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High precision blood lead radiogenic isotope signatures in a community exposed to Pb contaminated soils and implications for the current Pb exposure of the European population

Jérôme C.J. Petit [a,*], Nadine Mattielli [b], Jeroen De Jong [b], Elodie Bouhoulle [a], Wendy Debouge [b], Patrick Maggi [c], Geneviève Hublet [b], Nathalie Fagel [d], Catherine Pirard [e], Corinne Charlier [e], Remy Suzanne [a]

[a] *Institut Scientifique de Service Public, Rue du Chéra 200, 4000 Liège, Belgium*
[b] *Laboratoire G-TIME, Faculté des Sciences, Université Libre de Bruxelles, Av. F.D. Roosevelt 50 CP106/02 1050, Bruxelles, Belgium*
[c] *FPS Health, Food Chain Safety and Environment, Ecotoxicology Unit from Service Plant protection and Fertilising products, 5/2 Avenue Galilée, B-1210 Brussels, Belgium*
[d] *Laboratoire Argiles, Géochimie et Environnements sédimentaires (AGEs), Department of Geology, Faculty of Sciences, University of Liège, Liège B-4000, Belgium*
[e] *Laboratory of Clinical, Forensic and Environmental Toxicology, CHU of Liege, B35, B-4000 Liege, Belgium*

HIGHLIGHTS

- Soil Pb contributes to roughly 20 % of Blood Lead Levels in the study population.
- Exposure to soil Pb is not the main driver for changes in Blood Lead isotopes (BLI).
- BLI ratios differ by birth country and by the period the house was built.
- BLI remained stable over the last decade and still records Australian ore signature.

GRAPHICAL ABSTRACT

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ABSTRACT

Our study provides the most comprehensive dataset for high-precision radiogenic isotopes of lead (Pb) in blood for the western European population. It investigates their potential for elucidating the contribution of soil Pb to blood Pb using a human biomonitoring survey involving 81 adults and 4 children living in the urban area of Liège (Belgium). Soils in the area show moderate (median of 360 mg/kg) to high (95th percentile of 1000 mg/kg) Pb concentrations, due to former metal processing activities. Blood lead levels (BLL) measured in the study

* Corresponding author.
E-mail address: j.petit@issep.be (J.C.J. Petit).
URL: https://jcjpetit.wixsite.com/jcjpetit (J.C.J. Petit).

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Urban environment
Allotment garden
Historical metallurgy
Isotope forensics

population are, on average, quantitatively consistent with a ~ 20 % increase due to the exposure to Pb from soils, as estimated by a single-compartment biokinetic model. Consistently, its isotopic composition does not represent an endmember that fully accounts for the variability of Blood lead isotope (BLI) compositions measured in the study population. While some individuals show more thorogenic BLI ratios (relatively more enriched in ^{208}Pb), which could be consistent with a greater exposure to local soils and/or by their country of birth, the BLI data mostly follow a trend roughly parallel to the European Standard Lead Pollution (ESLP) line, within the European leaded gasoline field, even two decades after the withdrawal of this source. Differences in BLI are probably associated with factors related to the presence of Pb in dwellings (pipes, paint) and drinking water distribution system, suggesting that the anthropogenic Pb in use, relevant to human exposure, may contain ore components of different origins, including the Australian Pb ore signature.

1. Introduction

Lead (Pb), a toxic, non-essential metal, has played an important role in our technological development and remains one of today's most persistent and widespread anthropogenic pollutants. Exposure to Pb in the European population has strongly decreased over the last 40 years (e.g., Becker et al., 2003, Schulz et al., 2007, Smolders et al., 2010, Mielke et al., 2022), with median blood lead levels (BLL) currently in the range of ~10–30 μg/l (Nisse et al., 2017; Oleko et al., 2020). This trend is attributed to the ban on tetraethyl Pb gasoline, which lead to declining Pb levels in ambient air from around 2000 ng/m^3 in the early 1980s to <10 ng/m^3 today (Petit et al., 2015, Resongles et al., 2021), combined with other regulatory policies targeting dietary and non-dietary Pb sources, from consumer products to industrial emissions. Biomonitoring surveys performed in the general European population over the last two decades suggest that population BLL became stable or decreased at a much slower rate than previously. However, Pb remains a contaminant of public health concern, since current median biological exposure levels remain close to critical BLL implying neurodevelopmental (12 μg/l, children) and renal effects (15 μg/l, adults), according to the latest toxicity assessments (e.g. European Food Safety Authority, 2010). Lead shows toxicity to humans at low levels of exposure and still poses health risks for a large part of the population.

Studies of Pb source apportionment for the global European population shows that today ambient air has become a minor contributor to the total Pb exposure compared to dietary (food and water) intakes, which currently represent more than around 90 % of the total exposure (e.g. Sy et al., 2024). Other environmental sources, such as Pb contaminated soils and house dust, may be locally prevalent, especially for children (due to hand-to-mouth contact) and adults feeding on vegetables grown on contaminated soils. Indeed, cities built close to former metal-processing industries often have large residential areas whose soils show Pb concentrations at levels deemed unacceptable based on health risk assessments. Since current Pb sources, previously dominated by ambient air, have changed in absolute and relative proportions, identifying levers of action to further reduce BLL in local and general population becomes a difficult task for scientists and public authorities (Bierkens et al., 2011; Etchevers et al., 2017; Oulhote et al., 2011; Sy et al., 2024).

In this respect, Pb isotopes provide valuable insights into the origin of Pb within a sample, allowing for fingerprinting their source and quantify mixing relationships in various environmental media and scientific disciplines. Lead has one primordial stable isotope (^{204}Pb) and three radiogenic isotopes ^{206}Pb,^{207}Pb,^{208}Pb which are formed by radioactive decay from ^{235}U, ^{238}U and ^{232}Th respectively. Earth materials acquire their specific Pb isotopic signature depending on (i) the half-life of parent isotopes, (ii) the initial Pb, U and Th concentrations and (iii) the time elapsed since they were formed. Old geological materials with high U/Pb and Th/Pb ratios will have a more radiogenic isotopic signature, i.e. higher ^{20X}Pb/^{204}Pb ratios (with X = 6, 7 or 8), together with higher ^{206}Pb/^{207}Pb and lower ^{208}Pb/^{207}Pb ratios, as measured in European pristine topsoils (^{206}Pb/^{207}Pb = 1.20–1.30).

Along with Cd, Zn and As (Petit et al., 2022a), soils and other environmental medias receive additional inputs of Pb related to diffuse losses from the processing of Pb/Zn ores and the technological use of Pb. Anthropogenic Pb is refined from Pb ore deposits whose isotopic signatures are generally distinct from natural background values. In North-Western (NW) Europe, Pb ores are typically less radiogenic compared to the natural background. The isotopic composition of anthropogenic Pb can change in time in a given region (e.g. Sonke et al., 2008; Véron et al., 1999). In particular, imports of Australian Pb/Zn ores from the Broken Hill & Mont Isa districts characterized by extremely low ^{206}Pb/^{207}Pb (~1.03–1.04), occurred as early as 1900's to supply industrial Pb/Zn production in Western Europe (Sonke et al., 2002). This ore, even when mixed with ores of other origins (Véron et al., 1999), was responsible for the relatively less radiogenic isotopic signatures of tetra-ethyl Pb gasoline in NW Europe. The use of Pb gasoline drastically altered the isotopic composition of ambient air of NW Europe probably as early as in the 1930's until 2000, as shown by environmental archives ranging from lake sediments to Greenland ice cores (e.g. Shotyk et al., 1998; Weiss et al., 1999; Haack et al., 2003; Sonke et al., 2008).

In comparison, few studies have investigated the potential of Pb isotopes to address human exposure. Pioneering works by Manton et al. (2005) and Gulson et al. (2006) mainly focused on long-term residents of North America and Australia, respectively. They were initially conducted when BLL were high and, in Australia, strongly imprinted by the unique isotopic signature of Australian Pb ores. Gulson et al. (2006) evidenced a strong increase in the radiogenicity of BLI signatures with decreasing BLL in the Australian population over a decade (1990–2002), attributed to the combined effect of globalization (including the arrival of new residents from foreign countries) and environmental regulations on Pb. A similar temporal trend was also suggested by the data from Petit et al. (2015) for Belgium & Northern France urban areas. This latter trend has been related to the phasing out of leaded gasoline combined with the contribution of a more radiogenic Pb from dietary exposure. Consistently, Kamenov and Gulson (2014) have shown that Pb isotope data in teeth are reliable tracers to discriminate between area of birth. They provided additional evidences that today's western European BLI signatures may slightly overlap those of the Australian population, as related to how much Australian ores have pervaded the human exposome in Europe. Other studies on the use of Pb isotopes in health/exposure sciences have been more or less successful in fingerprinting environmental Pb sources to BLI signatures (e.g. Gwiazda and Smith, 2000, Patel et al., 2008, Oulhote et al., 2011, Cao et al., 2014, Li et al., 2015, Laycock et al., 2022, Becker et al., 2022), due to co-varying Pb isotopic ratios (e.g. Ellam, 2010) and limited accuracy when data were not acquired with TIMS or MC-ICP-MS (Gulson et al., 2018).

This study intends to complement the current knowledge on BLI signature and its evolution for the Western European adult population. In particular, it investigates the potential of high precision Pb isotope measurements in understanding the contribution of Pb from contaminated soil to Pb in blood in a community setting, while investigating also other potential sources of exposure potentially significant in explaining blood lead isotope signatures.

2. Material and methods

2.1. Study population and environmental setting

The cross sectional human biomonitoring survey took place during July–September 2018. Blood samples were collected from eighty-five adults ($n = 81$) and children ($n = 4$) living in a residential area of the city of Liège (Belgium), where soils show trace metal contaminations due to former industrial metal (mainly zinc) processing activities that took place over a century. All volunteers benefited from a collective 6-ha allotment garden existing since the 1920's. They were thought to be actively/more intensively exposed to Pb from soil than the general population because of their consuming and gardening habits on these moderate to highly Pb-contaminated soils. Higher blood Pb, as well as higher blood Cd, urine Cd and speciated urine As levels were also measured in the study population, as previously presented (Petit et al., 2022b).

Soils from the allotment garden have similar trace metal concentrations than those from the neighboring area. They showed moderate to high Pb levels (median concentration of 360 mg/kg, geometric mean (GM) of 500 mg/kg and 95th percentile at 1000 mg/kg, $n = 112$), while local vegetables and fruits ($n = 250$) had Pb contamination levels 10 to 40 times above those of commercial quality (ANSES, 2011). Potatoes, leaf and root vegetables growing on these soils showed high non-compliance frequencies (27 %, 47 % and 83 %, respectively) compared to EU 2006/1881 regulation on commercial food products (Petit et al., 2022b).

2.2. Analytical methodology

2.2.1. Sampling

For each volunteer, two aliquots of intravenous blood samples were collected in 10 ml gel free clot activator tubes. Volunteers also filled a questionnaire during a face-to-face meeting to provide information such as demographic characteristics (age, sex), allotment attendance, dietary habits, smoking status, presence of Pb water pipes at home, etc. Homes built before 1950 at are higher risk with respect to Pb since they combine the occurrence of Pb-rich paints and Pb drinking water pipes as indoor Pb sources.

All the personal data were treated confidentially in accordance with the General Data Protection Regulation (GDPR). The volunteers gave their explicit approval for the processing of their data within the context of the research objectives of this study by mean of an informed consent.

Soil sampling in the shared allotment garden and in the 1 km radius area took place in 2018 and 2019. They consisted in dried and 250 μm sieved top soils samples. Trace metal measurements were performed according to the ISO 54321:2020 for trace metal measurements in solid samples.

2.2.2. Pb concentrations in blood

Preparation and analysis of blood samples were performed at the Laboratory of Clinical, Forensic and Environmental Toxicology of CHU of Liege on a ICP-MS (Agilent 7700×) equipped with an ORS collision cell and an Integrated Sample Introduction System (ISIS). Methods and quality control were thoroughly described in a previous publication (Petit et al., 2022a, 2022b).

2.2.3. Pb isotopes

2.2.3.1. Chemistry. Dissolution of soil and blood samples and purification of Pb prior to isotopic analysis were carried out in a class 100 flow hood belonging to G-Time (ULB) clean rooms (class 1000), using only sub-boiled acids or ultrapure H_2O_2, and ultraclean Teflon consumables. Soil samples were prepared following the method described in Vanderstraeten et al. (2020). About 100 mg of dried calcinated powdered samples underwent conc. HF/HNO_3 dissolution in savilex® beakers at 120 °C for 48 h, followed by repeated cycles of dry evaporation and redissolution in HCl 6 mol/l until the solution was clear and without residue. Blood samples were mineralized from 2 to 6 ml aliquots by three repeated cycles involving 14 M sub-boiled HNO_3 with addition of concentrated. H_2O_2 (at room temperature, then at 90 °C) and dry-evaporation. A final step in HNO_3/HCl was also required. Blood and soil samples were finally dry-evaporated and redissolved in 2 ml HBr 0.5 mol/L prior to loading on the chromatographic column. Pb purification was carried out using triple-pass microcolumns filled with BIORAD AG1-X8 anion exchange analytical grade resin (200–400 mesh – single pass, and 100–200 mesh – double pass).

2.2.3.2. Analysis. Pb isotopes were measured on a Nu Plasma II high-resolution multi-collector-ICP-MS (Nu Instruments) at Laboratoire G-TIME (ULB). Analyses were performed in dry plasma mode using an Apex-Q Desolvating Nebulizer System with a minimum ^{204}Pb signal intensity of 70–100 mV and a total Pb beam of ~5 V. Isobaric interference by ^{204}Hg was corrected by monitoring ^{202}Hg and applying Retzmann et al. (2017) equations. Accuracy and reproducibility of the analyses were controlled by a series of repeated measurements of the NIST SRM 981 Pb standard solutions at the beginning of each session, and between every two samples. Instrumental mass bias was corrected using external normalization with thallium solution (added to every sample or standard solutions) combined to standard sample bracketing method with the NIST SRM 981 Pb standard solution (1 standard every two samples). The Pb/Tl ratio matched those for standards and was 20 ppb/8 ppb. All isotopic results were corrected using the recommended values of Abouchami & Galer (1998). More details about the analytical methodology and sample preparation before analysis can be found in Vanderstraeten et al. (2020).

Repeated analyses of NIST SRM 981 provided mean values of 36.7218 ± 0.0094, 15.4963 ± 0.0037 and 16.9405 ± 0.0033 (2sd as external standard deviation, $n = 86$) respectively for $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ (Table A1, supplementary material), consistent with the long-term laboratory measurement repeatability of NIST SRM 981 values and data reported by Weis et al. (2006), respectively of 36.7163 ± 0.0121, 15.4968 ± 0.0047 and 16.9407 ± 0.0036 (2sd, $n = 167$).

2.2.3.3. Quality controls. Quality controls are presented in Table A1. For soils, they consisted in 18 replicate measurements of an in-house peat sample measured during 6 analytical sessions. Their mean values and repeatability's (i.e., 2sd as an external standard deviation) were similar to the long-term values (38.2737 ± 0.0167, 15.6242 ± 0.0052, 18.2337 ± 0.0067, for $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ respectively) acquired in the lab. For blood, they consisted in duplicate chemistry and analysis for 4 blood samples and two certified reference materials (Seronorm Trace Element Whole Blood Level 2 (SERO210205) and level 3 (SERO210305). The latter showed similar Pb isotopic compositions, strongly enriched in radiogenic isotopes compared to blood samples and ore data that have been collected in this study. This probably reflects a particular isotopic signature of the Pb ore used in the manufacturing process of these reference materials. Duplicate chemistry and analysis of blood samples showed no >0.01 % relative difference for $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$ and generally agreed very well with the repeatabilities (2sd) determined for the in- house quality control and NIST standards.

2.2.4. Scanning electron microprobe

In order to investigate potential mineralogical tracers for Pb contamination in soils, scanning electron microscope (SEM) analyses were carried out at the CareM center (ULiège) on a FEI microscope (model ESEM XL 30), enabling secondary electron and back scattered electron image acquisition. Elemental point analyses on carbon plated soil sample powder were carried out using an EDS detector (XFlash 5010, Bruker). Analyses were performed at a working distance of 10 mm and an energy of 15 KeV.

2.3. Statistics

Statistical analyses were carried out with SPSS (IBM SPSS Statistics version 25). The model assumptions were evaluated with the Shapiro-Wilk test for normality. As Gaussian distribution was not confirmed, the non-parametric Mann-Whitney *U* test was used for categorical variables with 2 modalities ($k = 2$). The Kruskal-Wallis test was used for categorical variables with >2 modalities ($k > 2$), using the Bonferroni correction. Correlations between continuous variables were performed using Spearman's correlation coefficient, used for variables that do not follow a normal distribution. In the case of 2×2 tables, Fisher's Exact Test was used to determine the *p*-value, with 95 % confidence level. Multivariate linear regression was also used to build a statistical model using the stepwise method with variables showing *p*-values <0.1 with adult BLL. Homoscedasticity and normal distribution of residuals were also checked.

2.4. Data analysis – contribution from soil Pb to BLL prediction

In order to assess if Pb from soil significantly contributes to BLL measured in the study population (adults only), we used the US-EPA Adult Lead Model (Maddaloni et al., 2001) designed for human health risk assessment on Pb contaminated sites. This single-compartment biokinetic model predicts a BLL resulting from an incremental exposure to Pb from soil added to a baseline blood lead level, BLL_0. This latter parameter integrates all sources of Pb, including total dietary intakes as well as historical exposure and exposure variability at the population scale. The BLL_0 value selected in this study is the GM of BLL distribution for adults (18–74 years old) of the French general population survey ESTEBAN, i.e. 18.5 μg/l (Oleko et al., 2020).

The incremental Pb intake due to local soil depends on (i) the soil Pb concentration, Pb_S, (ii) the soil & soil-derived dust ingestion rate, $IR_{S,D}$ (0.03 g/d, U.S. Environmental Protection Agency, 2017), (iii) the soil & soil-derived dust Pb absorption factor $AF_{S,D}$ (0.12) and (iv) the Bio-Kinetic Slope Factor, BKSF (0.4 d/l) used to convert Pb intake into a BLL increment. Assuming (i) Pb exposure occurs 365 d/y and (ii) the Pb concentration in soil-derived and soil are the same, the resulting equation is (Eq. 1):

$$BLL = BLL_0 + BKSF^*Pb_S^*AF_{S,D}^*IR_{S,D} \quad (1)$$

3. Results

3.1. Pb in soil

Trace metal concentrations (Pb, Zn, Cd and As) of three soil samples are presented in Table 1. They were taken from the allotment garden and the residential area within a 1 km radius. Trace metal concentrations are consistent with a rather moderate to high level of soil contamination representative of a hotspot for the city of Liège. Mineralogical observation and analysis of Pb in soil samples by SEM revealed a single Pb bearing mineral with a structural formula $(Pb,Ca)_5(PO_4)_3Cl$ corresponding to pyromorphite, a very common and stable chemical phase for Pb in contaminated urban soils (e.g. Buatier et al., 2001, Vodyanitskii, 2006) showing a very low solubility at ambient soil pH. It occurs in more or less needle-like shaped polycrystalline aggregates around silicate grains (Fig. B1, supplementary material), probably indicating a secondary origin. Its presence brings no additional information on a particular mineralogical signature related to a specific ore or a particular Pb source.

Although they are several hundred meters apart, the soil samples display homogeneous Pb isotopic signatures. They are in the range of German Zn/Pb ores (originating from the same deposit district as Belgian ores), and close to the European leaded gasoline field (Komárek et al., 2008), as shown on Fig. 1). They also show a slight but significant offset towards a more thorogenic composition (enriched in ^{208}Pb compared to ^{206}Pb and ^{207}Pb) with respect to the European Standard Lead Pollution (ESLP) line (Haack et al., 2003). The latter is a general trend defined by various environmental samples resulting from the mixing of a more radiogenic signature attributed to pristine materials and a less radiogenic signature attributed to EU leaded gasoline (presenting a significant proportion of Pb from ores of Australian origin).

3.2. Blood Pb levels

The recruitment of children was very limited (4 volunteers). They were under 10 years old and had BLL mostly above the geometric mean of 10.84 μg/l (Table 2) for the corresponding age category in the ESTEBAN general population survey (2014–2016), which is the most relevant study for comparison (Oleko et al., 2020). As expected, children had a lower BLL than adults) due to the combination of their shorter exposure history and the bioaccumulative behavior of Pb.

Most of the interpretation on BLL for adults has already been

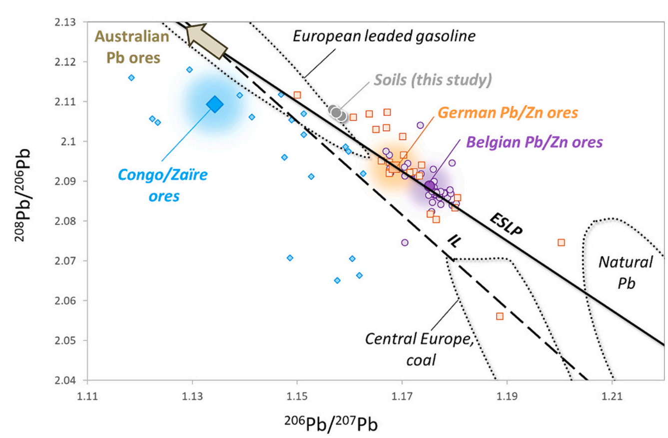

Fig. 1. Tri-isotope plot for anthropogenic and Natural Pb sources showing « EU Leaded Gasoline », « Natural Pb » and « Central Europe Coal » fields from Komárek et al. (2008), with soils data (this study). "Industrial Line" IL and « European Standard Lead Pollution » line ESLP are from Véron et al. (1999) and Haack et al. (2003), respectively. Data on Belgian ores (purple circles), German (orange squares) and Congo/Zaïre (blue diamonds) ores, and Australian ores (out of range) are compiled from Dejonghe, 1998; Doe and Rohrbough (1977) and Sangster et al. (2000), respectively. Larger symbol size corresponds to weighted average isotopic compositions of ores based on the number of analysis reported for each orebody.

Table 1
Trace metal concentrations (mg/kgDW) and Pb isotopic composition of three representative soil samples. Number in parenthesis refer to the error on the last significant digit for each isotopic ratio.

	As	Cd	Zn	Pb	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$
GC16720/10	34	5.2	1662	896	38.052 (2)	15.604 (1)	18.052 (1)	2.1079 (0)	1.1569 (1)
17J0988	35	5.8	1400	630	38.086 (3)	15.608 (1)	18.082 (1)	2.1063 (1)	1.1585 (2)
17J1046	46	4.6	1506	510	38.082 (2)	15.613 (1)	18.073 (1)	2.1071 (0)	1.1575 (1)

Table 2
Individual (children) and descriptive statistics (adults) for BLL (μg/l) and BLI compositions. GM: geometric mean; SD: standard deviation.

	BLL	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$
Adults, statistic descriptors (n = 81)						
GM	24.1	38.078	15.610	18.107	2.103	1.160
SD	18.5	0.139	0.011	0.099	0.005	0.006
p10	10.3	37.946	15.599	18.005	2.097	1.154
p25	16.6	38.000	15.604	18.061	2.100	1.157
p50	23.1	38.077	15.610	18.101	2.103	1.160
p75	36.0	38.124	15.614	18.142	2.106	1.162
p90	49.6	38.217	15.619	18.198	2.108	1.165
MIN	7.2	37.746	15.578	17.844	2.090	1.146
MAX	103.1	38.673	15.656	18.508	2.115	1.182
Children, individual samples						
TENV-2	14.1	38.084	15.609	18.106	2.103	1.160
TENV-3	22.0	38.057	15.606	18.076	2.105	1.158
TENV-66	10.7	38.097	15.609	18.128	2.102	1.161
TENV-67	12.4	38.094	15.611	18.120	2.102	1.161

presented in a previous publication (Petit et al., 2022b). Adults showed a geometric mean BLL of 24.1 μg/l (n = 81, see Table 3), higher than values measured in general French populations at the same period (e.g. Nisse et al., 2017; Oleko et al., 2020) and in the range of those measured 12–13 years earlier (Hutse et al., 2005, Falq et al., 2011) despite the general decreasing trend in BLL over time and even for similar age categories (Petit et al., 2022b). As in general population surveys, BLL in the study population were strongly correlated with age ($r^2 = 0.456$, p-value <0.001) but not with years spent in the study area. Differences in gender, country of birth or educational achievement were not associated with differences in BLL (p-value >0.05). However, BLL in the study population were positively associated with smoking status (p-value = 0.010), the presence of Pb pipes at home (p-value = 0.030), and tap water consumption (p-value = 0.035). Also, higher BLL were associated with several variables indicating that soil is a direct or indirect source of exposure, such as "allotment attendance" (p-value = 0.011), "cultivating several allotments" (p-value = 0.034), and "eating homegrown vegetables the week prior to blood sampling" (p-value = 0.001).

Multivariate linear regression provided a statistically significant model equation (Eq. 1) with a $r^2 = 0.518$ and a $F(5.76) = 15.291$, $p < 0.000$ – (see Table A2, supplementary material) for the prediction of the blood Pb concentrations, taking into account 5 predictor variables:

$$ln(\mathbf{BLL}) = 1.160 + 0.020^*(\mathbf{age}) + 0.265^*(\mathbf{type\ of\ water\ consumed}) + 0.358^*(\mathbf{homegrown\ vegetables\ consumption}) + 0.431^*(\mathbf{active\ smoker}) + 0.422^*(\mathbf{former\ smoker})$$

3.3. Blood Pb isotopes

Data on BLI signatures are summarized in Table 2. Children and adults in the study group did not significantly differ in BLI ratios (p-value = 0.582). Adults have geometric mean (+ − 1 SD) BLI ratios of 38.078 (0.139), 15.0610 (0.011) and 18.107 (0.099) respectively for $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$. Shapiro-Wilk statistic shows that Blood lead isotope ratios are not normally distributed (Fig. B2, supplementary material). Most BLI data follow a trend roughly parallel to the ESLP line (Fig. 2 and Fig. B3, supplementary material), within or close to the lower end of the EU gasoline field. However, some samples are characterized by a relatively more thorogenic signature.

Blood lead isotope ratios are not significantly correlated with BLL, nor age. Variables from the survey questionnaire showing statistically significant associations (p-value <0.05) with BLI are mostly different than those found with BLL. Statistically significant associations were not found simultaneously for all six Pb isotope ratios ($^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$). Table A3 (supplementary material) reports the variables for which statistically significant associations were found with at least two BLI ratios. The most significant ones were "period the house was built (before or after 1950)" (5/6), "country of birth" (4/6), "use of traditional food containers" (3/6) and, to a lesser extend (2/6), "allotment attendance frequency" and the "presence of Pb pipes at home".

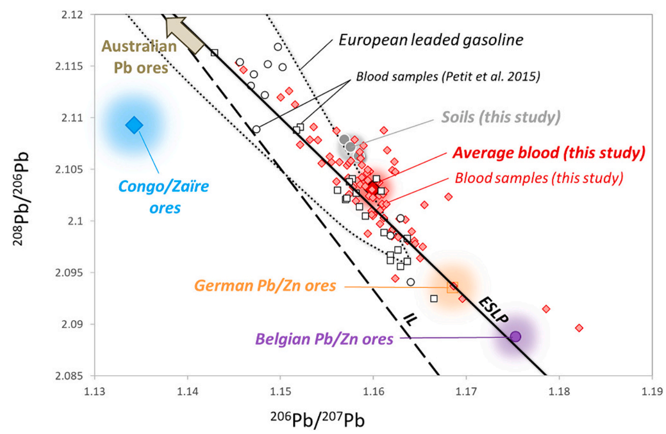

Fig. 2. Tri-isotope plot for blood lead data from this study (red diamonds - large symbol size corresponds to the population average) and from Petit et al. (2015) (1976–1978: white dots; 2008–2009: white squares). See Fig. 1 for additional information's and fig. B3 (supplementary material) for ^{204}Pb normalized tri-isotope plots.

4. Discussion

4.1. Sources of Pb to the contaminated soil

If the Pb isotopic signature for soils could apparently consist in a mixing between the (most) radiogenic Pb component from pristine soils with the least radiogenic component represented by combustion residues from Pb gasoline processed from (the least radiogenic) Australian Pb ores (see Fig. 1), other dominant Pb sources are at play in order to reach high soil Pb concentrations measured in soils in the Liege city. Industrial metallurgy that took place in Liege over a century has led to soil contaminations by Pb, Zn, Cd, and As (see Table 1) in relative concentrations that exclude the above hypothesis as the main one explaining the isotopic signature in soils. In addition, as shown elsewhere in Belgium (Sonke et al., 2002), Australian ores may have been processed at Liege for several decades as early as the 1910's, giving rise to abundant less radiogenic Pb by-products (slags, dust) as diffuse contaminations to nearby soils, that are not linked to the deposition of residues from leaded gasoline. At present, the limited knowledge on Pb isotope signatures in soils in Liege are not appropriate to build up a robust interpretation on the environmental sources of Pb responsible for the Pb isotopic signature measured in these contaminated soils.

4.2. The contaminated soil as a source of exposure

Unintentional ingestion of contaminated soil and soil-derived dust particles is generally known to be one of the main source of exposure to Pb for populations living on Pb contaminated soils. In fact, analysis of the survey questionnaires pointed out several significant associations between BLL and variables related to soil exposure in the study population (see Section 3.2.2).

Considering a $Pb_S = 360$ mg/kg (median Pb concentration in soils from the area, see section 2.1), the predicted BLL is 23.7 μg/l, which is consistent with the measured BLL value of 24.1 μg/l (GM of the study population, see Table 3) or 23.3 μg/l (GM of the study population excluding individuals above 74 y.o) in our study. When based on central values for exposure parameters and media concentrations, the US EPA biokinetic Adult Lead Model (see section 2.4) predicts that roughly 20 % of the BLL could result from the exposure to Pb from soil. Changes in $IR_{S,D}$ or Pb_S to upper percentile values (0.1 g/d and 1000 mg/kg, respectively) increase BLL values up to 32.9 and 35.8 μg/l, i.e. in the range of the 75th percentile of the BLL distribution. Even if homegrown vegetables consumption is omitted in the above model, the highest BLL observed are probably not only caused by the direct or indirect exposure to the contaminated soils.

Consistently, the three soil samples do not have Pb isotopic signatures representing an endmember that would fully account for the whole variability observed in BLI ratios for the study population. Soil Pb isotope ratios are close to the mean value of the BLI signatures measured in this study (Fig. 2). Blood Lead isotopes are mainly aligned with the ESLP line (Haack et al., 2003), overlapping BLI compositions measured in Belgium and Northern France in 1976–78 and 2008–2009 by Petit et al. (2015). They spread from lower $^{206/207}$Pb and higher $^{208/206}$Pb values, typical of Pb refined from Australian ores and formerly used in European gasoline, up to higher $^{206/207}$Pb and lower $^{208/206}$Pb in agreement with more radiogenic BLI compositions measured for urban population sampled in 2008–2009 (Petit et al., 2015), probably reflecting evolution of the main Pb sources through time. Since there is no relationship with BLI and BLL or with age in our study population, the more radiogenic signature probably reflects a higher impact of environmental and/or domestic Pb sources not related to the natural background signature. Soil Pb also shows a slight but consistent enrichment in ^{208}Pb (i.e. relatively more thorogenic, Table 1) that seem to be shared with some blood samples also showing more thorogenic isotopic signature compared to the ESLP.

Since Eq.1 provided realistic estimates for the contribution of soil Pb to BLL, it can be further modified into a binary mixing model for BLI compositions (Eq. 2). The isotopic composition of Pb in blood due to the exposure to Pb from soils, $^{20X}Pb/^{20Y}Pb_{0+S,D}$ (where X and Y = 4, 6, 7 or 8), can be determined from the isotopic composition of Pb in soil, $^{20X}Pb/^{20Y}Pb_{S,D}$ and the BLI composition attributed to the adult general population, $^{20X}Pb/^{20Y}Pb_0$, as follow:

$$BLL^*\left(\frac{Pb_{20X}}{Pb_{20Y}}\right)_{0+S,D} = BLL_0^*\left(\frac{Pb_{20X}}{Pb_{20Y}}\right)_0 + BKSF^*Pb_S^*AF_{S,D}^*IR_{S,D}^*\left(\frac{Pb_{20X}}{Pb_{20Y}}\right)_{S,D} \quad (2)$$

Using $^{20X}Pb/^{20Y}Pb_{0+S,D}$ and $^{20X}Pb/^{20Y}Pb_{S,D}$ values from this study, the biokinetic model allows to back-calculate the average BLI composition of the general adult population $^{20X}Pb/^{20Y}Pb_0$. The expected BLI composition of adults from the general population is estimated at 38.079; 15.610; 18.118; 1.161 and 2.102, respectively for $^{208}Pb/^{204}Pb$; $^{207}Pb/^{204}Pb$; $^{206}Pb/^{204}Pb$; $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$. This extrapolated value is closer to the ESLP line (Haack et al., 2003) while remaining close to the lower end of the European gasoline field (Komárek et al., 2008), as shown in Fig. 3. This suggests that the study population, and probably the general adult population as well, have BLI compositions that may still be partially affected by the isotopic signature of Australian Pb, despite the ban on leaded gasoline in the early 2000's.

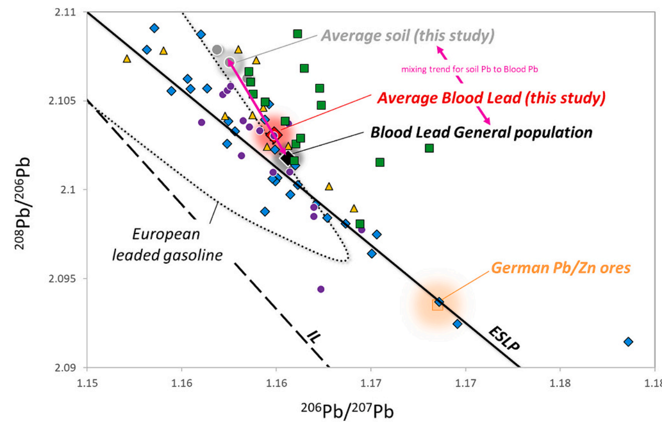

Fig. 3. Tri-isotope plot with soils and blood Pb mixing trend. The pink double arrow corresponds to the range of variation obtained from the one compartment biokinetic model showing the mixing between baseline BLL (general adult population, black diamond) and soils. Blue diamonds, yellow triangles, green squares and purple dots corresponds to population subgroups 1,2,3 and 4, respectively (see Fig. 5). See fig. B4 (supplementary material) for ^{204}Pb normalized tri-isotope plots.

If measured and predicted BLL mostly agree through a single-compartment biokinetic model applied to the study population, higher individual BLL cannot be solely attributed to a higher (direct and/or indirect) exposure to soil. Indeed, in addition to soil-related variables, age, smoking status, the type of water consumed (tap or bottled), and the presence of Pb pipes at home are also associated with observed BLL in the study population, and probably to BLI signatures as well. Statistically significant associations between BLI and (i) the presence of Pb pipes at home, (ii), the period the house was built (before or after 1950), as well as (iii) the use of traditional food containers (see Table A3, supplementary material) corroborate the hypothesis that different Pb sources presumably with contrasted isotopic signatures are at play. Yet, these sources would have a rather large range of isotopic compositions to explain the variability in BLI values measured in the study population.

A recent study by Kamenov et al. (2023) shows that the Pb isotopic composition of excavated Pb pipes used for municipal water supply (and by extension, the anthropogenic stock of Pb in use) are very variable at the scale of the U.S.A (i.e. $^{206}Pb/^{207}Pb$ varying from ~1.100 to ~1.383). This could hold true as well at the scale Europe regions where Pb refined from ores of various origin (Sonke et al., 2002) have been added to the stock of Pb in use for more than a century. Several factors could explain the persistence of Australian Pb isotope signature in the blood of the Western European population more than a decade after Pb gasoline withdrawal: (i) the release of bioaccumulated Pb from bones, recording more of the former signature when air Pb levels were high, (ii) the presence of Australian Pb in the in-use stock of manufactured Pb (Pb pipes, paints, solders and other consumer products relevant to chronic human exposure), (iii) the environmental resilience and secondary remobilization of Pb gasoline and/or diffuse Pb sources lost from their technological cycles, including smelting by-products, and (iv) food chain contamination from Pb contaminated soils (including fertilizers/sewage sludge amendments). This hypothesis was also proposed by Resongles et al. (2021) for urban aerosol in London sampled in 2018.

4.3. Review of BLI data and variations related to the country of birth

Other BLI data in the Western European population are mainly restricted to two studies:

- Oulhote et al. (2011) who provided a large dataset on a subpopulation of 125 French children aged 0.5 to 7 years old, sampled in 2008–2009, with measured BLL > 25 μg/l.
- Petit et al. (2015) who compared BLI signatures from 6 children and 26 adults from urban areas sampled in 1976–1978 (n = 11) and 2008–2009 (n = 21) in Belgium (n = 20) and Northern France (n = 12).

Despite the small individual sample size, data acquired by Petit et al. (2015) on adults sampled in 1976–1978 show a statistically significant difference in BLL and BLI signatures with those measured in 2008–2009 and those from our study, consistent with a former higher exposure to less radiogenic leaded gasoline (see also Fig. 2). In contrast, no statistically significant differences in BLI signature is observed between adults sampled in 2008–2009 and those sampled in our study, suggesting that the interplay of environmental sources has remained mostly stable over the last decade, when leaded gasoline was already withdrawn, which confirms that Pb-gasoline is not the main contributor to BLL and BLI in the general population anymore.

Blood Pb isotopes data from Oulhote et al. (2011), Petit et al. (2015) and the present study are among the most radiogenic ones reported by Gulson et al. (2006) for populations of various nationalities worldwide (native Australian or newcomer women in child-bearing age, sampled over a 10-year period between 1990 and 2000) (Fig. 4). In fact, adults from the current Western Europe population have a BLI composition characterized by a relatively high radiogenic signature, despite the likely persistence of Australian Pb component in blood, as experienced by the study population. Lead ores of economic interest may also show moderately radiogenic isotope compositions as for Belgian and in particular German ores (see Fig. 1), closer to Natural Pb. The lack of clear trend between BLI and BLL in our study is consistent with the occurrence of Antropogenic Pb refined from those ores in the in-use stock of Pb. BLI data also suggest that Congo/Zaire Pb ores, showing more uranogenic isotopic compositions (Sonke et al., 2002) are not significant source for anthropogenic Pb affecting BLI signatures of the study population.

As suggested by Gulson et al. (2006), the dependence of BLI signatures with nationality is certainly one of the first order feature to consider when interpreting BLI data, owing to the influence of the regional geochemical background and the signature of anthropogenic Pb that have entered the regional economies. In this respect, our study population showed a rather large spectrum of nationalities, mainly Belgian/French native (n = 35), Italian natives (1950's newcomers, n = 16), as well as Moroccan and Turkish natives (1970's newcomers, n = 17) and other nationalities (n = 18). Blood Pb isotopes ratios showed statistically different signature across these populations (Fig. 5 and Fig. B4, supplementary material). Despite the small sample size, statistically significant differences in BLI ratios are observed in the study population with Moroccan and Turkish natives compared to other categories for birth countries, with higher $^{208}Pb/^{204}Pb$; $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{207}Pb$ ratios, consistent with a more thorogenic isotopic signature (see also Fig. 3). In addition, more participants from this category declared using traditional food/beverage containers (Chi^2 test with p-value = 0.003), which was also associated with differences in BLI compositions (see Table A3). Statistically different BLI signatures for the Turkish and Moroccan subgroup could be attributed to the country of birth and tentatively related to the occurrence of an isotopically distinct in-use stock of lead in these two countries. It could also result from the more frequent use of non-EU traditional food/beverage containers for this particular study group, composed of Pb with a different isotopic signature.

If the spread of BLI data along the ELSP line towards the Australian Pb ore component is certainly the first order feature in the dataset, the relatively more thorogenic BLI signatures observed for some samples may be caused by the combination of (i) exposure to the local

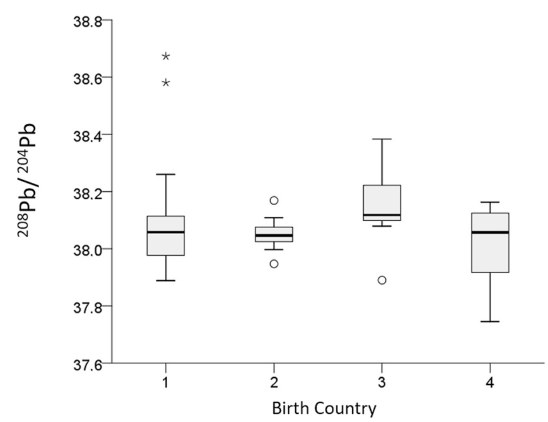

Fig. 5. Comparison by country of birth. Distribution of $^{208}Pb/^{204}Pb$ isotope ratio in blood for (1) Belgian and French natives; (2) Italian natives, (3) Moroccan / Turkish natives and (4) people with other country of birth from the study population.

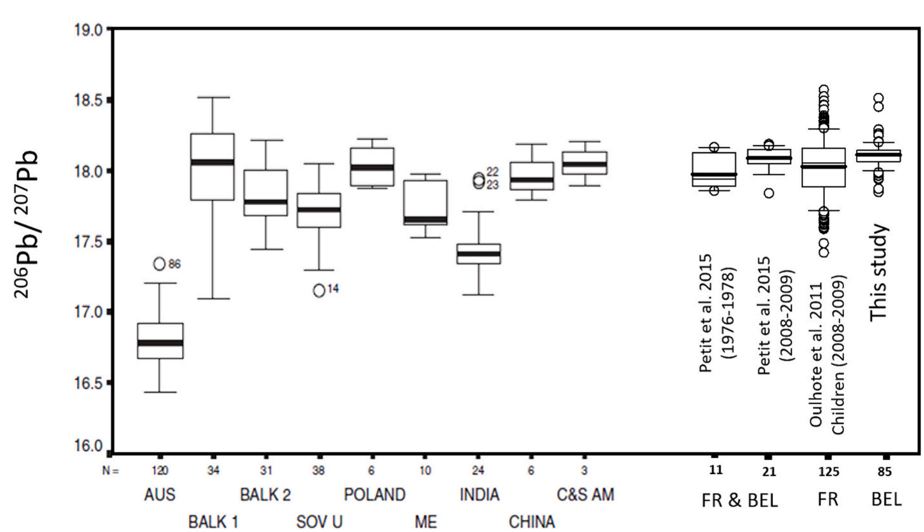

Fig. 4. Distributions $^{206}Pb/^{204}Pb$ in various population worldwide modified from Gulson et al. (2006), compared to those relevant to western Europe from Oulhote et al. (2011), Petit et al. (2015) and from this study, with n = number of individuals.

contaminated soil and/or (ii) by the particular BLI signature of people born in Morocco or Turkey. Other differences in blood Pb isotopes are also associated with variables related to housing characteristics such as the period the house was built (before or after 1950) and the presence of Pb pipes at home (see Table A3).

5. Conclusions

Blood lead levels and BLI data from 85 individuals exposed to Pb contaminated soils due to former metal processing activities in the city of Liege (Belgium) are interpreted with (i) a statistical analysis of the survey questionnaires, allowing to identify variables associated with significant differences in BLL and BLI and (ii) a one-compartment biokinetic-isotopic model for Pb, used to quantify BLL and changes in BLI signatures due to the exposure from Pb in soils.

The present study is, to date, the largest collection of high precision BLI data acquired in the Western European population.

There is no simple relationship between BLL and BLI in the study population, indicating complex interactions between different Pb sources. Higher BLL in adults are associated with factors indicating a higher exposure to Pb from soil, which is consistent with a BLL increment due to ingestion of soil & dust of about 20% compared to the general population, as estimated from a one-compartment biokinetic model. Soil Pb is not likely the main driver explaining variations in BLL. Other variables such as the smoking status, the type of water consumed and the presence of Pb pipes at home are important explaining factors as well for BLL in the study population. Consistently, local soils do not have a Pb isotope signature fully accounting for the variability of BLI, as being close to the average BLI measured in the study population. Statistically significant differences in BLI compositions are also observed depending on the presence of Pb pipes at home and the period the house was built, as well as the use of traditional food containers. The isotopic composition of Pb in blood spread along a trend close to the ESLP line mostly within the EU leaded gasoline field, thus likely recording, at least partially, an anthropogenic Pb component tracing the less radiogenic Australian ores, even nearly two decades after the withdrawal of leaded gasoline. In addition, some blood samples show a more thorogenic isotopic compositions that could be consistent with the isotopic signature of soils samples and/or result from the presence of particular subgroups of foreign origin in the study population.

Extrapolation of BLI data from the study group with a one-compartment biokinetic-isotopic model. model suggests that the general adult population still records the Australian Pb ore signature in blood. Comparison with the literature suggests that the interaction between environmental Pb sources and routes of exposure has not changed significantly during the last decade. In fact, the stock of metallic Pb in use as well as diffuse environmental contaminations relevant to human exposure likely integrates various isotopically distinct sources of Pb refined from ores of different origins including Australia. This may certainly account for the very variable BLI values observed in the study population.

A thorough assessment of the isotopic signature of the stock of Pb in use, also considering industrial history, would be necessary to confirm or refute this hypothesis. Scientific efforts should also be directed towards a more in-depth quantification of the isotopic composition of dietary Pb as it represents the major source of exposure to Pb in the general population.

CRediT authorship contribution statement

Jérôme C.J. Petit: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Nadine Mattielli:** Writing – review & editing, Validation, Investigation, Data curation. **Jeroen De Jong:** Validation, Methodology, Investigation, Formal analysis. **Elodie Bouhoulle:** Writing – review & editing, Formal analysis. **Wendy Debouge:** Resources, Investigation. **Patrick Maggi:** Validation, Formal analysis. **Geneviève Hublet:** Formal analysis. **Nathalie Fagel:** Investigation. **Catherine Pirard:** Investigation. **Corinne Charlier:** Investigation. **Remy Suzanne:** Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Petit reports financial support was provided by Walloon Public Service. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.174763.

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