Chemical and Isotopic Fractionation of Lead in the surface soils of Egypt

Waleed H. Shetaya[1,*], Ezzat R. Marzouk[2], Elham F. Mohamed[1], Elizabeth H. Bailey[3], Scott D. Young[3]

[1]Air Pollution Research Department, Environmental Research Division, National Research Centre, 33 El-Bohouth St., Dokki, Giza 12622, Egypt

[2]Division of Soil and Water Sciences, Faculty of Environmental Agricultural Sciences, Arish University, North Sinai, 45516, Egypt

[3]Division of Agricultural and Environmental Sciences, School of Biosciences, University of Nottingham, Sutton Bonington, Leicestershire LE12 5RD, UK

*Corresponding Author: Waleed H. Shetaya, +201012632019, wh.shetaya@nrc.sci.eg; waleed.shetaya@outlook.com

Abstract

Chemical fractionation via sequential extraction (SEP) combined with isotopic analysis of Pb was used to investigate the origins and reactivity of Pb in 66 topsoil samples collected from 12 different locations in Egypt. The total soil Pb concentrations (TPb) covered a wide range (~ 80 – 16,000 mg kg^{-1}), but were only elevated in four industrial and urban locations within Cairo and Alexandria. In all the other locations values of TPb were generally low and were close to the average crustal Pb concentration of 14 mg kg^{-1}. The largest Pb fraction in all soils, with the exception of two industrial locations, was the 'residual' fraction (38 – 63% of TPb) followed by Pb bound to 'organic' and 'metal oxide' phases. The Pb isotopic signatures ($^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$) of all samples in all SEP fractions were highly variable, suggesting a heterogeneous mix of Pb contamination sources; however, they aligned closely to a binary mixing line between geogenic and petrol Pb sources. There were similar patterns across all of the non-residual fractions with measureable data (F2 – F4) suggesting that the non-residual anthropogenic-Pb and geogenic-Pb have been assimilated into common pools within the soil. Binary and ternary source-apportionment models based on Pb isotopic ratios and abundances showed that the relative contribution of petrol-Pb and geogenic-Pb can be ascribed with reasonable certainty. However, the contribution of further sources can only be accounted for if the isotopic abundance of all end-members are known and are at the periphery of the soils dataset.

Keywords:

Environmental Pollution; Heavy Metals; Sequential Extraction; Stable Isotopes; ICP-MS

1. Introduction

Lead (Pb) is listed by the WHO as a chemical of major public health concern because of its high toxicity to living organisms (WHO, 2010). Long-term exposure of humans and animals to low levels of Pb through inhalation and/or ingestion may lead to a range of adverse clinical complications including neurological, cardiovascular and renal damage (Needleman and Bellinger, 1991). Geogenic Pb is composed of four stable isotopes: ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{204}Pb (1%); the only primordial isotope is ^{204}Pb, while the others are the fission products of uranium and thorium (Komárek et al., 2008). Therefore, the isotopic composition of Pb varies between different geological sources and this can be used as a tool to identify sources of pollutant Pb and to study its environmental fate (Veysseyre et al., 2001).

The large scale industrialization and urbanization of Egypt since the 1950's, in addition to the common practice of open air incineration of agriculture and other waste (Mohamed et al., 2015), were associated with the emission of large amounts of pollutants (including Pb) to the atmosphere. As a result, by the late 1980's and early 1990's Pb in the atmosphere of urban Egypt reached deleterious concentrations (Hassanien and Horvath, 1999, Nasralla and Ali, 1984, Shakour and El-Taieb, 1994). However, due to the introduction of the Environment Law in 1994 and the implementation of several environmental protection measures, such as relocating lead smelters and phasing out leaded petrol, the concentration of atmospheric Pb in urban Egypt reached safe levels by the end of the 1990's (Hassan et al., 2013, Hassanien et al., 2001, Rizk and Khoder, 2001, Safar and Labib, 2010). Nevertheless, most of the legacy anthropogenic-Pb which has been deposited on surface soils may not have been fully assimilated into the same soil fractions as geogenic-Pb. The bioavailability and mobility of contaminant Pb is therefore difficult to predict and it may be transferred to food and fodder crops and surface or ground waters more readily than geogenic-Pb.

Measuring total concentrations of heavy metals in soils may not always be a useful approach for risk assessment because, frequently, only a small proportion of soil metal is mobile under natural conditions (Tack and Verloo, 1995, Teutsch et al., 2001). It is therefore useful to estimate the labile, and potentially bioavailable, metal pool alongside the total concentration (Meers et al., 2007, Young et al., 2000). Sequential extraction protocols (SEP) have been used to investigate the chemical fractionation and

potential availability of heavy metals in soils. Possibly the most established SEP is the one developed by Tessier et al. (1979) which provides a guide to the likely chemical form of metals in soil or the adsorption phases with which the metals are associated. In the Tessier SEP, five operational fractions are identified: (F1) Exchangeable (metal fractions desorbed due to changes in the ionic composition of soil solution), (F2) Bound to carbonates (metal fractions reactive to pH fluctuations), (F3) Bound to Fe and Mn oxides (fractions that can be released by reduction of oxides under low Eh conditions), (F4) Bound to organic matter (metal fractions released under strong oxidizing conditions), and (F5) Residual (metal fractions held within the crystal structure of soil minerals).

The main aim of this work was to assess the current reactivity of Pb, and identify its origins, in Egyptian soils two decades after phasing out leaded petrol and implementing countermeasures to Pb pollution. This was achieved by studying the chemical fractionation and isotopic composition of Pb in some Egyptian surface soils and the soil properties likely to control them. A total of 66 soil samples that had been exposed to different degrees of Pb contamination were collected and characterized. Soil metals were chemically fractionated based on the SEP procedure of Tessier et al. (1979). The isotopic abundances of the four stable Pb isotopes were also measured in the SEP extracts by inductively coupled plasma mass spectrometry (ICP-MS). The objective was to assess the degree of assimilation of anthropogenic-Pb (mainly petrol-Pb) and geogenic Pb, into each soil Pb fraction (Shetaya et al., 2018). Moreover, multiple-sources models were used to try to identify the relative contribution of petrol, geogenic and industrial Pb sources, to different soil phases, based on their Pb isotopic signatures.

2. Materials and Methods

2.1. Soil sampling

Sixty six topsoil samples (0 – 20 cm) were collected, along a transect 0 - 100 m away from main roads, from 12 different locations in Egypt representing industrial, urban, agriculture and background sites (Table 1). Industrial locations included a cement factory (HE-I), inactive lead smelter (SH-I) and a major waste water treatment facility (CA-I). Urban soils were sampled around major motorways within the largest two urban conurbations in Egypt: Greater Cairo (CA-U and SH-U) and Alexandria (AX-U), in addition to Ismailia City (IS-U) and Assiut-Menya desert motorway (AM-U). Agriculture soils were collected from arable fields within Ismailia (IS-G) and Sharkia (SK-G) governorates. Reference (background) soils were sampled from 2 rural locations that were expected to have been exposed to minimal Pb deposition or discharge including sites in the Sinai Peninsula (SI-B) and Suez governorate (SZ-B). Soils were collected with a clean stainless steel trowel and sealed in plastic bags for transport.

Table 1. Sampling locations, codes and description. Letters I, U, G and B at the end of sample codes refer to the industrial, urban, agriculture and background nature of the sampling location, respectively.

Site nature	Location	Code	Number of Soil Samples	Coordinates
Industrial	Cairo - Helwan	HE-I (Cement Factory)	4	29.83N, 31.31E
	Cairo - Shubra	SH-I (Lead Smelter)	4	30.11N, 31.27E
	Cairo - Khanka	CA-I (Waste Water Treatment)	4	30.20N, 31.37E
Urban and Motorways	Cairo - Ring Road	CA-U	10	30.17N, 31.35E
	Alexandria	AX-U	5	31.15N, 29.97E
	Cairo - Shubra	SH-U	8	30.14N, 31.25E
	Ismailia	IS-U	8	30.59N, 32.27E
	Assiut - Minya	AM-U	4	27.93N, 30.57E
Agriculture	Ismailia	IS-G	4	30.68N, 32.05E
	Sharkia	SK-G	4	30.64N, 31.70E
Background	Sinai	SI-B	3	30.83N, 34.14E
	Suez	SZ-B	8	30.10N, 32.57E

2.2. Characterization of soil samples

Soil samples were air dried at room temperature and then sieved to <2 mm particle size; a fraction of each sample was finely ground with an agate ball mill (Retsch PM400). To measure soil pH, 5 g of the sieved soils, were suspended in 12.5 mL MQ water (18.2 MΩ cm) and shaken end-over-end for 30 min; pH was measured with a glass electrode allowing 5 min for equilibration. The organic carbon content of the soils was determined with a CN analyzer (Elementar VarioMax) after carbonates were removed with 50% HCl. Available phosphorus was extracted with 0.5 M sodium bicarbonate ($NaHCO_3$) solution

at pH 8.5 (Olsen et al., 1954) and assayed using a variation on the phosphomolybdate method (Drummond and Maher, 1995) by measuring absorbance in a 1 cm cell at 880 nm (CE 1011 spectrophotometer, Cecil Instruments). Amorphous (reactive) Fe, Al and Mn oxides were extracted from the finely ground soils by the citrate-bicarbonate-dithionite protocol developed by Kostka and Luther (1994); total Fe, Al and Mn concentrations in the filtered supernatants were assayed by ICP-MS. Total soil Pb (TPb) and total phosphorus (P) content were assayed by ICP-MS following digestion of 0.2 g finely ground soil samples in an acid mixture composed of Primar Plus™ or Analytical grade HF (2.5 mL; 40%), HNO_3 (2 mL; 70%), $HClO_4$ (1 mL; 70%) and H_2O (2.5 mL).

2.3. Sequential Extraction of Pb

All soil samples were extracted, in duplicate, by a sequential extraction procedure (SEP) adapted from that of Li and Thornton (2001) which was originally developed by Tessier et al. (1979) as shown below.

1- Exchangeable fraction (F1): 1 g soil samples (<2mm sieved) were extracted in polycarbonate centrifuge tubes for 20 min with 8 mL 0.5 M $MgCl_2$.
2- Bound to carbonate fraction (F2): the residues from F1 were extracted with 8 mL 1 M CH_3COONa (adjusted to pH 5 with CH_3COOH) for 5 hours.
3- Bound to iron and manganese oxides (F3): the residues from F2 were extracted with 10 mL 0.04 M hydroxylamine hydrochloride in 25% (v/v) CH_3COONa at 96^oC in a water bath for 6 h with occasional agitation.
4- Bound to organic matter (F4): the residues from F3 were extracted with 3 mL 0.02 M HNO_3 and 5 mL 30% H_2O_2 (adjusted to pH 2 with HNO_3) and tubes were heated to 85^OC in a water bath and maintained for 2 h with occasional agitation. Three mL H_2O_2 (adjusted to pH 2 with HNO_3) were then added and tubes were heated again for 3 h at 85^OC with intermittent agitation. After cooling, 5 mL 3.2 M CH_3COONa in 20% (v/v) HNO_3 were added and the tubes were agitated for 30 min.

Sample tubes were centrifuged after each extraction step and the supernatant solutions were syringe filtered and retained for multi-element and Pb isotopic analysis by ICP-MS; the remaining soil was retained for the next extraction step. Carry-over from the previous step was accounted for gravimetrically.

The concentration of Pb (mg kg^{-1}) in the residual phase (F5) was calculated by subtracting the summation of Pb concentrations (mg kg^{-1}) in the first four steps (F1-F4) from total soil Pb (TPb)

measured in the HF-$HClO_4$-HNO_3 acid soil digestates. For quality assurance, the recovery of the SEP procedure was tested on 11 samples in which the residual fraction was digested in a mixture of HF-$HClO_4$-HNO_3 for 19 h (Atkinson et al., 2011); 95 – 110 % recovery was achieved for Pb.

The individual isotopic concentrations of Pb in the residual fraction (F5) were obtained from the isotopic abundances (IA) of the total soil Pb and fractions F1 to F4. (Eq. 1).

$$^{X}Pb_{F5} = TPb\ ^{x}IA_{T} - (Pb_{F1}\ ^{x}IA_{F1} + Pb_{F2}\ ^{x}IA_{F2} + Pb_{F3}\ ^{x}IA_{F3} + Pb_{F4}\ ^{x}IA_{F4}) \quad (1)$$

where, $^{x}Pb_{F5}$ is the concentration (mol kg^{-1}) of a ^{x}Pb isotope (^{204}Pb, ^{206}Pb,^{207}Pb or ^{208}Pb) in the residual fraction (F5); TPb and $Pb_{F1,\ F2,\ F3\ or\ F4}$ are the total soil and non-residual fraction (F1, F2, F3 or F4) concentrations of Pb (mol kg^{-1}), respectively; $^{x}IA_{T}$ and $^{x}IA_{F1,\ F2,\ F3\ or\ F4}$ are the total soil and non-residual (F1, F2, F3 or F4) isotopic abundances of ^{x}Pb.

No attempts were made to investigate artificial isotopic fractionation of Pb during the sequential extraction procedure. However, heavy atoms e.g. Pb isotopes with very small fractional differences in atomic mass would not support mass-dependent fractionation during chemical processes on any significant level (Bacon et al., 2006, Komárek et al., 2008, Lee and Yu, 2016, Monna et al., 1997). This was also found to be true for even much lighter elements e.g. Fe and Cu with relatively large fractional differences in atomic mass (Roebbert et al., 2018).

2.4. Elemental and isotopic analyses by ICP-MS

Concentrations of Pb, P, Fe, Al and Mn in soil digestates and extracts were determined using ICP-MS (Model iCAPQ; Thermo Fisher Scientific GmbH, Bremen, Germany) as described in Shetaya et al. (2018). Briefly, samples and multi-element calibration standards (Certiprep/Fisher, UK) were diluted in 2% Primar Plus™ grade HNO_3 and measured in triplicate. Internal standards, including Rh and Ir in 2% HNO_3 were introduced to the sample stream via a t-piece. Limits of detection (LOD) were calculated from analysis of 16 blanks. Montana soil reference material (NIST 2711) was used for quality assurance and 96 ± 4% average recovery was achieved across all measured elements.

The ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb isotopic abundances in all samples were measured with a short dwell time of 2.5 ms and a total of 10,000 sweeps were used to mitigate the effects of 'plasma flicker' and achieve a high level of precision. For *internal* mass bias correction, a Tl solution (10 μg L^{-1}), was introduced directly to the internal standard line and the variations in the $^{203}Tl/^{205}Tl$ ratios were used to

correct shifts in Pb isotopic ratios (Blum and Bergquist, 2007, Shetaya et al., 2017). In addition, drift in mass bias was corrected *externally* by repeatedly assaying the certified Pb isotope standard NIST-981 and using linear interpolation to correct CPS ratios to isotopic ratios for samples (Atkinson et al., 2011, Marzouk et al., 2013b). To reduce polyatomic interferences from ^{92}Os-^{16}O (208 mass), ^{193}Ir-^{14}N (207 mass) and ^{205}Tl-H (206 mass), the ICP-MS was used in the kinetic energy discrimination (KED) mode with helium as a collision gas. The isobaric interference to ^{204}Pb from ^{204}Hg was corrected by determining intensity at m/z = 202 (^{202}Hg) and, from expected isotopic ratios, subtracting the intensity (CPS) attributed to ^{204}Hg within the instrument software. However, in practice the overall contribution of ^{204}Hg to the intensity at m/z 204 was trivial and the average ratio of ^{204}Hg/^{204}Pb in the measured soil factions was estimated as 0.0033. All solutions were diluted to ensure that the detector operated in 'pulse-counting' mode; data were rejected and sample analysis repeated, after appropriate dilution, if the detector 'tripped' to an analogue measurement in response to large count rates, typically > 1.5 million counts s^{-1} for the ^{208}Pb isotope (Marzouk et al., 2013a).

2.5. Binary and ternary source apportionment

Frequently, two identifiable sources of Pb are apparently present in soil, arising from (i) the petrol additive tetra-methyl Pb ('Petrol-Pb') and (ii) the underlying parent material ('Geogenic-Pb'). As a first approximation, we can then add a (single) third source, which is considered to originate from a range of industrial and power generation sources ('Industrial'). This may be similar to the Geogenic-Pb if there is a local source of coal or Pb ore.

The proportional contribution (%) of any two Pb sources (e.g. Petrol, Geogenic or Industrial), to total soil Pb (TPb) or total Pb concentration in any of the SEP fractions, was calculated from Eq. 2 (Lee and Yu, 2016, Mao et al., 2014).

$$\%Pb_A = \frac{IR_T - IR_B}{IR_A - IR_B} \times 100 \qquad (2)$$

where, $\%Pb_A$ is the proportion of TPb from source A; IR_A and IR_B are the Pb isotopic ratios (^{206}Pb/^{207}Pb or ^{208}Pb/^{207}Pb) of sources A and B, respectively; IR_T is the measured Pb isotopic ratio (^{206}Pb/^{207}Pb or ^{208}Pb/^{207}Pb) of the whole soil or any individual SEP fraction (F1 – F5).

The relative contribution of three different end-member (pure) sources was modeled using Eq. 3 and Eq. 4 adapted from Cheng and Hu (2010) and Luo et al. (2015).

$$\%Pb_A + \%Pb_B + \%Pb_C = 100\% \quad (3)$$

where, $\%Pb_A$, $\%Pb_B$ and $\%Pb_C$ are the proportions of Pb from sources A, B and C to TPb or total Pb in any of the five SEP fractions.

$$^{x}IA_T = \%Pb_A\ ^{x}IA_A + \%Pb_B\ ^{x}IA_B + \%Pb_C\ ^{x}IA_C \quad (4)$$

where, $^{x}IA_T$ is the isotopic abundance of a ^{x}Pb isotope (^{204}Pb, ^{206}Pb,^{207}Pb or ^{208}Pb) in soil or individual SEP fractions; $^{x}IA_A$, $^{x}IA_B$ and $^{x}IA_C$ are the isotopic abundances of the same isotope in the pure sources A, B and C.

The 'Solver' function in the software package Excel 2017 was used to minimize the residual standard deviation (RSD) between the modelled and measured isotopic abundances of all soils simultaneously. The operation was performed independently for total soil Pb (TPb) and for Pb in all of the five SEP fractions (F1 – F5).

The anthropogenic-Pb isotopic distribution, in any soil phase (total or F1 – F5), was calculated by subtracting geogenic-Pb from total Pb (TPb) assuming uniform distribution of geogenic-Pb across the studied terrains (Eq. 5).

$$^{x}Pb_{AT} = Pb_T\ ^{x}IA_T - Pb_G\ ^{x}IA_G \quad (5)$$

where, $^{x}Pb_{AT}$ is the anthropogenic concentration (mol kg^{-1}) of an isotope (^{204}Pb, ^{206}Pb,^{207}Pb or ^{208}Pb), in any soil phase (total or F1 – F5); Pb_T and Pb_G are the total soil Pb and geogenic-Pb concentrations (mol kg^{-1}), respectively (in the respective soil fraction); $^{x}IA_T$ and $^{x}IA_G$ are the isotopic abundances in total and geogenic Pb, respectively.

These approaches only present a simplified image of a complex geochemical system where soil Pb is a mixture of numerous sources. However, potentially they provide a means of quantifying the relative contribution of the two or three major Pb sources to each soil SEP fraction.

3. Results and Discussion

3.1. Soil Properties

Key soil parameters are shown in Table 2. Total soil Pb concentrations (TPb) in the studied locations are discussed in detail by Shetaya et al. (2018). Briefly, TPb was greatest at the lead smelter site (SH-I), peaking at ~ 31,000 mg kg^{-1} with an average of ~ 16,200 mg kg^{-1}. This was followed by the industrial location CA-I (waste water treatment) and the urban locations CA-U and AX-U within Cairo and Alexandria with average TPb values of 171, 160, and 82.6 mg kg^{-1}, respectively. However, significant difference ($p<0.05$; 2 sample t-test; Minitab 17) were only found between CA-I and AX-U locations. All other non-background locations showed relatively low TPb levels with an average of 17 mg kg^{-1} which is slightly above the Pb average crustal abundance of 14 mg kg^{-1} (Emsley, 2011) indicating generally low levels of Pb contamination in the soils of Egypt. All soils, with the exception of a few individual samples, were alkaline and organic-poor (pH 8 and 1% SOC on average) likely due to the calcareous and sandy marine origins of Egyptian soils (Shaheen, 2009).

282 **Table 2.** Soil parameters including total soil Pb (TPb), soil pH, organic content (%SOC), available P (Olsen) and total P, and reactive Al, Mn and Fe
283 oxides; n = number of samples in each location and NA = not available (not measured). Letters I, U, G and B at the end of sample codes refer to
284 the industrial, urban, agriculture and background nature of the sampling location, respectively.

Location	n	Total Pb (TPb) *(mg kg^{-1})*				pH		SOC *(%)*		Available P *(mg kg^{-1})*		Total P *(g kg^{-1})*		Al_2O_3 *(g kg^{-1})*		MnO_2 *(g kg^{-1})*		Fe_2O_3 *(g kg^{-1})*	
		Mean	SD	Max.	Min.	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Industrial																			
HE-I	4	19.5	2.83	23.5	16.9	9.7	1.3	0.95	0.19	27.9	7.47	0.24	0.06	1.08	0.77	0.02	0	3.21	1.01
SH-I	4	16201	15788	30808	2494	8	0.2	2.31	2.52	85.3	20.5	1.06	1.17	2.8	2.47	0.08	0.01	5.62	1.98
CA-I	4	171	14.2	184	157	8.3	0	3.48	0.61	215	23.1	0.14	0.11	2.5	1.35	0.23	0.33	4.6	5.68
Urban																			
CA-U	10	160	185	459	8.04	8.2	0.2	0.90	0.35	13.4	12.3	0.63	0.24	2.29	0.81	0.6	0.32	7.61	3.32
AX-U	5	82.6	94.6	247	18.3	7.8	0.7	3.20	1.92	NA	NA	0.4	0.05	30.5	8.68	0.59	0.12	30.3	9.84
SH-U	8	25.4	10.3	37.6	11.9	7.8	0.2	0.96	0.79	39.6	43.1	1.13	0.46	2.53	0.18	0.6	0.08	13.1	4.92
IS-U	8	18.7	11.1	40.5	6.47	7.9	0.2	0.52	0.50	13.2	10.7	0.28	0.15	1.31	0.32	0.09	0.05	2.67	0.79
AM-U	4	10.3	2.56	12	5.81	8.5	0.5	0.11	0.06	1.8	0.34	0.33	0.05	1.15	0.5	0.01	0.02	2.26	0.62
All data	35	68.5	119	459	5.81	8	0.4	1.33	1.49	18.6	25.5	0.57	0.39	9.09	13.3	0.44	0.3	12.9	12.1
Agriculture																			
IS-G	4	6.66	0.26	6.97	6.35	8.5	0.2	0.15	0.07	5.14	6.83	0.27	0.17	0.73	0.17	0.03	0.01	1.09	0.72
SK-G	4	11	0.73	11.6	10.2	7.8	0	0.29	0.04	9.24	5.95	0.59	0.04	2.03	0.03	0.21	0	3.51	0.05
All data	8	8.78	2.31	11.6	6.35	8.1	0.4	0.22	0.09	7.19	5.74	0.43	0.21	1.38	0.76	0.12	0.11	2.30	1.46
Background																			
SI-B	3	9.87	4.63	15.1	6.34	7.9	0.2	2.21	3.36	NA	NA	0.52	0.34	17.1	4.65	0.24	0.13	10.4	5.36
SZ-B	8	3.37	1.60	5.84	1.90	7.8	0.1	0.05	0.04	NA	NA	1.19	1.39	1.5	0.43	0.03	0.05	1.31	0.44
All data	11	4.96	3.21	15.1	1.90	8	0.2	1.07	1.53	NA	NA	0.68	0.75	15.5	12.8	0.15	0.11	7.38	5.38

285

286

287

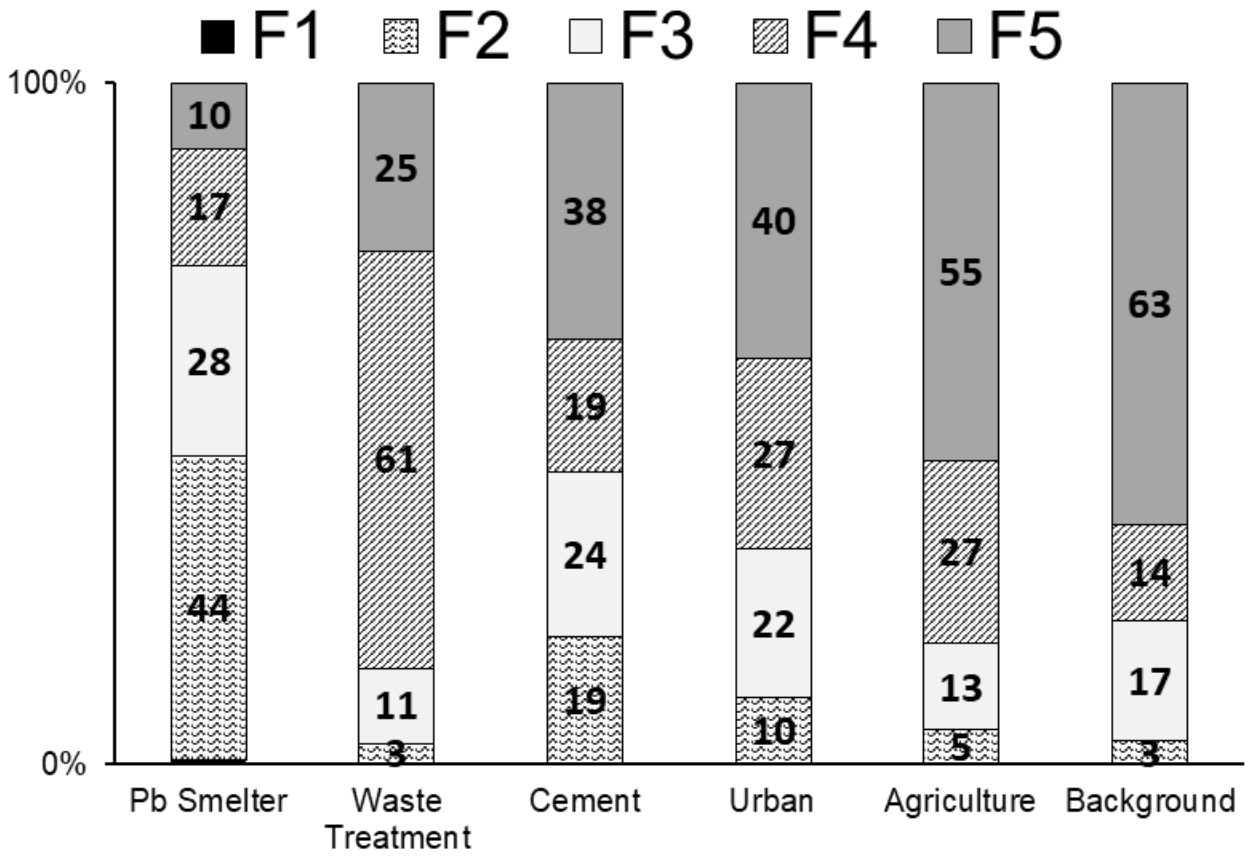
3.2. Geochemical fractions of Pb determined by sequential extraction (SEP)

The proportion (%) of residual (non-reactive) Pb fraction (F5-Pb) was highest in the background sites followed by agriculture, urban and industrial locations, respectively (Figure 1 and Table A.1); on average, F5-Pb was inversely proportional to TPb (R^2 = 0.97; power relationship) (Figure A.1). Since the residual fraction (F5) represents Pb in primary and secondary minerals, e.g. galena (PbS) and pyromorphite ($Pb_5(PO_4)_3Cl$), that hold Pb within their crystal structure (Cotter-Howells and Thornton, 1991, Tessier et al., 1979), the exchange of F5-Pb with other soil phases is likely to be extremely slow and limited. This means that any anthropogenic inputs of Pb will be almost exclusively distributed among the non-residual phases (F1-F4) and that F5-Pb is mostly geogenic in origin. As the anthropogenic input of Pb increased (higher TPb), Pb in F5-Pb proportionally decreased resulting in the inverse relationship between TPb and F5-Pb. This is also supported by the fact that F5-Pb was the largest fraction in the background, agriculture, urban and cement factory locations (relatively low TPb) as opposed to the lead smelter (SH-I) and waste water treatment (CA-I) sites (highest TPb) where the percentages of F5-Pb were only 10% and 25% of TPb, on average, respectively.

The second and third largest fractions in all soils, with the exception of SH-I and CA-I, were, respectively, F3 (bound to metal oxides) and F4 (bound to organic). In alkaline soils, these two phases are likely to be the most important non-residual phases for retention of heavy metals (Atkinson et al., 2011, Li and Thornton, 2001, Tipping et al., 1986)

Location CA-I (waste water treatment) was dominated by F4-Pb (61%) possibly due to its markedly elevated organic content (3.5% SOC) in comparison to all other locations ($P<<0.005$; paired t-test) (Table 1). The largest fraction (44%) in location SH-I (lead smelter) was F2 (bound to carbonates). Li and Thornton (2001) also reported high F2-Pb levels (24 – 55%) in mining and smelting sites with substantially elevated TPb concentrations. Although, in mining locations, the high concentration of F2-Pb was attributed to the sheer abundance of the thermodynamically favored cerussite ($PbCO_3$) (Brookins, 2012), the large F2-Pb fraction in smelting sites may be due to the ability of CH_3COONa to dissolve PbO (Clevenger et al., 1991) which is a primary emission product of lead smelters (Foster and Lott, 1980). Moreover, Murphy (1992) found that $PbCO_3$ is one of the major weathering products in the soils around old smelting facilities.

315 The exchangeable fraction (F1) was only detectable in locations SH-I (1%) and CA-U (0.3%) (Figure 1 and
316 Table A.1). In alkaline soils Pb ions are strongly adsorbed and exchangeable Pb (F1-Pb) is likely to be a
317 very minor fraction (McBride, 1994, Sparks, 2003). However, when Pb levels are largely elevated, such as
318 is location SH-I (lead smelter), Pb ions will occupy progressively weaker sorption sites and so the proportion
319 of exchangeable Pb increases (Degryse et al., 2009, Sastre et al., 2006, Tongtavee et al., 2005). In
320 addition, $PbSO_4$, which is an important component of Pb smelter emissions (Clevenger et al., 1991, Foster
321 and Lott, 1980), may be initially incorporated into the exchangeable phase (F1) (Harrison et al., 1981).



322

323 **Figure 1.** Proportion (%) of Pb estimated in each of the five SEP fractions: F1 (exchangeable), Fe (bound
324 to carbonates), F3 (bound to metal oxides), F4 (bound to organic matter) and F5 (residual). Industrial
325 locations (Pb smelter, waste water treatment, and cement factory) are displayed independently due to their
326 different nature, agriculture and background sites are grouped together by site type. Numbers inside the
327 boxes represent the proportion (%) of each fraction to total soil Pb (TPb). Detailed data is displayed in Table
328 A.1.

329

3.3. Isotopic fractionation of Pb in soil phases

The isotopic ratios (IR) $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ measured or calculated in all SEP fractions (F1 – F5) are shown in Table 3 for all sampling locations. Note that F1-Pb was below detection limit in most samples and the calculation of F5-Pb IR (Eq. 1) produced reliable results only in soils where F5-Pb concentrations were ≥ 40% of TPb (c. > 50% of the samples) due to compounded errors in Eq. 1 where F5 was a minor constituent of TPb. Shetaya et al. (2018) reported that petrol-Pb (IR of 1.11 ± 0.002 for $^{206}Pb/^{207}Pb$ and 2.385 ± 0.002 for $^{208}Pb/^{207}Pb$) and geogenic-Pb (IR values of 1.212 ± 0.004 for $^{206}Pb/^{207}Pb$ and 2.482 ± 0.006 for $^{208}Pb/^{207}Pb$) are likely to be the two major sources of Pb in the soils of Egypt. Figure 2 clearly shows that the IRs $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ for all soils in all five SEP fractions are aligned closely to a binary mixing line between the isotopic signatures of the two end members (nominally 'petrol' and 'geogenic'). This suggests that these are the two major contributors to both non-residual and residual Pb fractions in the studied soils with only minor contributions from other potential sources contributing to scattering of the data around the binary line. This agrees with the findings of other studies that adopted the binary plot approach to resolve the likely major sources of Pb using the isotopic signatures of two 'pure' end members. For example, Monna et al. (1997) found that the Pb isotopic signatures of various environmental samples from UK and France were aligned around a mixing line between geogenic-Pb ($^{206}Pb/^{207}Pb \approx 1.17 – 1.19$) and petrol-Pb ($^{206}Pb/^{207}Pb \approx 1.05 – 1.08$). Chenery et al. (2012), Izquierdo et al. (2012) and Mao et al. (2014) also found that the Pb isotopic signatures of their investigated UK samples (soils, plants and aerosols) indicated an almost exclusive mixing between petrol-Pb ($^{206}Pb/^{207}Pb \approx 1.06 – 1.09$) and Pb from indigenously mined coal ($^{206}Pb/^{207}Pb \approx 1.16 – 1.21$). This seems to be a universal pattern at least in the European environments where the Pb signatures of environmental samples align around a binary line between geogenic-Pb ($^{206}Pb/^{207}Pb \approx 1.22 – 1.24$) and petrol-Pb ($^{206}Pb/^{207}Pb \approx 1.12 – 1.14$) (Komárek et al., 2008).

To investigate the isotopic distribution of Pb in relation to their SEP phase, the $^{206}Pb/^{207}Pb$ IR of all soils were plotted against total soil Pb (TPb) (Figure 3). In all five SEP fractions (F1- F5), Pb isotopic signatures formed discrete clusters according to their origins. Soils from the background location (SZ-B) were grouped very close to the geogenic-Pb isotopic ratio while soils from urban (TPb < 100 mg kg^{-1}), agriculture and cement factory locations were distributed between geogenic-Pb and petrol-Pb indicating broadly similar

contributions from both sources. Waste treatment locations and urban soils with TPb > 100 mg kg^{-1} were more inclined toward the petrol-Pb isotopic signature. In all soil fractions, locations with higher values of TPb were inclined toward the petrol signature of $^{206}Pb/^{207}Pb$.

Lead smelter (SH-I) soils also formed clusters with $^{206}Pb/^{207}Pb$ IRs that fell between those of geogenic-Pb and petrol-Pb in all four non-residual Pb fractions (Figure 3 A – D); however, given the much greater Pb concentrations in these soils, it is likely that the smelter would generate a unique $^{206}Pb/^{207}Pb$ signature and the contribution of geogenic-Pb and petrol-Pb at this location was probably trivial in comparison. This is supported by the fact that the Pb smelting facility that was located in this site was recycling scrap lead from various industries and sources e.g. old batteries, and most of this recycled Pb was originally imported rather than indigenously mined (Labib et al., 2003, Safar et al., 2014). The measured $^{206}Pb/^{207}Pb$ ratios (1.151 – 1.155) in SH-I site, in all non-residual phases, agreed well with the average 'industrial' $^{206}Pb/^{207}Pb$ ratios (1.147 - 1.160) reported by Monna et al. (1997).

Most samples showed almost identical patterns across the non-residual (F2, F3 and F4) phases (Figure 3 B – D). Bacon et al. (2006) and Lee and Yu (2016) also reported homogenous distributions of Pb IRs among non-residual soil phases in spite of distinct Pb isotopic signatures between Pb sources, soil depths and sampling locations. In our work, the apparent consistency of Pb isotopic signatures among non-residual phases is also statistically supported (paired t-test; Minitab 17) by insignificant differences between $^{206}Pb/^{207}Pb$ or $^{208}Pb/^{207}Pb$ ratios of the non-residual fractions, with the single exception of $^{206}Pb/^{207}Pb$ when comparing F3 and F4 (Table A.2). Comparison with F1-Pb and F5-Pb isotopic signatures could not be discussed with confidence due to the limited number of valid results; however, the few available data points (Figure 3 A and E) appear to resemble those of F2, F3 and F4 (Figure 3 B - D).

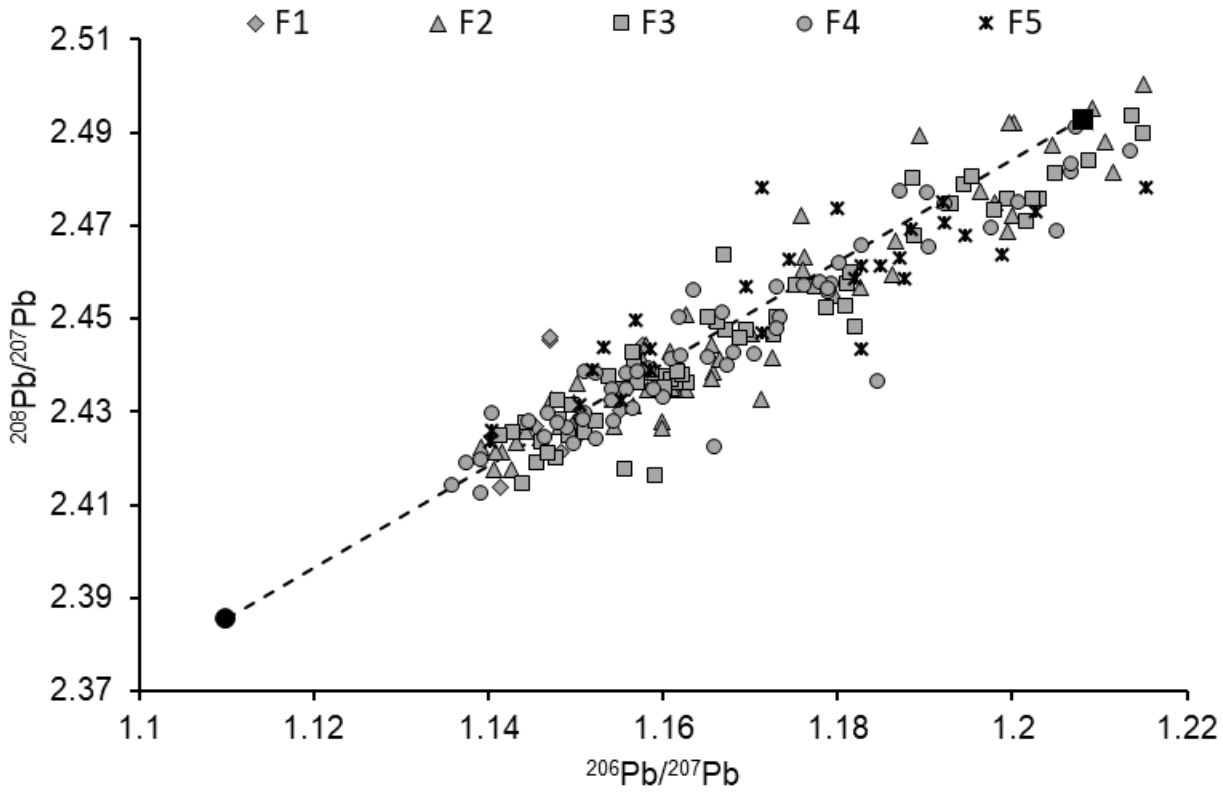
The similarity of isotopic signatures across the fractions (F1 - F5) may indicate that Pb from anthropogenic sources (petrol and other) may have no preferential affinity for specific non-residual or residual soil phases and has been sufficiently labile to be assimilated into common pools with geogenic-Pb due to prolonged contact with the soil. However, isotopic homogeneity between fractions should be interpreted carefully because differences in the Pb isotopic abundances between SEP fractions may only be measurable if a given Pb source, with a distinct isotopic signature, had a high chemical affinity for specific soil phases

385 resulting in limited mixing between fractions. This would depend on both the Pb source speciation and the
386 soil chemical properties. Our collection of soils fell within a relatively narrow range of properties (Table 2)
387 thus potentially contributing to the apparent Pb isotopic homogeneity between the non-residual (and
388 possibly residual) fractions. Furthermore, sequential extraction procedures are prone to re-adsorption
389 effects which may have contributed to the similarity in the Pb isotopic patterns between the non-residual
390 fractions. *Mass-dependent* fractionation of Pb between different soil phases is likely to be very small due
391 to the high mass of the Pb isotopes and would not be detectable by a quadrupole ICP.

392

Table 3. Isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) measured in the four SEP fractions: F1= exchangeable, F2=bound to carbonates, F3=bound to Fe/Mn reactive oxides, F4=bound to organic matter, F5=Resdiual. n = number of samples in each location, SD= standard deviation between soils sampled form the same site, ND = not detectable (below detection limit), NM= not measured and NA = not applicable.

Sampling Locations	n	F1				F2				F3				F4				F5			
		$^{206}Pb/^{207}Pb$		$^{208}Pb/^{207}Pb$		$^{206}Pb/^{207}Pb$		$^{208}Pb/^{207}Pb$		$^{206}Pb/^{207}Pb$		$^{208}Pb/^{207}Pb$		$^{206}Pb/^{207}Pb$		$^{208}Pb/^{207}Pb$		$^{206}Pb/^{207}Pb$		$^{208}Pb/^{207}Pb$	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Industrial																					
HE-I	4	ND	NA	ND	NA	1.159	0.011	2.441	0.008	1.161	0.012	2.437	0.013	1.161	0.014	2.437	0.014	1.149	0.013	2.431	0.011
SH-I	4	1.151	0.008	2.425	0.009	1.155	0.016	2.435	0.013	1.152	0.006	2.421	0.007	1.151	0.005	2.433	0.006	NA	NA	NA	NA
CA-I	4	ND	NA	ND	NA	1.141	0.001	2.419	0.002	1.144	0.002	2.425	0.002	1.139	0.001	2.420	0.007	NA	NA	NA	NA
Urban																					
CA-U	10	1.148	0.008	2.424	0.020	1.169	0.023	2.453	0.029	1.167	0.021	2.444	0.022	1.164	0.021	2.443	0.021	1.183	0.017	2.457	0.014
AX-U	5	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA
SH-U	8	ND	NA	ND	NA	1.161	0.004	2.437	0.006	1.166	0.006	2.444	0.008	1.163	0.011	2.443	0.009	1.257	0.143	2.822	0.430
IS-U	8	ND	NA	ND	NA	1.156	0.007	2.433	0.006	1.156	0.006	2.435	0.009	1.158	0.005	2.437	0.010	1.169	0.017	2.460	0.019
AM-U	4	ND	NA	ND	NA	1.199	0.014	2.474	0.013	1.202	0.015	2.483	0.011	1.190	0.019	2.467	0.020	1.165	0.021	2.450	0.017
All data	35	NA	NA	NA	NA	1.167	0.019	2.446	0.022	1.168	0.019	2.447	0.020	1.166	0.018	2.445	0.017	1.186	0.051	2.506	0.173
Agriculture																					
IS-G	4	ND	NA	ND	NA	1.172	0.013	2.448	0.028	1.172	0.010	2.451	0.010	1.172	0.016	2.457	0.021	1.162	0.013	2.445	0.013
SK-G	4	ND	NA	ND	NA	1.174	0.011	2.453	0.009	1.176	0.005	2.455	0.006	1.176	0.004	2.453	0.007	1.181	0.001	2.466	0.011
All data	8	ND	NA	ND	NA	1.173	0.011	2.450	0.020	1.174	0.007	2.453	0.008	1.174	0.011	2.455	0.015	1.168	0.014	2.452	0.016
Background																					
SI-B	3	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA	NM	NA
SZ-B	8	ND	NA	ND	NA	1.203	0.006	2.486	0.011	1.200	0.005	2.477	0.004	1.192	0.019	2.462	0.025	1.196	0.019	2.461	0.012
All data	11	NA	NA	NA	NA	1.203	0.006	2.486	0.011	1.200	0.005	2.477	0.004	1.192	0.019	2.462	0.025	1.196	0.019	2.461	0.012



399

400 **Figure 2.** Isotopic ratios ($^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$) of the F1, F2, F3, F4 and F5 SEP fractions in all soil
401 samples. Petrol-Pb (black circle) and geogenic-Pb (black square) signatures are also shown as two
402 possible end members; the dashed line is the mixing line between them. F5 fraction signatures are shown
403 for samples where F5-Pb was ≥ 40% of total soil Pb (TPb).

404

405

406

407

408

409

410

411

412

413

414

415

416

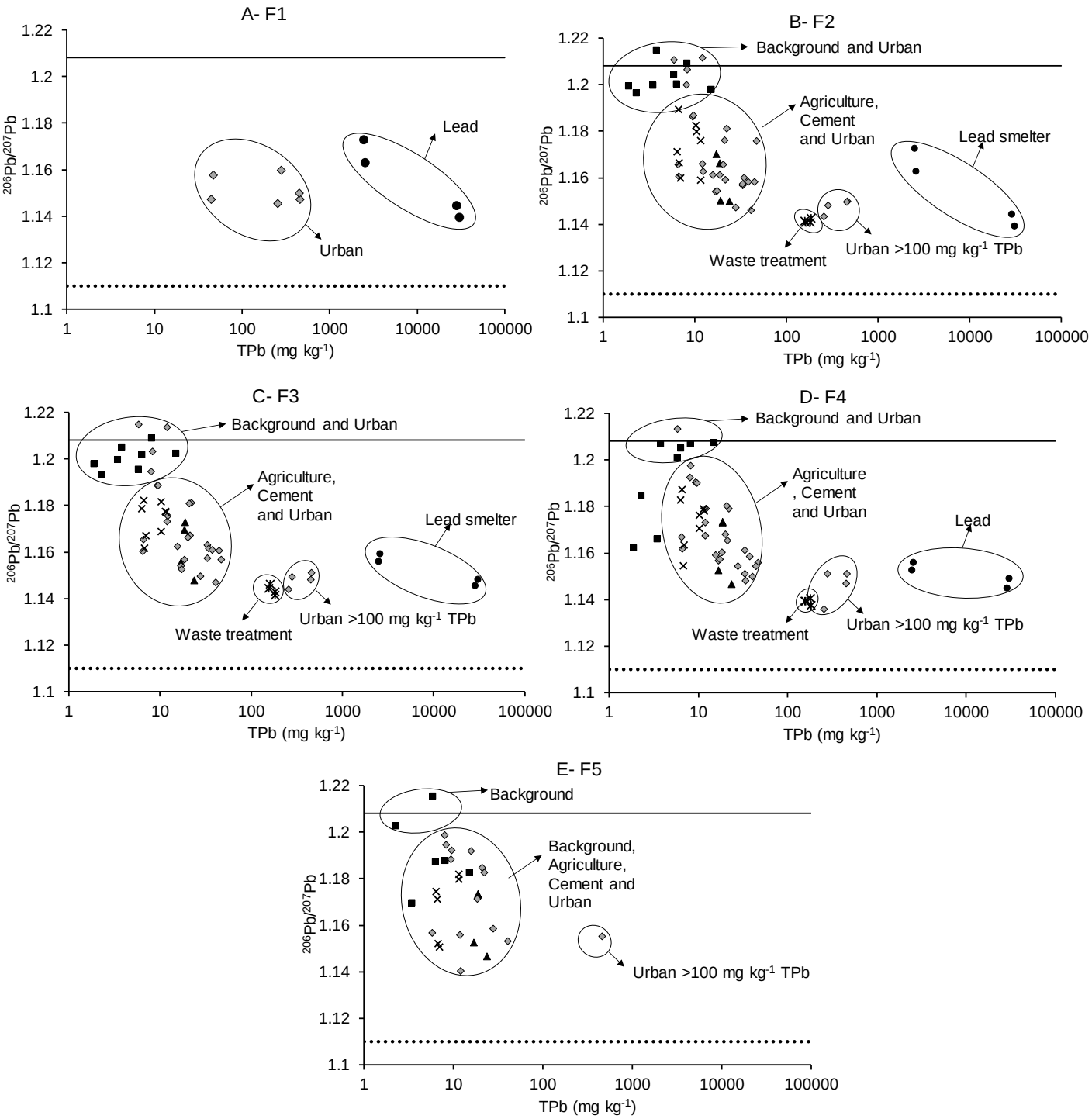


Figure 3. Isotopic ratios $^{206}Pb/^{207}Pb$ vs total soil Pb (TPb; mg kg^{-1}) for all SEP fractions: F1 (A), F2 (B), F3 (C), F4 (D) and F5 (E). Sampling locations included lead smelter (black circles), waste water treatment (asterisks), urban (grey diamonds), agriculture (crosses), cement factory (black triangles) and background (black squares). Solid and dotted lines represent the $^{206}Pb/^{207}Pb$ ratios of geogenic-Pb and petrol-Pb, respectively.

3.4. Relative contribution of geogenic and petrol Pb pools

The proportional contributions (%) of petrol-Pb and geogenic-Pb in non-residual fractions F2, F3 and F4 in all soils, except SH-I (lead smelter) soils, were estimated from Eq. 2. Figure 4 shows that the greatest proportion of petrol-Pb was found in the industrial location CA-I (wastewater treatment) with 66, 68 and 70% of Pb in fractions F3, F2 and F4, respectively. This was followed by the cement factory (HE-I) and urban locations where there were almost equal proportions of petrol-Pb and geogenic-Pb. Agricultural locations were characterized by low petrol-Pb contributions (34 – 36%) to all fractions while background locations were dominated (84 – 91%) by geogenic-Pb. Overall, higher total soil Pb (TPb) concentrations resulted in a greater proportion of petrol-Pb in all fractions.

It appears from Figure 4 that the proportion of Petrol-Pb was consistent within all fractions. As mentioned previously (section 3.3), measurable differences in the distribution of anthropogenic-Pb between soil phases would require a high affinity of the emitted Pb for one particular phase and very slow mixing between fractions. However, the evidence from this study suggests that the different sources of Pb have effectively mixed between (SEP) fractions.

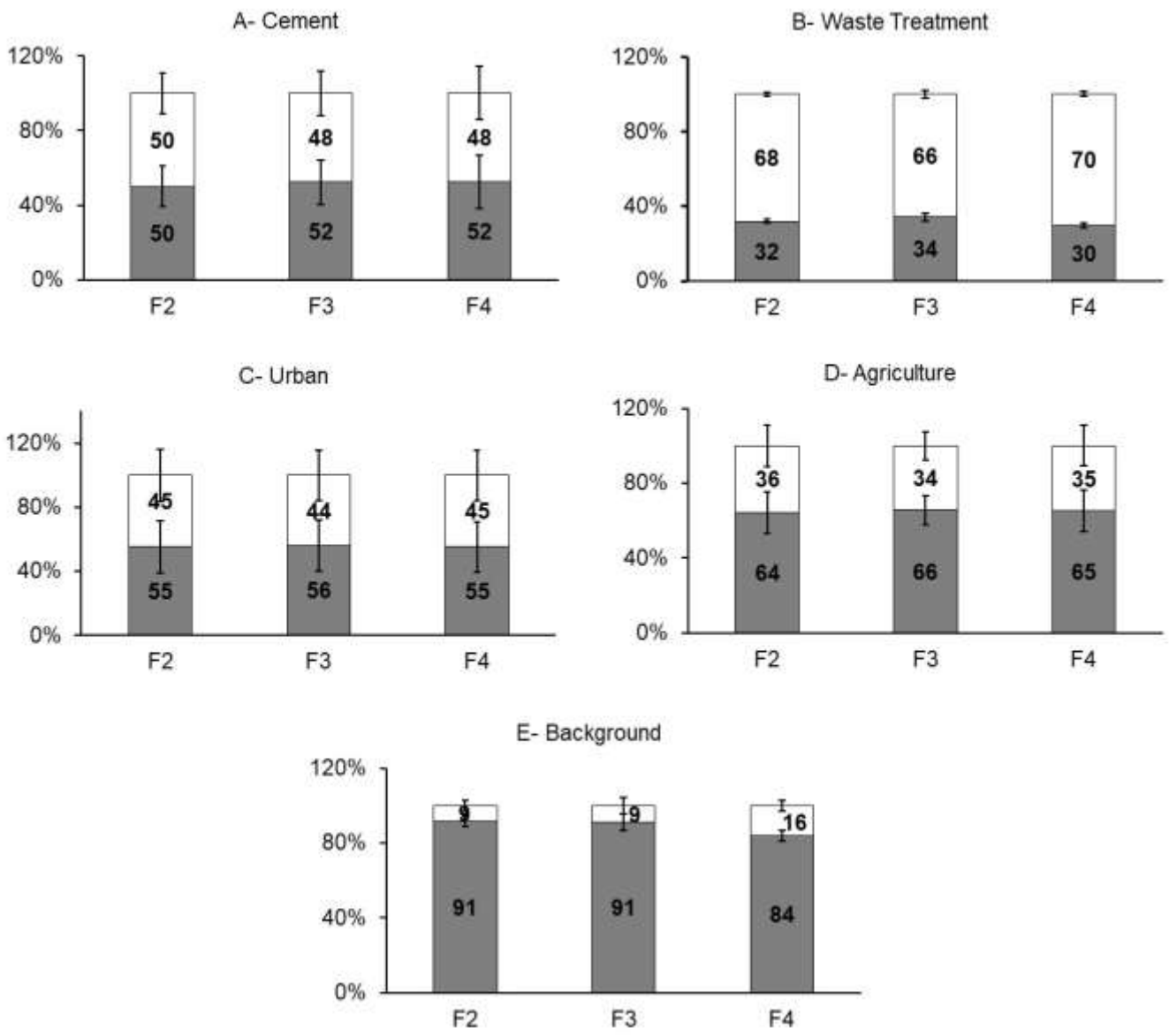


Figure 4. Proportion (%) of petrol-Pb (white boxes) and geogenic-Pb (dark grey boxes) in the non-residual fractions F2, F3 and F4 in all sampling locations, excluding the SH-I (lead smelter) samples. Numbers inside the boxes represent the proportion (%) of each fraction relative to total Pb in the respective soil phase. Error bars represent the standard deviation between soils from the same location.

3.5. Interpreting Pb isotopic signatures assuming three sources

We investigated the possibility of modelling the contribution of a third 'industrial' Pb contribution to the total Pb pool in addition to the geogenic-Pb and petrol-Pb end-members in all soil phases. As discussed previously (section 3.3), soils from the Lead Smelter location (SH-I) are likely to have a distinct isotopic signature (IR of 1.14 for $^{206}Pb/^{207}Pb$ and 2.41 for $^{208}Pb/^{207}Pb$ for total soil Pb) that is independent in origin from the other two definable sources (petrol-Pb and geogenic-Pb). This smelting facility recycled lead from various industries that used imported Pb metal, so it seemed possible that the Pb signature of the SH-I location soil may represent the range of Pb used industrially in Egypt. As such, the smelter site could be considered as representing a third Pb isotope end-member.

However, the IA values of ^{208}Pb in the smelter samples were too low to represent a discrete end member. To resolve a *hypothetical* third Pb source (designated 'industrial Pb'), it was necessary to lower the isotopic abundances (IA) of ^{204}Pb, ^{206}Pb, ^{207}Pb using a factor of 0.985, allowing the ^{208}Pb IA to compensate by keeping the sum of IA values equal to 1. The 'Solver' function of Excel together with Eq. 3 and Eq. 4 (as described in section 2.5) was then employed to find an optimum 'industrial' end-member for TPb and the SEP fractions across all soils simultaneously. The best fit between modelled and measured isotopic abundances of ^{206}Pb, ^{207}Pb and ^{208}Pb was achieved with IR values of 1.14 for $^{206}Pb/^{207}Pb$ and 2.48 for $^{208}Pb/^{207}Pb$ in the 'industrial' source (Figure A.2). The resulting contributions of all three hypothetical Pb sources (petrol, geogenic and industrial) are shown in Figure 5. The industrial-Pb source contribution was relatively uniform across all soils and soils fractions ranging from 13 – 28% of TPb. The relative contribution of petrol-Pb and geogenic Pb displayed similar patterns to that observed with the binary model (section 3.5; Figure 4) showing considerably higher geogenic-Pb contributions in the background and agriculture soils (Figure 5 D and E), almost equal contribution of both sources in the cement factory location (Figure 5 A) and a larger contribution from petrol-Pb in the waste treatment location.

In an alternative approach, the anthropogenic-Pb isotopic abundances were calculated by subtracting an estimate of the geogenic-Pb contribution from total Pb in all soil fractions (Eq. 5). Geogenic Pb isotope concentrations were estimated from the average Pb concentration and isotopic abundances of the background location SZ-B. This approach assumes a uniform distribution of geogenic-Pb in the studied

soils arising from similar underlying geological Pb concentrations and isotopic signatures across all the studied terrains. The molar concentrations of all four (anthropogenic) Pb isotopes were then calculated from Eq. 5. Figure 6 shows the isotopic signatures of the calculated anthropogenic-Pb in all soil fractions. However, it was apparent that the 'removal' of such a small background Pb content produced little change in the distribution of Pb isotopes and the 'anthropogenic' isotopic ratios of Pb were distributed between petrol-Pb and geogenic-Pb and well beyond the Pb smelter data (higher $^{206}Pb/^{207}Pb$ ratios) provisionally assumed to represent the 'industrial Pb' signature. The smelter Pb is certainly a candidate source for the mix of Pb in Egyptian soils – and this is consistent with the fact that it falls on the periphery of the soil Pb isotope ratio dataset (Figure 6). However, it is also clear from the position of the majority of the soil data in Figure 6 that the Pb smelter cannot serve as a single 'industrial-Pb' source in Egypt and must be regarded as a contributory factor. Figure 6 clearly indicates that a more general pool of (non-petrol) 'industrial-Pb' in Egypt must have a Pb isotope signature closer to that of Egyptian geogenic-Pb.

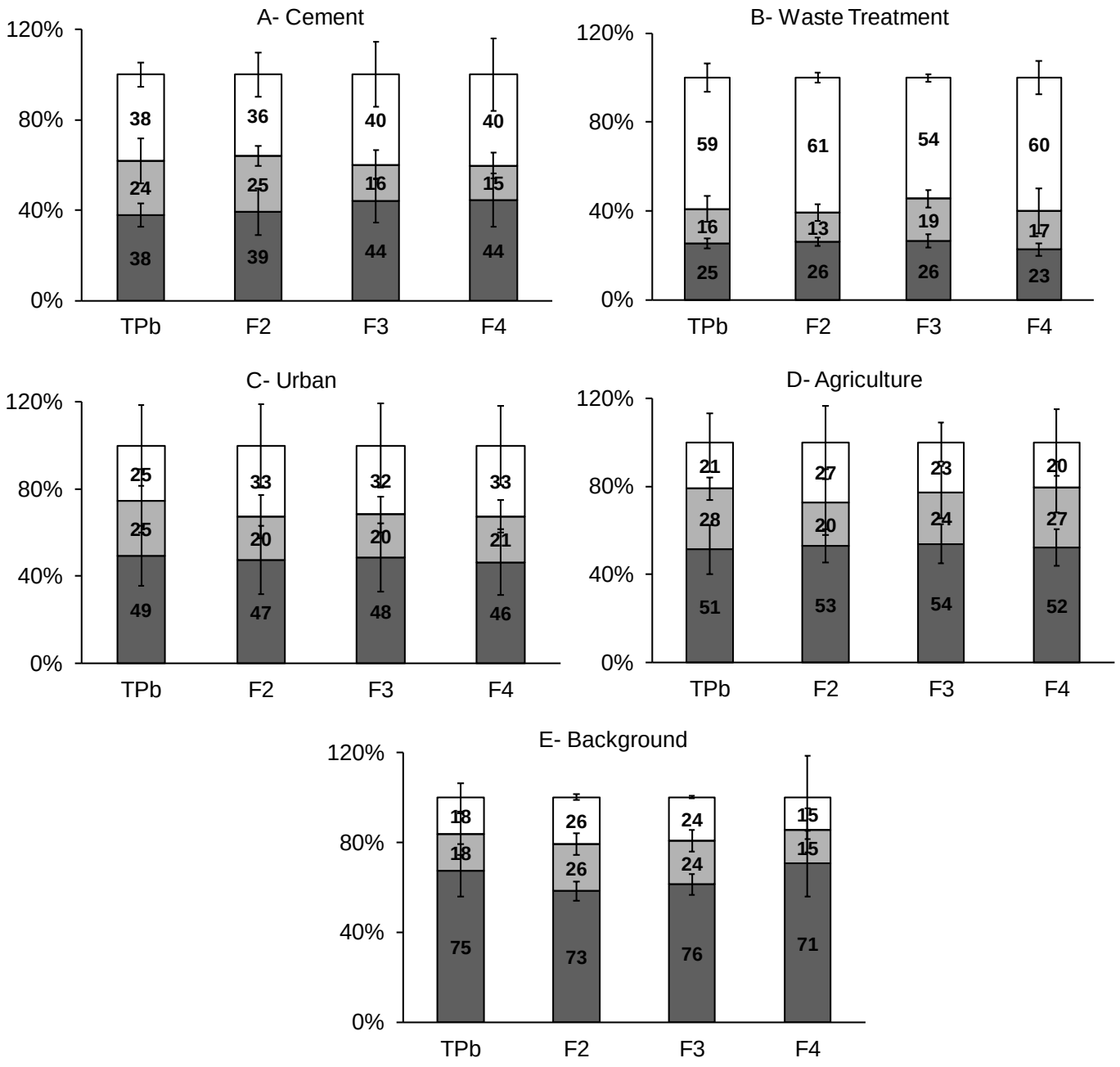
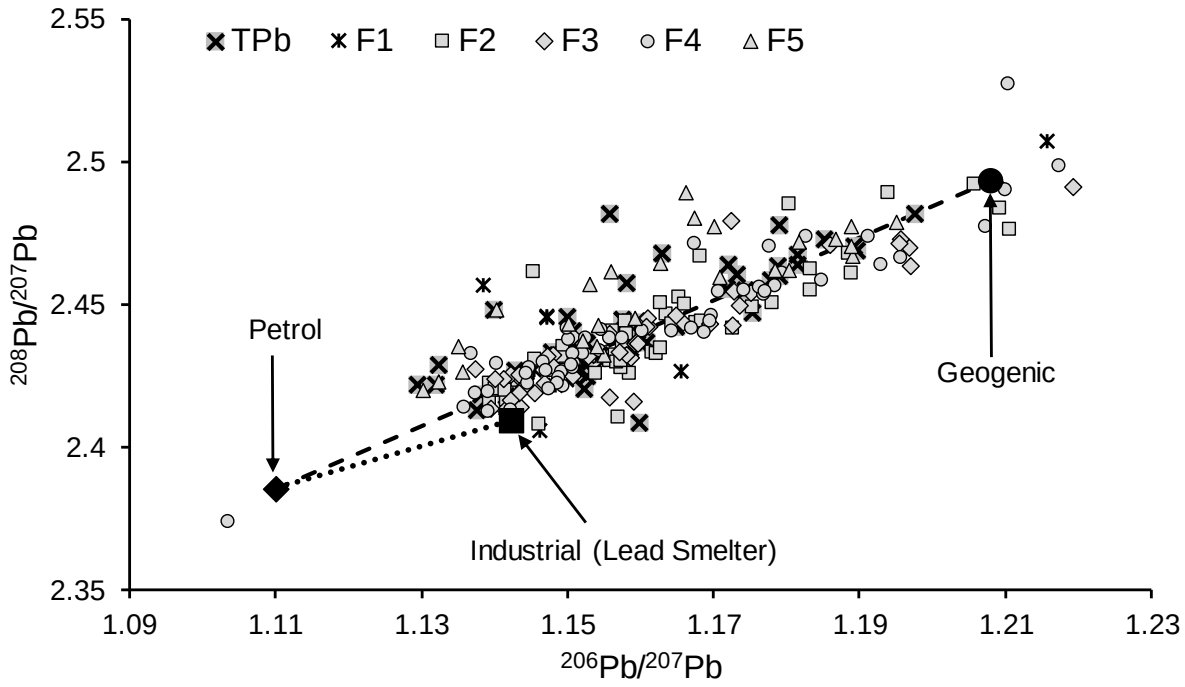


Figure 5. Proportion (%) of petrol-Pb (white boxes), industrial-Pb (light grey boxes) and geogenic-Pb (dark grey boxes) in the total soil Pb (TPb) and the non-residual fractions F2, F3 and F4 in all sampling locations excluding the SH-I (lead smelter) samples. Industrial-Pb signature was modelled by Solver from Eq. 3 and Eq. 4 with the hypothesis that all end-members isotopic signatures are locate at the periphery of the dataset. Numbers inside the boxes represent the proportion (%) of each fraction to total Pb in the respective soil phase. Error bars represent the standard deviation between soils from the same location or soil type.



579

580

581 **Figure 6.** *Anthropogenic-Pb* isotopic ratios ($^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$) of the whole soil and all five SEP
582 fractions, in all soil samples. Petrol-Pb (black diamond), industrial-Pb (black square) and geogenic-Pb
583 (black circle) signatures are also shown as possible end members. F5 fraction signatures are shown for
584 samples where F5-Pb is ≥ 40% of total soil Pb (TPb). Dashed line in the mixing line between petrol-Pb and
585 geogenic-Pb signatures while the dotted line is the mixing line between petrol-Pb and industrial-Pb (lead
586 smelter).

587

588

589

590

591

592

593

594

595

4. Conclusions

The concentrations of total soil Pb (TPb) in most of the studied soils were generally low and ranged around the background and crustal Pb levels of ~ 5 and 14 mg kg^{-1}, respectively. Substantially elevated TPb levels were only found in two industrial locations around a closed lead smelter (SH-I; ~ 16201 mg kg^{-1}) and a waste water treatment facility (CA-I; ~ 171 mg kg^{-1}), and in two urban locations around major motorways within Cairo (CA-U; ~160 mg kg^{-1}) and Alexandria (AX-U; ~ 83 mg kg^{-1}).

The residual fraction (F5-Pb) was the largest single fraction (38 - 63%) in all the studied locations with the exception of SH-I and CA-I sites which were dominated by the carbonate (F2-Pb; 44%) and organic (F4-Pb; 61%) fractions, respectively. Exchangeable Pb (F1-Pb) was only detectable in two locations: SH-I (1% TPb; ~ 162 mg kg^{-1}) and CA-U (0.3% TPb; ~1.6 mg kg^{-1}). Although this may suggest that the current risk of releasing considerable amounts of available Pb is exclusive to SH-I site (lead smelter), Pb in the other 3 non-residual fractions, in all locations including SH-I, may become available with any change in the soil Eh/pH conditions. For example, in location CA-I (waste water treatment), if the conditions become more oxidizing e.g. due to the waste treatment operations, the large organic (F4-Pb) pool will be released in available forms. Therefore, in the four locations with elevated TPb levels (SH-I, CA-I, CA-U and AX-U), despite their low/undetectable exchangeable-Pb, careful consideration should be taken to avoid mobilizing hazardous amounts of Pb to the surrounding environments.

The non-residual Pb isotopic signatures (F1 – F4; $^{206}Pb/^{207}Pb$) were dependent on the Pb source and level of contamination; however, they displayed very similar patterns between the non-residual fractions (F2 - F4). Similarly, the relative contribution of petrol-Pb to the non-residual Pb pools varied considerably between sampling locations and was apparently controlled by the concentration of TPb despite being almost identical in all the non-residual fractions (F2 - F4). This suggests no apparent difference in chemical affinity of any given anthropogenic-Pb source for specific non-residual fractions in soil. Any initial source-dependent distribution within the active soil fractions, following application to the soil, has apparently disappeared with time.

It was not possible to identify a *single* 'third Pb source' to explain the distribution of Pb isotope ratios. A major source, the Pb smelter in Cairo-Shubra, appeared to fall on the periphery of the dataset and could

be a significant contributor to Pb contamination in the country. However, removal of an assumed background geogenic source produced a dataset in which the majority of Pb isotope ratios fell beyond the range covered by the petrol and smelter sources. The suggestion is therefore that the majority of 'contaminant Pb' in Egypt has an isotopic signature close to that of geogenic Pb.

Acknowledgments

Waleed Shetaya acknowledges a postdoctoral fellowship (at the University of Nottingham, UK) funded by the Egyptian Government.

Conflicts of Interest

The authors declare no conflicts of interest.

Appendix A. Supplementary data

References

Atkinson, N. R., Bailey, E. H., Tye, A. M., Breward, N. & Young, S. D. 2011. Fractionation of lead in soil by isotopic dilution and sequential extraction. *Environmental Chemistry,* 8**,** 493-500.

Bacon, J. R., Farmer, J. G., Dunn, S. M., Graham, M. C. & Vinogradoff, S. I. 2006. Sequential extraction combined with isotope analysis as a tool for the investigation of lead mobilisation in soils: Application to organic-rich soils in an upland catchment in scotland. *Environmental pollution,* 141**,** 469-481.

Blum, J. D. & Bergquist, B. A. 2007. Reporting of variations in the natural isotopic composition of mercury. *Analytical and Bioanalytical Chemistry,* 388**,** 353-359.

Brookins, D. G. 2012. *Eh-ph diagrams for geochemistry*, Springer Science & Business Media.

Chenery S. R., Izquierdo M., Marzouk E., Klinck B., Palumbo-Roe B., Tye A. M. 2012. Soil–plant interactions and the uptake of Pb at abandoned mining sites in the Rookhope catchment of the N. Pennines, UK—a Pb isotope study. Science of the Total Environment, 433, 547–560.

Cheng, H. & Hu, Y. 2010. Lead (pb) isotopic fingerprinting and its applications in lead pollution studies in china: A review. *Environmental Pollution,* 158**,** 1134-1146.

Clevenger, T. E., Saiwan, C. & Koirtyohann, S. 1991. Lead speciation of particles on air filters collected in the vicinity of a lead smelter. *Environmental science & technology,* 25**,** 1128-1133.

Cotter-Howells, J. & Thornton, I. 1991. Sources and pathways of environmental lead to children in a derbyshire mining village. *Environmental Geochemistry and Health,* 13**,** 127-135.

Degryse, F., Smolders, E. & Parker, D. 2009. Partitioning of metals (cd, co, cu, ni, pb, zn) in soils: Concepts, methodologies, prediction and applications–a review. *European Journal of Soil Science,* 60**,** 590-612.

Drummond, L. & Maher, W. 1995. Determination of phosphorus in aqueous-solution via formation of the phosphoantimonylmolybdenum blue complex - reexamination of optimum conditions for the analysis of phosphate. *Analytica Chimica Acta,* 302**,** 69-74.

Emsley, J. 2011. *Nature's building blocks: An az guide to the elements*, Oxford University Press.

Foster, R. L. & Lott, P. F. 1980. X-ray diffractometry examination of air filters for compounds emitted by lead smelting operations. *Environmental Science & Technology,* 14**,** 1240-1244.

Harrison, R. M., Laxen, D. P. & Wilson, S. J. 1981. Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. *Environmental Science & Technology,* 15**,** 1378-1383.

Hassan, S. K., El-Abssawy, A. A., Abdel-Maksoud, A. S., Abdou, M. H. & Khoder, M. I. 2013. Seasonal behaviours and weekdays/weekends differences in elemental composition of atmospheric aerosols in cairo, egypt. *Aerosol and Air Quality Research,* 13**,** 1552-1562.

Hassanien, M. & Horvath, A. 1999. Lead risk assessment for children in hungary by predicting their blood lead levels using us epa integrated exposure uptake biokinetic model. *Central European journal of public health,* 7**,** 155-159.

Hassanien, M. A., Rieuwerts, J., Shakour, A. & Bittó, A. 2001. Seasonal and annual variations in air concentrations of pb, cd and pahs in cairo, egypt. *International journal of environmental health research,* 11**,** 13-27.

Izquierdo, M., Tye, A. & Chenery, S. 2012. Sources, lability and solubility of pb in alluvial soils of the river trent catchment, uk. *Science of the Total Environment,* 433**,** 110-122.

Komárek, M., Ettler, V., Chrastný, V. & Mihaljevič, M. 2008. Lead isotopes in environmental sciences: A review. *Environment International,* 34**,** 562-577.

Kostka, J. E. & Luther, G. W. 1994. Partitioning and speciation of solid phase iron in saltmarsh sediments. *Geochimica et Cosmochimica Acta,* 58**,** 1701-1710.

Labib, M. W., Safar, Z. & Khalil, M. H. 2003. Lead emission inventory in the greater cairo area during the life time of caip. *AWMA paper,* 70137.

Lee, P.-K. & Yu, S. 2016. Lead isotopes combined with a sequential extraction procedure for source apportionment in the dry deposition of asian dust and non-asian dust. *Environmental Pollution,* 210**,** 65-75.

Li, X. & Thornton, I. 2001. Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. *Applied geochemistry,* 16**,** 1693-1706.

Luo, X.-S., Xue, Y., Wang, Y.-L., Cang, L., Xu, B. & Ding, J. 2015. Source identification and apportionment of heavy metals in urban soil profiles. *Chemosphere,* 127**,** 152-157.

Mao, L. C., Bailey, E. H., Chester, J., Dean, J., Ander, E. L., Chenery, S. R. & Young, S. D. 2014. Lability of pb in soil: Effects of soil properties and contaminant source. *Environmental Chemistry,* 11**,** 690-701.

Marzouk, E. R., Chenery, S. R. & Young, S. D. 2013a. Measuring reactive metal in soil: A comparison of multi-element isotopic dilution and chemical extraction. *European Journal of Soil Science,* 64**,** 526-536.

Marzouk, E. R., Chenery, S. R. & Young, S. D. 2013b. Predicting the solubility and lability of zn, cd, and pb in soils from a minespoil-contaminated catchment by stable isotopic exchange. *Geochimica Et Cosmochimica Acta,* 123**,** 1-16.

Mcbride, M. 1994. Environmental soil chemistry. Oxford University Press, New York.

Meers, E., Du Laing, G., Unamuno, V., Ruttens, A., Vangronsveld, J., Tack, F. M. & Verloo, M. G. 2007. Comparison of cadmium extractability from soils by commonly used single extraction protocols. *Geoderma,* 141**,** 247-259.

Mohamed, E. F., El-Hashemy, M. A., Abdel-Latif, N. M. & Shetaya, W. H. 2015. Production of sugarcane bagasse-based activated carbon for formaldehyde gas removal from potted plants exposure chamber. *Journal of the Air & Waste Management Association,* 65**,** 1413-1420.

Monna, F., Lancelot, J., Croudace, I. W., Cundy, A. B. & Lewis, J. T. 1997. Pb isotopic composition of airborne particulate material from france and the southern united kingdom: Implications for pb pollution sources in urban areas. *Environmental Science & Technology,* 31**,** 2277-2286.

Murphy, S. 1992. Smelting residues from boles and simple smeltmills. *Boles and smeltmills***,** 43-47.

Nasralla, M. & Ali, E. 1984. Lead, cadmium and zinc around traffic roads. *Egyptian J. Occupat. Med,* 8**,** 197-210.

719 Needleman, H. L. & Bellinger, D. 1991. The health effects of low level exposure to lead. *Annual Review of*
720 *Public Health,* 12**,** 111-140.

721 Olsen, S. R., Cole, C. V., Watanabe, F. S. & Dean, L. A. 1954. Estimation of available phosphorus in soils
722 by extraction with sodium bicarbonate. *U.S. Dep. of Agric. Circ,* 939.

723 Rizk, H. F. & Khoder, M. I. 2001. Decreased lead concentration in cairo atmosphere due to use of
724 unleaded gasoline. *Central European Journal of Occupational and Environmental Medicine Hungary*.

725 Roebbert, Y., Rabe, K., Lazarov, M., Schuth, S., Schippers, A., Dold, B. & Weyer, S. 2018. Fractionation
726 of fe and cu isotopes in acid mine tailings: Modification and application of a sequential extraction
727 method. *Chemical Geology,* 493**,** 67-79.

728 Safar, Z., Labib, M. W., Lotfi, W. & Khalil, M. H. 2014. Characterization of contamination around the
729 largest lead smelter in egypt carried out through a cooperation program between USA and egypt. *Field*
730 *Actions Science Reports. The journal of field actions,* 7.

731 Safar, Z. S. & Labib, M. W. 2010. Assessment of particulate matter and lead levels in the greater cairo
732 area for the period 1998–2007. *Journal of advanced research,* 1**,** 53-63.

733 Sastre, J., Rauret, G. & Vidal, M. 2006. Effect of the cationic composition of sorption solution on the
734 quantification of sorption–desorption parameters of heavy metals in soils. *Environmental pollution,* 140**,**
735 322-339.

736 Shaheen, S. M. 2009. Sorption and lability of cadmium and lead in different soils from egypt and greece.
737 *Geoderma,* 153**,** 61-68.

738 Shakour, A. & El-Taieb, N. 1994. Effect of atmospheric lead exposure on urban children. *Egyptian J*
739 *Occup Med,* 18**,** 37-47.

740 Shetaya, W. H., Marzouk, E. R., Mohamed, E. F., Elkassas, M., Bailey, E. H. & Young, S. D. 2018. Lead
741 in egyptian soils: Origin, reactivity and bioavailability measured by stable isotope dilution. *Science of The*
742 *Total Environment,* 618**,** 460-468.

743 Shetaya, W. H., Osterwalder, S., Bigalke, M., Mestrot, A., Huang, J.-H. & Alewell, C. 2017. An isotopic
744 dilution approach for quantifying mercury lability in soils. *Environmental Science & Technology Letters,* 4**,**
745 556-561.

746 Sparks, D. L. 2003. *Environmental soil chemistry*, Academic Press, An imprint of Elsevier Science,
747 California, USA.

748 Tack, F. & Verloo, M. G. 1995. Chemical speciation and fractionation in soil and sediment heavy metal
749 analysis: A review. *International Journal of Environmental Analytical Chemistry,* 59**,** 225-238.

750 Tessier, A., Campbell, P. G. C. & Bisson, M. 1979. Sequential extraction procedure for the speciation of
751 particulate trace-metals. *Analytical Chemistry,* 51**,** 844-851.

752 Teutsch, N., Erel, Y., Halicz, L. & Banin, A. 2001. Distribution of natural and anthropogenic lead in
753 mediterranean soils. *Geochimica et Cosmochimica Acta,* 65**,** 2853-2864.

754 Tipping, E., Thompson, D., Ohnstad, M. & Hetherington, N. 1986. Effects of ph on the release of metals
755 from naturally-occurring oxides of mn and fe. *Environmental Technology,* 7**,** 109-114.

756 Tongtavee, N., Shiowatana, J., Mclaren, R. G. & Gray, C. W. 2005. Assessment of lead availability in
757 contaminated soil using isotope dilution techniques. *Science of the Total Environment,* 348**,** 244-256.

Veysseyre, A. M., Bollhöfer, A. F., Rosman, K. J., Ferrari, C. P. & Boutron, C. F. 2001. Tracing the origin of pollution in french alpine snow and aerosols using lead isotopic ratios. *Environmental science & technology,* 35**,** 4463-4469.

Who 2010. Exposure to lead: A major public health concern. Preventing disease through healthy environments. *Geneva, World Health Organization (http://www.who.int/ipcs/features/lead..pdf)* 6.

Young, S. D., Tye, A., Carstensen, A., Resende, L. & Crout, N. 2000. Methods for determining labile cadmium and zinc in soil. *European Journal of Soil Science,* 51**,** 129-136.