strong associations between Fe, Cu, Zn and Pb linked to vehicle sources in Wolverhampton (UK) whilst Robertson et al. (2003) found significant associations between Pb, Fe, Mn and Cu in Manchester, which were attributed to vehicular sources. The data in this study do not indicate a concomitant rise in Fe, Mn or Ti with Pb, Ca and associated elements with data grouped over the range 0–24 m to > 200 m (Supplementary materials Table SM-4) reducing the likelihood of contamination related to brake dust from vehicles being a dominant factor.

Mao et al. (2014) demonstrated that London soils have a relatively narrow range of $^{206}Pb/^{207}Pb$ falling on a mixing line between geogenic (UK coal and UK Pb ore; Shepherd et al., 2016) and UK leaded petrol (1.06–1.09 Shepherd et al., 2016; Chenery et al., 2012; Sangster et al., 2000) suggesting multiple sources of Pb contamination including petrol, paint, water pipes, coal ash. Whereas Total Pb does not correlate with $^{206}Pb/^{207}Pb$, it is the primary determinant of isotopically exchangeable Pb (Mao et al., 2014) as it is for bioaccessible Pb (Appleton et al., 2012). Equally, the narrow range of isotopically exchangeable Pb (16–26%) suggested a consistent assimilation and 'aging' of Pb from a wide range of sources, and this could reflect mixing of Pb over many decades (Mao et al., 2014). Mao et al. (2014) also concluded that whilst the Pb isotope data for London soils are impacted by petrol Pb they are likely to be most impacted by non-petrol Broken Hill Type Pb ($^{206}Pb/^{207}Pb$ 1.04) which was widely used in industrial application, including paint manufacture in the 20th century, as suggested by the sample with the lowest $^{206}Pb/^{207}Pb$ located close to an early 20th century 'White Lead Works' that possibly used BHT or Canadian Pb (Mao et al., 2014).

There is no significant difference between mean soil $^{206}Pb/^{207}Pb$ for pre-1940 (n = 41, mean 1.14) and post-1940 (n = 3, mean 1.13) urbanised areas, or never urbanised (n = 6, mean 1.15) although the latter fall towards the higher end of the range. Neither were statistical differences in $^{206}Pb/^{207}Pb$ detected between LCM2007 land cover

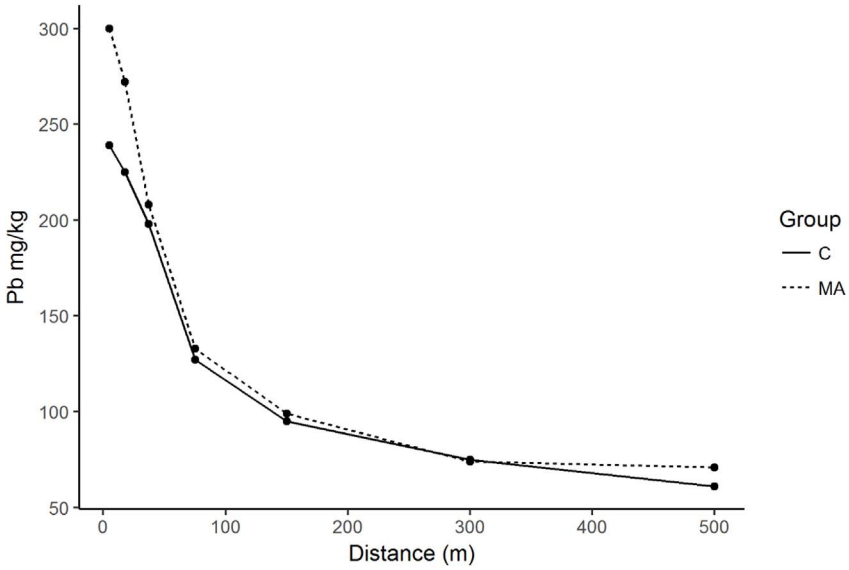

Fig. 8. Variation of median topsoil Pb concentration with distance from major (MA: motorway and A; n = 704) and minor, unclassified (C) roads (n = 5479). Data grouped into 0-10-25-50-100-200-400 m intervals and plotted at group centre distance; medians for data > 400 m plotted at 500 m. (Contains OS data © Crown copyright and database right (2017)).

classes (Table 2) nor between the BGS general land use classes (Supplementary material Table SM-1) although apart from domestic gardens/allotments (n = 24) the number of samples in each group is small (1–5). Only when the $^{206}Pb/^{207}Pb$ data are grouped into (1) built-up (Commercial and Residential, Domestic gardens/Allotments, Road verge, Urban open space; n = 37) and (2) Not built-up (Cemetery, Park, Recreational, Rough Grazing, Woodland and Forest; n = 13) is there a significant difference between means (Tukey Method). The built-up samples have a higher petrol Pb component although there is a substantial overlap between the ranges of $^{206}Pb/^{207}Pb$ values (Fig. 10) and the range of values for both classes is not substantially different to that for London airborne particulate matter (1.117-1.1152; Noble et al., 2008) with higher ratios corresponding to the period when leaded petrol was phased out in the UK. Atmospheric particles deposited onto the soil can be recycled into the atmosphere.

Mao et al. (2014) suggested that other markers of road traffic

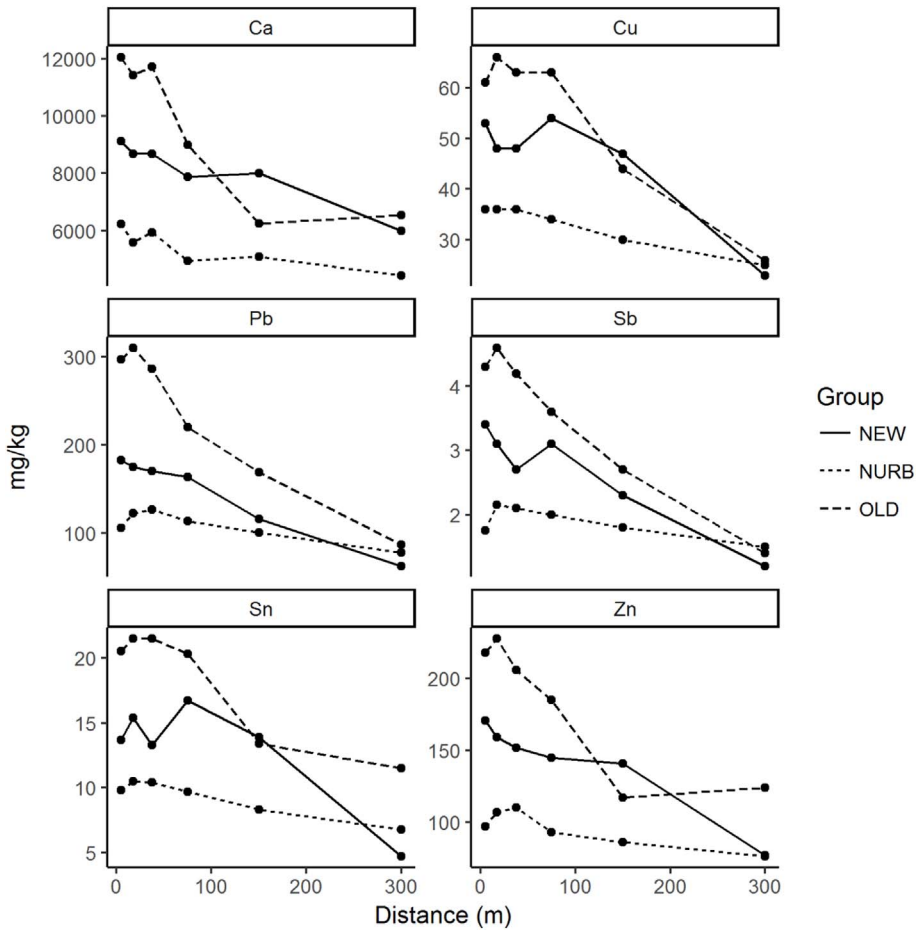

Fig. 9. Variation of median topsoil Ca, Cu, Pb, Sb, Sn, and Zn with distance from the nearest road grouped by urbanisation domain (OLD = pre-1940, NEW = post 1940, NURB = never urbanised). Based on soil samples overlying Thames Group clays and River Terrace Deposits. Data grouped into 0-10-25-50-100-200-400 m intervals and plotted at group centre distance; n = 3328 (Contains OS data © Crown copyright and database right (2017)).

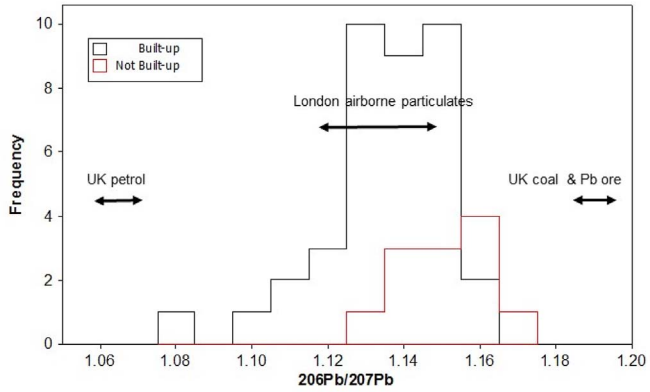

Fig. 10. Histogram of $^{206}Pb/^{207}Pb$ in soil samples from built-up and not-built-up areas (grouped using BGS site land use data) compared with the approximate ranges of $^{206}Pb/^{207}Pb$ in UK petrol, London airborne particulates, UK coal and Pb ores (see text for data sources).

sources such as Sb and Cu from brake liners may assist with contamination source identification, but there is no significant correlation between any of the Pb isotope ratios and other indicators including As, Ca, Cu, Sb, Sn and Zn in the 50 soil samples used by both Mao et al. (2014) and Appleton et al. (2012), although Ca, Cu, Pb, Sb, Sn and Zn all correlate (Pearson coefficient, p 0.05). Cu and Sb are not highest in the road verge samples (n = 5) whilst $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in road verge samples are lowest or next to lowest amongst all the land uses suggesting a high petrol Pb component, as would be expected, although the Pb isotope ratios are not substantially lower than for domestic gardens/allotments (n = 22) and urban open space (n = 5). No obvious spatial variation can be detected in $^{206}Pb/^{207}Pb$ within the GLA.

3.5. Other sources of contamination

P enrichment within the GLA as the result of fertilizer application is supported by the strong correlation between P and Cd. Whilst the lack of a corresponding enrichment in K suggests that fertilizer application may not be a major influence on soil chemistry, the higher solubility of the K component in NPK fertilizer may be a factor. Higher pH in the BU soils in the Richmond Parks area will reflect higher Ca although this cannot be dominantly due to application of phosphate fertilizer as P enrichment in the BU soils is not very high (1.2–1.5, Table 3).

4. Conclusions

Surface soil samples from currently built-up areas within the London GLA that were also built up in the pre-1940 have Ca, Cu, Ge, P, Pb, Sb, Sn and Zn median concentrations that are 1.2–1.75 times higher than in areas that have been built up (urbanised) since 1940. Ca, Cu, Pb, Sb, Sn and Zn are 2.2–3.2 times higher in areas built-up pre-1940 compared with areas that have never been built up in the GLA, and 2.1 to 5.2 times higher than in areas not built up outside the GLA but within the London Region. In all cases, Pb exhibits the highest enrichment ratios followed by Sn and Sb.

Enrichment (contamination) ratios suggest that an event or process that impacted the pre-1940 urban domain has caused soils to be enriched in Ca and to a lesser extent P, as well as some metals and metalloids. One possibility is that widespread destruction of buildings across large sectors of the London urban domain, especially during the period 1940–41, when more than 1 million houses were destroyed or severely damaged by strategic bombing, may have resulted in Ca-bearing cement and lime dust being incorporated into top soils. Similarly elevated Pb in the pre-1940 urban areas may be partly derived from leaded paint and lead pipes. Construction of new buildings using cement and concrete will also result in enhancement of Ca in the soil. The bomb density is spatially and statistically correlated with the soil Pb and Ca, but the correlation is not very strong. However, a progressive increase in Ca with proximity to bomb sites in the pre-1940 domain suggests that contamination related to destruction of buildings may be a significant factor, especially as Ca does not increase with proximity to bomb sites in the post-1940 domain. The variation of Ca, Pb and Zn medians in relation to distance from bomb sites is remarkably similar to the variation of the centred log-ratio (clr) medians for these elements.

Pb shows the strongest enrichment in soil samples taken 0–24 m from roads compared with those taken more than 200 m from roads and this is greater in the pre-1940 urban areas than in the post-1940 and never urbanised areas. High enrichment near to roads is also observed for Cu, Sb, Sn and Zn in both the pre-1940 and post-1940 urbanised domains and substantially lower in the never urbanised domain. The close spatial association of houses and other buildings with roads is a potentially confounding factor, especially in the urbanised sectors of London. The broadly comparable increase of Ca and Pb with proximity to roads in the urbanised domains suggests that Ca, Pb and some of the other metals derived from building debris could make up a relatively large contribution to the total amount of the metal contamination observed in London's soils. There is no concomitant rise in Fe, Mn or Ti with Pb, Ca and associated elements with proximity to roads, which reduces the likelihood of significant contamination being caused by brake dust from vehicles.

Only when the $^{206}Pb/^{207}Pb$ data are grouped into (1) built-up and (2) not built-up land uses is there a significant difference between means. The built-up samples appear to have a higher petrol Pb component although there is a substantial overlap between the ranges of $^{206}Pb/^{207}Pb$ values, and the range of values for both classes is not substantially different to that for London airborne particulate matter.

Soil data for areas classified as built-up using land cover data in 20 other urban centres in England and Wales exhibit enrichment in As, Cd, Cu, Pb, Sn and Zn in pre-1940 urbanised areas compared with post-1940 urbanised areas which is similar or stronger to that recorded in London.

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Bomb Site data base was compiled during a JISC-funded mapping project, called Bomb Sight, devised and managed by geographer Dr Kate Jones, formerly of the University of Portsmouth. OS Open Roads data set contains Ordnance Survey data © Crown copyright and database right 2013. The OS Open Roads data set also contains additional data sourced from third parties, including public sector information licensed under the Open Government Licence v1.0. Finally we thank Antonio Ferreira and Andrew Tye (BGS), Clemens Reimann (Associate Editor, Applied Geochemistry) and two anonymous reviewers for suggesting useful improvements to earlier versions of this paper.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2017.12.024.

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