Lability of Pb in soil: effects of soil properties and contaminant source.

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ENVIRONMENTAL CONTEXT

There is growing concern that lead (Pb) in the environment may cause adverse health effects in human populations. We investigated the combined use of isotopic abundance and isotopic dilution to show how the origins of soil Pb and soil characteristics affect lability. Soil pH and soil Pb content are the dominant controls on Pb lability; the lability of recent petrol-derived Pb is similar to that of other sources in urban soils but greater than geogenic Pb in rural roadside topsoils.

ABSTRACT

Lability of lead (Pb) in soils is influenced by both soil properties and source(s) of contamination. We investigated factors controlling Pb lability in soils from (i) land adjacent to a major rural road, (ii) a sewage processing farm and (iii) an archive of the geochemical survey of London. We measured isotopically exchangeable Pb (E-values; Pb_E), phase fractionation of Pb by a sequential extraction procedure (SEP) and inferred source apportionment from measured Pb isotopic ratios. Isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) of total soil Pb fell on a mixing line between those of petrol and UK coal or Pb ore. The main determinant of the isotopically exchangeable Pb fraction (%E-value) was soil pH: %E-values decreased with increasing pH. In rural roadside topsoils and there was also evidence that, petrol-derived Pb remained more labile (35%) than Pb from soil parent material (27%). However, in biosolid-amended and London soils %E-values were low (c. 25%), covered a restricted range, and showed no clear evidence of source-dependent lability.

1. Introduction

Industrial pollution, combustion of leaded petrol and mining activities have increased environmental Pb concentrations since the Industrial Revolution. The Agency for Toxic Substances & Disease Registry (ATSDR, 2012) lists Pb as the second most dangerous substance that threatens human health, not only because of its high toxicity but also due to its wide dispersion around the globe (Nriagu, 1996; Watmough and Hutchinson, 2004; Bacon et al., 2006). Human exposure to Pb, via inhalation of particles and ingestion of contaminated soil, can result in physiological damage, particularly to the nervous system. Due to these health concerns, the commercial use of Pb has been considerably reduced over the last three decades and unleaded petrol introduced to reduce aerial Pb deposition (Erel et al., 2002; Flament et al., 1996; Johnson et al., 1995). However, soils retain a large reservoir of anthropogenic Pb, derived partly from atmospheric deposition (Emmanuel and Erel, 2002; Sterckeman et al., 2000). Young children are at greatest risk from ingestion of soil contaminated with Pb because of their compulsive hand-to-mouth response (Wixson and Davies, 1994) and their greater sensitivity to Pb toxicity (Kayhanian, 2012). However, soil Pb may also enter the biogeochemical cycle through plant uptake, surface runoff and leaching into groundwater systems, depending upon the reactivity and solubility of the soil-borne Pb burden. Therefore, to fully quantify the risks associated with Pb it is also useful to assay the labile pool of Pb in soil, which is more closely linked to bioavailability and solubility than the total concentration in soil (Meers et al., 2007; Sauvé et al., 2000; Tongtavee et al., 2005).

The lability of cationic trace metals is generally lowest in alkaline soils with large mineral oxide and carbonate contents (Buekers et al., 2007; Tye et al., 2003). Trace metal binding to soil organic matter (SOM) and Fe/Mn oxides is also strongest at high pH (Tack, 2010); in contrast it appears that the effect of humus on lability is not consistent for all trace metals (Degryse et al., 2009). For Pb, lability may also be limited by formation of discrete mineral phases such as anglesite ($PbSO_4$) or Pb jarosite in acidic environments (Ruby et al., 1996) and chloropyromorphite ($Pb_5(PO_4)_3Cl$) which has been widely reported (Lang and Kaupenjohann, 2003). Association of Pb with discrete soil fractions has been investigated using sequential extraction procedures (SEP) by several workers (Bacon et al., 2006; Emmanuel and Erel, 2002; Imperato et al., 2003; Liu et al., 2003; Teutsch et al., 2001; Thornton et al., 2008). Attempts to identify the source of Pb in individual SEP extraction steps, using Pb isotopic ratios, have found that geogenic Pb was primarily associated with the residual fraction whilst anthropogenic Pb was distributed amongst carbonate, humus and Fe-oxide phases (Emmaunuel and Erel, 2002; Teutsch et al., 2001). However, the application of SEP assays in risk assessment may be limited because the labile Pb pool that controls solubility is unlikely to correspond to any single SEP fraction (Atkinson et al., 2011).

Isotopic dilution techniques can be used to determine the labile trace metal content of soils (Degryse et al., 2009). These methods can define the fraction of metal both in solid and solution phases that is 'isotopically exchangeable,' known as the 'E-value' (Smolders et al., 1999; Young et al., 2000). A small number of studies have used isotopic exchange with enriched stable isotopes to investigate lability of Pb in soils. Although variation in soil Pb solubility and lability is commonly ascribed to soil characteristics that affect adsorption strength (Gustafsson et al., 2011) it is likely that the original source of Pb is also a determining factor (Atkinson et al., 2011). Degryse et al. (2007) measured Pb_E in soils from 3 historically industrialized sites (pH 6.6-7.5) and found $\%Pb_E$ ranged from 45% to 78% (mean 58%). They suggested that high values of $\%Pb_E$ in soils contaminated with smelter fallout or battery production waste may arise because the Pb from these sources is more likely to enter the soil in a relatively soluble form. Similar $\%Pb_E$ values have been measured in acidic woodland and grassland soils (Marzouk et al., 2013a) whereas, in the same study, in alkaline minespoil soils with extremely high Pb concentrations (> 20,000 mg kg^{-1}) $\%Pb_E$ values were very low because of poorly soluble secondary carbonate or primary sulphide mineralogy; overall the range in $\%Pb_E$ was 7-99% when all soils were considered. In a second study of Pb lability in a contaminated catchment, Marzouk et al. (2013b) observed an inconsistent trend in $\%Pb_E$ value with soil metal:. They suggested that whereas an increase in soil Pb loading would reduce soil Pb adsorption strength it also increased the likelihood of poorly soluble minespoil minerals being present. Overall the range of $\%Pb_E$ values reported was <10% to >90% (n= 246).

The current study was an extension of work by Atkinson et al. (2011) who investigated Pb fractionation in four soils with distinctive metal sources and soil properties. The objective of this study was to broaden the investigation of the effect of soil properties and sources of contamination on Pb lability in soils, as determined by isotopic dilution. Soils (108 samples in total), covering a wide range of soil properties with both natural and anthropogenic sources of Pb, were obtained from three different localities (designated as 'Rural Roadside', 'Sewage Farm' and urban 'London' soils). Soil samples were analysed for chemical properties likely to affect Pb solubility, total Pb isotopic signature, fractionation by sequential extraction and isotopically exchangeable Pb (Pb_E); multivariate regression was used to examine the influence of soil properties within each set of soils. The sources of Pb in both labile and non-labile pools in the Rural Roadside soils were estimated by measuring the isotopic ratios $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in those fractions. An attempt was made to quantify the relative contribution from two likely sources (geogenic Pb and leaded petrol) to the isotopically exchangeable soil Pb fraction (%Pb_E) to determine whether Pb from petrol remains more labile than geogenic soil Pb despite the withdrawal of leaded petrol for several decades in the UK. Initially we regard 'Broken Hill Type' lead (BHT-Pb) as being synonymous with 'petrol-derived lead' but the limitations to this assumption are discussed in Section 3.5.

2. Materials and Methods

2.1 Soil sampling

Three sets of soils, with different sources of Pb contamination, were used in this study. Twenty one topsoils (0-20 cm) and twenty one subsoils at a range of depth intervals (between 20-60 cm) were collected from four sites along a major road (the A6) leading to the M1 motorway in a rural area of Nottinghamshire, UK (52°48'N, 1°16'W), where soils were likely to have received petrol-derived Pb from heavy traffic (designated 'Rural Roadside'). Sixteen topsoils were sampled from five fields at a sewage processing farm in Nottinghamshire, UK (52°57'N, 1°02'W) (designated 'Sewage Farm' soils). A further 50 topsoils (5-20 cm) were sub-sampled from the Geochemical Baseline Survey of the Environment (G-BASE) "London Earth" sample archive of the British Geological Survey (BGS) (Johnson et al., 2005). The 'London' soils selected were a subset from the systematic survey of the Greater London Authority area, chosen to cover 13 different land uses and a range of soil properties including pH, organic matter content and total Pb concentration.

2.2 Soil characterization

Soil samples were air-dried and sieved to < 2 mm. Soil pH was measured in 0.01 M $CaCl_2$ (1 : 2.5 soil : solution ratio) after shaking for 30 min. Soil organic matter content (SOM) was estimated from loss on ignition (%LOI) at 550°C for 7 hr. Available phosphate was determined using the Olsen method and a colorimetric assay (Rowell, 1994). Sub-samples of Rural Roadside and Sewage Farm soils were agate ball-milled and total Pb concentration was measured by ICP-MS (Thermo-Fisher Scientific, X-Series^{II}), following $HF/HClO_4/HNO_3$ mixed acid digestion, at the University of Nottingham (UoN). The Pb concentration in the London soil samples was determined on powder pellets by wavelength dispersive x-ray fluorescence spectrometry using PANalytical MagiX-PRO PW2440 and Axios-Pro spectrometers in BGS, each fitted with 4kW Rh-anode x-ray tubes. The manufacturer's

SuperQ software was used to account for matrix effects and correct for spectral line overlap interference. The XRF lower detection limit was 1.3 mg kg^{-1}, the calibration extended to 1,000 mg kg^{-1} and data were reported up to 10,000 mg kg^{-1}. Three of the London soils, in which total Pb concentrations exceeded 10,000 mg kg^{-1} were assayed by ICP-MS following acid digestion at the UoN.

2.3 Measurement of Pb isotopic abundances

The isotopic abundances of Pb isotopes (IA) in the $HF/HClO_4/HNO_3$ acid digestates of Rural Roadside and Sewage Farm soils were measured by ICP-MS (Thermo-Fisher Scientific, model X-Series^{II}) at the UoN. The London soil digestates were assayed at the BGS (Agilent, model 7500cx). The analytical method and instrument settings used at the UoN are described in Atkinson et al. (2011) and at BGS in Izquierdo et al. (2012). Both instruments employed a large number of sweeps with short quadrupole dwell times, to minimise plasma flicker, and used repeated assays of the Pb isotope CRM NIST-981 to drift-correct mass bias effects (Baker et al., 2004). The known Pb isotopic ratios (IR) for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in leaded petrol, UK Pb ore and UK coal, were used to assess the likely sources of Pb in the soils. The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios for petrol-derived Pb have been estimated at 1.067 ± 0.007 and at 2.340 ± 0.011 respectively (Monna et al., 1997). The Pb isotopic signature of galenas (PbS) from Derbyshire and Leicestershire were considered as representative for ore Pb with IR values of $^{206}Pb/^{207}Pb = 1.182 \pm 0.004$ and $^{208}Pb/^{207}Pb = 2.458 \pm 0.002$ (Rohl, 1996). For Pb in UK coal published average IR values for England and Wales were used (Farmer et al., 1999): $^{206}Pb/^{207}Pb = 1.184 \pm 0.005$ and $^{208}Pb/^{207}Pb = 2.461 \pm 0.012$. Regional Pb ore and coal are also used here as a proxy for soil parent material (i.e. geogenic Pb). The ratio of $^{206}Pb/^{207}Pb$ is generally adopted as the most sensitive to change in environmental studies (Bacon et al., 1996) because the similar isotopic abundance of the isotopes minimises instrumental bias and maximises precision.

The Pb isotopic abundances of the labile fraction for all soils were measured in the solution phase of a soil suspension (1 g soil (< 2 mm) in 30 ml of 0.01 M $Ca(NO_3)_2$) after shaking for three days. Quality assurance was confirmed by measuring the isotopic ratios $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in the $Ca(NO_3)_2$ solutions from eight Roadside soil suspensions at both institutions (UoN and BGS); the mean ratio of measured IR values for the two laboratories (UoN/BGS) was 1.003 for $^{206}Pb/^{207}Pb$ with SD = 0.002.

2.4 Lead lability measured by isotopic dilution

A method adapted from Gäbler et al. (1999) and Atkinson et al. (2011) was used to determine the concentration of labile Pb in soils. An enriched stable isotope ^{204}Pb was used as the spike isotope ($\geq$ 99.4% ^{204}Pb from ISOFLEX USA) and stored in 5% HNO_3. A spike, 0.4 ml of ^{204}Pb solution, was added to 1 g of soil suspended in 30 ml of 0.01 M $Ca(NO_3)_2$ following pre-equilibration on an end-over-end shaker for 3 days. The amount of ^{204}Pb added to each sample was sufficient to provide a 20% increase in the total background ^{204}Pb content; this was considered sufficient to accurately measure the change in the ratio ^{204}Pb/^{208}Pb without perturbing the Pb solubility equilibrium. Spiked soil suspensions were equilibrated on the shaker for a further 3 days and then separated by centrifugation (20 min; 2200 g) and filtration (< 0.2 µm) for determination of the isotopic abundance (IA) of ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb in the solution phase by ICP-MS. The value of Pb_E (mg kg^{-1}) was calculated from Eq. 1 adapted from Gäbler et al. (1999).

$$Pb_E = \left(\frac{M_{Pbsoil}}{W}\right)\left(\frac{C_{spk}V_{spk}}{M_{Pbspk}}\right)\frac{\left({}^{204}IA_{spk} - {}^{208}IA_{spk}R_{ss}\right)}{\left({}^{208}IA_{soil}R_{ss} - {}^{204}IA_{soil}\right)} \qquad (1)$$

where M_{Pbsoil} and M_{Pbspk} are the average atomic masses of Pb in soil and spike respectively, W is the weight of soil (kg), C_{spk} is the gravimetric concentration (mg L^{-1}) of Pb in the spike solution, V_{spk} is the volume of spike added (L), IA is the isotopic abundance (on a mole basis) of ^{204}Pb or ^{208}Pb in the spike or soil (0.01 M $Ca(NO_3)_2$ extracts), and R_{ss} is the IA ratio of ^{204}Pb to ^{208}Pb in the separated solution phase of the spiked soil suspension.

The isotopic compositions of the labile and non-labile Pb fractions were determined to investigate the source of Pb in each case. The isotopic abundance in the non-labile pool was calculated using Eq. 2 for both ^{206}Pb and ^{207}Pb, showing ^{206}Pb as an example in Eq. 2, which then enabled calculation of the isotopic ratio in the non-labile phase ($^{206/207}IR_{NL}$);

$${}^{206}IA_{NL} = \frac{{}^{206}IA_{total} - \left({}^{206}IA_L \times P_L\right)}{\left(1 - P_L\right)} \qquad (2)$$

where $^{206}IA_L$ and $^{206}IA_{NL}$ are the isotopic abundances of ^{206}Pb in the labile (0.01 M $Ca(NO_3)_2$ extracts) and non-labile (NL) pools respectively; $^{206}IA_{total}$ is the isotopic abundance of ^{206}Pb in the soil acid digestate ; P_L is the proportion of labile Pb in the soil calculated from %Pb_E.

The isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) of petrol Pb and coal Pb were used to estimate the proportion of each source of Pb in the labile and non-labile pools. The assumption that Pb came only from these two sources is a simplification but it indicates whether Pb from petrol is more labile than Pb from local parent material which has an isotopic signature similar to that of UK coal or Pb ore minerals. The concentration of petrol-derived Pb which is labile was estimated by linear interpolation of isotopic ratios (Eq. 3a & b):

$$Pb_{E(petrol)} = \frac{IR_{coal} - IR_{L}}{IR_{coal} - IR_{petrol}} \times Pb_{E} \tag{3a}$$

$$Pb_{total(petrol)} = \frac{IR_{coal} - IR_{total}}{IR_{coal} - IR_{petrol}} \times Pb_{total} \tag{3b}$$

where $Pb_{total(petrol)}$ and $Pb_{E(petrol)}$ are the total and isotopically exchangeable petrol-derived Pb respectively, IR_L and IR_{total} are the isotopic ratios ($^{206}Pb/^{207}Pb$ or $^{208}Pb/^{207}Pb$) of labile Pb (0.01 M $Ca(NO_3)_2$ extracts) and total soil Pb ($HF/HClO_4/HNO_3$ acid digestion) respectively; Pb_{total} is total soil Pb concentration (mg kg^{-1}) measured by acid digestion. The proportion of the petrol-derived Pb which is labile can then be calculated by dividing $Pb_{E(petrol)}$ by $Pb_{total(petrol)}$. Equations 3a and 3b are extensions of a widely used simple binary mixture model, based on interpolation between the isotopic ratios of prescribed end-members, discussed by Komárek et al. (2008). It should be noted that, although interpolation between the IR values of end members is commonly used, this approach incurs a small error. By assuming an IA value of 0.014 for ^{204}Pb in both end members and comparing results from IR interpolation with calculations of isotopic abundance (IA) we estimate that there is a maximum error of about 1.3% in source apportionment; this occurs at the midpoint across the full range of possible source compositions (i.e. 0 – 100% petrol-derived Pb).

2.5 Relating the labile fraction of Pb to soil properties

Two approaches were used to investigate the relationship between Pb lability ($\%Pb_E$) and soil properties; a logistic model and multiple regression. The parameters in the logistic model (pH_{50} and k_S Eq. 4) were optimized using the Solver function in Microsoft Excel, on all three sets of soils to examine the relationship between $\%Pb_E$ and pH :

$$\%Pb_{E} = \frac{100}{1+\exp\left[k_{S}\left(pH-pH_{50}\right)\right]} \tag{4}$$

where pH_{50} is the pH at which $\%Pb_E$ is 50% and k_S is a spreading factor that determines the shape of the curve. Equation 4 provides limits of 0 and 100% on the value of $\%Pb_E$ and assumes that pH value is the primary determinant of %E-value in a manner analogous to the adsorption behaviour of trace metals in soils.

The relationships between the labile fraction of Pb (Pb_E) and soil characteristics including pH, %LOI, available phosphate (P_{Olsen}, mg kg^{-1}) and total Pb concentration (Pb_{total}, mg kg^{-1}) in soils were also investigated using multiple regression (Eq. 5); the constants ($k_1 - k_4$) were optimized using the stepwise regression function in *Minitab 16.*

$$\log_{10}Pb_E = k_1\log_{10}Pb_{total} + k_2pH + k_3\%LOI + k_4P_{Olsen} \qquad (5)$$

Correlation coefficients between measured and modelled values of $\log_{10}Pb_E$ and residual standard deviations (RSD) for the model fit were used to assess the contribution of each soil variable to the prediction of labile Pb.

2.6 Sequential extraction of Pb

A sequential extraction procedure (SEP, adapted from Li and Thornton, 2001) was applied to 32 soil samples selected to cover a range of values of the variables in Eq. 5 (Pb_{total}, pH, %LOI and P_{Olsen}). Soils included 10 Rural Roadside (both topsoils and subsoils), 12 Sewage Farm and 10 London soils with a range of land uses. Full details of the SEP are summarized in Table 1. The concentration of Pb in the residual fraction (F5) was determined by difference between Pb_{total}, measured independently, and the summation of F1 to F4 of the SEP.

3. Results and discussion

3.1 Soil characteristics

Soil characteristics are shown in Table 2. Rural Roadside sites had a wide range of pH values (3.9 - 7.6) with slightly lower values of %LOI at depth in the subsoils. Available phosphate concentration (P_{Olsen}) and total Pb concentration were relatively low compared to the other two sets of soils. The average Pb concentration in Rural Roadside topsoils was approximately double that in subsoils suggesting anthropogenic inputs. Sewage Farm soils had a narrower pH range (5.9 - 6.7), greater %LOI (mean=16%) and very large available phosphate content (53-380 mg kg^{-1}). Lead concentrations varied from 55-712 mg kg^{-1} with lower concentrations in fields where pH was slightly higher and %LOI and available phosphate were lower suggesting lower historical sewage sludge inputs. For comparison, the BGS G-BASE dataset for soils in Nottinghamshire (BGS; 636 samples) gives a background Pb concentration range from 13.8 to 976 (mg kg^{-1}) with an average of 145 mg kg^{-1} and median of 100 mg kg^{-1}. The London soils covered a wide pH range (3.3-7.3) and had similar values of %LOI (mean =

9.7%) to those of the Rural Roadside soils. Available phosphate was greater than for the Rural Roadside soils but much lower than for soils from the Sewage Farm. Lead concentrations were very high in the London soils (median= 940 mg kg^{-1}) and showed greater variation (99-22600 mg kg^{-1}) between different land uses, than soils sampled elsewhere. Many urban sites in the UK are heavily contaminated with metals; the G-BASE dataset for urban soils (BGS; 13583 samples) gives a median value of 128 mg kg^{-1} and a range of 2.1 to 10,000 mg kg^{-1}. The latter figure is certainly exceeded and simply represents the maximum quantification limit for XRF.

The isotopic characteristics of the 108 soils are shown in Fig. 1 alongside typical values for leaded UK petrol, UK ore and UK coal. The range of values measured indicates that Pb in the soils investigated had multiple origins (Bacon et al., 1996). The majority of samples fell close to a mixing line, formed by a plot of IR values for ^{208}Pb/^{207}Pb against ^{206}Pb/^{207}Pb, which strongly suggests that soil Pb originated from both the geogenic and leaded petrol sources used as indicative end members.

The Rural Roadside *subsoils* had isotopic signatures for Pb that were close to those of geogenic Pb (Fig. 1b). This is as expected considering the joint influences of the local Derbyshire Pb ore field and Nottinghamshire-Leicestershire coalfields on alluvial and fluvio-glacial deposits in the Trent Valley and surrounding areas. In contrast, Rural Roadside *topsoils* had isotopic signatures closer to that of petrol Pb at the surface. The majority of London soils (Fig. 1), fell in a range similar to that of the Rural Roadside topsoils (1.127 – 1.146) and consistent with values reported for London aerosols of c. 1.135 (Noble et al, 2008), suggesting a similar mix of Pb from both geogenic and petrol sources. The origins of Pb in urban soils are difficult to identify unequivocally by isotopic ratio because there are so many possible sources. McGill et al. (2003) suggested that Pb in urban soils may come from paint, roofing materials, water pipes, coal burning, etc., and each manufactured source may be a mix of parent sources. In the Sewage Farm soils, fields with lower Pb concentrations, indicating lower sludge inputs, showed a greater influence from geogenic Pb (UK ore or coal) whereas soils with greater Pb contents showed a stronger influence of petrol-derived Pb, suggested by Atkinson et al. (2011) to arise from run-off to sewers from roads. There was therefore a strong correlation (r = -0.92) between the isotopic ratio (^{206}Pb/^{207}Pb) and the total Pb content in the Sewage Farm soils which implies a single source of background (geogenic) soil Pb and a consistent isotopic signature in the sewage sludge input which is closer to that of petrol. The same situation may broadly apply to the Rural Roadside topsoils (r = -0.72).

For London soils however, the correlation coefficient between isotopic ratio (^{206}Pb/^{207}Pb) and total Pb content was not significant, suggesting a more complex mix of source materials. Farmer et al. (2011) studied the relationship between total Pb concentration and the isotopic ratio ^{206}Pb/^{207}Pb in 27 urban soils in the city of Glasgow, Scotland and also suggested that the isotopic ratio of total soil Pb represented a complex mixture of Pb deposited from a variety of contaminant sources since the Industrial Revolution.

3.2 Pb lability in soils affected by soil properties and sources of contamination

In a study of Pb bioaccessibility, the source of Pb was found to be less important than the concentration and physico-chemical influences of soil properties (Farmer et al., 2011). In the current investigation, the median Pb lability values (%Pb_E) measured for the Rural Roadside topsoil and subsoil, Sewage Farm and London soils were quite similar at 31%, 30%, 24% and 22% respectively. However, Fig. 2 also shows a wider range of Pb lability in the Rural Roadside subsoils than in both the Sewage Farm and London soils.

Rural Roadside soils

Alkaline subsoils from the Rural Roadside sites, had the lowest values of %Pb_E, ranging from 0.6-12.7%, where Pb from parent material is likely to be fixed within soil particles or may be in the form of discrete Pb minerals such as cerrusite ($PbCO_3$) or pyromorphites (Li and Thornton, 2001). Lead-containing particles from petrol would be expected to dissolve in soils and adsorb to geocolloidal phases. Teutsch et al. (2001) found that petrol Pb was predominately bound to carbonate and Fe-oxides but presumably this will depend on soil composition.

Sewage Farm soils

Although the mix of sources of Pb contamination in the Sewage Farm soils may have been similar to those from the Rural Roadside sites, 75% of %Pb_E values fell in the lower range of 20-27% (Fig. 2). This was probably because of the relatively limited range of pH values in the Sewage Farm soils and their extraordinarily high phosphate concentration (Tye et al., 2003). Contaminant Pb in the Sewage Farm soils is almost exclusively from sewage sludge but the history of sludge application also determines the concentrations of soil humus and available phosphate. There was therefore a strong co-variance between the soil Pb content and the factors likely to affect its lability (Brazauskiene et al., 2008): soil Pb content was highly correlated with both %LOI (r= 0.97) and P_{Olsen} (r= 0.75). This, coupled with an on-site liming policy to maintain a limited range of soil pH values, around pH 6.5 (Severn Trent Ltd, pers. comm.), probably explains the low and very restricted range of %Pb_E values observed so that Pb_{total} explained 96% of the variation in Pb_E. A flat, non-significant, relationship was observed between %Pb_E and P_{Olsen} (not shown) which would appear to suggest that phosphate had no effect on Pb fixation in these soils. This seems intuitively unlikely as a soil subject to increasing phosphate inputs might be expected to show a negative trend in %Pb_E against soil P content. However, the absence of such a trend may arise as a consequence of the co-addition of Pb and phosphate to the soil, in a 'pre-reacted' form, in sewage sludge. Furthermore, there was a strong negative correlation between P_{Olsen} and soil pH (r = -0.73), probably arising from oxidation of sludge components (organic carbon, ammonium), so that the lower pH values at high phosphate (and sludge) loadings would elevate %Pb_E against the expected trend arising from phosphate fixation of Pb.

London soils

In the fifty London soils, although land use, soil properties and possible sources of Pb all covered a wider range than at the other two sites, the range of Pb lability was relatively small with 75% of the %Pb_E values falling in the range 16−26% (Fig. 2). This was a larger range than found in the Sewage Farm soils but much smaller than seen for the Rural Roadside soils and so soil properties appeared to have only a minor effect on Pb_E with Pb_{total} accounting for 90% of the variation in Pb_E. Appleton et al. (2012) studied the bioaccessibility of Pb on the same subset of London soil samples and concluded that total Pb concentration was the single significant predictor of bioaccessible Pb. Soil pH in the London soils was relatively high (mean pH=6.6; SD = 0.75), and accounted for only 0.7% of the variation in $Log_{10}Pb_E$ and an improvement in RSD of just 0.05 and may have contributed to the relatively narrow range of %Pb_E values. However, it is difficult to draw general conclusions regarding the factors controlling Pb lability in the London soils because of the complex mix of historical and current Pb sources and land uses. The highest level of lability found in a London soil (74.9%), was from a park planted with deciduous woodland with an exceptionally low pH value (for this dataset) of 5.28.

Predicting Pb_E from soil properties

Predicted values of %Pb_E as a function of soil pH using a logistic model (Eq. 4), is shown in Fig. 3a, with model constants, RSD and R^2 given in Table 3. Using the logistic model in preference to linear regression ensures an asymptote in %Pb_E of 100% at low pH and zero at high pH. Plotting data from all three sources together suggests only a very broad trend in Pb lability (%Pb_E) with soil pH. Whilst pH was a reasonable predictor of %Pb_E for the Rural

Roadside soils this was not the case for the London and Sewage Farm soils which had a more restricted range of pH and Pb_E values. It is difficult to incorporate further soil variables (eg P_{Olsen}, %LOI) into the structure of Eq. 4 in a meaningful form and so it is not possible to say whether the scatter around the model line (Fig 3a) arises from variation in soil properties or contaminant characteristics. Therefore to test the importance of other soil properties we also used a regression approach (Eq. 5) to test the dependency of Pb_E on total soil Pb concentration (Pb_{total}; mg kg^{-1}, log_{10} scale), pH, %LOI and $P_{Olsen.}$ Both %LOI and P_{Olsen} (k_3 and k_4 in Eq. 5) were found to be non-significant in improving the prediction of $log_{10}Pb_E$ when all three sets of soils were treated as a single dataset. The inclusion of Pb_{total} and pH produced an almost identical model performance to the logistic model (Table 3). A separate stepwise regression for each of the three sets of soils showed that soil pH was the dominant parameter in predicting Pb_E in Rural Roadside soils, accounting for 40.6% of the total variance. However, values of Pb_E were over-predicted from soil properties for deeper Rural Roadside subsoils with high pH values (>7.5) and low amounts of labile Pb (< 0.4 mg kg^{-1}, Fig. 3b), probably originating almost entirely from soil parent material. For the Sewage Farm and London soils, with their restricted range of pH values, soil Pb content was the primary determinant of Pb_{E}, accounting for 96% and 90% of the variance respectively.

3.3 Fractionation of lead as measured by a sequential extraction procedure (SEP)

Figure 4 shows the mean proportion of Pb in each SEP fraction and the proportion of Pb that was labile (isotopically exchangeable) or non-labile. The SEP results indicate that the ‘inert’ residual pool (F5) was the largest fraction for all three sets of soils (37.2% for Rural Roadside soils, 77.6% for Sewage Farm soils, and 41.8% for London soils), which corresponds qualitatively with the results from other studies of Pb in contaminated soils (Thums et al. 2008; Thornton et al. 2008; Liu et al. 2003). Within the limitations of fractionation provided by SEP’s the non-residual Pb was notionally bound mainly to Fe and Mn oxides (F3) and to humus (or sulphide) (F4).

A comparison of mean $\%Pb_E$ values with SEP fractions is appropriate where the range of both variables is very restricted, as in the case of the Sewage Farm and London soils (Figure 2). There was no consistent agreement between Pb_E and any single SEP fraction, as also found for Pb by Atkinson et al. (2011) and for Cd by Ahnstrom and Parker (2001). However, in the Sewage Farm soils, the average SEP residual fraction (78%) could be identified closely with the non-labile pool of Pb (76%). This may be because the high concentration of phosphate in these soils caused formation of a discrete Pb-phosphate phase (e.g.

chloropyromorphite $K_{sp} = 10^{-84.4}$, Shevade et al., 2001), which may resist complete dissolution in the SEP extractants given the relatively short duration of each step (Xie & Giammar, 2007). The most likely dissolution stage for chloropyromorphite, apart from F5, would be F4 (pH 2). For both the Rural Roadside and London soils, however, Pb bound into other fractions also contributed to the non-labile pool. Average non-labile Pb in the Rural Roadside soils (68%) corresponded quite well with a combination (70%) of F3 (oxides) + F5 (residual) of the SEP. A similar situation applied for most of the London soils, where the average non-labile fraction (76%) also corresponded with F3 and F5 combined (74%) by omitting one exceptionally acidic soil (pH 3.29). For the 10 London soils tested there was also a significant correlation (r = 0.85) between the non-labile fraction and SEP fractions F3 and F5 combined. It is perhaps less likely that humus-bound Pb (F4) contributes substantially to the non-labile Pb fraction (Atkinson et al., 2011).

3.4 Differences between the isotopic signature of labile and non-labile pools of Pb

Previous studies have suggested that Pb from petrol and coal combustion particulates is more soluble in dilute acid extractions than geogenic soil Pb which tends to be associated with the residual pool of SEPs (Erel et al., 1997; Li et al., 2011). To investigate possible differences in lability between the Pb sources we plotted the ratio of the IR value for $^{206}Pb/^{207}Pb$ in the non-labile fraction to the equivalent IR value in the labile fraction as a function of $^{206}Pb/^{207}Pb$ in the whole soil ($R_{NL,L}$; Equation 6; Figure 5).

$$R_{NL,L} = \frac{\text{Non-Labile IR}(^{206}\text{Pb}/^{207}\text{Pb})}{\text{Labile IR}(^{206}\text{Pb}/^{207}\text{Pb})} \tag{6}$$

Complete mixing of petrol-derived and geogenic Pb would produce a uniform value of 1.0 for $R_{NL,L}$ (Y-axis, Figure 5) for all soils. Values > 1 are generated by samples that have proportionately greater representation of geogenic Pb in the non-labile pool. Data for the Sewage Farm and London soils is scattered either side of the $R_{NL,L} = 1$ line, broadly within a range of ± 0.010, across the range of IR values for the whole soil (X-axis). This implies that Pb from petrol and geogenic sources in these soils has become distributed between labile and non-labile forms in the same proportions following prolonged contact with the soil. Of course, effects arising from the original form of Pb cannot be discounted. For example reaction between phosphate and Pb *during* sewage sludge production could reduce the lability of petrol-derived Pb prior to introduction to the soil.

By contrast, the Rural Roadside topsoils provided some evidence of a link between isotopic signature and Pb_E, with consistent and significant elevation above the $R_{NL,L}$ = 1.0 line. This suggests greater lability within petrol-derived Pb compared to the geogenic soil Pb pool. An isotopic distinction between labile and non-labile Pb is most likely where there is a small background Pb concentration into which the major pollutant source is petrol-derived Pb. With approximately 1/8th the Pb content of the Sewage Farm soils and 1/40th that of the London soils (Table 2), but with high local traffic densities, it is perhaps not surprising that the Roadside soils alone show a consistent deviation from 1.0 in $R_{NL,L}$ values.

The proportion of petrol-derived Pb in the Rural Roadside *subsoils* was very small: IR values ($^{206}Pb/^{207}Pb$) for soils (X-axis, Figure 5 and Figure 1b) were ≥ 1.15 compared to topsoils with IR values ≤ 1.17. There was a clear split in the range of values for $R_{NL,L}$ when the Rural Roadside subsoils were divided into two group: acid soils (mean pH 4.4) were spread across the $R_{NL,L}$ = 1.0 line but alkaline soils (mean pH = 7.3) were clustered above the line, suggesting labile Pb had a lower IR for $^{206}Pb/^{207}Pb$. This may seem a surprising result for the alkaline Rural Roadside subsoils, in which petrol-derived Pb is virtually absent. However it is important to recognise that the range of $R_{NL,L}$ values on the Y-axis in Figure 5 is very small: the average $R_{NL,L}$ value for the alkaline subsoils, 1.02, produces a shift in $^{206}Pb/^{207}Pb$ ratio for the labile Pb pool from (e.g.) 1.184 for UK coal to 1.16 which is still within the overall range observed for the Rural Roadside subsoils (Figure 1). There are also some confounding factors which complicate the interpretation of the data in Figure 5. The Pb ascribed to geogenic sources in the topsoil, on the basis of IR($^{206}Pb/^{207}Pb$) values, is actually likely to include recently deposited Pb from the nearby coal-burning power station, at Ratcliffe on Soar (52°51’55”N, 1°15’23”W). This Pb, (PbO particulates) is likely to be more labile than the true geogenic Pb (from the underlying parent material) and so boosts the apparent lability of geogenic Pb in the topsoil and would suppress the values of $R_{NL,L}$ in Figure 5. Furthermore, the soil conditions in the topsoil (high organic matter content, lower pH, greater biological activity) are all likely to encourage greater mixing of the two Pb sources, compared to conditions in the alkaline subsoil. Again, this would have the effect of lowering the values of $R_{NL,L}$ in Figure 5 for the topsoil (towards 1.0) and, again, could help explain why the Rural Roadside topsoil and alkaline subsoil appear to have a similar displacement from 1.0 even though, intuitively, we would expect that the ratio for the topsoil would be greater. Similarly, values of $R_{NL,L}$ for the acidic roadside subsoil samples are closer to unity (1.0) suggesting greater mixing of the two Pb sources in the soil. It would be more likely to see petrol-derived Pb in the alkaline subsoil if movement was by earthworm activity but less likely if Pb leaching in solution was responsible.

It is also conceivable that the displacement from an $R_{NL,L}$ value of 1.0 seen in Rural Roadside topsoils could arise from a small systematic error in ICP-MS measurement. We took all the measures we could to avoid this, including 'in sample run' mass bias correction with an isotopic standard (NIST 981), diluting all samples to a restricted Pb concentration range (typically 5 – 50 µg L^{-1}) to avoid detector mode changes, running inter-laboratory comparisons between UoN and BGS and correctly setting the detector dead time correction factor to avoid systematic shifts in IR measurements with Pb concentration. However, although the random errors for $R_{NL,L}$ values in Figure 5 were extremely small there is no way to be certain that the very small shifts in IR being measured are valid.

Figure 6 shows the proportion of labile Pb (%Pb_E) in petrol-derived and geogenic fractions (from Eq. 3) for topsoils from the three sites as a box and whisker diagram. The Rural Roadside subsoils were not included in this figure, as it is difficult to give a confident estimation of the proportion of petrol-derived Pb in these soils. The values of IR_{total} were very close to or beyond the isotopic signature of Pb coal (1.181) from England and Wales (Fig. 1). In Rural Roadside topsoils, there was a small but significant difference in Pb lability between petrol-derived Pb (35%) and geogenic Pb (27%) (paired t-test). As found for the overall %Pb_E values, there was a reasonably strong correlation between soil pH and the labile proportion of both geogenic Pb ($r = -0.70$; $p<0.001$) and petrol-derived Pb ($r = -0.60$; $p<0.005$). For Sewage Farm and London soils, the values of %Pb_E for Pb originating from petrol and geogenic sources were not significantly different. For some of the Sewage Farm soils, as suggested by Atkinson et al. (2011), the co-existence of large phosphate concentrations may cause rapid fixation of petrol-derived Pb during sewage sludge processing which then contradicts the pattern seen in the Rural Roadside soils where petrol-derived Pb was clearly more labile. For the London soils, despite having the widest range of possible Pb sources (Fig. 1), the proportions of petrol- and geogenic Pb that were isotopically exchangeable were very close (average of 23.1% and 22.1% respectively). This suggests a remarkably consistent level of assimilation into the soil and a geochemical "aging" to a similar reactivity for Pb from all sources and is consistent with the narrow range of Pb_E seen across this dataset (Fig. 2).

3.5 Limitations to the binary model of Pb source apportionment

There are substantial limitations to the assumption that Pb in soil originates from just two major sources. First, the assumption that a clear linear mixing line between two end members indicates the presence of just two sources can be challenged. The analytical constraints of quadrupole ICP-MS, which preclude accurate determination of small differences in ^{204}Pb isotopic abundance, have encouraged a reliance on plots such as $^{208/207}$Pb against $^{206/207}$Pb (Fig. 1) in source apportionment studies. However, as Ellam (2010) has shown, multiple geological sources of Pb are likely to cover a limited range of values on such plots. This factor combined with the low IR value for ^{206}Pb/^{207}Pb in the 'Broken Hill Type' lead (BHT-Pb) used in petrol, tends to produce an apparently linear plot, erroneously suggesting that there are mixtures of just two end members. The second, more obvious, problem arises from the simple assumption that BHT-Pb is synonymous with petrol-derived Pb. In fact, imported BHT-Pb was widely used in industrial applications in the UK in the 20th century (Vane et al., 2011; Chenery et al., 2012). Thus Bacon et al. (1996) found that the historical trend in the $^{206/207}$Pb ratio in archived Park Grass herbage samples declined ahead of the introduction of tetra-ethyl Pb in petrol, indicating industrial inputs from BHT-Pb into atmospheric aerosols in the UK from as early as 1900. For the three datasets presented in the current study, it may be reasonable to assume that Pb in the Rural Roadside soils is predominantly a combination of petrol-derived and geogenic Pb. The Sewage Farm soils, historically amended with sewage from Nottingham, must have a greater input of non-petrol BHT-Pb even though Pb from urban road runoff is likely to form a substantial part of the soil Pb burden. The London soils, although also substantially affected by petrol Pb, are likely to be the most affected by non-petrol BHT-Pb. An extreme example from the London dataset is Sample 654432 (Electronic Annexe 1) with a soil Pb content of almost 23,000 mg kg^{-1} and the most pronounced BHT signature of all the soils studied ($^{206/207}$Pb ratio = 1.081 (BGS, total Pb) and 1.082 (UoN, labile Pb)). Intuitively it is highly unlikely that most of the soil Pb originated from petrol; we estimate that this would have required the equivalent of Pb from more than 30 L petrol per kg soil. The sample site is located close to a dockland area and scrutiny of a local map from the early 20th century, shows the historical presence of a 'White Lead Works' ($2PbCO_3{\cdot}Pb(OH_2)$ for paint etc.) within 400 m of the site – possibly using imported Australian or Canadian lead.

The current challenge to source apportionment is perhaps to combine Pb isotopic ratio data, including consideration of ^{204}Pb, with other markers of industrial and road traffic sources, such as Sb and Cu from brake liners (Fujiwara et al., 2011; Huang, 1994; Weckwerth, 2001)

4. Conclusions

In summary, both soil properties and sources of contamination influence the isotopic exchangeability (lability) of Pb. Although soil pH was the only soil factor tested which significantly affected Pb lability (%Pb_E) the influence of the original Pb source and/or contact time limits the prediction of Pb_E from soil properties alone. In Rural Roadside soils, there was a relatively clear distinction between Pb from parent material and the main source of aerial contamination (petrol-derived Pb). In the Sewage Farm soils, with a limited range of soil pH values (c. pH 6.5) and high organic matter contents, the co-application of large phosphate and Pb concentrations from sewage sludge may have restricted the magnitude and range of Pb lability possibly indicating formation of Pb-phosphate minerals within the sludge; this remains difficult to confirm. Despite a wide range of land uses, and possible Pb sources, the Pb lability of most of the London soils fell into a remarkably restricted range (16-26%). This may be because of relatively high soil pH values (mean=pH 6.6; SD=0.75), but it is difficult to draw an unequivocal conclusion because of the complex mix of Pb sources present. However, this limited range in %Pb_E values may greatly simplify generic risk modelling in that it validates correlation of risk factors with total soil Pb content for urban soils with a restricted range of pH values.

There was no consistent agreement between Pb_E and any single SEP fraction in all three sets of soils. However, the non-labile Pb in both Rural Roadside and London soils was likely to be a combination of Pb occlusion within Fe oxides (F3) and primary minerals (F5 of the SEP), whilst for Sewage Farm soils, the SEP residual fraction (78%) could be identified very closely with the (isotopically) non-labile pool of Pb (76%) – possibly a consequence of Pb-phosphate interactions prior to biosolid application.

There was evidence in Rural Roadside topsoils that petrol-derived Pb remained more labile than Pb from geogenic ore or coal, and the proportion of petrol-derived Pb that was labile was strongly correlated with soil pH. There was also limited evidence, from comparison with the Rural Roadside alkaline subsoils, of greater mixing of sources in the Rural Roadside topsoils and in the acidic subsoil. However, both petrol-derived and geogenic (coal) Pb contributed to both the labile and non-labile fractions and contributions to the labile Pb pool from aerial inputs of coal-derived Pb from a nearby power station may have complicated the relationship between source and locality.

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Table 1: Summary of the modified Li and Thornton sequential extraction procedure (SEP)

	Reagents	**Extraction time**	**Soil: solution ratio (g : mL)**
F1: exchangeable	0.5 M $MgCl_2$	0.33 h	1 : 8
F2: carbonate	1 M NaOAc (adjusted to pH 5 with HOAc)	5 h	1 : 8
F3: Fe/Mn oxide	0.04 M $NH_2OH.HCl$	6 h at 96°C	1 : 20
F4: OM and sulphide	0.02 M HNO_3 and H_2O_2, 3.2 M NH_4OAc	5 h at 85°C; 0.5 h at 20°C	1 : 16 in stages
F5: residual	Total Pb ($HNO_3/HF/HClO_4$) – $\sum$(F1,F2,F3,F4)		

*Ac, acetate (NaOAc, sodium acetate)

Table 2: Land use and soil characteristics for the three site locations studied.

		pH in 0.01 M $CaCl_2$			Loss on ignition (%)			Available phosphate (mg kg^{-1})			Total Pb content (mg kg^{-1})		
Land use	**n**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**
Rural Roadside	**42**	**5.67**	**3.92**	**7.57**	**8.31**	**2.59**	**20.1**	**7.88**	**1.92**	**29.7**	**51.5**	**14.0**	**233**
Surface	21	5.71	4.17	7.01	11.8	7.05	20.1	9.31	1.92	29.7	65.7	25.1	233
Subsoil	21	5.62	3.92	7.57	4.84	2.59	8.20	6.44	1.99	26.3	37.2	14.0	161
Sewage Farm	**16**	**6.32**	**5.86**	**6.74**	**16.2**	**5.42**	**29.3**	**194**	**53.0**	**380**	**390**	**55.4**	**712**
Field 1	4	6.29	6.14	6.57	10.9	9.60	11.8	167	142	190	273	229	324
Field 2	2	6.66	6.58	6.74	6.47	6.38	6.56	138	128	147	78.8	55.4	102
Field 3	6	6.14	5.86	6.47	24.7	19.7	29.3	283	182	380	610	433	712
Field 4	2	6.44	6.34	6.53	21.4	19.5	23.4	171	126	216	592	511	673
Field 5	2	6.49	6.44	6.53	5.78	5.42	6.14	61.1	53.0	69.1	74.8	67.8	82.0
London	**50**	**6.58**	**3.29**	**7.31**	**9.70**	**4.25**	**17.5**	**22.0**	**1.09**	**207**	**1990**	**99.2**	**22600**
Commercial and residential	4	7.05	6.93	7.14	9.55	6.66	14.4	18.1	10.5	25.8	1850	166	3970
Deciduous woodland established	2	5.11	3.29	6.92	16.9	16.6	17.3	21.6	14.7	28.5	1220	162	2280
Domestic Garden	22	6.73	4.95	7.25	9.02	5.35	16.9	13.5	1.09	42.4	1850	172	7210
Grass moor	2	6.12	5.00	7.24	5.10	4.25	5.95	1.61			548	99.2	996
Graveyard	1	6.76			5.45			n.a			115		
Hospital Grounds	1	7.31			6.11			13.5			420		
Major roads/verge	2	6.39	5.57	7.20	9.07	8.98	9.17	15.8	14.6	17.0	468	428	507
Minor metalled* roads/verge	3	6.23	5.56	6.69	12.3	7.89	17.5	122	37.2	207	755	213	1730
Park	4	6.00	5.28	6.88	10.9	9.50	12.4	19.1	6.31	28.2	3260	217	9040
Recreational area	3	6.92	6.70	7.07	12.0	9.73	15.4	33.7	1.41	80.8	3330	641	6600
School	1	5.98			8.27			2.25			193		
Urban open space	2	6.51	6.40	6.61	12.0	9.90	14.0	n.a.			370	205	534
Urban open space tended but unproductive	3	7.00	6.78	7.30	8.59	4.96	11.5	27.3	19.8	34.9	3850	123	22600

n.a. not available (limited amount of sample); * A metalled road is one surfaced with small or crushed stones.

Table 3: Constants, RSD and R^2 values for the prediction of Pb_E using logistic (Eq. 4) and linear regression (Eq. 5) models. The logistic model (Eq. 4) was parameterized against measured values of $\%Pb_E$; modelled values of $\%Pb_E$ were then multiplied by measured Pb_{total} values to estimate $\log_{10}(Pb_E)$. The regression model (Eq. 5; three variants) was used to predict $\log_{10}(Pb_E)$ directly.

Logistic Model (prediction of $\%Pb_E$):

All soils	**pH_{50}**	**k**	**RSD**	**R^2**
	4.00	0.50	0.26	0.93

Regression Model (prediction of $Log_{10}Pb_E$):

All soils	**k_1 ($\log_{10}Pb_{total}$)**	**k_2 (pH)**	**RSD**	**R^2**
Pb_{total}	0.745	-	0.399	0.85
Pb_{total} , pH	1.181	-0.179	0.237	0.92

List of Figures:

Figure 1: (a) Lead isotopic characteristics in soils from three sites: Rural Roadsides (n = 21) (top- and subsoils), a Sewage Farm (n = 16) and the G-BASE London Earth geochemical survey (n = 50). Isotopic ratios ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb are shown as a mixing line with median values for UK coal (Nottinghamshire-Yorkshire-Derbyshire), South Pennine Pb ore and Broken Hill Type lead (BHT-Pb), the source of lead in petrol, shown for comparison. (b) Lead isotopic ratio ^{206}Pb/^{207}Pb shown as a box and whisker plot; the higher and lower quartile represents the highest and lowest 25% of the data respectively; whiskers indicates variability outside the upper and lower quartiles; the horizontal broken lines show values for the range of reference sources (mean ± SD), the mean value (×) and outliers are marked as an asterix.

Figure 2: Box and whisker plot showing lability of Pb (%Pb$_E$) for soils from Rural Roadside (n=42), Sewage Farm (n=16) and London (n=50) sites; the box represents the lower boundaries of the first and third quartile, the whiskers extend to the furthest data point within 1.5 box heights (of the box); outliers beyond the whiskers are shown as asterisk symbols; the mean (×) and median (line) values are shown.

Figure 3: (a) Predicted Pb lability (%Pb$_E$) from soil pH (0.01 M $CaCl_2$) using the logistic model (Eq. 4) with Rural Roadside, Sewage Farm and London soils. The solid line represents predicted %Pb$_E$. (b) Measured and predicted Pb$_E$ $\log_{10}$(mg kg^{-1}) for all soils (calculated from the predicted %Pb$_E$ in Eq. 4 and total soil Pb); dashed lines around the 1:1 line represent ± SD.

Figure 4: Comparison of average soil Pb fractions (%), determined by (a) sequential extraction procedure, and (b) with isotopically exchangeable Pb (%Pb$_E$) for a sub set of soils from Rural Roadside, Sewage Farm and London sites. Error bars represent standard deviation of data.

Figure 5: The ratio of ^{206}Pb/^{207}Pb in the non-labile Pb fraction to ^{206}Pb/^{207}Pb in the labile Pb fraction ($R_{NL,L}$) for all three sets of soils as a function of the isotopic ratio ^{206}Pb/^{207}Pb in the whole soil (from acid digestate) for Rural Roadside topsoils (○), and acidic (×) and alkaline subsoils (∆); sewage farm (▲) and London (●) soils. The single error bar symbol shows the average standard error for replicate rural roadside soils. The dashed lines are y = 1 ± SD (0.0038) for London soils.

Figure 6: Box and whisker plot showing the estimated proportion (%) of petrol derived BHT-Pb or coal-Pb that is labile in the Rural Roadside topsoil, Sewage Farm and London soils; the box represents the lower boundaries of the first and third quartile, the whiskers extend to the furthest data point within 1.5 box heights (of the box); outliers beyond the whiskers are shown as asterisk symbols; the mean (×) and median (line) values are shown.

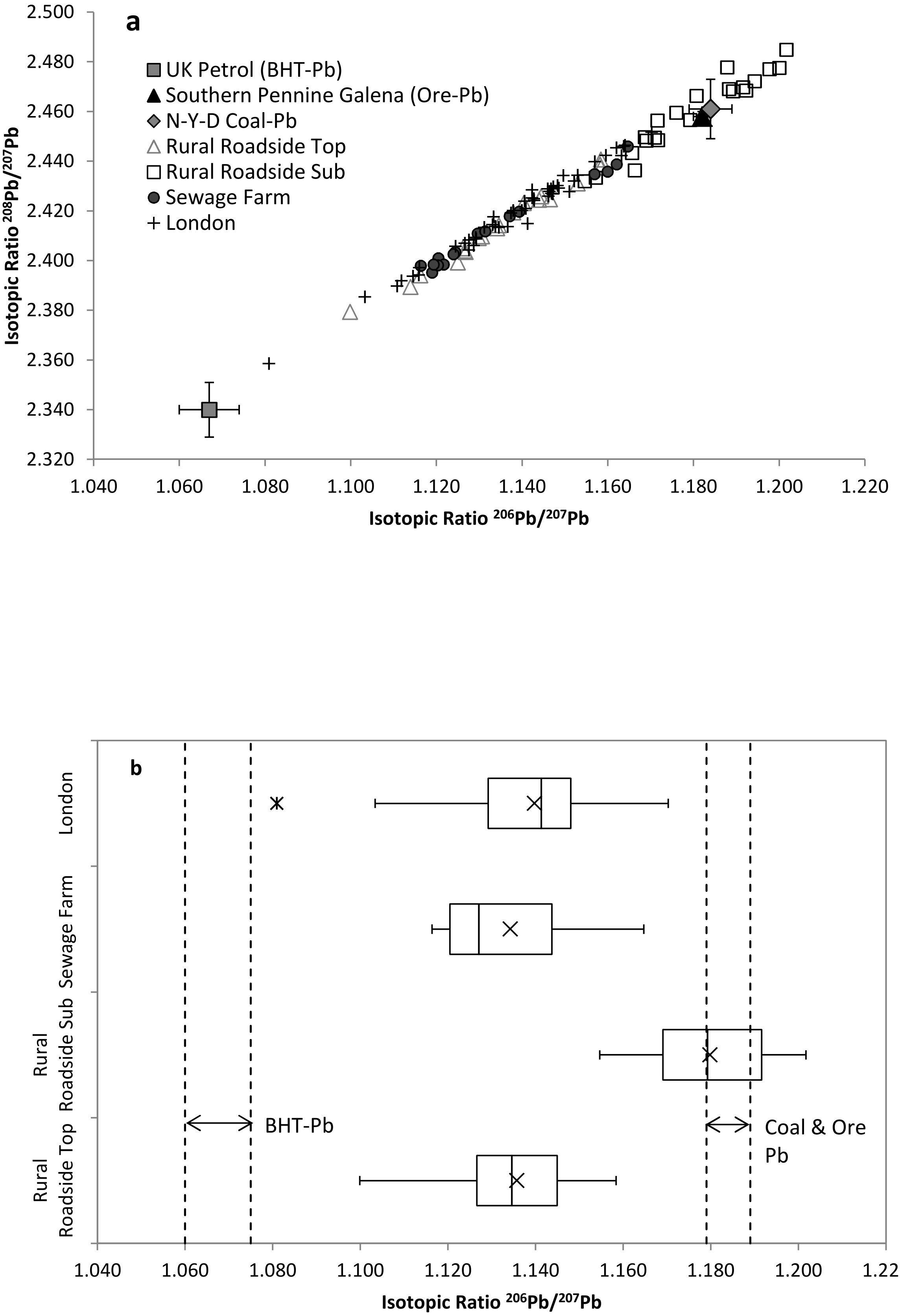
a
UK Petrol (BHT-Pb)
Southern Pennine Galena (Ore-Pb)
N-Y-D Coal-Pb
Rural Roadside Top
Rural Roadside Sub
Sewage Farm
London
Isotopic Ratio ^{208}Pb/^{207}Pb
2.500
2.480
2.460
2.440
2.420
2.400
2.380
2.360
2.340
2.320
Isotopic Ratio ^{206}Pb/^{207}Pb
1.040
1.060
1.080
1.100
1.120
1.140
1.160
1.180
1.200
1.220
b
London
Sewage Farm
Rural Roadside Sub
Rural Roadside Top
BHT-Pb
Coal & Ore Pb
1.040
1.060
1.080
1.100
1.120
1.140
1.160
1.180
1.200
1.220
Isotopic Ratio ^{206}Pb/^{207}Pb

Figure 1

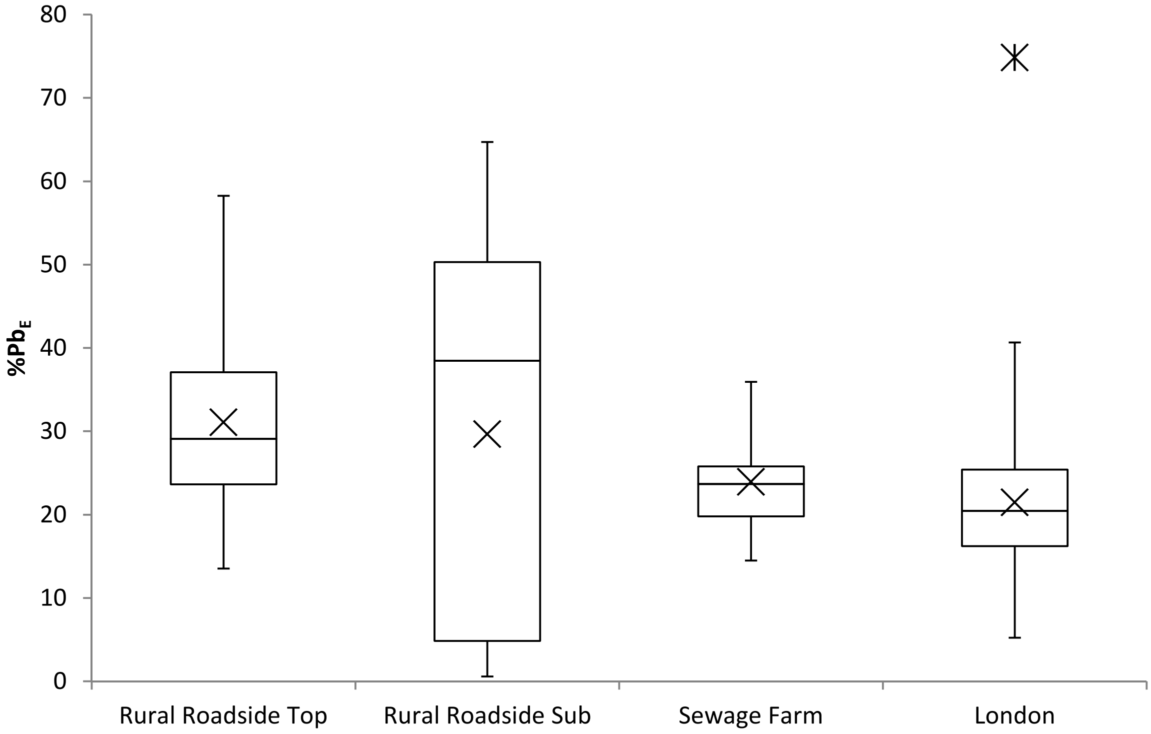
80
70
60
50
40
30
20
10
0
%Pb$_E$
Rural Roadside Top
Rural Roadside Sub
Sewage Farm
London

Figure 2

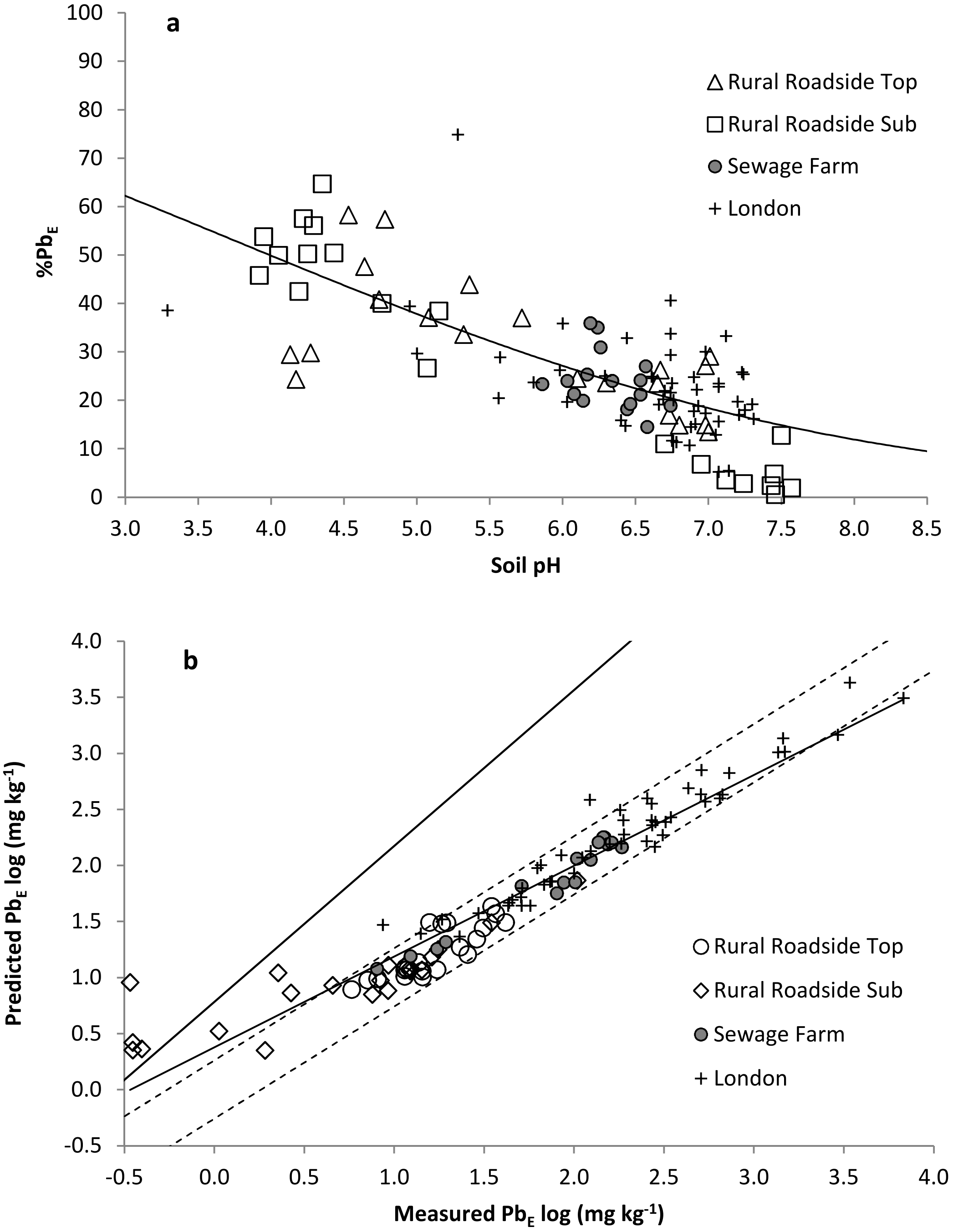
a
100
90
80
70
60
50
40
30
20
10
0
%Pb$_E$
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
Soil pH
△ Rural Roadside Top
□ Rural Roadside Sub
● Sewage Farm
+ London
b
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
Predicted Pb$_E$ log (mg kg^{-1})
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Measured Pb$_E$ log (mg kg^{-1})
○ Rural Roadside Top
◇ Rural Roadside Sub
● Sewage Farm
+ London

Figure 3

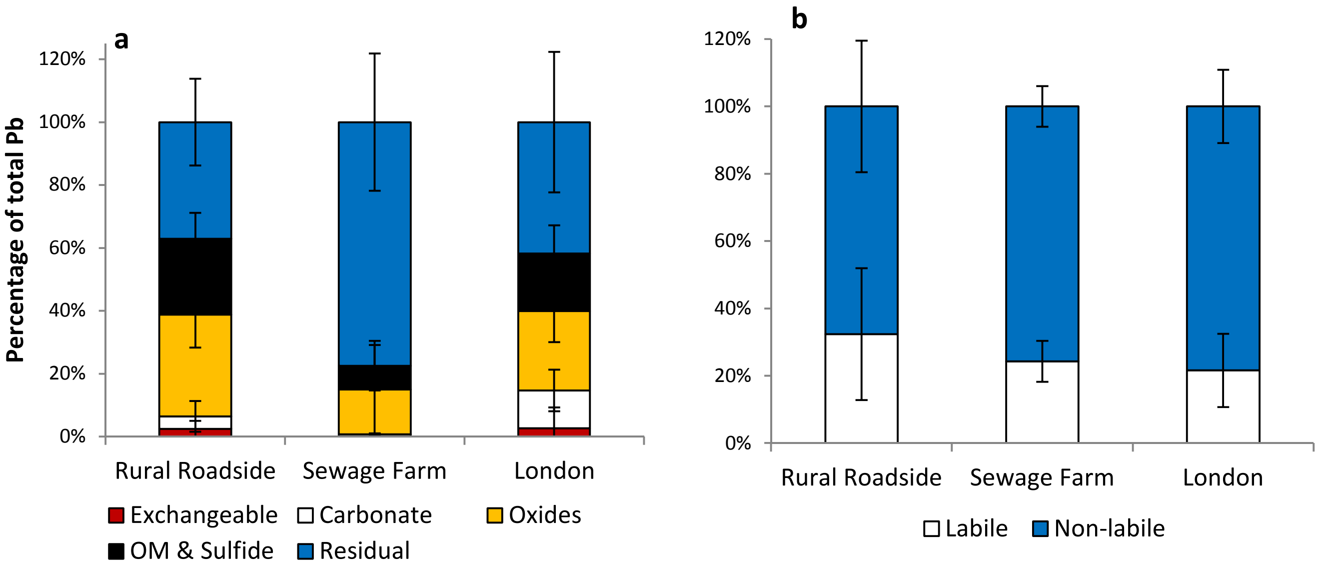
a
Percentage of total Pb
120%
100%
80%
60%
40%
20%
0%
Rural Roadside
Sewage Farm
London
🟥 Exchangeable
☐ Carbonate
🟨 Oxides
■ OM & Sulfide
🟦 Residual
b
120%
100%
80%
60%
40%
20%
0%
Rural Roadside
Sewage Farm
London
☐ Labile
🟦 Non-labile

Figure 4

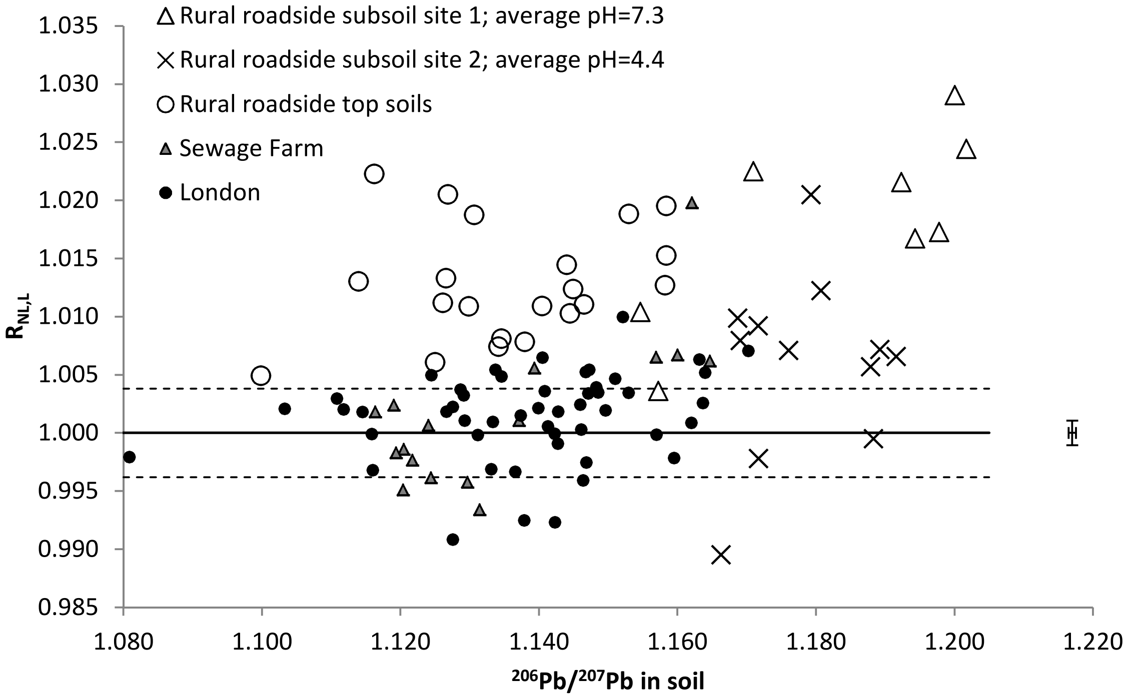
Rural roadside subsoil site 1; average pH=7.3
Rural roadside subsoil site 2; average pH=4.4
Rural roadside top soils
Sewage Farm
London
1.035
1.030
1.025
1.020
1.015
1.010
1.005
1.000
0.995
0.990
0.985
$R_{NL,L}$
1.080
1.100
1.120
1.140
1.160
1.180
1.200
1.220
$^{206}Pb/^{207}Pb$ in soil

Figure 5

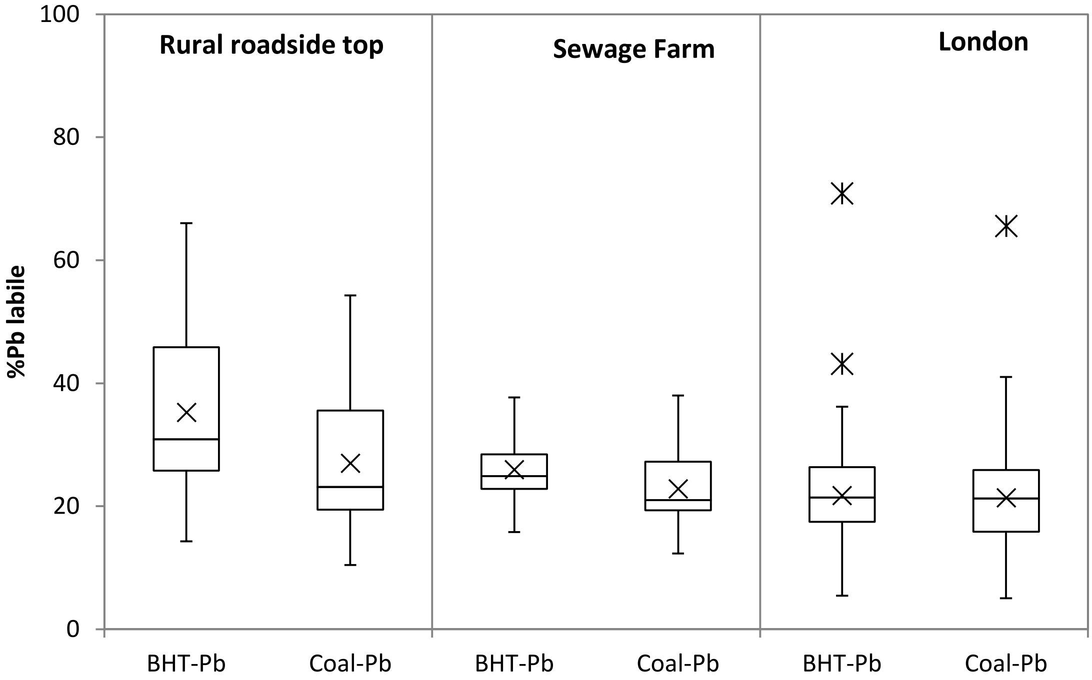
Rural roadside top
Sewage Farm
London
%Pb labile
100
80
60
40
20
0
BHT-Pb
Coal-Pb
BHT-Pb
Coal-Pb
BHT-Pb
Coal-Pb

Figure 6

Supplementary Information.

Lability of Pb in soil: Effects of soil properties and contaminant source.

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The following Tables provide additional details for the Rural Roadside, Sewage Farm and London archive soils, including; selected soil properties, Pb content and lability, and the isotopic ratios $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in both the whole soil and the labile pool of soil Pb.

Rural Roadside Soils

Soil	Depth	Soil pH	Total soil Pb content	E-value (Pb_E)	LOI	Available-P	Isotopic ratios: Total soil Pb		Isotopic ratios: Labile soil Pb	
Sample	(cm)	(0.01 M $CaCl_2$)	(mg kg^{-1})	(mg kg^{-1})	%	(mg kg^{-1})	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Site 1_1	0-20	6.10	47	12	8.8	4.2	1.138	2.419	1.131	2.408
Site 1_2	0-20	6.80	48	7	8.5	1.9	1.140	2.423	1.131	2.408
Site 1_3	0-20	6.73	48	8	8.8	4.4	1.144	2.424	1.133	2.411
Site 1_4	0-20	6.30	48	11	14.6	3.2	1.144	2.426	1.135	2.413
Site 1_5	20-26	6.95	39	3	5.8	3.0	1.157	2.433	1.154	2.430
Site 1_6	26-30	7.50	15	2	4.4	6.1	1.202	2.485	1.180	2.452
Site 1_7	30-40	7.46	60	0	4.2	3.9	1.166	2.443	1.178	2.445
Site 1_8	0-20	7.00	43	6	7.1	5.9	1.153	2.431	1.137	2.418
Site 1_9	20-26	7.12	63	2	5.3	2.0	1.171	2.449	1.150	2.430
Site 1_10	26-30	7.45	22	1	4.1	3.1	1.194	2.472	1.179	2.455
Site 1_11	30-40	7.57	18	0	4.1	5.2	1.192	2.468	1.170	2.444
Site 1_12	0-20	6.65	49	11	7.1	3.1	1.147	2.425	1.135	2.412
Site 1_13	20-26	6.70	41	5	5.7	2.4	1.155	2.432	1.143	2.420
Site 1_14	26-30	7.24	14	0	3.8	5.3	1.200	2.478	1.171	2.445
Site 1_15	30-40	7.43	15	0	3.6	6.4	1.198	2.477	1.179	2.462
Site 2_1	0-20	4.64	66	31	15.5	5.5	1.127	2.403	1.118	2.400
Site 2_2	0-20	4.27	66	20	13.0	12.2	1.127	2.404	1.119	2.396
Site 2_3	0-20	4.17	65	16	11.2	4.9	1.134	2.413	1.130	2.407
Site 2_4	0-20	4.13	62	18	11.4	20.8	1.130	2.409	1.123	2.399
Site 2_5	20-30	3.95	30	16	5.9	9.3	1.169	2.450	1.161	2.446
Site 2_6	30-40	3.92	25	12	4.9	2.0	1.176	2.460	1.169	2.446
Site 2_7	40-50	4.05	25	12	4.8	11.1	1.169	2.448	1.162	2.435
Site 2_8	50-60	4.25	24	12	5.2	3.8	1.172	2.456	1.162	2.434
Site 2_9	0-20	4.53	71	42	13.2	23.6	1.125	2.399	1.120	2.398
Site 2_10	20-30	4.35	161	104	7.6	11.4	1.172	2.448	1.174	2.453
Site 2_11	30-40	4.22	25	14	3.4	7.0	1.181	2.466	1.174	2.451
Site 2_12	40-50	4.19	20	8	3.0	2.5	1.188	2.478	1.183	2.463
Site 2_13	50-60	4.29	17	9	2.6	2.3	1.188	2.469	1.189	2.466
Site 2_14	0-20	5.32	109	37	16.1	9.4	1.145	2.518	1.134	2.416
Site 2_15	20-30	4.43	69	35	8.2	26.4	1.166	2.436	1.176	2.453
Site 2_16	30-40	4.76	44	18	5.1	14.3	1.179	2.457	1.160	2.444
Site 2_17	40-50	5.07	35	9	5.1	2.7	1.189	2.468	1.183	2.463
Site 2_18	50-60	5.15	20	8	4.9	5.4	1.192	2.470	1.185	2.465
Site 3_1	0-20	5.08	32	12	8.4	2.7	1.158	2.439	1.147	2.426
Site 3_2	0-20	4.74	33	14	8.5	3.9	1.158	2.441	1.147	2.423
Site 3_3	0-20	4.78	25	14	8.1	2.7	1.158	2.437	1.148	2.421
Site 4_N1	0-20	5.72	63	23	16.6	29.7	1.135	2.414	1.127	2.403
Site 4_N2	0-20	5.36	65	29	20.1	25.3	1.126	2.405	1.117	2.395
Site 4_N3	0-20	6.67	55	14	10.6	11.3	1.131	2.410	1.118	2.395
Site 4_S1	0-20	6.98	233	35	10.3	7.3	1.100	2.379	1.104	2.384
Site 4_S2	0-20	6.98	64	17	11.4	5.6	1.116	2.394	1.107	2.385
Site 4_S3	0-20	7.01	88	26	18.0	7.8	1.114	2.389	1.096	2.377

Sewage Farm soils

Soil Sample	Soil pH (0.01 M $CaCl_2$)	Total soil Pb content (mg kg^{-1})	E-value (Pb_E) (mg kg^{-1})	LOI %	Available-P (mg kg^{-1})	Isotopic ratios: Total soil Pb $^{206}Pb/^{207}Pb$	 $^{208}Pb/^{207}Pb$	Isotopic ratios: Labile soil Pb $^{206}Pb/^{207}Pb$	 $^{208}Pb/^{207}Pb$
6A	6.14	256	51	11.4	153.7	1.137	2.418	1.136	2.415
6B	6.57	324	88	10.8	190.4	1.130	2.411	1.133	2.416
6C	6.24	229	80	9.60	183.7	1.139	2.420	1.135	2.416
6D	6.19	282	101	11.8	141.8	1.131	2.412	1.136	2.418
7A	6.58	55	8	6.56	146.8	1.165	2.446	1.159	2.437
7B	6.74	102	19	6.38	128.5	1.157	2.435	1.151	2.431
8A	6.26	596	184	24.5	291.7	1.116	2.398	1.115	2.401
8B	5.86	631	147	23.8	379.9	1.120	2.401	1.122	2.402
8C	6.03	433	104	19.7	252.8	1.122	2.398	1.124	2.409
8D	6.08	683	145	25.5	314.9	1.119	2.395	1.117	2.397
8E	6.17	608	154	29.3	276.4	1.120	2.398	1.125	2.402
8T	6.47	712	137	25.2	182.4	1.119	2.398	1.121	2.400
9A	6.34	673	162	23.4	216.3	1.124	2.403	1.128	2.410
9B	6.53	511	124	19.5	126.1	1.124	2.403	1.123	2.411
10A	6.53	82	17	6.14	53.0	1.160	2.436	1.154	2.432
10B	6.44	68	12	5.42	69.1	1.162	2.439	1.144	2.434

London Soils

Soil Sample	Soil pH (0.01 M $CaCl_2$)	Total soil Pb content (mg kg^{-1})	E-value (Pb_E) (mg kg^{-1})	LOI %	Available -P (mg kg^{-1})	Isotopic ratios: Total soil Pb		Isotopic ratios: Labile soil Pb		Land use
						^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	
641188	7.30	1416	272	9.3	n.a.	1.138	2.420	1.145	2.426	Unproductive open space
641198	7.14	2237	123	6.7	25.8	1.142	2.425	1.142	2.425	Commercial and residential
641201	6.93	1006	190	10.0	n.a.	1.147	2.430	1.142	2.423	Commercial and residential
641221	6.98	641	111	9.7	1.4	1.164	2.446	1.161	2.446	Recreational area
641228	7.07	166	9	7.1	n.a.	1.149	2.429	1.145	2.425	Commercial and residential
650221	7.07	2762	432	15.4	80.8	1.170	2.452	1.163	2.450	Recreational area
650266	6.88	1864	270	9.5	28.2	1.150	2.434	1.148	2.427	Park
650324	6.98	2154	647	7.5	23.1	1.147	2.427	1.149	2.424	Domestic garden
650373	5.56	320	65	11.5	37.2	1.152	2.432	1.143	2.422	Minor metalled roads/verge
650436	7.07	1512	345	7.3	27.5	1.128	2.408	1.136	2.425	Domestic garden
650499	5.28	9044	6771	10.4	6.3	1.141	2.415	1.141	2.417	Park
650763	6.74	7212	2933	6.7	19.9	1.153	2.434	1.151	2.433	Domestic garden
650773	7.24	996	253	6.0	n.a.	1.133	2.418	1.133	2.416	Grass moor
650803	6.74	1828	536	9.2	12.0	1.143	2.425	1.144	2.422	Domestic garden
650903	5.98	193	51	8.3	2.3	1.140	2.420	1.138	2.417	School
650930	6.90	245	43	6.8	15.6	1.129	2.406	1.125	2.408	Domestic garden
650932	5.57	428	124	9.2	17.0	1.111	2.390	1.109	2.390	Major roads/verge
651006	6.69	213	43	7.9	n.a.	1.127	2.407	1.125	2.405	Minor metalled roads/verge
651013	6.92	2284	507	16.6	28.5	1.160	2.442	1.162	2.445	Deciduous woodland
651021	6.43	1731	255	17.5	207.4	1.116	2.397	1.119	2.400	Minor metalled roads/verge
651100	6.40	534	85	14.0	n.a.	1.137	2.414	1.140	2.423	Urban open space
651133	5.80	217	51	11.3	22.8	1.147	2.427	1.144	2.425	Park
651344	7.21	927	158	15.5	4.7	1.112	2.392	1.110	2.389	Domestic garden
651438	5.00	99	29	4.3	1.6	1.164	2.446	1.160	2.433	Grass moor
651654	3.29	162	62.5	17.3	14.7	1.141	2.421	1.137	2.419	Deciduous woodland
651871	6.74	919	311	7.3	4.1	1.134	2.414	1.130	2.407	Domestic garden
651954	6.75	1546	180	15.5	42.4	1.146	2.428	1.151	2.432	Domestic garden
651975	6.87	172	18	7.7	n.a.	1.125	2.406	1.120	2.401	Domestic garden
652570	6.74	1247	269	9.7	15.6	1.133	2.415	1.136	2.417	Domestic garden
652631	7.23	2587	668	10.0	5.9	1.157	2.440	1.157	2.440	Domestic garden
652900	6.66	237	45	10.1	20.2	1.129	2.409	1.128	2.412	Domestic garden
653407	6.29	301	75	10.3	n.a.	1.135	2.413	1.130	2.410	Domestic garden
653570	6.70	6600	1450	10.9	19.0	1.162	2.445	1.161	2.441	Recreational area
653588	4.95	187	74	5.7	1.9	1.151	2.428	1.148	2.426	Domestic garden
654281	6.62	1153	283	8.2	1.1	1.143	2.424	1.141	2.423	Domestic garden
654432	6.91	22572	3409	11.5	34.9	1.081	2.359	1.082	2.360	Unproductive open space
654464	7.20	507	100	9.0	14.6	1.146	2.426	1.146	2.426	Major roads/verge
654542	7.12	845	281	6.9	8.7	1.147	2.429	1.143	2.426	Domestic garden
654699	7.25	4056	729	16.9	6.3	1.146	2.429	1.144	2.427	Domestic garden
654950	6.75	779	183	5.3	11.5	1.129	2.409	1.126	2.410	Domestic garden
654976	7.05	3974	511	14.4	10.5	1.131	2.413	1.131	2.412	Commercial and residential
655376	6.76	115	23	5.5	n.a.	1.163	2.442	1.157	2.435	Graveyard
655522	6.78	123	14	5.0	19.8	1.137	2.419	1.136	2.417	Unproductive open space
655783	7.07	1377	323	6.4	3.8	1.115	2.394	1.113	2.393	Domestic garden
655952	6.00	3798	1363	5.7	1.2	1.142	2.429	1.148	2.430	Domestic garden
656000	6.44	4530	1488	12.0	37.9	1.103	2.386	1.102	2.382	Domestic garden
656271	7.31	420	68	6.1	13.5	1.128	2.404	1.125	2.406	Hospital Grounds
656359	6.61	205	51	9.9	n.a.	1.141	2.424	1.135	2.424	Urban open space
656463	6.03	952	188	12.4	n.a.	1.148	2.430	1.145	2.427	Park
656571	6.90	230	57	7.8	7.3	1.116	2.394	1.116	2.399	Domestic garden