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Variable Pb sources found in garden soils in Szklary Górne and Szklary Dolne (Lower Silesia)

Abstract

Garden soils from the vicinity of Szklary Górne and Szklary Dolne (Lower Silesia) have variable Pb isotope composition consistent with at least two sources of Pb contamination. The profiles from Szklary Dolne have similar Pb isotope characteristic, which can be attributed to the atmospheric contamination by mixed pollution coming from coal burning and ore smelting. The $^{206}Pb/^{207}Pb$ ratios in these soils are 1.17–1.18, similar to those observed in various soils from Lower Silesia. This confirms that such an isotope ratio is characteristic of the predominant atmospheric Pb source, which is of the anthropogenic origin. On the other hand, the soils in the vicinity of Szklary Górne have variable isotope characteristic with two profiles having $^{206}Pb/^{207}Pb$ ratios below 1.17. The low values and the variability could be attributed to pollution from leaded gasoline, as the traffic is more intense close to Szklary Górne than Szklary Dolne, because the active quarry is situated in the close proximity to Szklary Górne. Alternatively, the source of Pb may be related to construction works, because a cable was found at the bottom of the profile with the lowest $^{206}Pb/^{207}Pb$ ratios. The implication of this local study is that the garden soils offer a detailed insight into potential pollution sources present in the area, which help to identify and characterize sources that are masked by more general pollution signal in the regional scale.

Geoscience Notes 2.2, 2014

Streszczenie

Gleby ogrodowe w pobliżu Szklar Górnych i Szklar Dolnych (Dolny Śląsk) mają zróżnicowany skład izotopów ołowiu, który mógł powstać wskutek zanieczyszczenia z co najmniej dwóch źródeł. Profile ze Szklar Dolnych mają podobną charakterystykę izotopową, którą można przypisać zanieczyszczeniom atmosferycznym związanym ze spalaniem węgla i hutnictwem. W tych glebach stosunek izotopowy $^{206}Pb/^{207}Pb$ wynosi 1.17-1.18 i jest zbliżony do stosunku $^{206}Pb/^{207}Pb$ zbadanego w innych, zanieczyszczonych glebach Dolnego Śląska. To może dowodzić, że taki stosunek jest związany z zanieczyszczeniami atmosferycznymi i jest pochodzenia atmosferycznego. Profile z okolic Szklar Górnych mają różne charakterystyki izotopowe, a w dwóch z nich stosunek izotopowy $^{206}Pb/^{207}Pb$ opada poniżej wartości 1.17. Niskie wartości i zmienność stosunków izotopowych mogą być przypisane zanieczyszczeniu gleb benzyną ołowiową, ponieważ ze względu na bliskość czynnej kopalni ruch samochodowy jest większy w okolicy Szklar Górnych niż w okolicy Szklar Dolnych. Inną możliwością jest kontaminacja gleby związana z robotami ziemnymi w tym rejonie. W odkrywce o najniższym stosunku izotopowym ołowiu na dnie znajdował się przewód elektryczny/światłowodowy. Nasze badania wskazują na możliwość wykorzystania terenów takich jak przydomowe ogrody do prowadzenia szczegółowych badań nad źródłami zanieczyszczeń gleb. Często te źródła zanieczyszczeń nie są możliwe do zidentyfikowania w badaniach składu izotopowego gleb w skali regionalnej.

Keywords: garden soils, Pb isotopes, anthropogenic Pb sources, Lower Silesia

Introduction

Lead isotopes in soils are used to track different sources of Pb, for example to estimate proportions between natural and anthropogenic Pb (e.g. Erel et al. 1997; Haack et al. 2003; Ettler et al. 2004; Walraven et al. 2013; Bińczycki et al. 2014) and to identify different types of pollutants (e.g. Cicchella et al. 2008; Saint-Laurent et al. 2010). For example low $^{206}Pb/^{207}Pb$ ratios (1.10–1.16) in European soils are attributed to pollution by Pb derived from leaded petrol (e.g. Walraven et al. 2013), whereas higher ratios (1.16–1.18) may indicate contamination related to processing of European ores (e.g. Ettler et al. 2004; Kierczak et al. 2013; Tyszka et al. 2014). The study by Tyszka et al. (2012) and Kierczak et al. (2013) showed that Pb pollution in soils of Lower Silesia is dominated by Pb coming from coals and ore processing. The authors analysed different soils in Lower Silesia (Poland), both located far from and close to pollution sites such as factories, slag heaps and busy roads. The analysed soils were located in forest and showed uniform Pb isotope ratios in the upper horizons of 1.17–1.18. In this study we analysed garden soils in order to see if the soils are characterized by similar Pb isotope ratios as previously analysed forest soils. Garden soils were not analysed before in Lower Silesia and therefore provide possibility to identify new sources of Pb pollution. Generally, Pb distribution and isotope characteristic differ between the garden, agricultural and forest soils (Moir and Thornton 1989; Waterlot et al. 2011). Both garden and agricultural soils may show more variable Pb isotope composition due to additions of various products like fertilizers. They may be also affected by human activities, which is not the case for forest soils, e.g. ploughing, cropping or building and construction works of nearby houses. Generally, due to these practices, garden soils may have higher concentrations of potentially toxic elements compared to other soil types (Waterlot et al. 2011). Therefore, analysing different types of soils should provide more complete information on Pb sources in the area.

Study area and soil characteristic

Six soil profiles were investigated in this study. The study area extended between two villages, Szklary Górne and Szklary Dolne, three soil profiles were located near each of the two villages (Figure 1). Geologically the area is situated between the Fore Sudetic Block and the Sudetic Monocline (Figure 1). The basement is composed of Precambrian to Palaeozoic crystalline rocks, which are overlain by Permian and Cenozoic sediments. The youngest sediments include sands, conglomerates, clays and muds.

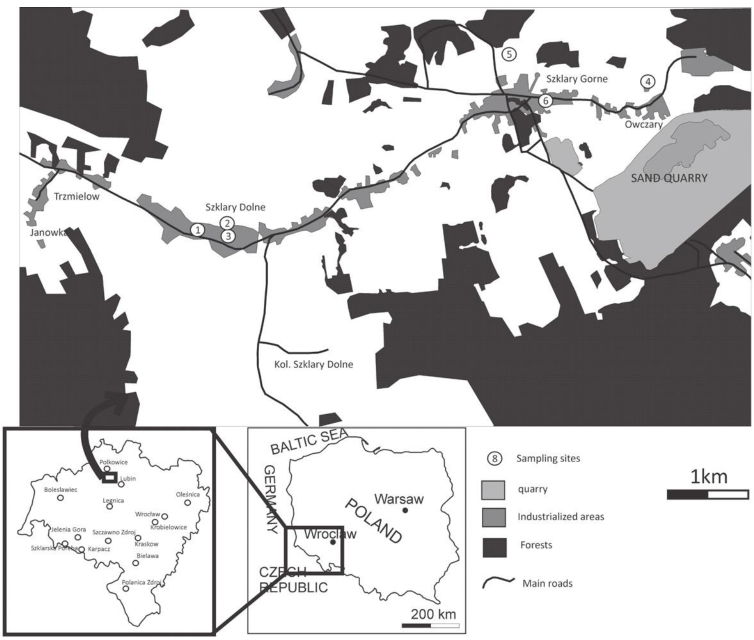

Figure 1. Detailed map showing the sampling sites

The analysed soils are located within private gardens under grass vegetation. The soil profiles show various structural characteristic (Figure 2). Profile 1 consists of anthropogenic soil with fragments of charcoal and brick throughout the whole depth of the profile (Figure 2a). Profiles 2, 3 and 4 do not show distinct horizons to the depth of 60 cm (Figure 2b,c,d). The profile 5 includes distinct horizons (Figure 2e). In profile no. 6 the horizons were disturbed probably during technical works, as a cable is present at the depth of 60 cm (Figure 2f). All of the soils are to some extent affected by human activity and can be classified as Anthrosols, specific classification based on field observations and physicochemical characteristic was done for three profiles and is presented in Table 1.

Table 1. Particle size distribution and classification of the studied soils.

Profile	Depth [cm]	Type of soil (WRBSR-FAO classification)	Silt + clay (< 0.05 mm)	Sand (0.05-2 mm)	Gravel (>2 mm)
Profile 1	0-30	Urbic Technosol (Arenic)	32 %	64 %	4 %
	> 30		24 %	70 %	6 %
Profile 3	0-30	Hortic Anthrosol (Siltic)	49 %	48 %	3 %
	> 30		45 %	48 %	7 %
Profile 5	0-30	Hortic Anthrosol (Arenic)	35 %	63 %	2 %
	> 30		32 %	67 %	1 %

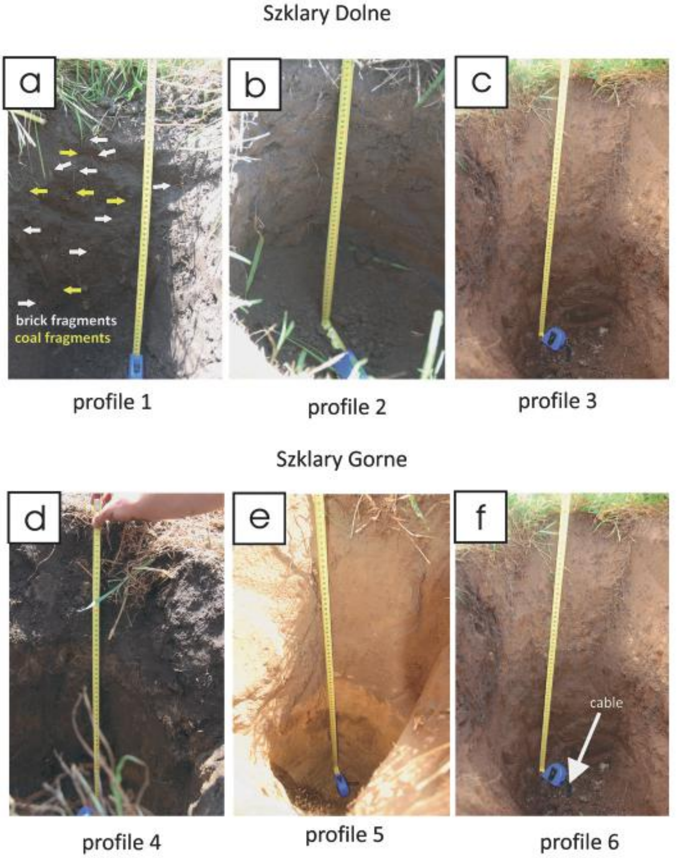

Figure 2. Field photos of the soil profiles

Materials and methods

The soil samples were collected during summer 2010. Two soil samples were collected per each soil profile (a) the upper part consisting of the upper 30 cm of the soil, and (b) the lower part consisting of soil collected from 30 to 60–70 cm. The samples are mixed soils taken from the whole indicated depth ranges (below 30 cm and from 30 to 60 cm).

The soil samples were dried and homogenized in laboratory. For analytical procedure 0.1 g of each sample dissolved in 10 mL of 40% HF and 0.5 mL $HClO_4$ for 2.5 h at 150 °C and in 5 mL of 40% HF with 0.5 mL $HClO_4$ for another 2 h. The residue in HNO_3 was analysed for metal and metalloids contents and subsequently for Pb isotopes: ^{206}Pb, ^{207}Pb, ^{208}Pb using quadrupole-based inductively coupled plasma mass spectrometry (ICP MS, X Series 2, Thermo Scientific). The details of analytical procedure are described in Mihaljevič et al. (2011). The samples were analysed in the same run as samples described in Tyszka et al. (2012). The standard errors for metal and metalloids concentrations were 0.5–4 %, and the mean standard errors for isotope were 0.4%.

Results

The analysed profiles show diverse Pb distribution and Pb isotope composition. Lead is usually found in lower concentrations in the lower parts of the profile, but the decrease in Pb from the upper to the lower horizon varies from slight in the profile no. 1 (Figure 3), through approximately 2-fold in the profiles no. 3 and no. 5, to 4–8-fold in the remaining profiles. The larger increase is observed in the soils from Szklary Górne, which are characterized by better developed horizons. The Pb content in upper parts of the soils varies from approximately 20 mg/kg in profiles no. 1, 3 and 5 to 110 mg/kg in profile no. 6 (Table 2). The lower parts of the sampled soils have the Pb range from approximately 5 mg/kg in profiles no. 4 and 5 to 30 mg/kg in profile no. 6 (Table 2). Usually the soils containing higher contents of Pb have also higher contents of other potentially toxic metals e.g. Cu, Ni, Zn, Cd, Sb (Figure 4). Mobile elements such as Zn and Cd are very well positively correlated ($R^2 = 0.95$, $p=0.005$, Figure 4). The highest concentrations of mobile elements were observed in the soil rich in brick and coal fragments in the profile no. 1.

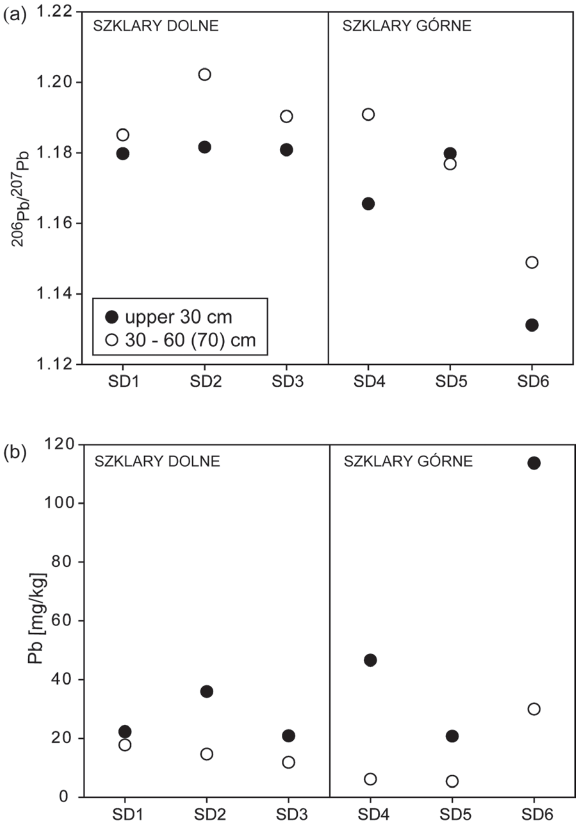

Figure 3. (a) Pb isotope ratios and (b) Pb concentrations in upper and lower soil horizons from Szklary Górne and Dolne area

Table 2. Concentrations of potentially toxic elements and isotope composition of the studied soils

	Cu [mg/kg]	Ni [mg/kg]	Zn [mg/kg]	As [mg/kg]	Cd [mg/kg]	Pb [mg/kg]	$^{206/207}Pb$	$^{208/206}Pb$
SZD1 upper	13.5	11.2	39.8	6.0	0.24	22.3	1.180	2.071
SZD1 lower	13.0	4.2	41.4	14.4	0.20	17.7	1.185	2.081
SZD2 upper	18.1	7.2	102.5	4.3	0.51	36.0	1.182	2.060
SZD2 lower	6.8	5.0	39.7	3.8	0.27	14.6	1.202	2.050
SZD3 upper	17.5	6.8	38.6	7.1	0.27	20.8	1.181	2.071
SZD3 lower	4.7	1.9	15.9	5.9	0.13	11.8	1.190	2.058
SZD4 upper	50.3	7.2	55.5	13.0	0.31	46.6	1.166	2.080
SZD4 lower	3.2	2.6	8.5	2.2	0.10	6.1	1.191	2.062
SZD5 upper	9.2	1.8	21.6	4.2	0.19	20.8	1.180	2.088
SZD5 lower	1.3	0.4	6.0	1.4	0.06	5.4	1.177	2.076
SZD6 upper	39.4	14.2	67.2	12.7	0.32	113.7	1.131	2.136
SZD6 lower	6.8	4.2	28.4	3.5	0.20	30.0	1.149	2.103

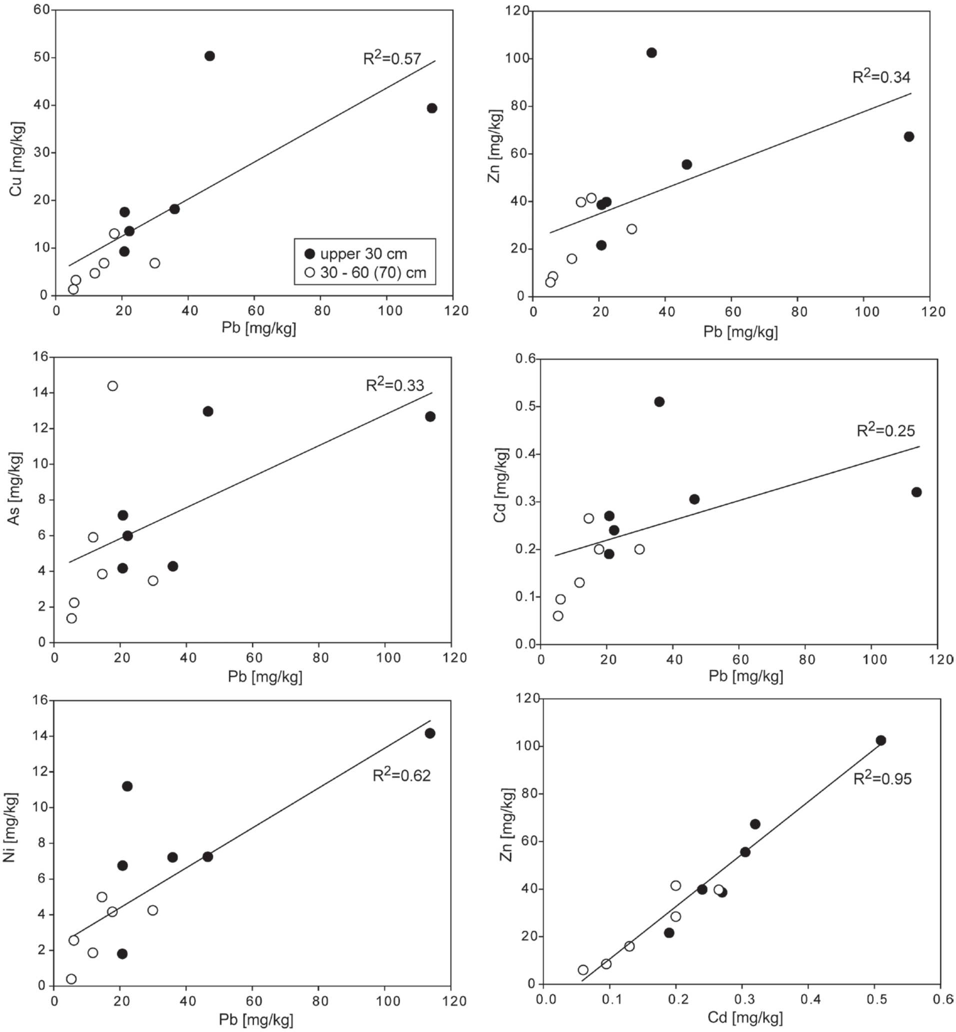

Figure 4. Correlations between Pb, Cu, Zn, Cd, As and Ni in soil horizons from Szklary Górne and Dolne area. Correlation coefficients are shown for the full dataset (upper and lower horizons together)

Lead isotope ratios do not vary much within each profile, but differences occur between the profiles and between the localities. The three profiles from the vicinity of Szklary Dolne have uniform $^{206}Pb/^{207}Pb$ of 1.18 in the upper part of the profiles, whereas the lower parts have slightly higher and more variable $^{206}Pb/^{207}Pb$ of 1.19–1.20 (Figure 3). On the other hand each of the profiles in the vicinity of Szklary Górne have different isotope characteristic with the most notable being profile no. 6 characterized by very low $^{206}Pb/^{207}Pb$ of 1.13 in the upper part of the profile and 1.15 in the lower part. Low $^{206}Pb/^{207}Pb$ ratios are observed also in the profile no. 4 in its upper part (1.16), whereas the values in the lower part are 1.19. The profile no. 5 has uniform $^{206}Pb/^{207}Pb$ of 1.18 throughout the profile.

Discussion and conclusions

Garden soils vary in composition and structure and they can be contaminated from various sources including nearby industrial sites, traffic, addition of composts and fertilizers and dusts coming from the housings (e.g. Kelly and Thornton 1996; Cheng et al. 2011). Even soils located in non-industrial sites may have elevated concentrations of Pb and other potentially toxic elements (e.g. Kelly and Thornton 1996) and may pose health risks (e.g. Murray et al. 2011). Garden soils analysed in this study have relatively low, but variable total concentrations of Pb and also variable Pb isotope composition. As such they offer possibility to identify different sources of Pb present in the area. Topsoils from the profiles 1, 3 and 5 have Pb concentrations similar to background concentrations observed in polish soils (arithmetic mean 14.2–25.2 mg/kg, Kabata-Pendias and Pendias 1999). Topsoils from the profiles 2, 4 and 6 have higher concentrations than mean background values and these profiles are also characterized by larger enrichments in Pb between the lower and upper parts of the profile and the largest variations in Pb isotope composition (Figure 3). The implication is that the upper parts of soils in profiles 2, 4 and 6 are the most affected by contamination.

Analyses of Pb isotopes in soils in this study offer a look at a different scale and soil type compared to the previous studies of Pb isotopes in the Lower Silesian soils. The garden soils were never analysed in Lower Silesia before and the soil profiles are located within a relatively small area, also the point source of possible contamination is absent in the area. Tyszka et al. (2012) analysed the range of soils in contaminated sites and the sites far from contamination sources, extending all over Lower Silesia, but all of them were located in the forest. The soil profiles analysed in the Rudawy Janowickie sampled small area dominated by contamination from the surrounding historical slag heaps and the profiles were also located in the forest. Comparison of the Pb isotope composition of the forest soils with those analysed in this study shows that garden soils composition extends to lower $^{206}Pb/^{207}Pb$ and higher $^{208}Pb/^{206}Pb$ ratios than that of previously analysed soils (Figure 5). Therefore, the new Pb source was identified using the garden soils. So far most of the upper soil horizons (O and A) analysed in Lower Silesia were characterized by $^{206}Pb/^{207}Pb$ of 1.17–1.18 (Tyszka et al. 2012) and similar ratios are observed in four out of six analysed profiles in Szklary Dolne and Szklary Górne, which is consistent with the predominance of atmospheric Pb, with such isotope composition, in Lower Silesia. It is not surprising since both polish metal ores and coals are characterized by $^{206}Pb/^{207}Pb$ of 1.17–1.18. On the other hand, the Pb source with $^{206}Pb/^{207}Pb$ lower than 1.17, which contributed Pb to profiles no. 4 and no. 6 must have a distinct origin with Pb derived from the leaded gasoline being the most probable. Alternatively an unknown contamination linked to the construction works can be responsible for the low $^{206}Pb/^{207}Pb$ ratios.

Leaded gasoline was an important substance polluting the air and soils throughout the Europe. It was characterized by low Pb isotope ratios because Pb coming from old Australian ores was commonly used as the knock-out additive (Novak et al. 2003). In Poland the leaded gasoline had been used until 2005 and its signal should still be present in soils. The lowest Pb isotope ratios were observed in the profile no. 6, which is disturbed, as an electric cable was placed at some point within the soil. Therefore, the construction works taking place at this site could have contaminated the soil. However, the profiles no. 4 and 6 are also those located the nearest to the active quarry (Figure 1) and the traffic and dusts related to the works in quarry could have also be the possible contamination source.

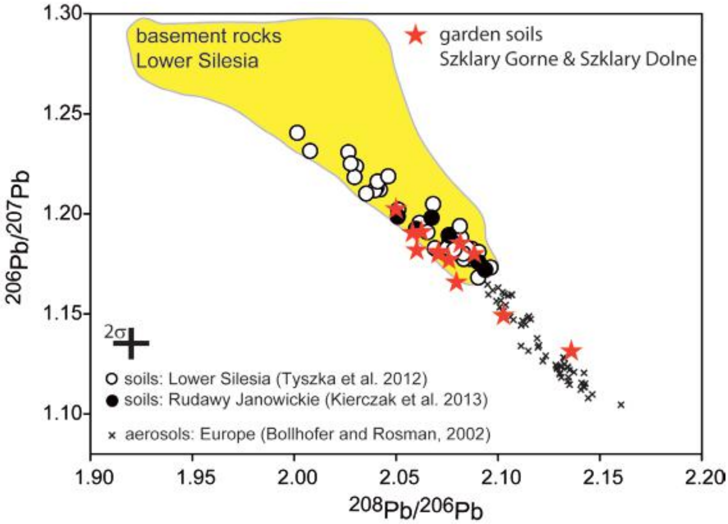

Figure 5. Comparison of Pb isotope composition of soils from Lower Silesia, composition of atmospheric dusts in Central Europe analysed by Bollhöfer and Rosman (2002) is also shown

Summarizing, the results from the analysed profiles show that the analyses of garden soils in the local scale complement the previous analyses of soils in the regional scale in Lower Silesia. In detail, the Pb isotope investigation of soils offer additional opportunities to identify and characterize different pollution sources in the area. In the studied soil profiles the pollution was probably dominated by air born material, as it affected mostly upper soil horizons. However, especially in the profile no. 6, the contamination from construction works cannot be excluded.

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