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RADIOCARBON, TRACE ELEMENTS AND PB ISOTOPE COMPOSITION OF PINE NEEDLES FROM A HIGHLY INDUSTRIALIZED REGION IN SOUTHERN POLAND

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ABSTRACT. We determined the chemical composition of pine needles to monitor environmental contamination in an urban forest environment in the most industrialized part of southern Poland. The concentrations of radiocarbon (^{14}C), trace elements (Cr, Co, Ni, Cu, Zn, Rb, Sr, Ba, Ce, Pb) and the Pb isotope composition were measured in needles from *Pinus sylvestris* L. growing in nine urban forests near five factories. The investigated young pine needles were collected in January 2013 and September 2013, respectively. ^{14}C concentration was determined by liquid scintillation counter, trace elemental concentration and Pb isotope ratio were determined by ICP-MS and MC-ICP-MS, respectively. Analysis of trace metal pollution is based on the assumption that element concentrations in tree foliage represent element availability in the environment. Different space-time patterns of element accumulation in pine needles were observed. The variation in isotopic composition reflects a mix between different anthropogenic sources.

KEYWORDS: contemporary pollution, Pb isotopes, pine foliage, radiocarbon, trace elements.

INTRODUCTION

Human activities resulting in the emission of different pollutants to the atmosphere affect the physiological processes that control tree growth. The determination of tree-ring and foliage properties is crucial in the investigation of local and global environmental changes. Tree-ring analysis and the determination of the chemical composition of wood and foliage are useful in ecosystem biomonitoring, in particular when assessing the impacts of soil, air, and water pollution (e.g., Kabata-Pendias and Pendias 1992; Rovinsky et al. 1993; Dmuchowski and Bytneroicz 1995; Adriano 2001; Pomierny and Ciepał 2004; Prasad et al. 2006; Jelaska 2007; Savard 2010; Malik et al. 2012; Przybysz et al. 2014; Sensuła et al. 2017). In this context, the monitoring of trace heavy metals is important, and based on the elemental and isotopic composition of pine needles as well as tree-ring analysis, we can identify the sources of air contamination (Łukaszewski et al. 1988; Kabata-Pendias and Pendias 1992; Rovinsky et al. 1993; Alfanie et al. 1996; Adriano 2001; Prasad et al. 2006; Jelaska 2007; Savard 2010; Pazdur et al. 2013; Przybysz et al. 2014; Sensuła 2015, 2016). Environmental biomonitoring can be used to measure the cumulative impact of different types of environmental pressures, including air contaminants emitted from different sources as well as soil and water contamination.

Scots pine (*Pinus sylvestris*) needles have widely been used as bioindicators for reforestation success in post-mining areas in central Europe, mainly because this species can survive on acidic and dry soils (Białobok 1976; Dmuchowski and Bytnerowicz 1995; Baumann et al. 2006; Kuznetsova et al. 2010). Most heavy metals are derived from anthropogenic sources, such as different industrial activities (e.g., metal refining, waste incineration, burning of coal and wood, coal and petroleum combustion, mining, metallurgy and metal smelting, barning of waste, and cement production), private householders, and motor vehicles. The contamination of air, rain, and soil can be a source of foliar injury. Geochemical analyses

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of Scots pine (*Pinus sylvestris* L.) needles have been performed previously (Dmuchowski and Bytnerowicz 1995), because this species is able to survive and grow on reclaimed mine soil (Białobok 1976; Pietrzykowski et al. 2014).

Plants can take up nutrients via the roots or the stomata. The stomata facilitate active exchange between leaf and atmosphere, representing the active interface between plants and their atmospheric environment. The local carbon cycle is very important to understand biological and chemical process and different interaction in the environment. Human activities over the past two hundred years have significantly increased the amount of carbon in the atmosphere, by emitting it directly (e.g., by fossil fuel combustion) or by changing ecosystems' ability to extract CO_2 from the atmosphere (e.g., by deforestation). Not only carbon concentration, but also the carbon isotopic composition of the Earth's atmosphere has been modified by human activities. Fossil fuels combustion have also diluted the $^{14}CO_2$ in the air (Suess effect, Keeling 1979). Human nuclear activities (connected with nuclear tests, nuclear power plant) increase anthropogenic $^{14}CO_2$ in the air. The analysis of contemporary samples of pine needles and tree rings growing in different sampling sites around three industrial factories in Silesia (Sensuła et al. 2018), shown high concentration of radiocarbon (^{14}C).

Elements taken up from the soil via roots can be accumulated in roots and leaves. While some elements taken up by plants are essential for growth and development, some are toxic (Kabata-Pendias and Pendias 1992). The most toxic metals for higher plants are Hg, Cu, Ni, Pb, Co, Cd, and possibly Ag, Be, and Sn. The assessment of toxic concentrations and effects of trace elements on plants is highly complex because it depends on several factors that cannot be measured on a linear scale (Kabata-Pendias and Pendias 1992). Elements taken up by plants from the atmosphere can provide clues about air pollution, whereas elements taken up via the roots can provide information about past contamination, as some elements can remain in the soil over several years. For example, Pb is mainly derived from anthropogenic sources (De Vleeschouwer et al. 2007, 2009) and can remain in the soil for thousands of years. The concentration of the elements in soil and air is area-specific. For instance, Steinnes et al. (2005) measured the highest concentrations of lead in the surface layer of soils in southern Poland ($\leq$ 142 mg/kg). The following threshold concentrations have been established for soils of coniferous forest sites in southern Poland: copper (150 mg/kg), zinc (500 mg/kg), and lead (1500 mg/kg) (Zwoliński 1995); these elements are largely linked to industrial emissions in the area.

In Silesia, southwestern Poland, high levels of pollution were recorded from 1960 to 1990, mainly caused by the industrial sector. Trees respond differently to environmental stress, e.g., by decreased growth, increased heterogeneity of tree-ring growth, reduced sensitivity to short-term environmental impulses, and changes in wood composition. After a significant reduction in pollution loads in the early 1990s, pines quickly recovered (Sensuła et al. 2015a, 2015b, 2017). Different investigations have been conducted in Silesia, mainly near factories, to assess the impacts of anthropogenically caused contamination on pine tree stands (for example, Norman 1999; Malik et al. 2012; Sensuła 2016; Sensuła et al. 2017). In such investigations, the determination of the chemical properties of tree rings and foliage is crucial to evaluate environmental changes. In particular, the monitoring of heavy metals stands out, as they not only impact plant growth and development, but also human health.

In this context, we used trace metal and Pb isotopes measured in pine needles as bioindicators of the accumulation of elements emitted into the atmosphere and deposited in foliage, focusing on Cr, Co, Ni, Cu, Zn, and Pb in young needles.

MATERIAL AND METHODS

Pine needles (*Pinus sylvestris* L.) from the current year were collected from forests located at different distances from factories (Figure 1, Table 1) within nine communes or cities in the highly populated and industrialized southern part of Poland.

Three sampling sites were located in Opole Province near the Petrochemia-Blachownia chemical factory (BL) and a nitrogen factory (KK, ancient name: Zakłady Azotowe Kędzierzyn-Koźle), on the highway A4 within the communes of Sławięcice (50°20′15.7″N; 18°19′52″E, site 1), Rudziniec (50°20′3.6″N; 18°24′29.9″E, site 2), and Rudno (50° 21′26.4″N; 18°28′14.5″E, site 3). The other six sampling sites were located in the province of Silesia. Of these, six were near the Łaziska Power Plant (LA) in the communes of Wyry (50°9′38.8″N; 18°56′4.4″E, site 4), Mikołów (50°10′35.1″N; 18°58′52.8″E, site 5), and Podlesie (50°8′55.4″N; 18°53′4.9″E, site 6), while three were near a coking plant (KO) and a steel factory (HK, Huta Katowice/ArcelorMittal Poland Oddział) in Dąbrowa Górnicza, in the communes of Dąbrowa Górnicza (50°21′48.5″N; 19°19′24″E, site 7), Łazy (50° 24′58.4″N; 19°22′56.8″E, site 8) and Ogrodzieniec (50°26′27″N; 19°29′30.6″E, site 9). According to the environmental reports of Chief Inspector of Environmental Protection (http://www.gios.gov.pl/), these factories were listed as some of the most polluting factories up to the late 1990s. Nowadays, air contamination due to industrial emissions is not as significant as it was in 20th century, but emissions from transport and domestic coal burning are still a matter of concern.

The sampling sites were selected to be in the direction of the dominant winds. In January 2013, we sampled young pine needles formed in 2012 (sample numbers 1–9, collected from sites 1–9). The samples were collected on the same day to avoid weather influences. In addition, needles were also collected in 2013 for three of the sampling sites. The needles formed in 2013 were collected in September 2013 (sample numbers 10–12, collected from sites 4, 5, and 6, respectively).

Needles were collected from the tree crowns, placed in plastic bags, and separated manually in the laboratory. Prior to geochemical analysis, samples were lyophilized. For ^{14}C analysis and fraction modern determination (^{14}F), the needles were prepared using a standard acid-alkali-acid treatment in a three-step treatment: (1) 2% HCl at 80ºC for 2 hr, neutralization with deionized water, (2) 2N NaOH at 80ºC for 2 hr, neutralization with deionized water, (3) 2% HCl at 80ºC for 2 hr, neutralization with deionized water and dried, then washed with distilled water to neutral pH, thus NaOH, samples were converted to benzene for LSC (liquid scintillation counter) measurements. Measurement of (^{14}C) concentrations in pine needles was performed with a β-radiation liquid spectrometer of the Quantulus 1220 type (Pazdur et al. 2013). The background $F^{14}C$ was equal to 0.019 pMC. The reference material ANU Sucrose (Rozanski 1991) was used and the fraction modern was calculated according to Mook and van der Plicht (1999).

For ICP-MS and MC-ICP-MS analyses, the samples were first dried at 90ºC for 24 hr, manually ground into a powder, and combusted at 550ºC for 4 hr to remove organic matter. Combusted samples were transferred to Teflon vials and digested via two steps: (1) a mixture of 4 mL of HF 36N and 1 mL of HNO_3 14N was added, and the samples were kept at 120ºC for 48 hr; (2) HCl 6N was added, and the samples were kept at 140°C for 48 hr. Each step was followed by evaporation at 90ºC. Subsequently, the samples were dissolved in 1 mL of 5% HNO_3 and divided into two parts. The first part, i.e., 200 μL of

Table 1 Sampling sites.

No.	Sampling site commune	Lab code	Localization, distance from factories
1	Sławięcice	KK_5	6.5 from a nitrogen factory, 3 km from the chemical factories Petrochemia-Blachownia
2	Rudziniec	KK_10	11 from a nitrogen factory, 7 km from Petrochemia-Blachownia
3	Rudno	KK_15	16 from a nitrogen factory, 10 km from Petrochemia-Blachownia, and ca. 1–2 km from the highway
4	Wyry	LA_5	3 km from Łaziska, a combined heat and power plant, and 3 km from the local road
5	Mikołów	LA_10	7 km from Łaziska and 2 km from the local road
6	Podlesie	LA_15	10 km from Łaziska
7	Dąbrowa Górnicza	HK_5	3 km from the steel factory Huta Katowice and a coking plant
8	Łazy	HK_10	11 km from the steel factory Huta Katowice and a coking plant
9	Ogrodzieniec	HK_15	19 km from the steel factory Huta Katowice and a coking plant; close to a local road

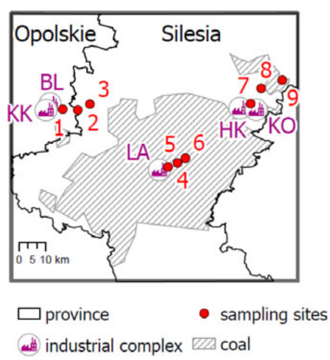

Figure 1 Location of nine sampling sites near different factories (BL-Petrochemia-Blachownia and KK-nitrogen factories in Kędzierzyn Koźle, LA-power plant in Łaziska, KO-coking plant and HK-steel factory in Dąbrowa Górnicza) in the provinces of Opolskie and Silesia. The coal basin is indicated on the map (geoportal.pgi.gov.pl: http://geoportal.pgi.gov.pl/css/surowce/images/2012/mapy/large/large_8.jpg).

the solution, was transferred into a Teflon vial for elemental analysis and then evaporated to dryness at 90ºC. The second part, corresponding to 800 µL of the solution, was used for lead isotope analysis. This part was evaporated at 90ºC, and the dried residue was dissolved in 500 µL of HBr 0.8N prior to chromatographic separation. Lead separation was made by using anion-exchange chromatography by successive adding of HBr and HCl in the clean class-100 laboratory at the University of Liège (Belgium) (De Vleeschouwer et al. 2007). The eluted Pb solution was evaporated and stored prior to analysis.

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Before the analysis, the ICP-MS instrument was calibrated and linearity was checked for the BHVO2 standard concentrations of 0, 0.01, 0.1, 5, 10, and 20 ppb. Repeated blank measurements were used to determine the limit of detection for each element. Replicates (i.e., run of the same samples twice) and duplicate (i.e., repetition of the analyses with different aliquots of the same samples) were performed. The standard deviation of each result was $\leq 5\%$.

Lead isotopes (Table 3) were measured using the Nu Instruments Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the Laboratoire G-Time (Université Libre de Bruxelles, Belgium). For MC-ICP-MS, the standard NBS981 was repeatedly measured in alternation with samples to control any daily instrument drifts.

RESULTS AND DISCUSSION

The spatial and temporal variations of the element levels (Cr, Co, Ni, Cu, Zn, Pb) are reported in Figures 2 and 3. The results of ^{14}C analysis and fraction modern determination and trace element concentrations in the pine needles from different sites are presented in the Table 2. The needles were characterized based on the concentrations of Cr, ranging from 0.05 to 0.7 mg/kg, Co, from 0.005 to 0.075 mg/kg, Ni, from 0.12 to 0.66 mg/kg, Cu, from 0.49 to 1.0 mg/kg, Zn, from 3.9 to 14 mg/kg, and Pb, from 0.06 to 0.53 mg/kg. These values represent the minimum concentrations, as some contamination deposited on the needle surface may have been removed by precipitation or wind.

The spatial and temporal variations of the lead isotope ratios are shown in Figure 4 and Table 3. The range of Pb isotope ratios was relatively narrow. In the area near the chemical factories in Kędzierzyn-Koźle, $^{206}Pb/^{207}Pb$ isotope ratios ranged between 1.15 (KK_5) and 1.17 (KK_10), whereas $^{208}Pb/^{206}Pb$ varied between 2.09 (KK_10 and KK_15) and 2.11 (KK_5). Near the Power Plant in Łaziska, $^{206}Pb/^{207}Pb$ isotope ratios ranged between 1.163 (LA_5 and LA_15) and 1.168 (LA_10), whereas $^{208}Pb/^{206}Pb$ varied between 2.093 (LA_10) and 2.097 (LA_15). Near the steel factory "Huta Katowice" in Dąbrowa Górnicza, $^{206}Pb/^{207}Pb$ isotope ratios ranged from 1.168 (KK_10) to 1.174 (HK_15) and $^{208}Pb/^{206}Pb$ from 2.082 (HK_5) to 2.094 (HK_15).

Radiocarbon

Plants convert CO_2 from the air into cellulose and while living, plants are in equilibrium with their surroundings by exchanging carbon with the atmosphere. In the highly populated Silesia region, where a burning fossil fuels is the largest source of CO_2 emission and which is located far from nuclear power plant, a Suess effect (Keeling 1979) a ^{14}C depletion in pine needles relative to clean air, was expected, we have found that higher concentration of ^{14}C in the needles relative to clean air. Review of the literature describes the pathway and associated fractionation of ^{14}C and $\delta^{13}C$ in CO_2 during photosynthesis, respiration and dissolution by groundwater (Białobok et al. 1993; Dawson et al. 2002; Trumbore 2006). The changes in carbon isotopes fractionation during these processes are smaller than differences in ^{14}C composition of the ^{14}C in current atmospheric background (Hammer and Levin 2017) in pine foliage in Silesia. We suppose that, in the region of Silesia localized far from nuclear power plant, that the observed enrichment in ^{14}C in pine needles can be connected with point-source emitters, where products enriched in ^{14}C, are utilized and combusted (for example products used in ^{14}C-labeling in medical sector, or probably also household wood burning). To confirm or to reject this hypothesis, additional analyses will be done in future.

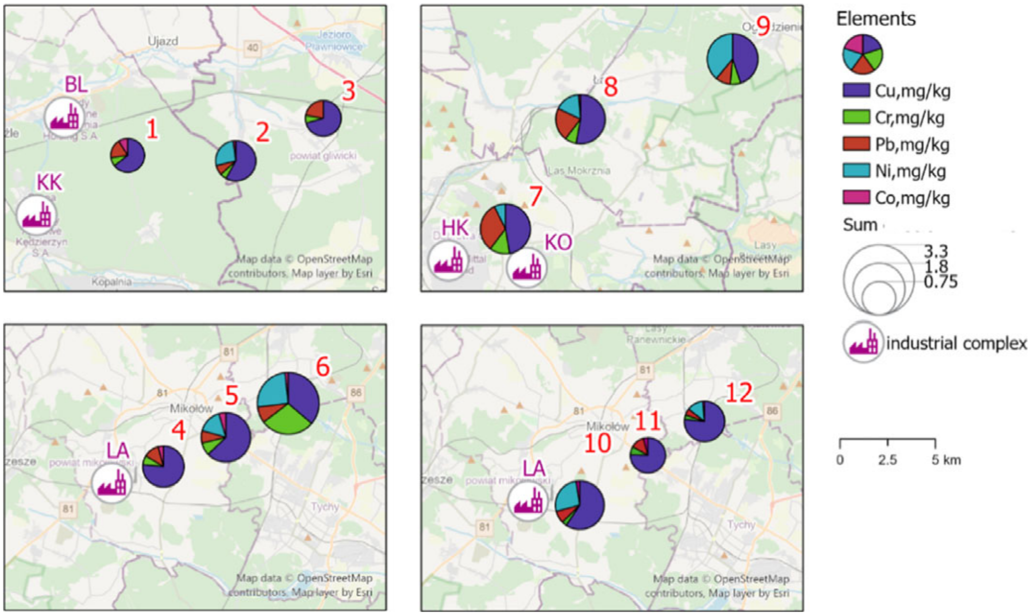

Figure 2 Accumulation of Cu, Cr, Pb, Ni, and Co in pine needles formed in 2012 (samples no. 1–9) and 2013 (samples no. 10–12) in areas near different factories, i.e., Petrochemia-Blachownia (BL) and nitrogen factories (KK), Łaziska Power Plant (LA), coking plant Przyjaźń (KO), and the steel factory Huta Katowice (HK).

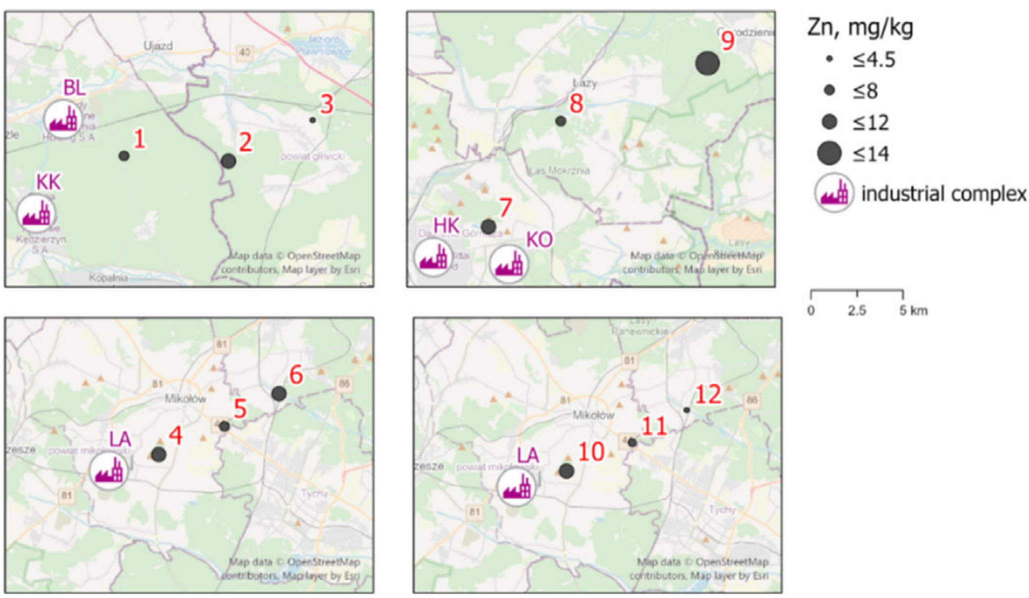

Figure 3 Accumulation of Zn in pine needles formed in 2012 (samples no. 1–9) and in 2013 (samples no. 10–12) in areas near different factories, i.e., Petrochemia-Blachownia (BL) and nitrogen factories (KK), Łaziska Power Plant (LA), coking plant Przyjaźń (KO), and the steel factory Huta Katowice (HK).

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Table 2 Radiocarbon concentration and trace elements accumulation in annual pine needles collected in 2013 in three cities of Opole and six cities in Silesia Voivodeship. Standard deviation for trace elements was always 5% or lower. Values below the detection limit are marked as "*". The reference value of BHVO-2 was adopted from Chauvel et al. (2010). LD is the limit of detection, a. Replicate corresponds to a re-run of the same sample solution; b. Duplicate corresponds to the analyses of two different aliquots from the same sample. We determined minimum, maximum, average, median, and standard deviations for all samples.

Sample	Site	Year of needles formation	Sampling	Lab code	$\Delta^{14}C$ pMC	$u(\Delta^{14}C)$ pMC	Cr mg/kg	Co mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Rb mg/kg	Sr mg/kg	Ba mg/kg	Ce mg/kg	Pb mg/kg
1	Sławięcice	2012	Jan. 13	KK_5_2012	103.49	0.65	0.063	0.068	*	0.49	7.3	1.5	2.72	3.47	0.022	0.139
2	Rudziniec	2012		KK_10_2012	103.37	0.65	0.056	0.023	0.29	0.63	8.4	1.8	1.44	1.79	0.031	0.086
3	Rudno	2012		KK_15_2012	102.95	0.65	0.06	0.005	*	0.6	4.3	0.5	0.24	0.27	0.064	0.188
4	Wyry	2012		LA_5_2012	103.36	0.51	0.082	0.048	*	0.87	11.1	2.2	1.78	0.7	0.016	0.138
5	Mikołów	2012		LA_10_2012	103.47	0.81	0.136	0.075	0.26	1.02	7	0.6	1.72	1.76	0.05	0.132
6	Podlesie	2012		LA_15_2012	102.44	0.52	0.719	0.042	0.64	0.92	8.5	1.8	4.41	4.41	0.113	0.216
7	Dąbrowa G.	2012		HK_5_2012	102.81	0.84	0.214	0.016	0.12	0.78	10.4	1	0.97	0.5	0.035	0.534
8	Łazy	2012		HK_10_2012	102.98	0.63	0.123	0.021	0.27	0.86	6.4	1.7	0.41	0.36	0.029	0.353
9	Ogrodzieniec	2012		HK_15_2012	101.7	0.62	0.113	0.014	0.66	0.76	14	4.5	0.77	1.05	0.049	0.162
10	Wyry	2013	Sept.2013	LA_5_2013	103.69	0.52	0.058	0.046	0.474	1.058	8.977	2.327	6.113	1.393	0.027	0.145
11	Mikołów	2013		LA_10_2013	103.29	0.78	0.071	0.04	*	0.705	7.57	0.524	0.778	0.736	0.016	0.117
12	Podlesie	2013		LA_15_2013	104.92	0.59	0.045	0.018	0.159	0.932	3.942	1.196	2.025	2.104	0.016	0.064
			BHVO-2				28	45	119	127	103	9-Jan	396	131	37.5	Jan-54

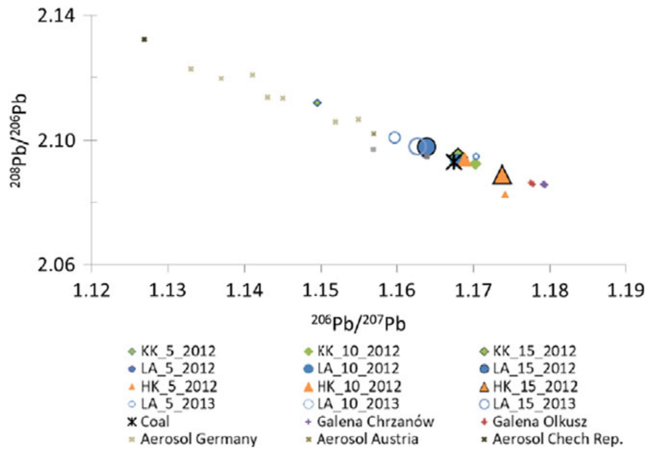

Figure 4 Variation in ^{208}Pb/^{206}Pb isotope ratio versus ^{206}Pb/^{207}Pb in pine needles (current studies), coal from Katowice, Galena from Olkusz and Chrzanów (De Vleeschouwer et al. 2009), and aerosols (after Bollhöfer and Rosman 2001).

Trace Elements

The elements Ni, Cr, Zn, Pb, Co, Cu were mainly derived from anthropogenic sources, whereas Rb and Sr derived from the erosion of the continental crust (Bowen 1979). In the last decades, different industrial sectors and transport (leaded petrol combustion) have released large amounts of heavy metals into the atmosphere (Nriagu and Pacyna 1988), while private households have also become a significant source of air contamination. Elements absorbed by leaves are partly translocated to roots and are also leached from plant foliage, especially by acid rain. Under specific conditions, and especially with atmospheric pollution, a high proportion of trace metals may enter plant tissues.

Heavy Metals

In the province of Opolskie province nearby nitrogen factories (KK) and Petrochemia-Blachownia (BL), the Cr concentration in the needles was stable and low, while Ni was only detected in KK_10. Copper and zinc were detected in the three studied sites, with highest concentrations in KK_10. The Pb concentration differed with different distances from the factories. Higher levels were found for pines in close proximity to factories; at a distance of 10 km, the concentrations were lower and further decreased with decreasing distance to the highway.

In the areas near the power station Łaziska (Silesia Voivodeship), higher concentrations of Cr and Ni were found in pine needles from sites located farther from the factory; the larger the distance, the higher the concentrations. The Cu levels were similar across the area. Regarding Zn, the highest concentration has been observed in the commune located nearest to the factory and the lowest at a distance of 7 km; the Cu concentration slightly increased with increasing distance from the factory. Heavy metal accumulation in the needles differed between January and September. In September, the highest total heavy metal concentration was observed in the sampling sites closest to the factory.

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Table 3 Ratio of the Pb isotopic composition in annual pine needles collected in 2013 in three cities of Opole and six cities in Silesia Voivodeship. "R" indicates replicate, i.e., a re-run of the same sample solution. 26 – refers to the accuracy calculated via two standard deviations. We determined minimum, maximum, average, median, and standard deviation values for all samples.

Sampling site	Lab code	$^{208}Pb/^{204}Pb$	2 σ	$^{207}Pb/^{204}Pb$	2 σ	$^{206}Pb/^{204}Pb$	2σ	$^{208}Pb/^{206}Pb$	2 σ	$^{207}Pb/^{206}Pb$	2 σ
Sławięcice	KK_5_2012	37.8918	0.0021	15.60729	0.00055	17.94149	0.00066	2.111933	0.000037	0.869902	0.000013
Rudziniec	KK_10_2012	38.252	0.0018	15.62147	0.00067	18.28245	0.00067	2.092314	0.00004	0.854453	0.000012
Rudno	KK_15_2012	38.2091	0.0017	15.61909	0.00067	18.24392	0.00074	2.094404	0.000047	0.856135	0.000014
Wyry	LA_5_2012	38.0707	0.0019	15.614	0.00081	18.16953	0.00083	2.095321	0.000036	0.85934	0.000014
Mikołów	LA_10_2012	38.184	0.0025	15.61861	0.00084	18.24022	0.00088	2.093403	0.000048	0.856269	0.000012
Podlesie	LA_15_2012	38.1171	0.0017	15.61211	0.00072	18.17229	0.00081	2.097578	0.000036	0.859124	0.000013
Dąbrowa Górnicza	HK_5_2012	38.2213	0.0021	15.63187	0.00069	18.35484	0.00069	2.082357	0.000045	0.851657	0.000012
Dąbrowa Górnicza[R]	HK_5_2012	38.2223	0.0023	15.63192	0.00082	18.35431	0.00079	2.082446	0.000054	0.851674	0.000015
Łazy	HK_10_2012	38.2158	0.0021	15.61644	0.00076	18.25403	0.0008	2.093607	0.000055	0.855516	0.000015
Ogrodzieniec	HK_15_2012	38.3651	0.0017	15.64687	0.00072	18.36692	0.00077	2.088815	0.000043	0.851909	0.000013
Wyry	LA_5_2013	38.3067	0.0021	15.6264	0.00078	18.2894	0.001	2.094511	0.000045	0.854405	0.000013
Mikołów	LA_10_2013	38.036	0.0021	15.6114	0.001	18.1057	0.001	2.100799	0.000042	0.862237	0.000013
Podlesie	LA_15_2013	38.0875	0.0037	15.6147	0.0014	18.154	0.0016	2.098026	0.000048	0.860112	0.000021

In the sites near the steel factory (HK) and the coking plant (KO) in Dąbrowa Górnicza (Silesia province), Ni levels were higher in the needles from stands further away from the factories. The opposite pattern was observed for Cr and Pb. Copper concentrations were similar for all investigated sites. The highest Zn concentration was observed in the commune nearest to the factory and the lowest at a distance of 11 km from the factory, with a further slight increase up to a distance of 19 km.

The concentrations of Zn, Cu, and Pb in pine needles measured in this study were lower than those obtained previously for pines growing near mining sites (Pietrzykowski et al. 2014). In a study from 2009, the average heavy metal concentrations in pine needles were as follows: Zn from 33 to 77 mg/kg, Cu from 3.0 to 28 mg/kg, and Pb from 0.8 to 3.2 mg/kg, measured in Poland near Smolnica, Szczakowa, and Piaseczno, respectively. In another study, the concentrations of heavy metals in the needles of different pine species varied, with Cu ranging from 7 to 10 mg/kg, Ni from 41 to 90 mg/kg, and Zn from 42 to 119 mg/kg (Parzych et al. 2017). Previous studies have shown that the heavy metal concentrations in foliar dust differ among different regions; for example, in Spain, Aboal et al. (2004) found the following mean values: Cr: 0.235 mg/kg, Cu 3.52 mg/kg, Ni 3.71 mg/kg, Zn 19.06 mg/kg, Pb 0.059 mg/kg. In a study in China, Pb ranged from 434.0 to 512.0 mg/kg (Yuan et al. 2009), while in another Chinese study, Ni ranged from 50.4 to 388.6 mg/kg, Zn ranged from 162 to 2152 mg/kg, and Cu ranged from 43 to 218 mg/kg (Yin et al. 2013). Although the toxicity of heavy metals for plants is widely known (Kabata-Pendias and Pendias 1992), the underlying mechanisms have not yet been fully elucidated (Pietrzykowski et al. 2014).

Figures 2 and 3 show the distribution of heavy metals in pine trees growing at distances of 3–19 km from factories; the median concentrations followed the order Cr < Pb < Cu < Zn, which is in agreement with previous findings from the same area (Sensuła et al. 2017). However, the industrial factor is not the only source of air contamination; household emissions and emissions by traffic are also considerably high. Some heavy metals can be transported by wind over long distances. It should be noted that the needles collected in winter (in January) had been formed in the spring of the previous year, accumulating elements for nearly 1 year. The samples collected in September consisted of young needles from May in the same year.

Lead Isotopes

The study area is characterized by spatial variations in the Pb isotopic composition of the needles (Figure 3, Tables 2 and 3). The $^{208}Pb/^{206}Pb$ ratio ranged from 2.08 to 2.11 and the $^{206}Pb/^{207}Pb$ ratio between 1.15 and 1.17. The heterogeneity of Pb isotope ratio indicates that there are different sources affecting the Pb isotopic composition of pine needles (Figures 4–6). The samples are aligned along a linear trend that may be interpreted by a mixing line between different anthropogenic Pb sources (e.g., Bollhöfer and Rosman 2001; Doucet and Carignan 2001; Cloquet et al. 2006). The three main sources of Pb are related to the exploitation of galena ores, coal burning, and aerosols. In addition to industrial activities, a significant part of the pollution derived from coal combustion is probably due to low emissions by private households and coal burning for heating. The Pb isotopic composition of the atmosphere in Central Europe has been measured via aerosol samplers (Bollhöfer and Rosman 2001), and the results for Eastern Europe suggest a mix of alkyllead compounds from different sources, mainly related to industrial activities and coal

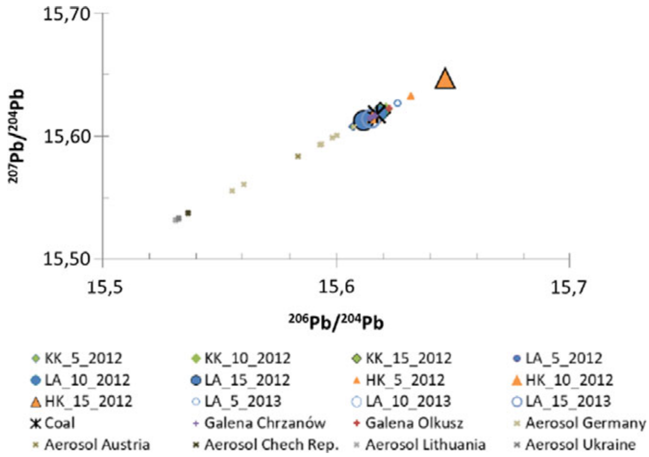

Figure 5 Variation in $^{207}Pb/^{204}Pb$ isotope ratio versus $^{206}Pb/^{204}Pb$ in pine needles (current studies), coal from Katowice, Galena from Olkusz and Chrzanów (De Vleeschouwer et al. 2009) aerosols (after Bollhöfer and Rosman 2001).

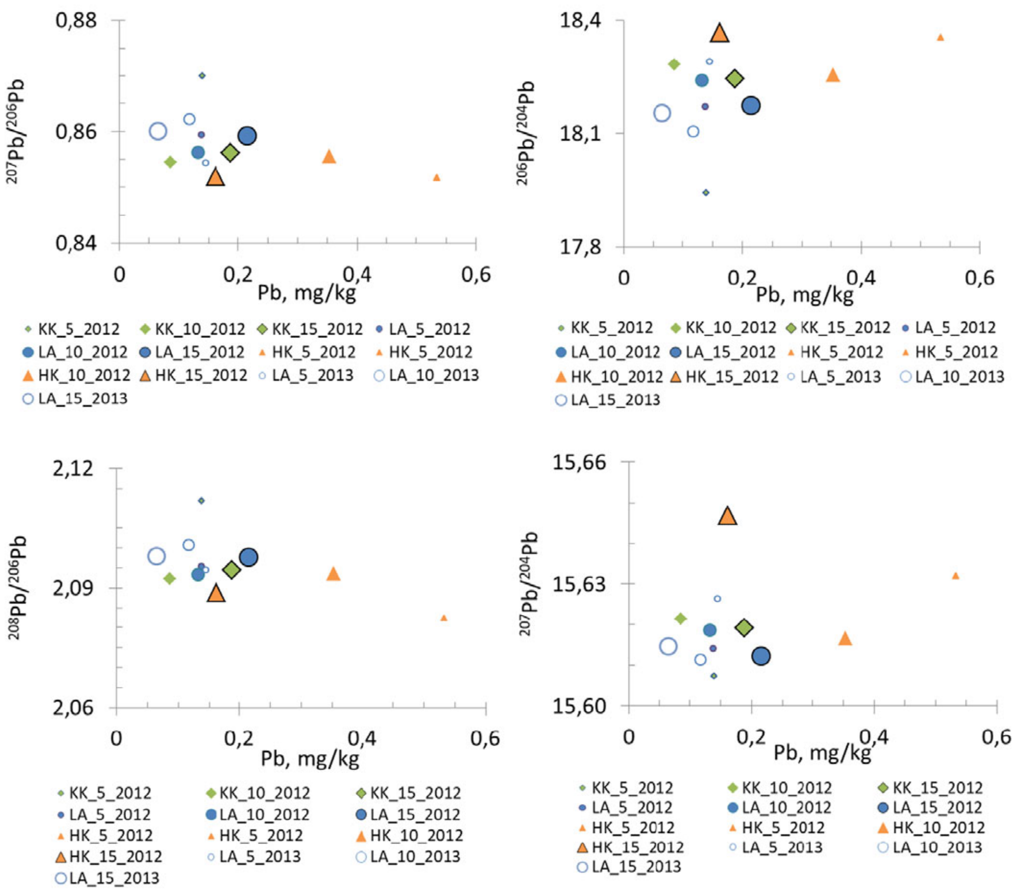

Figure 6 Distribution of Pb isotopic ratio in comparison with lead concentration.

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burning (Bollhöfer and Rosman 2001). Lead from the industrial sector, associated with coal and steel plants, was enriched in ^{206}Pb and ^{207}Pb compared to ^{204}Pb. Depletion in ^{206}Pb and ^{207}Pb compared to ^{204}Pb (i.e., ^{206}Pb/^{204}Pb $<$ 17.7), ^{207}Pb/^{204}Pb $<$ 15.58, respectively) corresponds to the European gasoline lead origin. The end-member with a low ^{206}Pb/^{207}Pb isotope ratio is most probably influenced by traffic (Bollhöfer and Rosman 2001).

Although lead gasoline was banned in the year 2000 in Poland, plants may still accumulate lead from other sources. Analysis of the lead isotopic ratio ^{208}Pb/^{206}Pb versus ^{206}Pb/^{207}Pb showed that local coal and galena are the two main sources of lead, although previous Pb pollution cannot be excluded. Lead can remain in the soil over several years and can be taken up by plants via the roots. However, Dalenberg and van Driel (1990) have calculated that 73 to 95% of the total ^{210}Pb content of field crops are derived from aerial deposition on leaf surfaces.

CONCLUSIONS

We determined radiocarbon, trace element accumulation, and Pb isotope ratios in pine needles collected in a heavily industrialized area of Poland to evaluate the degree of air contamination. Most of the elements were derived from anthropogenic activities. The temporal and spatial variations were evident. All sampling sites are characterized by high levels of radiocarbon. Also high level of zinc and copper, and lead was detected in pine needles. The variation in the radiocarbon indicates a mix between different sources of ^{14}C, also lead isotopic composition indicates a mix between different sources Pb, respectively. Industrial activity, private households, and transport are a source of atmospheric contamination in the provinces of Opolskie and Silesia.

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