Applied Geochemistry 145 (2022) 105397

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Lead and stable lead isotopes as tracers of soil pollution and human health risk assessment in former industrial cities of Hungary

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ARTICLE INFO

Editorial Handling by: Jiubin Chen

Keywords:
Urban soil
Industrial lead pollution
Stable lead isotopes
Contamination source
Health risk assessment

ABSTRACT

Lead is a toxic heavy metal that has become much more prevalent in the environment since industrialization and causes considerable health problems. The current study investigated the spatial distribution and sources of lead from urban soils in former heavy industrial cities, Salgótarján and Ózd (northeastern Hungary). Even today, industrial byproduct (e.g., coal ash, smelter slag) dumps in both cities pose a real threat to the residents. Our analytical results acquired on samples from kindergartens, playgrounds, parks, roadside, etc. indicated a heterogeneous lead distribution with 8.5–1692 mg kg-1 for Salgótarján and 6.6–1674 mg kg-1 for Ózd. The enrichment of Pb results from the high variability of the potential anthropogenic contamination sources, such as iron and steel work, coal mines, coal-fired power plant, smelter slag, vehicle emission, etc., in the studied areas. The potential lead emission sources were defined by $^{206}Pb/^{207}Pb$ – $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ – $^{208}Pb/^{204}Pb$ isotopic ratios in urban soil samples and the local endmembers: namely brown forest soil ($^{206}Pb/^{207}Pb$: 1.20 in Salgótarján and 1.21 in Ózd), brown coal ($^{206}Pb/^{207}Pb$: 1.18 in Salgótarján and 1.26 in Ózd), and industrial byproducts ($^{206}Pb/^{207}Pb$: 1.18 coal ash in Salgótarján and 1.12–1.16 smelter slags in Ózd). A positive correlation between TOC, TN, Mn, and Pb in Salgótarján and between Fe, Mn, and Pb in Ózd, shows that the urban soil characteristics play a significant role in Pb distribution in the sampling sites. Our study confirms that coal ash in Salgótarján and smelter slag in Ózd can be considered primary anthropogenic Pb contamination sources, resulting in low chronic health risks for residents.

1. Introduction

Lead (Pb) and its compounds have been used in various products since the ancient time of the Roman Empire and increased dramatically after industrialization (Komárek et al., 2008; Riva et al., 2012). Over centuries, anthropogenic activities (mining, manufacturing, industrial activities, etc.) have resulted in widespread Pb contamination in urban areas that jeopardizes the well-being of residents and the environment (Galušková et al., 2014; Hiller et al., 2017; Ljung et al., 2006). In addition, these industrial and corresponding activities introduced various chemical forms of Pb into the environment that are widely regarded as persistent components (Saint-Laurent et al., 2010). Their principal increase occurred after using Pb in various industrial products (e.g., pipes, steel, glass, gasoline, paint, battery, ammunition, etc.) due to its chemical and physical characteristics, such as low melting point and corrosion resistance, density, and malleability.

Soil contamination is a primary environmental concern because of its interactions with the hydrosphere, atmosphere, and biosphere. Due to its high affinity for specific soil components (e.g., clay minerals, iron and manganese oxides, organic matter), Pb can be retained by the soil matrix or with high solubility under oxidative conditions it can be mobilized by particle and colloids to different environments (Ibanez et al., 2007; Löv et al., 2018; Hooda 2010). Hence, in the biogeochemical cycle, numerous Pb contaminants have remained within the biosphere and continue to be an exposure source for organisms. Human exposure occurs mainly through the food chain, drinking water, inhalation, and

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https://doi.org/10.1016/j.apgeochem.2022.105397
Received 18 February 2022; Received in revised form 25 June 2022; Accepted 18 July 2022
Available online 31 July 2022

direct or indirect contact (Zacháry et al., 2015; Zhang et al., 2010).

Due to its adverse health effects, the Agency for Toxic Substances and Disease Registry has listed Pb as the second element of the highest public health concern (ATSDR 2019). Once Pb enters the organism, it can cause a wide range of physical and mental issues. At high levels of human exposure to Pb (>10 μg/dL in blood; CDC . Centers for Disease Control, 2012), there is damage to nearly all organs and organ systems, most notably the central nervous system and kidneys that are resulting in death (Dapul and Laraque 2014). In addition, children are exposed and intake up to 40% more Pb than adults because of their behavior and physiology. Consequently, around 18 million children suffer from constant brain damage from Pb poisoning (WHO 2011).

Lead in urban soil indicates a highly variable origin and is derived over long periods from numerous sources, such as coal ash and bottom slag produced by coal combustion, metallurgical smelters, gasoline, paints, natural sources, etc. One of the major sources, leaded gasoline, was introduced to the market in the 1920s (Komárek et al., 2008). During the 1980s in Europe and North America, engine Pb emissions rapidly dropped after the average Pb content of petrol was decreased to 0.15 g/l (Bollhöfer and Rosman, 2001; Löfgren and Hammar 2000), resulting in a robust decline of Pb concentration in the atmosphere and hydrosphere (Zhu et al., 2010).

Recently, Pb stable isotopes have been used to track potential sources and origins of Pb to differentiate its anthropogenic and geogenic (natural) sources in environmental studies (Reis et al., 2016). The method is called "isotopic fingerprinting" and is based on the fact that, in the natural environment, Pb has four stable isotopes (i.e., ^{204}Pb (1.4%, primordial), ^{206}Pb (24.1%, partially radiogenic, parent: ^{238}U), ^{207}Pb (22.1%, partially radiogenic, parent: ^{235}U) and ^{208}Pb (52.4%, partially radiogenic, parent: ^{232}Th), which can be expressed in various ratios (e.g., ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb, ^{206}Pb/^{204}Pb, ^{208}Pb/^{204}Pb) in environmental sciences for anthropogenic and geogenic source identification of potential endmembers (Komárek et al., 2008; Reimann et al., 2016; Liu et al., 2016). Furthermore, it is known that natural (e.g., chemical weathering) and industrial/technological processes (e.g. chemical treatment) do not affect considerably to the isotopic composition of Pb (Nakata et al., 2017), making the method a powerful tool.

In this paper, we studied soil samples from urban areas such as kindergartens, playgrounds, parks, etc., indicating anthropogenic contamination as a result of industrial activity in and around residential areas. The primary goals of this study are to 1) determine the spatial distribution of Pb and its contamination level in two former industrial cities, 2) utilize stable Pb isotope ratios to identify contamination sources and their influence on urban soils, and 3) assess the health risk for the residents. Due to the limited research in Hungary on Pb and stable Pb isotopes, the current study contributes to the Pb database of Central and Eastern Europe.

2. Material and methods

2.1. Sampling area and sites

Sampling was performed in two former industrial cities of Hungary, Salgótarján and Ózd. The cities are located in approx. 40 km distance from each other (Fig. 1A), and were significant brown coal, iron, and steel suppliers of Hungary for more than a century. The elevation ranges from 250 to 500 m for Salgótarján and 120–250 m for Ózd above sea level, and the highest elevations are framed at the northern margins of the cities. The relief is characterized by hills and valleys with several creeks; the wind is northern dominated. Geological edifices consist of Neogene sedimentary formation with sandstone, marl, aleurolite, brown coal, rhyolitic pyroclasts in Ózd and additionally lava rocks, such as basalt and andesite in Salgótarján (Kercsmár et al., 2015). In both cities, the surrounding area covered by brown forest soils.

Salgótarján and Ózd cities cover 103 km^2 and 92 km^2 areas with around 32,000 populations, respectively (Fig. 1B and C). In Salgótarján, foundation and development of ironwork started in the mid-18th century when brown coal deposits were discovered in the settlements. Due to the iron and steel manufacturing, glassworks, mining machine factory, stove factory, and ferroalloy factory functioned along the main roads, Salgótarján was considered a multi-industrial city. The city and its adjacent area were provided by energy from the coal-fired power plant, which was supplied by the local brown coal mines (Fig. 1B). In Ózd, the iron and steelwork were established in the city center in the mid-18th century and ~150 years later was extended to the north-eastern part of the city, where its activity continues as of today (Ózd Steelworks Ltd.; Fig. 1C). The energy consuming iron works and later steel metallurgy was supplied by local brown coals.

In 1980s, industrial production started to decrease, and after the collapse of the communist system, the shutdown of coal mines and most of the industries (Fig. 1B) dramatically changed the employment rate, life standard, and population of the whole region. This economic and social shift resulted in remarkable changes in the landscape of the cities, where the reconstruction of commonwealth establishments (particularly buildings of schools and kindergartens) and open recreation areas (playgrounds and parks) started. However, the footprint of the significant and long-term (at least 170 years) heavy industrial activities (coal mining, heavy industry, and later road and train transportation) can be recognized even today in both cities due to the presence of potential contamination sources (e.g., ruins of former smelters, coal mines, coal-fired power plant, 'slag hill', 'ash cone', etc.) (Fig. 1B and C).

2.2. Sampling

Soil samples were collected in residential areas of Salgótarján and Ózd, including samples from surrounding sites, like steel factories, coal mines, different dumps, coal-fired power plant, and surrounding forests (Fig. 1B and C). A 'zig-zag' sampling strategy (Alloway 2013) was followed from each 1 × 1 km grid for both cities, where randomly picked points, based on the availability of desired site categories as kindergarten, playground, park, and 'other' (i.e., roadsides, cemeteries, soccer pitch, and gardens) were selected for urban soil sampling. A total of 39 urban soils from Salgótarján and 64 urban soils from Ózd were collected from 5 to 15 cm depth to study (upper 5 cm soil was removed due to plant residues). A local coal ash sample was taken from an ash cone of the former coal-fired power plant in Salgótarján (Fig. 1B), and smelter slag samples from the former and the active smelter dumps in Ózd (Fig. 1C). Moreover, brown coal samples (from the same Neogene geological formations) were acquired from the former coal mines, Inászó (eastern part of Salgótarján) and Farkaslyuk (former part of Ózd) that were obtained from the collection of the Department of Physical and Applied Geology of Eötvös Loránd University, Budapest. The local geochemical background samples, i.e., brown forest soils (Fig. 1B and C), were taken from the nearby forest area, far (~7 km away) from all potential contamination sources (e.g., former iron and steel works, road systems) in both cities. Our urban soil sampling followed the EuroGeoSurveys Geochemistry Expert Group Sampling Protocol (e.g., Demetriades and Birke, 2015; Zacháry et al., 2015; Völgyesi et al., 2014). To avoid cross-contamination, samples were collected and delivered to the laboratory in plastic bags.

2.3. Methods

2.3.1. Sample preparation and chemical analysis

The urban soils were air-dried in the laboratory and passed through 2-mm sieves to obtain a representative portion. For homogenization, the coning and quartering procedures were applied. Visible organic materials (e.g., worms, grasses, roots) and urban debris (e.g., bricks, concrete,

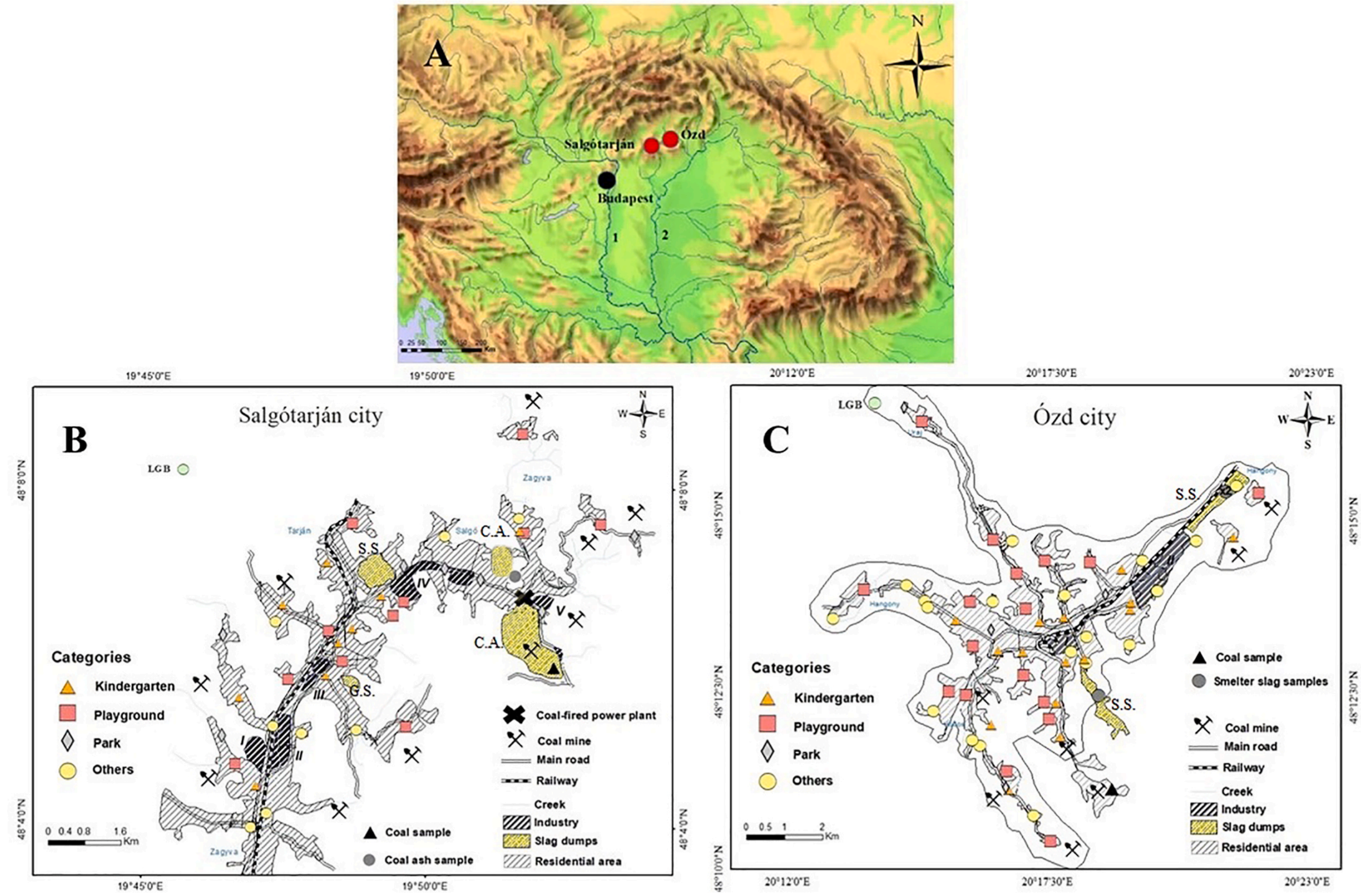

Fig. 1. A. Carpathian-Pannonian region shows the geographic environment of the two studied cities (Salgótarján and Ózd). Brown color - mountains (like the Carpathian Chain), green color - plains (Pannonian Basin), blue color - major rivers (Danube −1 and Tisza - 2). **B.** Map of Salgótarján and **C.** Map of Ózd, showing the sampling sites and their categories, residential areas, locations of the industry and coal mine, slag landfills, and coal-fired power plant. Abbreviation for Salgótarján: I - former mining machine factory, II - former glassworks, III - stove factory, IV - former steelworks, V - former ferroalloy factory, and **C.** Map for Ózd: I - former steelworks, II - present steelwork. GS-glass slag, SS-steel slag, CA-coal ash. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

waste) were removed before grinding. The rest of the sample preparations (such as mortaring, pulverization, etc.) were performed at Bureau Veritas Global Company[1] in Canada (Bureau Veritas, 2021). The soil samples were digested by modified aqua regia digestion (1:1:1 HNO_3: HCl: H_2O) method at 95 °C on 15 g of <0.075 mm milled aliquots for low to an ultra-low determination of Pb, as well as Fe and Mn in soils (Reimann et al., 2009). The isotopic (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) and elemental contents (Fe, Mn) of soil samples were analyzed by quadrupole-based ICP-MS (The detection limit is 0.01 mg kg-1) at the Bureau Veritas Global Company in Canada (Bureau Veritas, 2021). For homogeneity and heterogeneity identification, a total of 10 (7 from Salgótarján and 3 from Ózd) urban soil duplicate samples were used.

The analytical quality was controlled using certified reference materials NIST981 (common Pb standard, USA), NIST983 (radiogenic Pb isotopic standard, USA), and DS11 (internal standard for Fe and Mn). The analytical precision of stable Pb isotopes was found to be <3.6% RSD for ^{204}Pb, 2.1% for ^{206}Pb, 2.9% for ^{207}Pb, and 2% RSD for ^{208}Pb.

Analyzed and expected concentrations for the NIST981 SRM are 0.28 mg kg-1 and 0.2851 mg kg-1 for ^{204}Pb, 4.8475 mg kg-1 and 4.8288 mg kg-1 for ^{206}Pb, 4.4525 mg kg-1 and 4.4167 mg kg-1 for ^{207}Pb, 10.453 mg kg-1 and 10.469 mg kg-1 for ^{208}Pb, respectively. Analyzed and expected concentrations for the NIST983 SRM are <0.01 mg kg-1 and 0.0068 mg kg-1 for ^{204}Pb, 18.248 mg kg-1 and 18.43 mg kg-1 for ^{206}Pb, 1.3275 mg kg-1 and 1.3122 mg kg-1 for ^{207}Pb, 0.26 mg kg-1 and 0.251 mg kg-1 for ^{208}Pb, respectively. The procedural blanks were measured for each isotope and is < 0.01 mg kg-1 for ^{204}Pb, <0.03 mg kg-1 for ^{206}Pb, <0.02 mg kg-1 for ^{207}Pb, and <0.07 mg kg-1 for ^{208}Pb. A standard Hg correction was used for ^{204}Pb isotope measurements, and the results were negligible due to the low Hg content of the samples.

The grain size fraction analysis of soil samples was performed with around 0.5 g of soil, mixed with an optimal amount of Na-pyrophosphate ($Na_4P_2O_7$) to disaggregate particles (Abdulkarim et al., 2021), which was further performed by applying to ultrasonic. The mixture was allowed to stand overnight, so that the aggregates are dispersed and then analyzed by the Laser Scattering Particle size distribution analyzer PARTICA 950-V2 LA instrument at the Research and Instrument Core Facility of Sciences, Eötvös Loránd University. The particles were divided into three grain size fractions: <8 μm (clay), 8–63 μm (silt) and >63 μm (sand fraction) (Thomas et al., 2021).

The organic content (organic carbon, total nitrogen, ammonia, nitrate) of the soil samples was estimated at the Institute for Soil Sciences and Agricultural Chemistry by the loss-on-ignition method (Wright et al., 2008). The air-dried soil samples were mixed with 10 ml of distilled water for Eh-pH analysis. The mixture was kept rotating for 30 min. Soil pH and conductivity (Eh) were tested in deionized water in a 1:10 soil-water ratio with a digital “Eijkelkamp 18.52.01 Multimeter”

[1] A global leader in Testing, Inspection and Certification of geochemical, geoanalytical and mineral analysis.

instrument (Yu and Rinklebe 2015).

2.3.2. Data analysis and mapping

The data was analyzed and displayed by R v4.0.2 (R Core Team, 2020) and OriginLab v9.5.1 softwares. Sampling locations (Fig. 1B and C) were recorded by GPS and processed by ArcGIS v10.3 software. Surface maps were created by the Inverse Distance Weighting (IDW) method, which was used to transform the values from the erratically distributed sampling points to regular grid-based variograms. Class divisions for Pb distribution color maps are based on a manual classification to compare Pb data in both cities and indicate the internationally accepted soil Pb threshold value (300 mg kg-1; CSTEE, 2000).

A ternary mixing model (Luo et al., 2015; Reis et al., 2016; Wang et al., 2019) was used to distinguish the proportion of industrial, brown coal and natural Pb input in urban soil samples. The calculations include $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios by the following equations:

$$(^{206}Pb/^{207}Pb)_{sample}=(^{206}Pb/^{207}Pb)_1*f1+(^{206}Pb/^{207}Pb)_2*f2+(^{206}Pb/^{207}Pb)_3*f3 \quad \text{(eq. 1)}$$

$$(^{208}Pb/^{207}Pb)_{sample}=(^{208}Pb/^{207}Pb)_1*f1+(^{208}Pb/^{207}Pb)_2*f2+(^{208}Pb/^{207}Pb)_3*f3 \quad \text{(eq. 2)}$$

$$f1+f2+f3=1 \quad \text{(eq. 3)}$$

The subscript of f1, f2, and f3 represent the potential local geogenic and two primary anthropogenic Pb sources (e.g., coal ash, smelter slag, brown coal, etc.) expressed in ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$, respectively, and f1, f2, and f3 are the approximate contribution (in %) of each source (transferred to % after calculations).

2.4. Health risk assessment

Non-carcinogenic human health risk assessment is calculated by a health risk model suggested by the US Environmental Protection Agency (US EPA, 1989a, 1989b; RAIS, 2017). The study covers only the ingestion pathway exposure (as the inhalation and dermal reference doses are missing/uncertain for Pb (Rapant et al., 2011)), which can result from hand-to-mouth action, dropped food, or direct soil or dust consumption.

The non-carcinogenic risk assessment was done by the following equations (RAIS, 2017):

$$CDI_{children/adults}=(C*EF*ED*IR*CF)/(AT*BW) \quad \text{(eq. 4)}$$

$$HQ^i=CDI^i/RfD^i \quad \text{(eq. 5)}$$

CDI represents the daily intake of metal(loid)s; C – concentration of Pb at sampling site ($mg*kg^{-1}$); EF – exposure frequency that is 350 days/year; ED – exposure duration that is considered 6 years for children and 30 years for adults; IR – ingestion rate that is 200 $mg*kg^{-1}$ for children and 100 $mg*kg^{-1}$ for adults; AT – average time = 365*ED; BW - average body weight, which is 15 kg for children and 70 kg for adults. Hazard Quotient (HQ) >1 indicates possible adverse health effects, whereas HQ <1 means no adverse health effect. Oral reference dose (RfD) for Pb is 3.60E-03 (US EPA, 1989a, 1989b; RAIS, 2017).

3. Results and discussion

3.1. Pb distribution

Results showed that the average Pb concentrations of urban soil samples for both cities are similar: 82 mg kg-1 in a range of 8.5 and 1692 mg kg-1 for Salgótarján and 80 mg kg-1 in a range of 6.6 and 1674 mg kg-1 for Ózd (Table 1; Tables S1 and S2). The spatial distributions of the data (Fig. 2A and B) show that elevated Pb concentrations in urban soils are highly characteristic, especially in industrial sites (Tables S1 and S2).

The three outlier Pb concentrations in Salgótarján are encountered at a park (STN09: 81 mg kg-1), a playground (SNT24: 1692 mg kg-1) in the city center close to the north-south main road, and at a site of a roadside (STN30: 433 mg kg-1) close to the western coal mining area (Fig. 3A and B). In Ózd, the four outlier Pb concentrations derived from the former (OZD38: 596 mg kg-1) and current steel industry sites (OZD54: 1674 mg kg-1), at a kindergarten (OZD13: 173 mg kg-1) close to the former smelters and a playground (OZD42: 251 mg kg-1) near the former loading station of the "dinkey" line (Fig. 2A and B, Fig. 3A and B, Tables S1 and S2). Comparable results from kindergarten, playground and park soils of surrounding countries were published, where Pb values ranged from 11.0 to 190 mg kg-1 for fifty-nine kindergarten and nineteen park soils, as well as from 13.2 to 163 mg kg-1 for hundred playground soils of Bratislava (Slovakia) due to the effect of industrialization (Hiller et al., 2017, 2020). In Ostrava (Czech Republic), the Pb concentration of nine urban parks ranges from 27 to 125 mg kg-1, indicating a slight effect of airborne particle deposition from industries (Galušková et al., 2014), In Maribor (Slovenia), Pb values in one hundred eighteen top soils show wide range with elevated concentration: 19–626 mg kg-1 (Gaberšek and Gosar 2018) (Table 1). Among our studied urban soil samples, two Salgótarján (STN24 - playground, STN30 - roadside) and two Ózd samples (OZD38 – old industry, OZD54 – new industry) show higher Pb content than the safe soil Pb value accepted by the European Commission (300 mg kg-1, CSTEE, 2000). In comparison to the local geochemical background (LGB) values (STN: 16.7 mg kg-1, and Ózd: 17.5 mg kg-1), Pb content in most of the urban soil samples desplayes high concentration, but in the outlier samples it shows approximately 10–100 times higher values (Table 1, Fig. 2A and B, Fig. 3A and B). High enrichment of Pb at the industrial sites is consistent with the results (up to 5260 mg kg-1) reported on hundred twenty two soil samples from urban areas of Bytom city (Poland), which is one of the most disastrous industrial areas of Europe (Ullrich et al., 1999).

For around a century, brown coal mining, the dominant energy source, was one of the essential and widespread anthropogenic activities in Salgótarján and Ózd. The Pb concentrations of Neogene brown coal samples in Salgótarján and Ózd are 2.7 mg kg-1, and 1.9 mg kg-1, respectively (Table 1). These values fall below the word brown coal average (3.5 ± 11.3 mg kg-1; Keegan et al., 2006) and are far below the Neogene brown coal of Portugal (19 mg kg-1) and Romania (17 mg kg-1)

Table 1

Summary (minimum, mean, median, and maximum values) of lead concentration (mg kg-1) in urban soil samples from Salgótarján, Ózd, and other comparative cities. Local brown coal, coal ash from Salgótarján, smelter slag from Ózd, and brown forest soil (as local geochemical background) data are also included, respectively. Salgótarján coal ash is from the coal-fired power plant, Ózd smelter slag samples derived from two smelter slag dumps (slag1, slag3).

Cities	Urban soils				Coal	Coal ash Smelter slag			Brown forest soil	References
	Minimum	Mean	Median	Maximum						
Salgótarján	8.5	82 ± 47.44	20.5	1692	2.7	14.2			16.7	This study
Ózd	6.6	80 ± 31.64	29.8	1674	1.9	28.48	3.26	200.20	17.5	This study
Shanghai	19.1	64.9	–	308						Li et al., 2011a
Bytom	69	627	430	5260						Ullrich et al. (1999)
Ostrava	27	58 ± 28	49	125						Galušková et al., 2014
Bratislava	11	30.9	24	190						Hiller et al. (2017)
Maribor	19	60.5	44	626						Gaberšek and Gosar (2018)

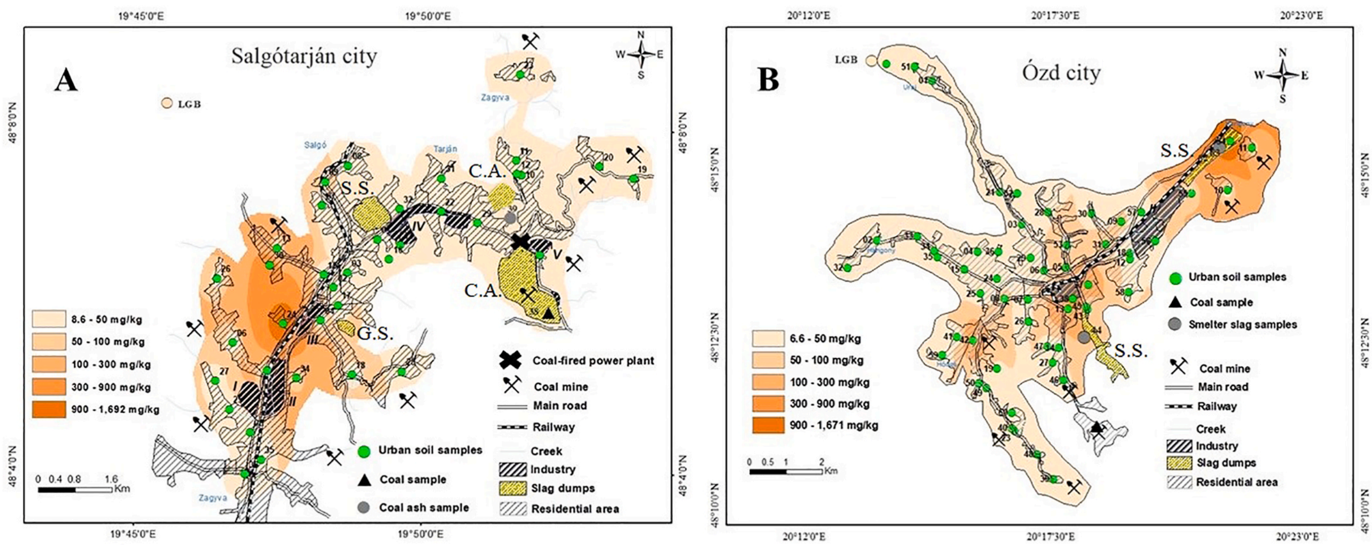

Fig. 2. Spatial distribution maps of Pb in Salgótarján (A) and Ózd (B) cities showing sampling sites, locations of ash, slag, and coal, and relative information from Fig. 1B–C. Distribution of Pb concentrations (mg kg-1) in both cities is indicated and makes the city maps comparable. Class divisions (Pb concentration ranges) are set on manual classification involving the internationally accepted soil Pb threshold value (300 mg kg-1; CSTEE, 2000). Local geochemical background (LBG) samples (brown forest soils) are also shown. GS-glass slag, SS-steel slag, CA-coal ash. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

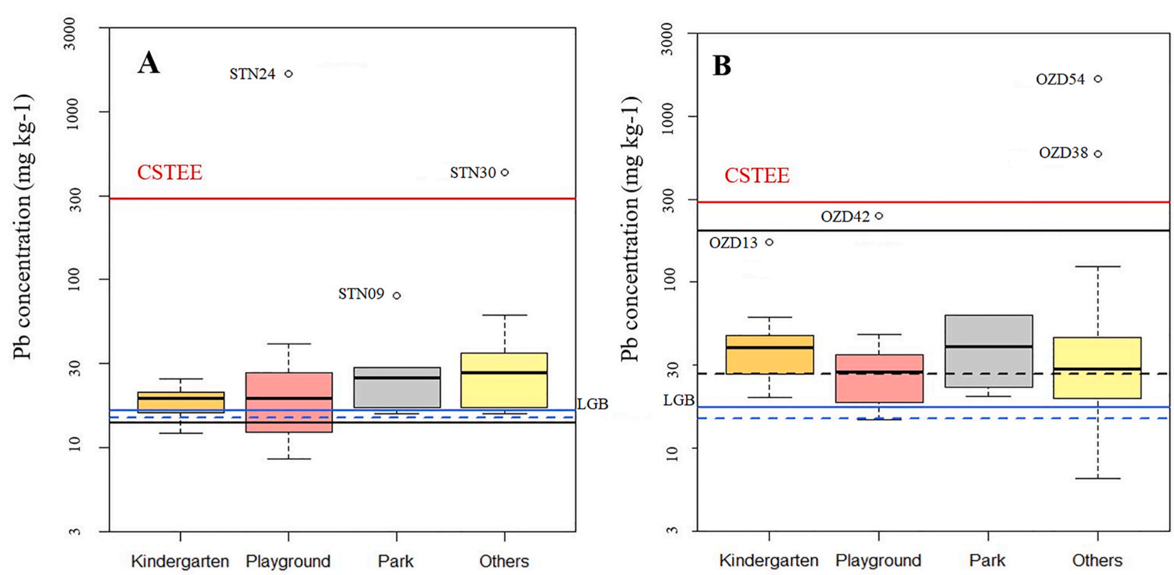

Fig. 3. Box and whiskers diagrams showing Pb concentration (mg kg-1) distribution in Salgótarján (A) and Ózd (B) based on sampling categories in log10 scale. Blue dashed line represents the background value of FOREGS for Hungary (Zacháry et al., 2015), blue line represents brown forest soil (local geochemical background: LGB) for both cities. Black line denotes coal ash for Salgótarján and smelter slag for Ózd (OZD44 slag3 (showing the highest value). Red line indicates the permitted maximum (300 mg kg-1) soil Pb concentration of the European Union (CSTEE, 2000). Outlier samples (Salgótarján: STN24, STN30, STN09; Ózd: OZD54, OZD38, OZD42, OZD13) are numbered. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(Díaz-Somoano et al., 2009). Though Pb concentrations of the studied Salgótarján and Ózd brown coal samples are very low, a long period of coal combustion in the coal-fired power plant at Salgótarján and different smelters, particularly in Ózd, could accumulate a significant amount of Pb in the urban environment in the form of coal ash and smelter slag, respectively (e.g., Raj et al., 2019). However, Pb concentration of Salgótarján coal ash (STN39) and two Ózd smelter slag samples (OZD62 slag1 and OZD63 slag2) (Fig. 2A and B) reflect low concentrations of Pb (14 mg kg-1 for Salgótarján, and 28.5 mg kg-1 and 3.3 mg kg-1 for Ózd, respectively) (Tables S1 and S2). Similar results were reported from coal ash of the South Moravia (3–69 mg kg-1) in the Czech Republic (Pešek et al., 2005), and Upper Silesian and Belchatov basins (3.4–131 mg kg-1) in Poland (Bielowicz 2021). The potential reason for the unexpectedly low Pb content of our studied coal ash and two smelter slag samples could be the result of the long-term (approx. 50–100 years) physical and chemical weathering process on different dumps, which was also concluded by Lottermoser, 2002), studying smelter slag deposits at North Queensland, Australia. Therefore, in Salgótarján, around the former steel factory (STN01- kindergarten and STN32 - park) and the coal ash cone (STN21- roadside) Pb concentration is relatively low and there is no sign for spatial enrichment (Fig. 2A). However, the high lead concentration in sampling sites could be explained by their proximity to local contamination sources. In the Salgótarján playground (STN24) and roadside (STN30) samples, the observed high Pb content might indicate the effect of the closest former glasswork and/or former mining machine factory (Fig. 1A). Other studies have demonstrated increased contents of trace elements, including Pb, in surface soils around glass factory and dumps (Hiller et al., 2020; Jani and Hogland 2017). This could be one of the reasons for Pb enrichment in the soil samples, though two sampling sites, next to the glasswork at the roadside (STN33 and STN34), have low Pb content (Fig. 1A). The Ózd urban soils collected in the city center (where the former steelwork operated with its surrounding area) and in site of the recent steelwork show several folds higher Pb content than the local LGB value (OZD54 - recent industry, OZD13 - kindergarten, OZD38 - former industry and OZD37 – roadside). Furthermore, one of the three metallurgic smelter slag samples (OZD44 - slag3), from dump of the former industry also shows elevated concentration of Pb (200 mg kg-1) (Figs. 2B and 3B, and Table S2) that allows us to explain the Pb enrichment in Ózd urban soil samples. The highest concentration of Pb (1674 mg kg-1; Figs. 2B and 3B, and Table S2) was measured in the recent industrial area, which indicates the usage of coal as an energy source in the iron industry or the usage of smelter slag from old industry. Additionally, it is observed that in both cities, sampling sites with elevated Pb content are mainly the result of the presence of coal ash and smelter slag below the topsoil layer, noted during soil sampling (Fig. S2). These byproducts were used to cover or fill up stream beds, holes, mining galleries, openings, etc. Thus, a part of the former Salgótarján smelter slag deposit from 'slag hill' (Fig. 2A) has already been removed, and the urban soil samples around this deposit do not show sign of high Pb content (discussed above). This approach was encountered frequently in Salgótarján regardless of sampling site categories (e.g., STN09 - park, STN14 - playground, STN16 - playground, STN24 - playground) and in Ózd at playground sites (e.g., OZD13 - kindergarten, OZD42 - playground) (Fig. 1B and C, 2A-B, 3A-B). Despite the evident Pb concentration differences in Salgótarján and Ózd sampling categories (Fig. 3A and B, Tables S1 and S2), they indicate no correlation with Pb enrichment. Therefore, for interpretations, the sampling sites were rather treated as individual locations (not categories).

3.2. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ distribution in the studied areas

To further understand the potential origin of Pb in urban soils, the stable Pb isotopic ratios were studied, and the obtained data shown in Tables S1 and S2, and their basic statistics are summarized in Table 2. Lead isotopic ratios in Salgótarján urban soil samples fall within a narrow range of 1.15–1.24 for $^{206}Pb/^{207}Pb$ and 2.34–2.57 for $^{208}Pb/^{207}Pb$. In contrast, Ózd urban soil samples show a wider range and lower isotopic ratios of $^{206}Pb/^{207}Pb$ (ranging between 1.08 and 1.24) and $^{208}Pb/^{207}Pb$ (ranging between 2.14 and 2.50), respectively (Table 2, Tables S1 and S2).

The spatial distribution maps of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic ratios for Salgótarján (Fig. 4A-B) and Ózd (Fig. 4C-D) show random patterns, and most urban soil samples show medium to low Pb isotopic ratios compared to those of the local geochemical backgrounds (Table 2). The isotopic ratio ranges partially coincide with the park soils of the Ostrava (1.20–1.80 for $^{206}Pb/^{207}Pb$ and 2.42–2.49 for $^{208}Pb/^{207}Pb$; Galušková et al., 2014) and Shanghai (1.12–1.95 for $^{206}Pb/^{207}Pb$ and 2.40–2.49 for $^{208}Pb/^{207}Pb$; Li et al., 2011) values (Fig. 5), showing similar industrial activities (i.e., iron and steel works).

High $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios (Fig. 4A and B) were observed at the southwestern corner (a segment of agricultural area: STN36 - cemetery) and the northern side of Salgótarján, around the former steel factory (STN22 - roadside, STN29 - park, and their surroundings: STN10 - playground, STN11 - park and STN12 – kindergarten). The latter is a partially residential and partially meadow environment, which should have been interacted and contaminated by production of metallurgy, coal ash, traffic and coal mining, which provided characteristic high Pb isotopic ratios (Fig. 4A and B) with low Pb concentration (Fig. 2A). The nearby coal-fired power plant was ceased ~50 years ago, whereas the byproducts, coal ash deposits, are still spread in the city (Fig. 1B). In Ózd, some small clusters with low $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios (Fig. 4C and D) were detected especially in the former industrial sites (OZD13 - kindergarten, OZD44 - smelter slag3). Therefore, we assume that the long-term and continuous activity of the steel factory in the central part of the city (Figs. 2B and 4C) produced characteristic by-product that dispersed and decreased Pb isotopic ratio (Fig. 4A and B) in soils around former industrial area. A similar effect was observed due to Pb smelter activity in Příbram soils, Czech Republic (Ettler et al., 2004). On the contrary, entire western part of the city and some sampling sites located inside city (e.g., OZD58 - roadside, OZD12 - kindergarten, OZD56 - recent industry) show high $^{206}Pb/^{207}Pb$ ratio (Fig. 4C), whereas the Pb concentrations are relatively low (~22–32 mg/kg) (Fig. 2B). The low isotopic ratios can be associated with contiguous agricultural land use where heavy industrial activity was not present. Although, Reimann et al. (2012) and Kelepertzis et al. (2016) reported that the continental-scale distribution of the $^{206}Pb/^{20}Pb$ isotope ratios in the European agricultural soils is higher, especially in northern Europe due to the granitic bedrock, compared to the rest of the territory, and the isotopic ratio ranges between 1.12 and 1.73 with the median value of 1.20. Our isotopic data (Table 2) from Salgótarján and Ózd support this statement, and the $^{206}Pb/^{207}Pb$ isotopic ratios of the studied urban soils (Fig. 4A and C) fall within the lower part of the European range.

Table 2
Summary (minimum, mean, median, and maximum values) of commonly used Pb isotope ratios in urban soil samples from Salgótarján and Ózd cities. Data on local brown coal, coal ash, smelter slags and brown forest soils (local geochemical background) were also included, respectively.

Salgótarján	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
STN Urban soil samples (36):				
Minimum:	1.14	2.34	17.96	36.81
Mean:	1.19 ± 0.004	2.47 ± 0.008	18.65 ± 0.132	38.58 ± 0.310
Median:	1.20	2.47	18.51	38.20
Maximum:	1.24	2.57	22.74	47.74
STN38:Brown coal	1.18	2.47	22.33	47.00
STN39:Coal ash	1.18	2.46	18.68	39.11
STN37:Brown forest soil	1.20	2.44	18.44	37.57
Ózd	**$^{206}Pb/^{207}Pb$**	**$^{208}Pb/^{207}Pb$**	**$^{206}Pb/^{204}Pb$**	**$^{208}Pb/^{204}Pb$**
OZD Urban soil samples (55):				
Minimum:	1.08	2.14	15.75	31.87
Mean:	1.19 ± 0.004	2.41 ± 0.009	18.23 ± 0.094	36.84 ± 0.230
Median:	1.19	2.41	18.28	36.90
Maximum:	1.24	2.50	19.22	39.60
OZD61:Brown coal	1.26	2.46	24.50	48.00
OZD62:Smelter slag1	1.16	2.40	21.06	43.56
OZD63:Smelter slag2	1.14	2.38	16.20	33.80
OZD44:Smelter slag3	1.12	2.28	15.70	32.06
OZD00:Brown forest soil	1.21	2.46	19.44	39.52

3.3. Identification of potential Pb emission sources

The application of different three-isotopic ratio plots of $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$ (Fig. 5A) and plot of $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$(Fig. 5B) is a powerful tool to distinguish the local Pb pollution sources (e.g., Li

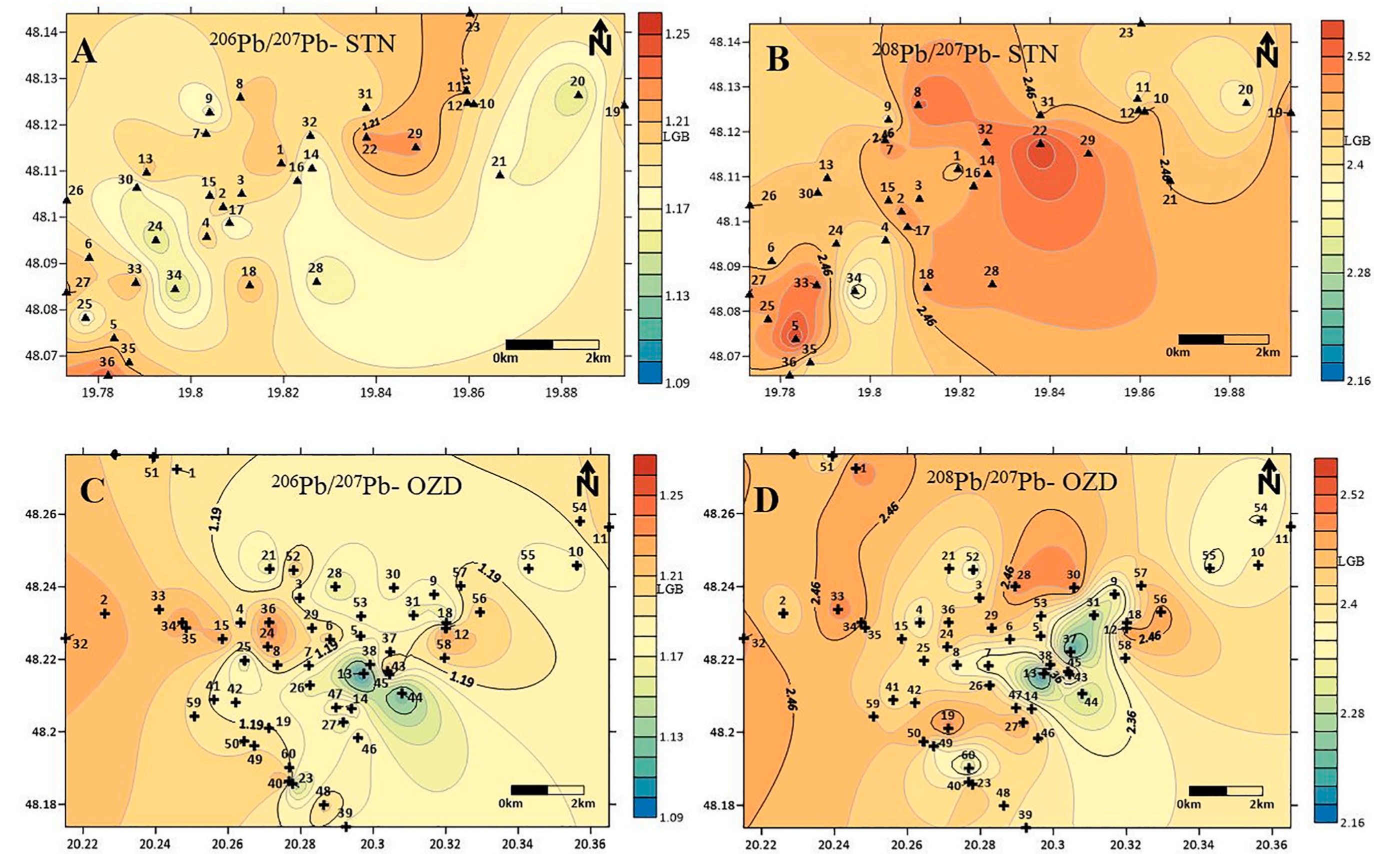

Fig. 4. Isotopic distribution maps of $^{206}Pb/^{207}Pb$ ratio (A-B) and of $^{208}Pb/^{207}Pb$ ratio (C-D) for Salgótarján (STN) and Ózd (OZD) urban soils, respectively. Sampling site numbers are the same as shown in Fig. 2A and B. Isotope ratios of brown forest soils (local geochemical background – LGB) are marked on scale bars as LGB. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

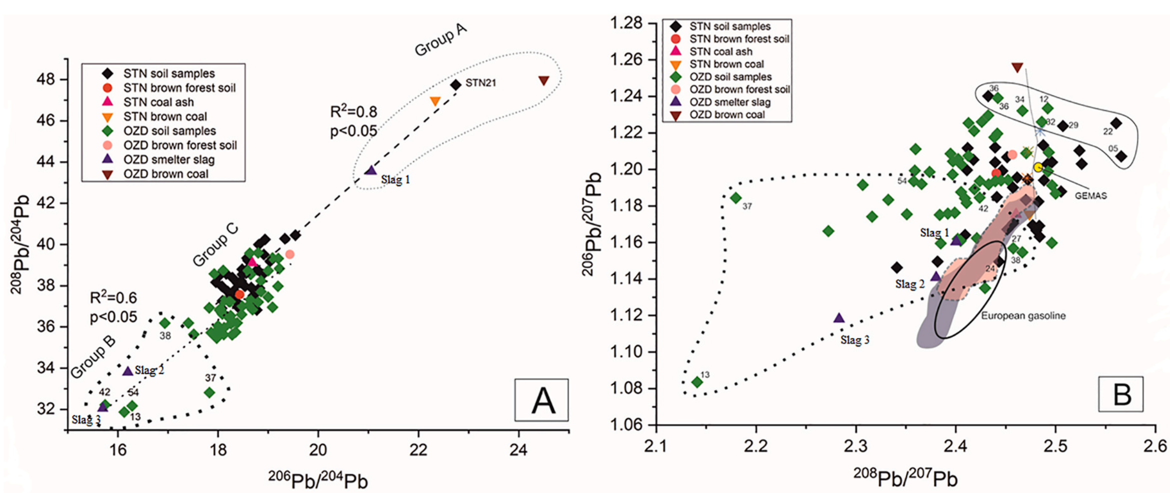

Fig. 5. Variation of $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$ (A) and $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ (B) isotopic ratios of Salgótarján and Ózd urban soil samples. The brown forest soil samples from both studied cities (as geochemical background - LGB), local coal samples, coal ash from Salgótarján, and smelter slag samples from Ózd are shown on A and B. On A,dotted and dashed line represent samples with impact of the relevant contamination sources: smelter slga for Ózd and caol ash for Salgótarján, separately. On B, grey area represents urban soils from Shanghai (Li et al., 2011), and pink area represents urban soils from Ostrava (Galušková et al., 2014). The range for European gasoline is from Kelepertzis et al., 2016b); Komárek et al., (2008); Monna et al., (1997). The GEMAS data represents the isotopic ratio of Hungarian agricultural soils from the GEMAS project (Reimann et al., 2012). Coal samples were connected by a line and represents Hungarian (green asterisk), Portuguese (red asterisk), and Romanian (blue asterisk) samples published by Díaz-Somoano et al., 2009. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

et al., 2011). Substantially distinct patterns were obtained by $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$ isotopic ratio plot (Yu et al., 2016; Sucharová et al., 2014) and distinguished the Salgótarján and Ózd data into three groups (Fig. 5A). Notably, Group-A represents both coal samples from Salgótarján and Ózd, OZD62-slag1 (from recent industrial area), and an urban soil sample (STN21 - roadside) collected next to the Salgótarján coal-fired power plant (Fig. 2A and B, Fig. 5A). This particular urban soil sample contains high coal ash content (Fig. S1) and is reasonable proxy of the characteristic coal ash signature from the Salgótarján coal-fired power plant. The STN coal ash sample exposed to chemical weathering and caused a depletion of trace elements (inc. Pb) as was discussed earlier and reported by various researchers (Lottermoser 2002; Stefaniak et al., 2015). Sample OZD62 smelter slag1 derived from recent industrial site shows distinct isotopic ratio, similar to coal samples, which can be explained by its fine grain size fraction containing relatively high coal components (Fig. 5A).

Group-B contains urban soil samples (OZD13 - kindergarten, OZD37 - roadside, OZD38 - former industry, OZD042 - playground, and OZD54 - recent industry) which illustrate the highest isotopic ratios and are comparable to Ózd smelter slag2 (OZD63) and smelter slag3 (OZD44) (Fig. 5A). These samples are characterized by high Pb content and are located around the former and recent iron-steel factories (Fig. 2) that describes the significant input of contaminants from local industries on soils (Kelepertzis et al., 2020; Yang et al., 2018). Group C includes most of the urban soils and two local brown forest soils (local geochemical background - LGB), and the weathered Salgótarján coal ash (STN39). Majority of the Salgótarján urban soils falls between Salgótarján brown forest soil and STN21 urban soil (the latter is proxy of the coal ash). In contrast, almost all of the OZD urban soils fall between Ózd brown forest soil and Ózd63 slag3 samples (the latter is a smelter slag deposit, close to the former factory (Fig. 2B). Therefore, urban soil samples from both cities can be considered as mixtures of local brown forest soil (as geogenic) and local STN coal ash/local OZD smelter slag (as anthropogenic) components in various degrees (Fig. 5A).

A wide $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ isotopic distribution with partial overlap is seen in urban soil samples from the studied cities, and comparative Shanghai and Ostrava isotopic data originated from similar urban environment (Fig. 5B). This indicates a high possibility of mixing of the potential end members (coal, coal ash in Salgótarján, and smelter slag in Ózd) with urban soils, which could form the high variability of Pb isotopic ratios in urban soil (see also Fig. 4A and B). Sampling sites with the highest $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic ratios have relatively moderate to low Pb content and they considere natural soils since the majority of these sites are far from the industry (see Ózd sampling sites) or significant landscape change/recultivation processes (see Salgótarján sampling sites), which reduced the effect of former industrial activity. Particularly, the roadside samples (e.g., STN05 and STN22) might be exposed to various transported pollutants, meanwhile the upper soil layer was replaced by artificial soil layer, which explains the isotopic deviation (Fig. 5A and B). In terms of low $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotopic ratios, the isotopic similarity of some Ózd urban soil samples (OZD13, OZD37, OZD38, OZD42, OZD54) to smelter slag samples (OZD63, OZD44) make them a good example of industrial effects (Fig. 5B), which is corresponding to elevated Pb concentration, in agreement with the spatial distribution maps (Fig. 4C and D). Whereas Salgótarján urban soil samples do not represent any characteristic local pollution sources (Fig. 5B) probably because of its multi-industrial history. However, most of the STN samples show similar isotopic ratios to local geochemical background, which is ideintical to that of Ózd and those of GEMAS project from the region (Reimann et al., 2012). Besides, the samples with lower isotopic ratio than STN local geochemical background sample might carry the isotopic signatures of coal ash, one of the biggest anthropogenic sources in Salgótarján (Fig. 5B).

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic ratios of brown coal are 1.18 and 2.47 for Salgótarján, and 1.26 and 2.46 for Ózd (Fig. 4A–D, 5B, Table 2). The Ózd coal sample shows the highest $^{206}Pb/^{207}Pb$ and intermediate $^{208}Pb/^{207}Pb$ isotopic ratio. The same isotopic values for Salgótarján coal is intermediate and highly comparative to the local geochemical background ($^{206}Pb/^{207}Pb = 1.20$ vs $^{208}Pb/^{207}Pb = 2.44$) values (Table 2, Fig. 5B). Similar isotopic ratios from brown coals of Czech Republic were reported by Mihaljevič et al., 2009. The presented data shows that the $^{206}Pb/^{207}Pb$ Ózd coal ratio (Fig. 5B) is higher than the Salgótarján coals (Table 2), whereas the data points fell on the 'coal line' obtained by data of Díaz-Somoano et al., 2009) for Hungarian, Portuguese, and Romanian brown coals (formed during Neogene time). It is known that during the coal combustion process, Pb vaporates, however, when temperature decreases, it condenses and attaches to fine particles (Pudasainee et al., 2020), that explains the significant impact of coal ash on Pb isotopic distribution. Thus, the usage of the local coal for the coal-fired power plant in Salgótarján resulted in a high similarity of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic ratios for coal and coal ash (Fig. 5B; Table 2), which are the main emission sources of the city.

On the contrary, smelter slag samples collected from Ózd revealed a wide range of isotopic ratios: $^{206}Pb/^{207}Pb$ ranges from 1.12 to 1.16 and $^{208}Pb/^{207}Pb$ from 2.28 to 2.40 (Table 2; Fig. 5B). We assume that the existence and distribution of smelter slag, related to former iron work, in both studied cities produced especially low $^{206}Pb/^{207}Pb$ isotopic ratios that can cause these variations by mixing with urban soils. Besides, low isotopic ratios may suggest the impact of additional sources, such as leaded gasoline.

Vehicular emissions can be considered another essential origin of Pb contamination (e.g., Nriagu, 1990; Komárek et al., 2008). Though the sale and use of leaded gasoline were banned in Hungary in 1999 (e.g., Salma et al., 2000), the burning of leaded gasoline for several decades had left a legacy of alkyl Pb additives embedded in the environment. Also, early aerosol analysis from Budapest indicates a strong influence of Russian Pb-ores due to higher radiogenic Pb isotopes than Western European aerosol data (Bollhöfer and Rosman 2001; Novák et al., 2003). Despite that, the exact origin of Pb in Hungarian petrol has not been defined (Bollhöfer and Rosman 2001; Hopper et al., 1991; Mukai et al., 2001; Novák et al., 2003). Therefore, we assume the average isotopic composition of Pb in Hungarian gasoline was in the range of European gasoline (average $^{206}Pb/^{207}Pb = 1.11$–1.16 and $^{208}Pb/^{207}Pb = 2.38$–2.45, (Fig. 5B); Kelepertzis et al., 2016; Komárek et al., 2008; Monna et al., 1997). Isotopic distribution of samples STN24 - playground, OZD23 - kindergarten, OZD27 - playground, and OZD38 - former industry similar to European gasoline data (Fig. 5B) could be a sign of leaded gasoline impact in both cities due to active traffic (e.g., road transportation of iron and steel productions and of coal from close mines), operating in and between the two studied industrial cities (Fig. 5B). Sipos et al., 2013 report that aerosols data collected from Budapest aerosols in the 1990s showed a strong sign of European gasoline. In fact, a general impact of leaded gasoline in both study areas (Salgótarján and Ózd) is expected, but due to reduced traffic density (following 1990), a ban on leaded gasoline in the past 30 years (Sucharová et al., 2014), local landscape changes, and reconstructions we do not consider it as a significant local pollution source.

It is obvious that Pb in both cities originated from more than one source, whereas the relative proportion of the sources requires additional calculations. The relative percentage contribution of potential local endmembers, having characteristic Pb isotopic signatures, on Ózd urban soil samples was calculated using mixing binary models - Eqs. (1)–(3) (Li et al., 2011; Kelepertzis et al., 2020) (Table S3). Input data includes the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic ratios of the following local end members: smelter slags, local coal, and local brown forest soil as geochemical background providing the natural geogenic Pb contribution (Table 2). Due to long and highly complex industrial and mining history, sporadic soil changes in parks, playgrounds, kindergartens, and similarity in coal ash and coal Pb isotopic ratios (Table 2), such calculations for Salgótarján could not be performed. The mean Pb isotopic ratios of Ózd smelter slags (slag1-2-3) are regarded as representative of the iron and steel industrial emissions. Lead contribution from the three mentioned sources was considered 100%, which resulted in, on average 51% smelter slag, 37% coal, and 12% natural relative Pb contribution. The industrial value reflects the general impact of the local iron and steel works in Ózd (operated for several decades), which caused a widespread smelter slag in the city (Fig. 2B). The impact of extensive industrial byproducts on surface soils in urban areas is one of the significant environmental problems..

Taking all previously discussed factors into account, we could consider that the various types of Pb products were mixed in urban soils and that the average Pb isotope ratios have changed. Hence, the isotopic ratios of samples most likely represented a combination of industrial (by)-products, local coal, brown forest soil and even reflected an effect of former petrol emissions (Fig. 5B). Additionally, we cannot exclude the possibility that other unidentified minor sources have influenced the Pb isotopic composition of urban soil at some sites.

3.4. Soil physicochemical properties and its connection to Pb distribution

The characteristics of Pb content in urban soils are related to their physical and chemical properties, which play an essential role in their accumulation and mobility (Csorba et al., 2014; Hiller et al., 2016). Thus, the content of Pb together with basic soil properties (pH, Eh, total nitrogen, ammonium, nitrate, total organic carbon, inorganic carbon, Fe- and Mn-content, and soil texture) were measured in the urban soil samples (Tables S5 and S6).

To identify and highlight the strength of interrelationship between Pb concentration of the studied urban soils and physicochemical parameters of the study areas, Spearman rank correlation coefficients were calculated for Salgótarján and Ózd, respectively (Table 3 and Table 4). A significant ($p < 0.05$) positive correlation was found between Pb content and physicochemical parameters, which show their strong association in both cities. Notably, Spearman correlation coefficient indicated a significant correlation between Pb and total nitrogen (TN), total organic carbon (TOC), and Mn content in Salgótarján (Table 3), whereas in Ózd, significant ($p < 0.05$) correlation was observed between Pb, Fe and Mn (Table 4). All of these indicate that the mentioned parameters highly affect the distribution and mobility of Pb in urban soils. This finding is consistent with the study by Hiller et al. (2016), which found a link between Pb and Fe and organic matter content in urban soils. Also, previous studies report that the abiotic redox reactions are the main factors controlling the mobility and transformation of Pb on the surfaces of Fe(III)- and Mn-oxides, as well as ferrous species and humic substances (Alloway 2013; Caporale and Violante, 2016). These statements suggest that, in Salgótarján soils, TOC, TN, and Mn, whereas, in Ózd soils, Fe and Mn are most likely constraints on Pb mobility, thus bioavailability in the surface environment. Though the organic content of some urban soil samples indicates high values in Ózd soils (Table S6), no significant connection was observed between soil organic matter and Pb content. This observation is in agreement with published data from contaminated urban areas of Naples (Imperato et al., 2003), where the organic content decreased if the metal content increased. This might be the result of the high content of heavy metal(loid)s, including Pb, in polluted soils, which could slow down the mineralization rate of soil organic matter as the experiment of Zhang and Wang, 2007 shows. Additionally, contaminated urban soils are characteristic of high sand fractions. Due to their nature, sandy soils contain less organic material than clay and silt fraction, which is the reason for organic content depletion in most urban samples (Seddaiu et al., 2013). Based on the average pH values (7.2 in Salgótarján and 7.5 in Ózd), the urban soil samples are slightly alkaline, and it is relatively high in Pb elevated sites (Table S5), which were similarly reported in Naples (Imperato et al., 2003), Athens (Kelepertzis et al., 2016), and Maribor (Gaberšek and Gosar 2018). However, no significant correlation was noted between pH and Pb content in the urban soils of the current study.

3.5. Health risk assessment

The health estimation based on the concentration of Pb represents a long-term risk and can overrate the authentic health risk (Liu et al., 2016). In Salgótarján and ózd, the Pb concentration analysis of the urban soils alerted four sampling sites (Salgótarján: STN24 - playground, and STN30 - roadside, Ózd: OZD38 - former industrial zone, and OZD54 - recent industrial site; Fig. 2A and B, 3A andB and Tables S1 and S2), which are considered as highestly contaminated areas. At these sites, the Pb content exceeds the maximum threshold value (300 mg/kg) for the acceptable concentration of Pb in soils assigned by the European Commission (CSTEE, 2000). This value represents the dependence of the soil Pb concentration, from a digestion point of view, on the permitted blood Pb level (max.10 μg/dL: CDC . Centers for Disease Control, 2012). Therefore, we performed an additional assessment of human health risk according to US EPA models (US EPA, 1989a, 1989b; RAIS, 2017) on Pb content to reveal the risk possibility of high Pb-contaminated areas in Salgótarján and Ózd (Fig. 2A and B). A summary of chronic health risk assessment results for Pb was presented in Table 5 and Table S4.

Despite the differences in minimum and maximum values, the average non-carcinogenic risk assessment values are similar in Salgótarján and Ózd (Table 5). Results indicate that the hazard quotient (HQ) of Pb for adults is below the safe value ($HQ < 1$) in both cities, however in two sampling sites of Salgótarján (STN24 - playground and STN30 - roadside) and two sampling sites of Ózd (OZD38 - former industrial site and OZD54 - recent industrial site; Fig. 2A and B) are higher than safe level with the values of 6.01E+00, 1.54E+00, 2.12E+00, and 5.94E+00, respectively (Table S5). These sampling sites could carry possible risk to children's health ($HQ > 1$). Similar studies on Pb contamination in urban areas (Gržetić and Ghariani, 2008; Tepanosyan et al., 2017) indicated that urban environments pose a high non-carcinogenic health risk for children compared to adults.

However, the severity and exposure level depend on the interaction

Table 3
Spearman correlation coefficient between soil physicochemical parameters, Fe, Mn and Pb content in urban soils from Salgótarján. TN - total nitrogen, NH4+ - ammonium, NO3- -nitrate, TOC - total organic carbon. The significance values were obtained after Bonferroni correction and shown by the * sign (*<0.05, **<0.001).

	TN	NH4+	NO3-	TOC	CaCO3	pH	Eh	clay	silt	sand	Pb	Fe	Mn
TN	1												
NH4+	0.52	1											
NO3-	0.26	0.49	1										
TOC	**0.93****	0.48	0.20	1									
CaCO3	−0.26	−0.27	0.14	−0.17	1								
pH	−0.53	−0.45	−0.12	−0.40	**0.59***	1							
Eh	0.52	0.45	0.12	0.39	**−0.58***	**−1.00****	1						
clay	−0.34	−0.05	−0.15	−0.39	−0.16	−0.12	0.12	1					
silt	0.42	0.32	0.22	0.37	−0.38	−0.52	0.52	0.11	1				
sand	−0.20	−0.32	−0.10	−0.12	0.45	0.50	−0.50	**−0.68****	**−0.74****	1			
Pb	**0.57***	0.17	0.01	**0.60***	−0.29	−0.31	0.30	−0.29	0.16	0.02	1		
Fe	0.10	−0.12	−0.31	0.11	−0.14	−0.15	0.14	0.12	0.04	−0.08	0.44	1	
Mn	0.46	0.24	−0.11	0.50	−0.40	−0.25	0.24	−0.12	0.17	−0.08	**0.59***	0.38	1

Table 4
Spearman correlation coefficient between soil physicochemical parameters, Fe, Mn and Pb content in urban soils from Ózd. TN - total nitrogen, NH4+ - ammonium, NO3- -nitrate, TOC - total organic carbon. The significance values were obtained after Bonferroni correction and shown by the * sign (*<0.05, **<0.001).

	TN	NH4+	NO3-	TOC	CaCO3	pH	Eh	clay	silt	sand	Pb	Fe	Mn
TN	1												
NH4+	**0.77****	1											
NO3-	0.35	0.20	1										
TOC	0.95	**0.72****	**0.29****	1									
CaCO3	−0.14	−0.25	0.09	−0.09	1								
pH	−0.27	−0.43	0.21	−0.21	**0.74****	1							
Eh	0.38	**0.49***	−0.17	0.31	**−0.71****	**−0.91****	1						
clay	−0.15	−0.05	−0.13	−0.25	−0.34	−0.27	0.28	1					
silt	0.36	0.26	0.21	0.23	−0.18	−0.10	0.24	**0.48***	1				
sand	−0.13	−0.14	−0.04	0.00	0.34	0.23	−0.33	**−0.83****	**−0.86****	1			
Pb	0.06	−0.20	0.01	0.21	0.28	0.37	−0.33	−0.38	−0.21	0.36	1		
Fe	−0.15	−0.18	0.08	−0.01	0.20	0.35	−0.31	−0.20	−0.30	0.27	**0.71****	1	
Mn	0.09	−0.01	0.07	0.22	0.21	0.42	−0.38	−0.33	−0.11	0.24	**0.62****	**0.60****	1

Table 5
Summary of chronic health risk assessment of lead for Salgótarján and Ózd cities. The exposure duration for chronic risk was considered 30 years for adults and 6 years for children. The detailed calculations are shown in Table S5 Appendix E.

City		Chronic risk (based on hazard quotient - HQ)	
		Adults (30 years old)	Children (6 years old)
Salgótarján	min	3.24E-03	3.02E-02
	mean	3.12E-02	2.91E-01
	max	6.44E-01	6.01E+00
Ózd	min	2.49E-03	2.33E-02
	mean	3.04E-02	2.84E-01
	max	6.37E-01	5.94E+00

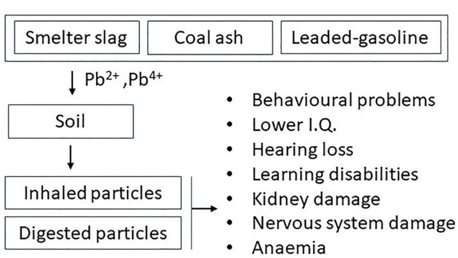

Fig. 6. The sources of lead and possible exposure by digestion pathway in children.

degree with Pb contaminants and ingestion rate (Fig. 6; RAIS, 2017). Therefore, the studied areas in both cities might be hazardous and pose a real health threat, especially in kindergartens (n = 9 in Salgótarján and n = 21 in Ózd), playgrounds (n = 11 in Salgótarján and n = 19 in Ózd), and parks (n = 6 in Salgótarján and n = 4 in Ózd) due to daily use by children (Tepanosyan et al., 2017). It is also proven that the transport of Pb-bearing particles by air and water (i.e., creeks, runoff water, subsurface water) causes potential health concerns not only in the vicinity where industrial activities took place but also in the surrounding region similarly to study of Callender (2013). Thus, long-term industrial activities in Salgótarján and Ózd not only contaminate the industrial areas but also disperse the contaminants all around the cities and pose a health threat.

4. Conclusion remarks

This paper examined Pb content and Pb isotopic compositions in urban soils (kindergarten, playgrounds, parks, and other sites) from former heavy industrial cities of Hungary. The local Pb content variations of more than 90 sampling sites in both cities demonstrate the effect of distinct Pb sources.

1) The results showed that the content of Pb on average is 82 and 80 mg kg-1 in Salgótarján and Ózd urban soils, respectively, and those values are approximately five times higher than that of local brown forest soil (16.7 mg kg-1 in Salgótarján and 17.5 mg kg-1 in Ózd). The Pb content rapidly increased in industrial areas, reaching extreme contamination levels up to 1692 mg kg-1 in Salgótarján and 1671 mg kg-1 in Ózd.
2) Areas with high Pb content were characteristic with low $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic ratio distribution. The results were reaffirmed by $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ three-endmember plots, where smelter slag, coal ash and coal-bearing samples formed distinct clusters by their specific isotopic ratios. The study areas were affected especially by two primary sources, smelter slag and coal ash contaminants, however, the impact of additional sources (e.g., leaded gasoline) cannot be excluded.
3) Soil organic matter (TOC, TN) and Mn content in Salgótarján and Fe and Mn content in Ózd regulate the distribution of Pb in urban soils.
4) The non-carcinogenic health risk assessment indicates both cities as safe areas for adults but can be risky to children's health (HQ > 1). Especially, two sampling sites in Salgótarján (a playground and a roadside sample) and Ózd (former and recent industrial sites) were defined as carrying potential health risks for residents where the soil Pb content is above the EC-permitted level.

Our study suggests using the combination of Pb concentration and isotopic ratio data to express the contamination sources effectively and the studied cities to take further measures to treat the contaminants at the risky sampling areas.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Stipendium Hungaricum and ELTE Doctoral School of Environmental Sciences. The research is financially supported by the ÚNKP-21-4 (ÚNKP-21-4-I-ELTE-272 to GA) New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development, and Innovation Fund. We are grateful to all the LRG members for their help in completing the project: Áron Bognár, Do Le Tan, Diego M. B. Santanna, Lívia Luczek (sampling and sample preparation), Boglárka Jaloveczki, Szilvia Koczur, Cintia Kollárik(sampling), Margit Kereskényi, Júlia Fehér (sample preparation), Department of Physical and Applied Geology of Eötvös Loránd University for providing brown coal samples from Salgótarján and Ózd, Dr. Gyozo Jordan for fruitful discussion, as well as local authorization and residents to assist during sampling. This is the 110th publication of the Lithosphere Fluid Research Lab at ELTE.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2022.105397.

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