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Analysis of Trace Elements in Tree Rings of Pines Growing Nearby Steelwork in Southern Poland during the Industrial and Post-Industrial Periods

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Abstract: The current study explores for the first time the contrasts and similarities between the elemental (Na, Mg, Fe, Ni, Cu, Zn, and Pb) composition of pines that grow in a polluted industrialized area, located close to a steelworks, and that of pines growing in a comparative site, far from industry. Radial trace element profiles were determined by LA-ICPMS. The results are compared with the rainfall load at the monitoring station in Katowice, the nearest one to sampling sites, over the years 1999–2012, received from the Chief Inspectorate of Environmental Protection (GIO). The results show that in annual tree rings, there is no direct linear correlation between rainfall load and concentration of the studied elements in wood of the annual rings. The element concentrations in trees may reflect the sum of different factors that impact the ecosystem, including pollution from large sources and local point sources, immission, load of the rainfall level, and also specific plant physiology processes.

Keywords: biological archive; atmospheric pollution; pine; LA-ICP-MS; trace elements

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1. Introduction

The rapid and significant development of industry and urban agglomerations in the last century caused significant changes in the natural environment and a modified biogeochemical cycle of trace elements in the biosphere. Trees have been used as bioindicators, as their physiological processes and growth are affected by environmental factors [1–10]. Over the years, dendrochronological monitoring has been successfully used to monitor the development of different types of industrial production. It has been found, *inter alia*, that the reduction in tree-ring width (TRW) is affected by the chemical composition of pollution [1,10,11]. The width reduction depends on trees' sensitivity to environmental changes but also on local factors, such as, for example, weather conditions or air pollution. One of the most important species of coniferous trees that grows in Europe, used as a sensitive bioindicator of environmental changes, is the Scots pine (*Pinus sylvestris* L). Combining different research methods allows obtaining more complete information about the relationship between the environment and this tree, used in biomonitoring of the environment on a local, regional, and global scale. Dendrochronological studies are supplemented by analyses of stable isotopes, radiocarbon, or elemental composition in leaves and trees' wood performed using spectrometric methods. Since the beginning of the twentieth century, there has been much discussion about how external environmental factors affect the physiological processes that control tree growth.

Based on the elemental and isotopic composition of plant tissue, it is possible to analyze the cumulative impact of different types of environmental pressures, including air contaminants emitted from different sources, as well as soil and water contamination, e.g., [4–8,11–15]. Most heavy metals are emitted from various industrial activities (e.g., refining of metals, waste burning, burning of coal and wood, burning of coal and oil, mining, metal manufacturing, metal smelting, waste banning, and cement production), private households, households, and motor vehicles. Pollution of air, rain, and soil may cause leaf damage that may be reflected in tree rings.

Trees absorb CO_2 molecules from the atmosphere, and during photosynthesis, plants convert CO_2 and H_2O to cellulose, which is the basic structural component of the cell walls of plants. During photosynthesis, trees absorb not only CO_2 and H_2O but also other elements. Some of these elements are important for plants, but some of them can be toxic. In pine, photosynthesis and transport of saccharides from the foliage to the trunks and roots is very important in tree ring formation and occurs throughout the year. Carbohydrates are synthesized in the autumn and stored in the trunk in the winter, and they are used to start the radial growth of the trunk in the spring. Spare materials are used to produce the first cell layers of early wood. Later cell layers of the early wood are formed from photosynthetic products freshly transported from needles. In early spring, part of the assimilated carbon is stored in the needles, and part of this is transported to other parts of the tree or to the roots. Saccharide transport stops when new needles start to grow and begins again when their formation is finished (mid-July). Until the middle of July, annual needles are a source of carbon for new needles. In the middle of July, the ability of new needles to assimilate is similar to that of older needles [16]. Research showed that the annual needle mobility of the assimilation products was the fastest in summer. In late summer and fall, when the buds are budded and after maturation, the needles are assimilated only down to the trunk and roots; however, nutrients can also be stored in the needles. Assimilates are used primarily for the development of xylem and root growth, and excess is stored. The transport of different elements by pine has been described in detail by Bialobok et al. [16]. Review articles in the scientific literature have shown that tree foliage can act as an 'air filter' and trees can be used to monitor heavy metal pollution [12,13,17–19]. Some studies show that trees may not provide reliable information on the yearly scale of past variations in contaminated soils, and soil acidity also plays a key role because the absorption of elements. However, on the other hand, reviews of the scientific literature have shown that tree rings yearly formed in wood are a wide and complex source of data, potentially offering hints on the impact of atmospheric pollution. They can provide material for dating events at a high temporal resolution, i.e., yearly or seasonally. Furthermore, given their wide spatial distribution, trees offer possibilities of correlations over vast territories. In research on local and global environmental changes, the determination of tree properties can be crucial.

The aim of research conducted over several years in Silesia has been to analyze the impact of climate change and the anthropogenic effect and to monitor the impact of human activity on the environment during industrial and post-industrial periods, with particular emphasis on the period of implementation of pro-ecological policy in Silesia (Poland). In Silesia, different investigations were carried out, especially near factories, to evaluate the effects of human-induced contamination on pine trees e.g., [20–23].

The input of pollutants to the atmosphere has increased significantly since the middle of the twentieth century due to increased industrial activities all over the world. In Poland, the highest levels of dust and gaseous pollutants were recorded in the 1980s. Since the 1980s, pro-ecological policy and pro-ecological investments have been implemented in most of the factories in Poland, similarly to elsewhere in eastern and central Europe. The further reduction in contamination emission was related to restrictive governmental regulations on emissions according to EU legislation. Even trace metals in soils have been shown to be very useful indicators of environmental pollution and sources of pollution. In the research areas analyzed in our study, there is a problem with using soil samples as bioindicators due to mechanical destruction of soil surfaces in this region. Between 1960 and 1990, high levels of pollution were recorded in Silesia, mainly due to industrial pollution. Trees respond differently to environmental stresses, for example, by decreasing growth, increasing tree rings, reducing sensitivity to short-term environmental impulses, and changing wood composition. After a significant reduction in pollution in the early 1990s, pine trees quickly recovered [20–23].

The variability in tree-ring width, stable oxygen and carbon isotopes, and radiocarbon of annual tree rings of *Pinus sylvestris* L. in different parts of the highly populated and industrialized Silesia region have recently been investigated [10,11,17–23], with the use of complementary dendrochronological and mass spectrometric methods since about 15 years. However, until now, the elemental composition of annual tree rings in Silesia was conducted only in one sampling site—near Kędzierzyn-Koźle [22].

Using laser ablation–inductively coupled plasma mass spectrometry (LA-ICPMS), it is possible to investigate radial variations in selected element concentrations in pine wood from a selected area and to compare these results with other data, for example, surface load of the elements of the area of Silesia Voivodeship with pollutants brought by precipitation.

The current study explores for the first time the contrasts and similarities between the elemental composition of pines that grow in a polluted industrialized area, located close to a steelworks, and that of pines growing in a comparative site, far from industry. The results are compared with the rainfall load at the nearest monitoring station in Katowice. In Poland, access to spatial and time data of wet deposition is limited due to a small number of instruments and also changes in the administrative division in the 1990s. Usually, there is an access to data given by the appropriate inspectorate for environmental protections, who extrapolate instrumental data for Katowice.

2. Materials and Methods

The investigated Scots pine population was studied at two sites (Figure 1). Both were pine stands of approximately 100 years in age, growing in mixed coniferous forest habitats. The first was localized in site HKF2, near the village of Hutki-Kanki (50.403856 N, 19.472666 E), about 17 km from the ArcelorMittal Poland steelworks in Dąbrowa Górnicza, in line with the most frequent winds in this region, blowing from the south-west direction. The second was in the comparative site OLE in Olesno (50.802278 N, 18.389217 E), localized 100 km from industrial region.

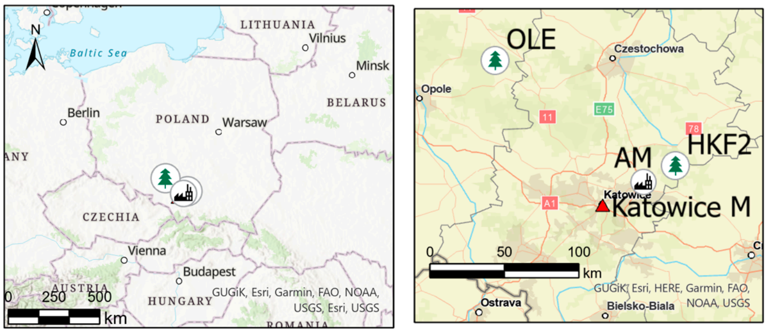


Figure 1. Sampling sites: HKF2, near the village of Hutki-Kanki (HKF2), the comparative site in Olesno (OLE), and the locations of monitoring station in Katowice (Katowice M) and Arcelor Mittal Steelworks (AM).

Meteorological data received from the station in Katowice, from IMiGW, indicate that from 1960–2010, the annual average temperature was ca. 8.15 °C, and an increase in the average air temperature (0.02 °C/year) can be observed. Even though the mean annual sum of precipitation remains at the same level (720 mm/year) since the 1990s, some episodes with a significantly higher amount can be observed over a short period of time compared to prior periods (Figure 2). The impact of pluvial and thermal conditions on trees growing in selected areas has already been discussed [21,23].

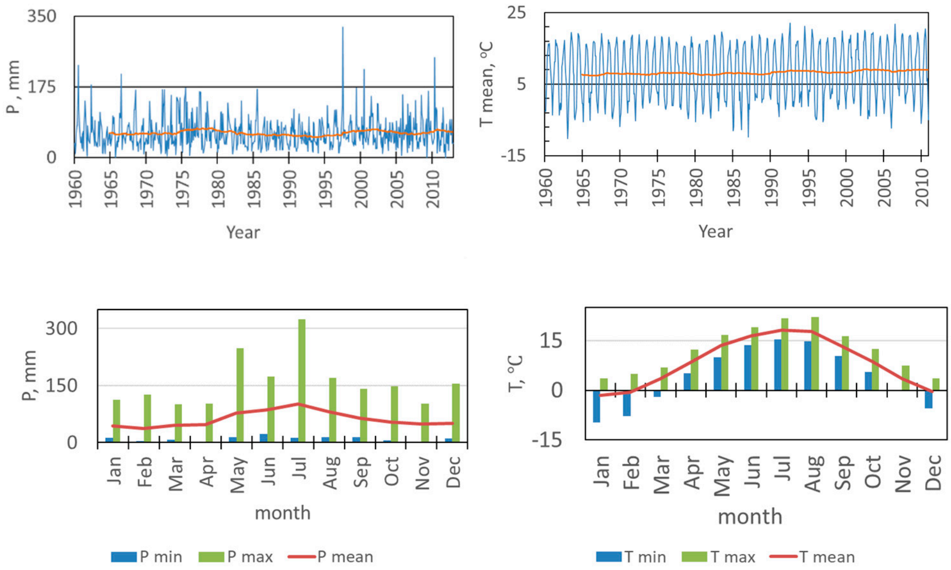


Figure 2. Fluctuation in the monthly air temperature and the monthly sum of precipitation from 1960–2010.

Initial detailed dendrochronological studies carried out in both sampling sites [21,23] allowed the selection of representative research sites and trees for elemental studies (increment core/tree and two increment cores per site were chosen). The main selection criteria were determined by dendrochronologists: the degree and duration of the period of reduction in the width of the annual growth of trees related to air pollution. When comparing both sites, in the area nearby the steelworks, a reduction in tree-ring width associated with an increase in pollution emission in Silesia was observed [20–23]. Similar effects have been observed in 15 other sampling sites located in different industrial areas of Silesia [20–23]. This reaction of reducing tree-ring width was not evident in 20 samples collected in Olesno [23]. For the current research, two cores were selected, i.e., HKF2 covered the period of time from 1886 until 2010, and OLE covered the period of time since 1910. The TRW of all samples was measured with the use of the LINTAB 6 device (accuracy of 0.01 mm) with a microscope and the TSAPWin software [24]. Results were verified by the COFECHA program [25]. Normalization of the TRW series was carried out using ARSTAN computer software [26]. Differences in chronology (TRW and RWI) and the impact of climate factors on tree-ring width were previously studied, and results have been presented [21,23].

2.1. Emission of Contaminants from Steelworks ArcelorMittal

Figure 1 shows a clear decrease in the emission of contaminants from ArcelorMittal since the late 1970s, while the level of steel production remains at a similar level or slightly decreased (Figure 3). The increase in emissions and, consequently, in the immission of contaminants in Silesia observed in recent decades has been associated with the combustion of fossil fuels in industry (including mining, metallurgy), households, and road transport.

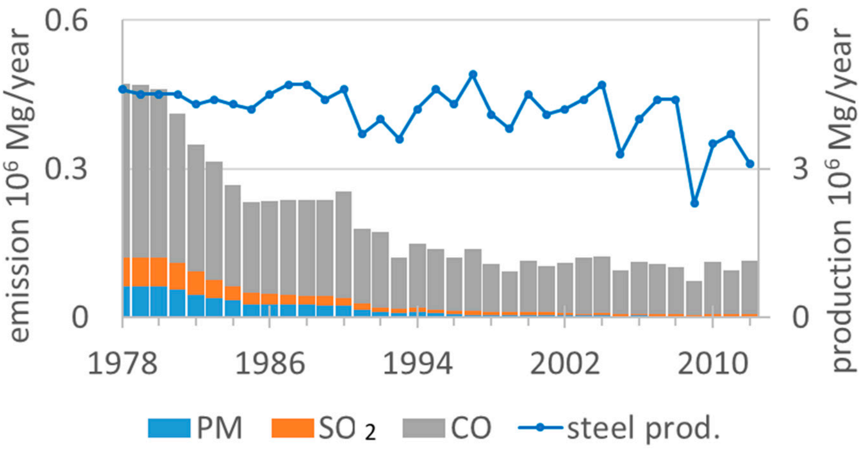


Figure 3. Example of reduction in emissions of pollution into the atmosphere during the production of steel by Huta Katowice in Poland (1978–2012), data given by the company.

2.2. Mass Spectrometric Analysis by LA-ICP-MS

For mass spectrometric analysis, only a subset of the samples were taken into analysis, which covered the period beginning in the 1960s. The limitation of the analysis was caused by the time limitation of access to the instrument and costs of the analysis. However, beginning analysis with the 1960s created the possibility to conduct research on a period of strong development of the industry in the region, following the preindustrial period of time, and to analyze similarities and contrasts in the adaptation of trees to environmental changes, including increasing and limited emission of pollution by steelworks in comparison to pine growing in a relatively clear area.

The cores (HKF2 and OLE) of two healthy pines were analyzed for the total concentration of the following elements: Na, Mg, Fe, Ni, Cu, Zn, and Pb. Radial trace element profiles were determined by LA-ICP-MS (Laser ablation, New Wave Research UP-193 FX Fast Excimer; ICP-MS, Thermo Scientific X-Series2 with CCT Collision Cell Technology) at Royal Museum for Central Africa (Belgium). This method provides a high-spatial-resolution, repeatable, minimally destructive, and sensitive method to determine many elements of wood tissue [27,28]. The ablated material, from the 10-microns crater produced by the laser ablation system, was swept directly into the plasma of ICP-MS by the He-Ar flow of the sample cell. Afterward, the sample particles were ionized, and the ions were separated and detected by the mass spectrometer. The measurement was carried out in continuous ablation with 100-µm line at a speed of 15 µm/s. The spatial resolution between each measurement was 14 µm. The laser was fired with an energy of 10 J/cm^2 and a repetition rate of 40 Hz. Before analysis, the operating conditions of LA-ICP-MS were optimized by ablation on the standard reference material NIST SRM 612 (from the National Institute of Standards & Technology, USA). The two certified MACS-1 and MACS-3 standards (from the United States Geological Survey) were used for calibration. Both standards were analyzed with each series of samples to control the instrumental drift. The precision was below 10%, and the accuracy was better than 6%. The total element blanks were negligible and below their detection limit (2.64 mg/kg for Na, 0.93 mg/kg for Mg, 1.16 mg/kg for Fe, 0.60 mg/kg for Ni, 0.50 mg/kg for Cu, 0.27 mg/kg for Zn, and 0.03 mg/kg for Pb). The quantification limit was calculated from the standard deviation and intensity measurements of 20 blanks. As an internal standard, ^{13}C was used and assumed to be 45% (in concentration).

2.3. Statistical Analysis

The radial trace element profiles were checked again, smoothed for spike removal, and fit to annual tree-ring width. The median concentration of selected elements was used in the analysis, because a median is a more outlier-resistant measure of the center of a distribution than the arithmetic mean. JSAP [29] software was used in statistical analysis, such as Pearson's correlations, Pearson heatmap, PCA, and path diagram. PCA analysis allows one to determine the number and contribution of principal components that describe the correlation between each component and each variable. Uniqueness represents the variance that is unique to the variable and not shared with other variables. The greater the 'uniqueness', the lower the relevance of the variable in the factor model [30].

The enrichment factor, used to compare the concentration of the selected element in wood and the rain load, was calculated according to the following formula.

$$EF = C_{wood}/C_{load} \quad (1)$$

where C_{wood} is the concentration of selected element in the annual tree ring of pine growing in industrialized area (HKF2) and the comparative site (OLE); C_{load} is the concentration of selected element in the rainfall load.

2.4. The Silesia Region—Pollutant Loads Brought with Precipitation

Data on the amounts of pollutant loads brought with precipitation to the area represented by monitoring station in Katowice, the nearest to sampling sites, over the years 1999–2012 were received from the Chief Inspectorate of Environmental Protection (GIOŚ). GIOŚ is an office of government administration responsible, in particular, for the control of entities that use the environment in terms of compliance with environmental protection regulations and the conduct of state environmental monitoring.

The descriptive statistics on the yearly amounts of pollutant loads brought with precipitation to the area represented by the monitoring station in Katowice, the closest to sampling sites, in the years 1999–2012 are presented in Table 1.

Table 1. Statistical data on the yearly amounts of elements in the loads brought with precipitation to the area (including the mean, standard deviations, median, range, minimum and maximum values, and percentile distribution) from Silesia, based on data from monitoring station in Katowice.

	Load of Elements in the Rainfall kg/ha								
Element	**Median**	**Mean**	**Std. Deviation**	**Range**	**Minimum**	**Maximum**	**25th Percentile**	**50th Percentile**	**75th Percentile**
Na	4.2	3.94	0.76	2.2	2.7	4.96	3.29	4.2	4.4
Mg	1.03	1.07	0.30	1.03	0.65	1.68	0.92	1.03	1.15
Cr	0.003	0.004	8.2×10^{-4}	0.003	0.003	0.005	0.003	0.003	0.004
Fe	0.367	0.368	0.083	0.31	0.26	0.566	0.30	0.37	0.40
Ni	0.008	0.009	0.003	0.010	0.006	0.017	0.008	0.008	0.01
Cu	0.072	0.075	0.023	0.096	0.045	0.141	0.061	0.072	0.084
Zn	0.70	0.71	0.18	0.54	0.43	0.971	0.54	0.70	0.87
Pb	0.048	0.050	0.022	0.092	0.026	0.118	0.037	0.048	0.051

3. Results

3.1. Element Load in Rainfall

Figure 4 and Tables 1 and 2 provide an overview of the data from GIOŚ of the pollutant loads in rainfall. Table 2 reveals a relationship between the yearly amounts of element loads brought with precipitation to the area represented by the monitoring station in Katowice, the closest to the sampling sites, over the years 1999–2012. Table 2 and Figure 5 provide an overview of the principal component loadings and a path diagram with only one factor, based on principal components analysis.

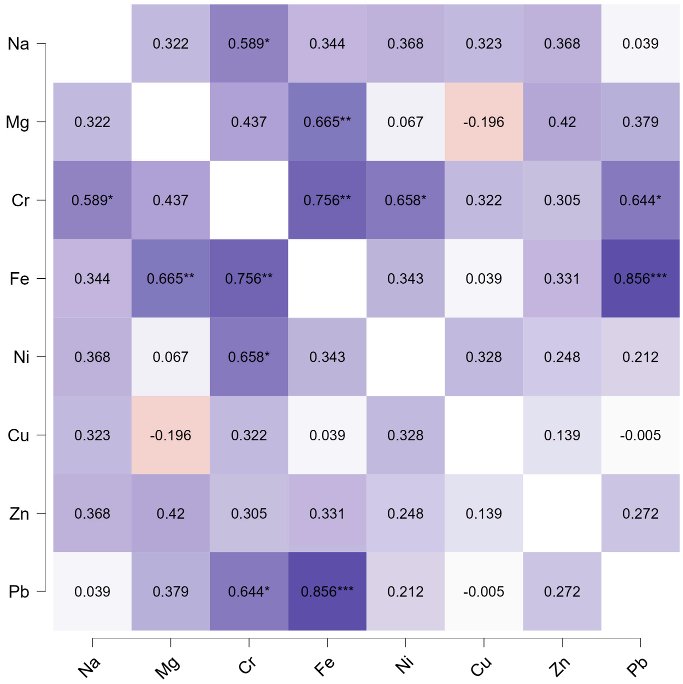


Figure 4. Pearson r heatmap showing the relationship between the elements and pollutant loads in rainfall. Significant correlations are flagged: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Table 2. Results of the Principal Components Analysis (PCA). Component loadings, element loads in rainfall, and uniqueness. The applied rotation method was promax.

Component Loadings		
Element	**RC1**	**Uniqueness**
Cr	0.792	0.373
Fe	0.782	0.388
Ni	0.64	0.591
Pb	0.6	0.639
Mg	0.48	0.77
Na	0.467	0.782
Cu		0.921
Zn		0.853

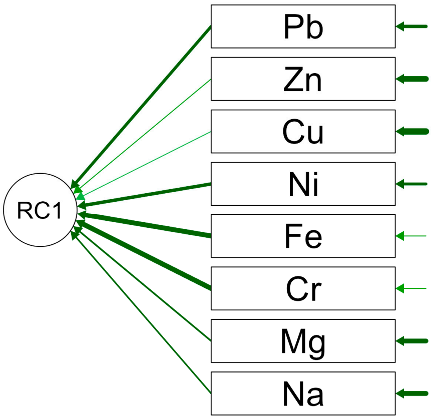
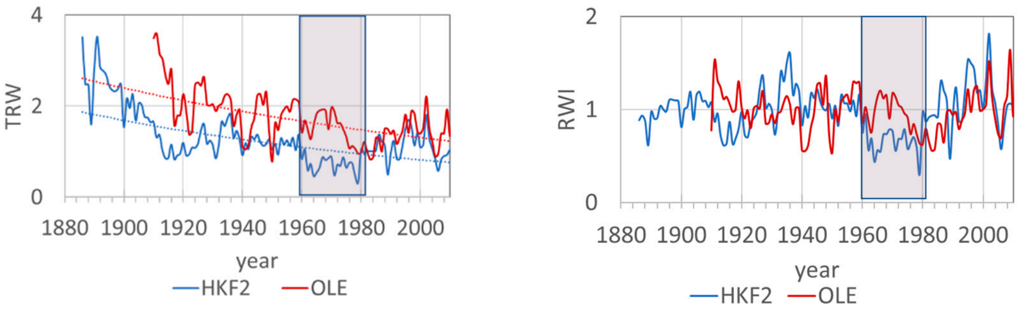


Figure 5. A path diagram of Principal Components Analysis (PCA) for element loads in rainfall.

3.2. Trace Elements in Wood Samples

A difference between chronologies (TRW—tree-ring width, RWI—ring width indexes chronology) for pine and a decreasing trend due to the industrial sector's development and thus relatively higher emission of the pollution linked to higher production have been observed only in the industrialized area in 1960–1980 (Figure 6). Detailed dendrochronological studies of trees growing in Olesno and in different parts of Silesia, including the Hutki-Kanki region, have already been presented [17,20–22]. Figure 6 provides an overview of the fluctuations in tree-ring width and ring width index data for pines growing in the industrialized area and in the comparative site over the years 1960–1980.



(**a**) (**b**)

Figure 6. Difference between pine chronologies (TRW—tree-ring width (**a**), RWI—ring width index chronology (**b**)) growing in Hutki-Kanki (HKF2) and Olesno (OLE).

3.2.1. Hutki-Kanki

Figure 7 and Tables 3 and A1 provide an overview for the LA-ICP-MS data of the wood sample HKF2. The detailed results of the element concentration in individual annual tree rings include radial variation in the element concentration (see Figure 7), descriptive statistics (see Table 3), the relationships between the element concentrations as determined by Pearson's r heatmap (see Figure 8), and component loadings and a path diagram based on principal components analysis (see Figure 9, Table 4).

Table 3. Statistical data (including mean, standard deviations, median, range, minimum and maximum values, and percentile distribution) of yearly concentration of selected elements in pine wood from industrialized area (HKF2).

				Concentration, mg/kg					
Element	**Median**	**Mean**	**Std. Deviation**	**Range**	**Minimum**	**Maximum**	**25th Percentile**	**50th Percentile**	**75th Percentile**
Na	25	31	33	211	3	214	17	25	36
Mg	51	58	21	99	28	126	46	51	60
Cr	1.02	1.08	0.23	1.03	0.90	1.93	0.94	1.02	1.10
Fe	4	10	14	72	0	73	2	4	9
Ni	0.17	0.23	0.27	1.75	0.6	1.81	0.12	0.17	0.25
Cu	1.0	1.7	2.4	12.3	0.4	12.7	0.7	1.0	1.7
Zn	12.1	13.0	4.5	25.8	7.0	32.7	10.9	12.1	13.6
Pb	0.44	0.47	0.23	1.22	0.16	1.38	0.31	0.44	0.57

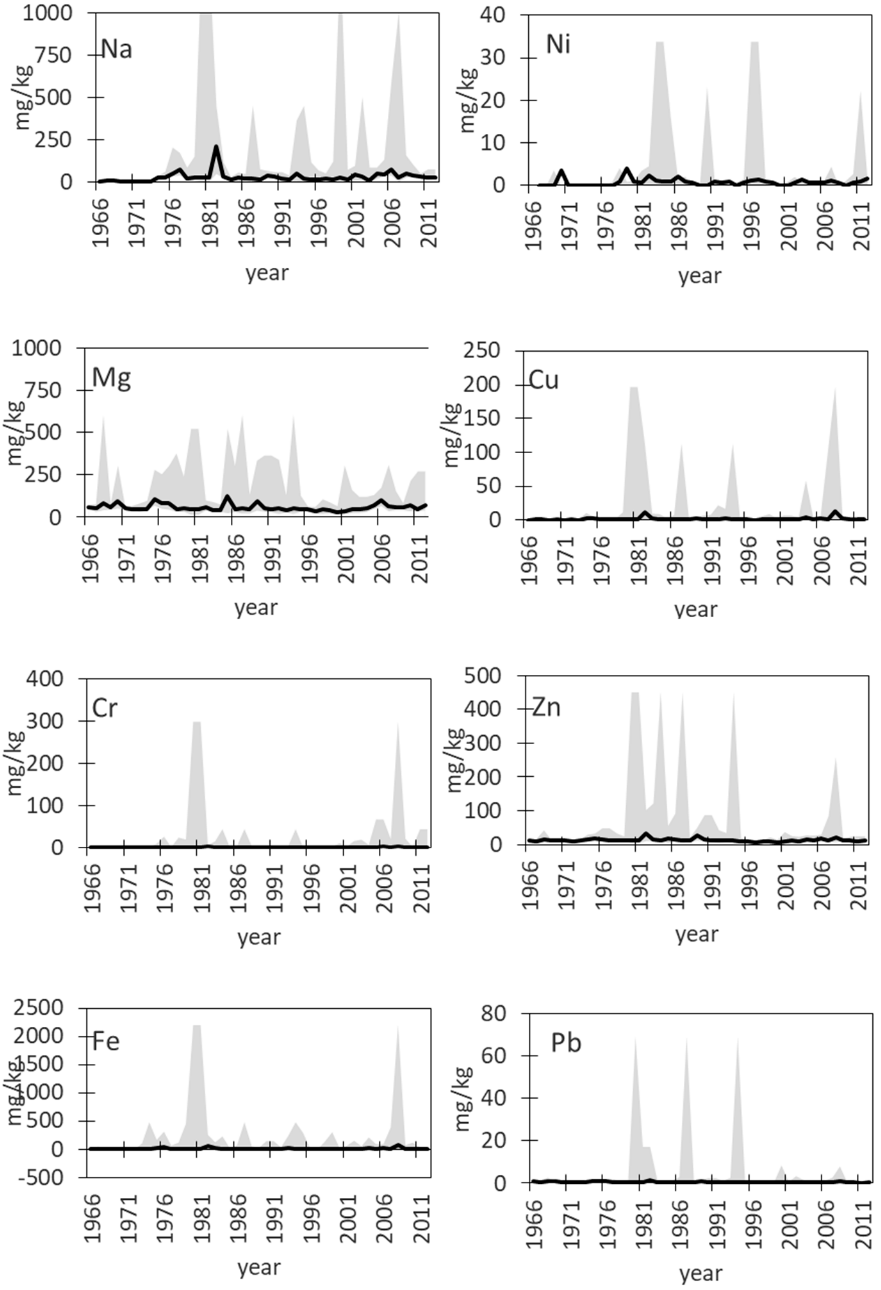
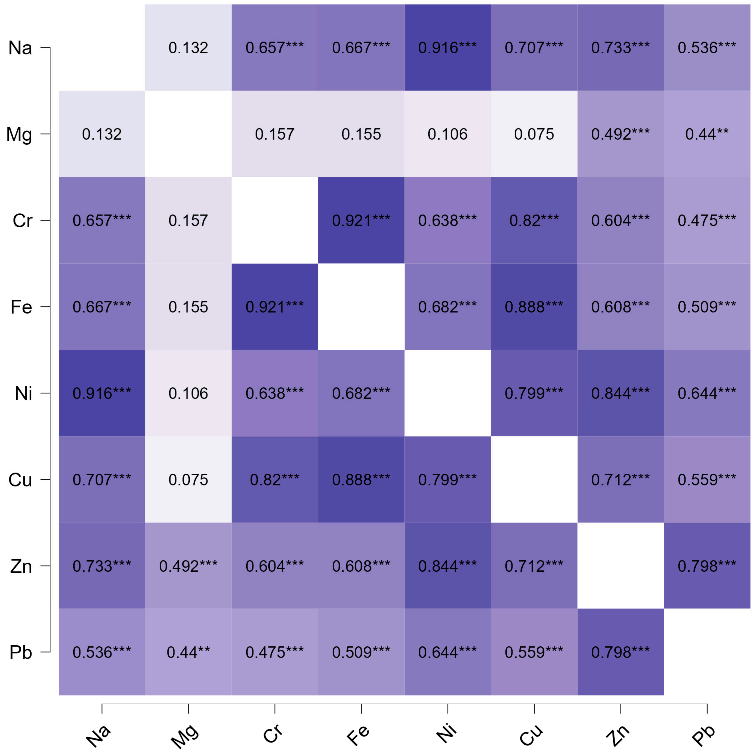


Figure 7. Radial variations in the element concentrations of Na, Mg, Fe, Ni, Cu, Zn, and Pb in the wood pine growing in the industrial area HKF2. Black lines indicate median contents of elements, and grey area indicates the maximum concentration of the element in annual tree ring. In the late 1970s and early 1980s, a spike can probably be observed.



	Na	Mg	Cr	Fe	Ni	Cu	Zn	Pb
Na		0.132	0.657***	0.667***	0.916***	0.707***	0.733***	0.536***
Mg	0.132		0.157	0.155	0.106	0.075	0.492***	0.44**
Cr	0.657***	0.157		0.921***	0.638***	0.82***	0.604***	0.475***
Fe	0.667***	0.155	0.921***		0.682***	0.888***	0.608***	0.509***
Ni	0.916***	0.106	0.638***	0.682***		0.799***	0.844***	0.644***
Cu	0.707***	0.075	0.82***	0.888***	0.799***		0.712***	0.559***
Zn	0.733***	0.492***	0.604***	0.608***	0.844***	0.712***		0.798***
Pb	0.536***	0.44**	0.475***	0.509***	0.644***	0.559***	0.798***	

Figure 8. Pearson's r heatmap: relationship between concentrations of selected elements in the wood of pine that grows in an industrialized area (HKF2). Significant correlations are flagged: ** $p <$ 0.01, *** $p <$0.001.

Table 4. Results of the principal components analysis (PCA). Component loadings and uniqueness of element concentration in pine growing in industrialized area (HKF2).

	Component Loadings HKF2		
Element	**RC1**	**RC2**	**Uniqueness**
Cu	0.988		0.117
Fe	0.958		0.173
Cr	0.929		0.223
Ni	0.877		0.165
Na	0.855		0.244
Zn	0.566	0.545	0.097
Mg		1.014	0.169
Pb		0.621	0.252

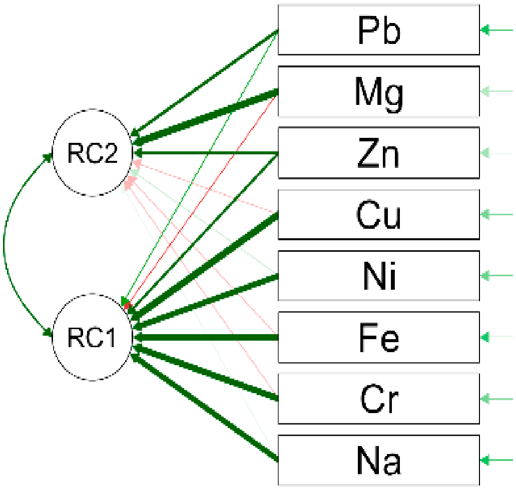


Figure 9. A path diagram of the Principal Component Analysis (PCA) of the concentration of elements in pine growing in industrialized area (HKF2).

3.2.2. Olesno

Figure 10 and Tables 5 and A2 provide an overview of the data from the LA-ICP-MS analysis of the wood sample OLE. Detailed results of the element concentration in individual annual tree rings include radial variation in element concentrations (Figure 10), descriptive statistics (Table 5), relationship between elements' concentration as determined by Pearson's r heatmap (Figure 11), and component loadings and a path diagram based on principal components analysis (Figure 12, Table 6).

Table 5. Descriptive statistics of the yearly concentration of selected elements in wood pine (OLE) growing far from industrial factories in Olesno (1965–2010).

	Element Concentrations, mg/kg								
Element	**Median**	**Mean**	**Std. deviation**	**Range**	**Minimum**	**Maximum**	**25th Percentile**	**50th Percentile**	**75th Percentile**
Na	57	80	60	197	13.86	210	25	58	131
Mg	102	102	17	75	67	142	92	103	112
Cr	2.8	3.1	1.2	4.2	1.6	5.7	2.1	2.8	3.7
Fe	50	53	33	116	10	126	27	50	73
Ni	1.0	1.1	0.49	3.1	0.7	3.8	0.89	0.99	1.18
Cu	4.5	5.2	3.4	18	1.1	19	3.2	4.5	6.1
Zn	10.4	10.3	2.3	9.0	5.1	14	9.2	10.4	11.8
Pb	1.06	1.08	0.61	2.48	0.16	2.6	0.6	1.05	1.67

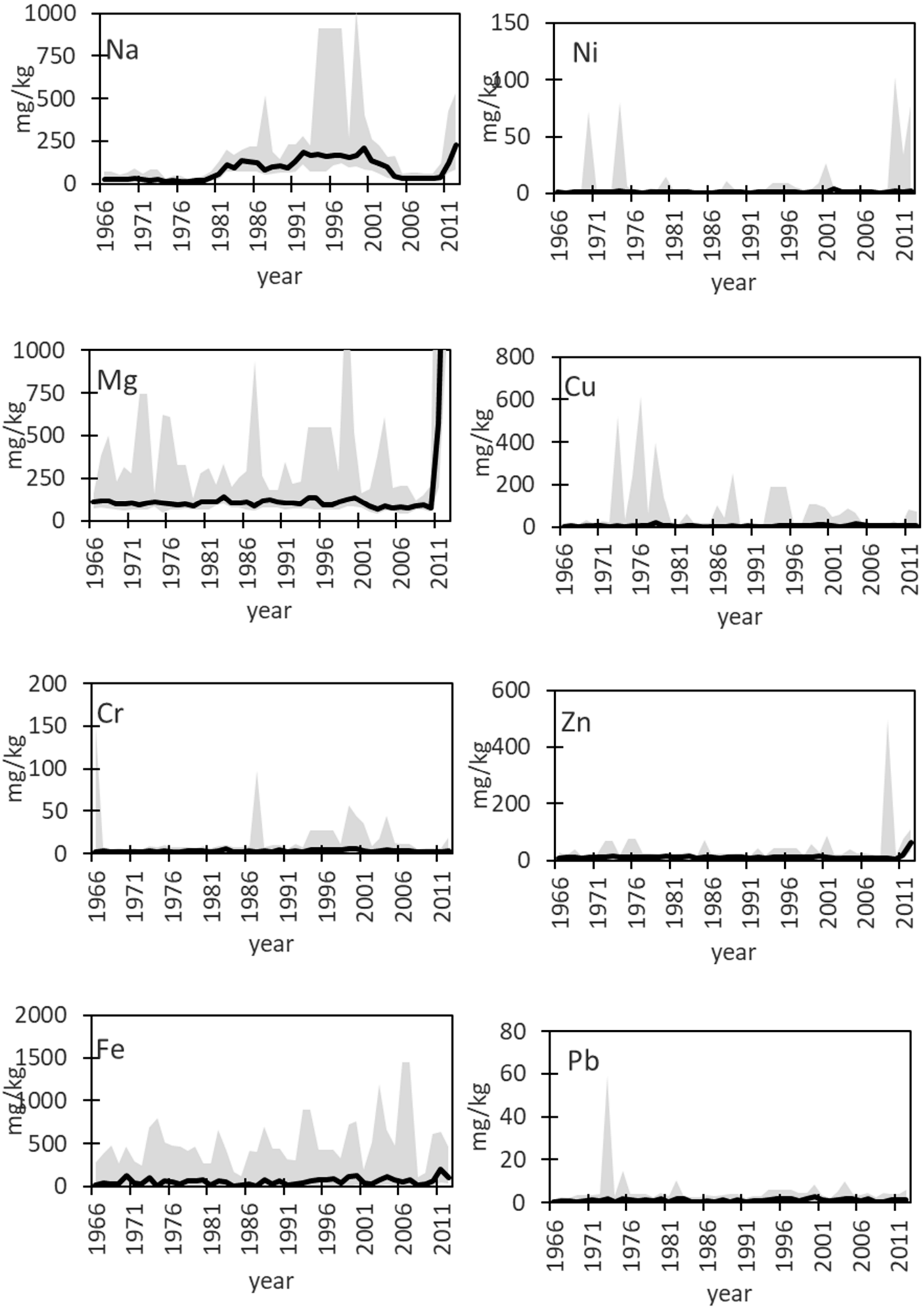


Figure 10. Radial variations in the element concentrations of Na, Mg, Fe, Ni, Cu, Zn, and Pb in wood pines that grow far from the industrial factories in Olesno. Black lines indicate median contents of elements, and grey area indicates the maximum concentration of the element in annual tree ring.

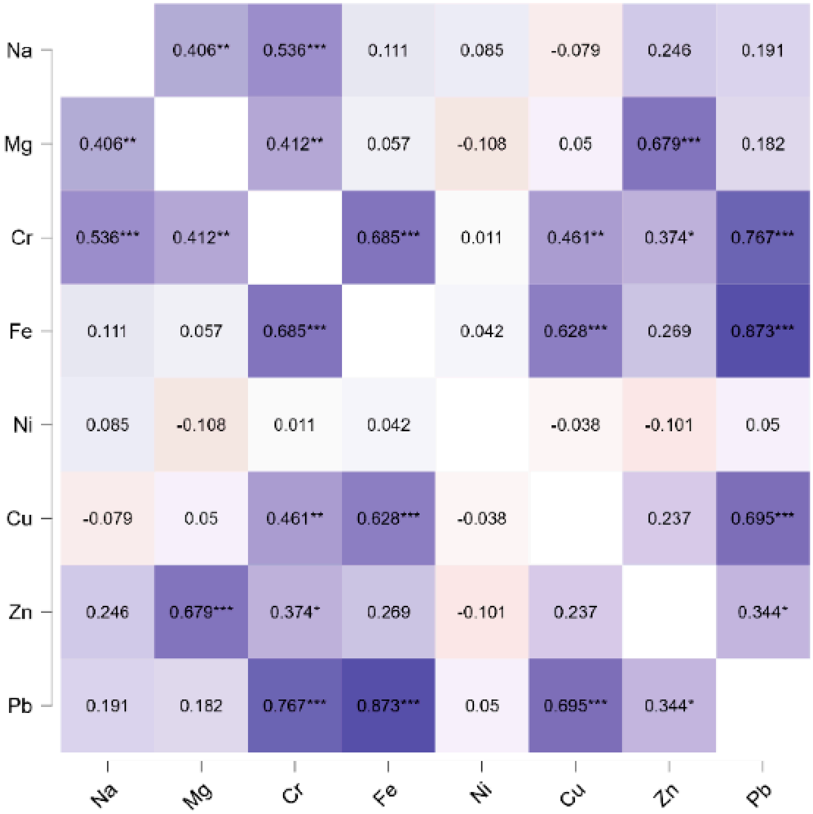


Figure 11. Pearson's r heatmap: relationship between concentrations of selected elements in wood of pine growing far from industrialized area. Significant correlations are flagged: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Table 6. Results of the principal components analysis (PCA). Component loadings and uniqueness of element concentration in pine growing far from the industrialized area (OLE). The applied rotation method was promax.

	Component Loadings OLE		
Element	**RC1**	**RC2**	**Uniqueness**
Fe	0.951		0.141
Pb	0.949		0.082
Cu	0.869		0.311
Cr	0.675	0.413	0.205
Mg		0.918	0.207
Zn		0.729	0.391
Na		0.711	0.51
Ni			0.979

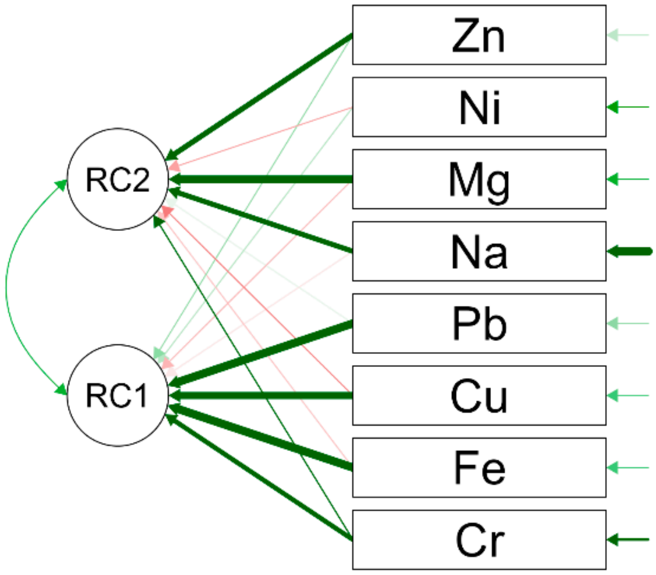


Figure 12. A path diagram of the Principal Component Analysis (PCA) of the concentration of elements in pine growing in industrialized area (HKF2).

3.2.3. Comparison of the Trends in Trace Element Concentration

Figure 13 compares the trends in medians of element concentrations (Na, Mg, Fe, Ni, Cu, Zn, Pb) in pine growing in both industrialized and comparative areas (since 1960–2010s) and the loads of Na, Mg, Fe, Cu, Zn, and Pb in rainfall (1999–2010), along with the enrichment factors. The ratio of the median element contents (Na, Mg, Cr, Fe, Ni, Cu, Zn, Pb) in the wood of pines growing in the industrialized area (HKF2) and the comparative site (OLE) to the median contents of elements of the load in rainfall (load) in Katowice in the period of time from1999 to 2010 is presented in Figure 14. The median concentrations of the elements in the individual annual tree rings of HKF2, from 1965–2010, followed the order Ni < Pb < Cr < Cu < Fe < Zn < Na< Mg. In the case of OLE, they followed the order Ni < Pb < Cr < Cu < Zn < Fe < Na < Mg. The median concentrations of elements in the rainfall load during 1999–2010 followed the order Cr < Ni< Pb < Cu < Fe < Zn < Mg < Na. In pines, it is slightly different than in rain. OLE followed a different order (i.e., Ni < Pb < Cr < Cu < Fe < Na < Zn < Mg) with higher concentration of Zn for the period 1999–2010.

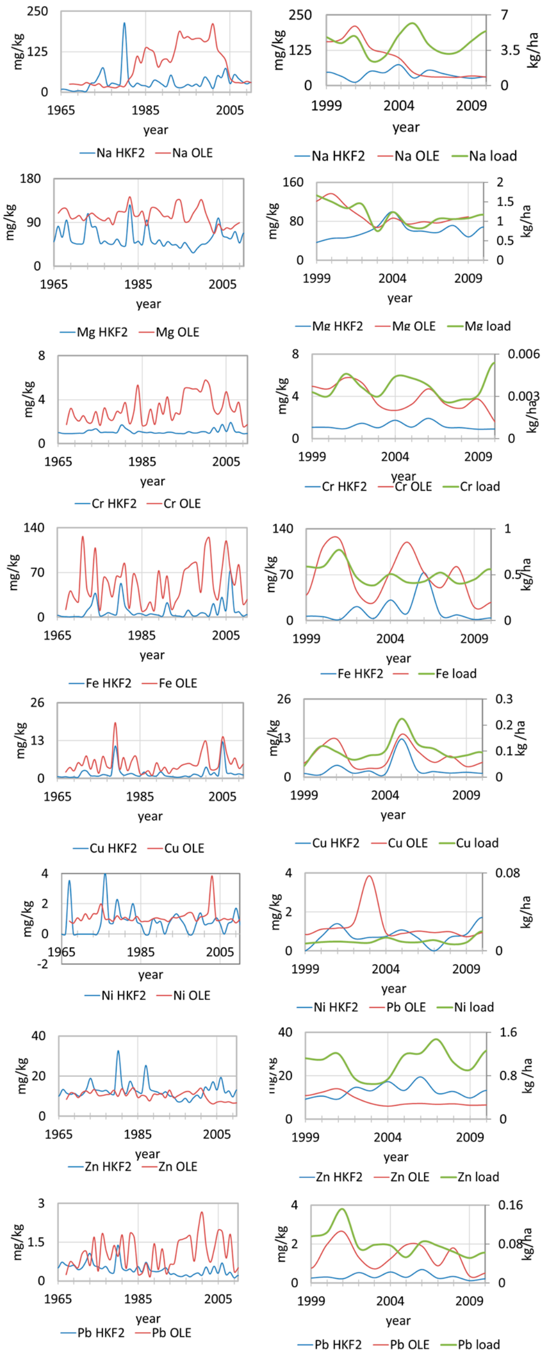


Figure 13. Comparison of the trends in median elements (Na, Mg, Cr, Fe, Cu, Zn, Pb) in pines growing in both industrialized (HKF2) and comparative (OLE) sites, from 1965–2010, and loads of Na, Mg, Fe, Cu, Zn, Pb in rainfall load in Katowice (1999–2010).

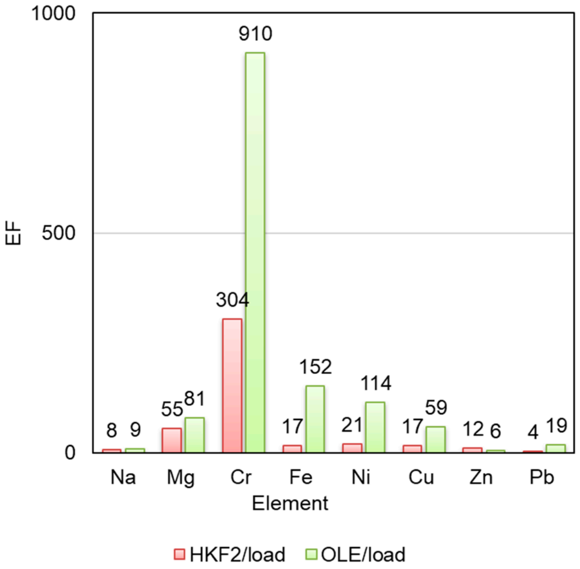


Figure 14. The ratios of the median elements (Na, Mg, Cr, Fe, Ni, Cu, Zn, and Pb) in wood of pines growing in industrialized area (HKF2) and the comparative site (OLE) to the median element contents of the rainfall load in Katowice during 1999 to 2010.

4. Discussion

The results are in part in agreement with previous findings from other areas in Kędzierzyn-Koźle, in Poland [22]. In the investigated period of time, analyzing the correlation between the amount of annual rain and the concentration of elements in tree rings, no direct link was observed between climatic factors and the accumulation of elements by trees. Furthermore, a short-term moving correlation between climatic data and elemental components of trees was conducted and did not show a significant correlation in this region. Even though there are also no linear dependences between rain load and elements accumulated in annual tree rings, the changes in amplitude distribution of the load are reflected by tree wood’s elemental composition for some elements. However, other scientists [4] found that the Mn, Cu, Cd, Pb, Zn, and Ni contents in tree rings may correlate with climate-induced drought conditions, which explains the increase in elemental contents after 1980. In this moment, we cannot exclude that there is no dependence; we can note that if there is any relationship between data, it cannot be analyzed on a linear scale. Higher concentrations of some elements were found in the pine that grows in Olesno, far from the industrial area. A hypothetical explanation can be associated with (1) the physiological response to some natural environmental stress, (2) the effect of other local small point sources of emission (such as traffic or householders), or (3) soil contamination, especially in Olesno, i.e., a region strongly contaminated by radionuclides during the accident in Chernobyl in 1986 [31]. Pines growing in Olesno without the effect of continuous industrial air contamination absorb more elements during photosynthesis, and stomata conductance has not been limited. According to [32], the trees that have been growing in this region did not show any impact of emissions related to industrial pollution.

In Silesia’s industrial forests, also in the area nearby steelworks and Hutki-Kanki, trees significantly reduced their stomata conductance in the first decade of the 2000s [23]. This reduction in stomata conductance may probably affect the air amount, and in consequence the elements, taken in by plant leaves during respiration. However, the impact of other local point sources cannot be excluded. Pearson correlation and PCA analysis showed that element concentrations in rainfall load cannot be divided into clusters, whereas, the analysis of element concentrations in wood indicate two factors that visually identify two clusters. In the case of pine growing in an industrial area (HKF2), the first component is correlated with Cu, Fe, Cr, and Ni, and the second component is correlated with Na, Zn, Mg, and Pb. Meanwhile, in the sample collected in the area far from the industrial area, the first component is related to Fe, Pb, Cu, and Cr, and the second component is correlated with Mg, Zn, Na, and Ni. Both samples show that one of the components is related to the concentrations of Cu, Fe, and Cr and the second one to Mg, Zn, and Na. The difference in cluster divisions is related to Pb and Ni. It could be due to the fact that the Olesno site is closer to the road and traffic has been a source of lead emission due to use of lead gasoline in Poland up to 2000. The HKF2 site has been under strong impact from steelworks, from which Ni emission during the production process is evident [33]. However, on the other hand, emission of Ni can also be associated with traffic [32]. In the future, it will be a challenge to try to identify those initial factors, and this identification of the factors will require additional, more complex and detailed investigations.

Most trace elements (Cr, Cu, Fe, Mn, Ni, Pb, Zn) are derived from mining, metal smelting, coal and petroleum combustion, oil burning, waste incineration, cement production, and other industrial activities [5,32,34–37]. Pb emission and also Zn and Ni could be found in petrol and motor oil; therefore, motor vehicles could be an important source of these contaminants. Currently, it is likely that urbanization and high traffic are the main reasons for high concentrations of these metals [6,35]. It has been observed that vegetation intercepts the aerosol and that the concentrations of elements are high in samples of plants from industrial areas. A review of the scientific literature shows that trees can absorb some elements from the air by leaves and also by roots from the soil that can be polluted by industry, traffic, and household activities [38–41]. Meanwhile, some studies show that trees did not provide reliable information at the yearly scale on past variations in contaminated soils, and a key role in absorption of elements is also played by soil acidity. It seems that two other aspects should be taken in account for the interpretation of trace element concentration, i.e., (1) migration of the elements within the soil profile from the top part to the roots of the plant and (2) migration of the elements within trees. Different groups of elements in terms of availability for plants and the risk of contamination of the food chain, using the theory of the soil–plant barrier, have been distinguished [42]: (i) elements that are not dissolved in the water, which are collected in small amounts (Cr); (ii) elements quite easily collected by the roots but transported in small quantities to the aerial parts (Pb); and (iii) elements that are readily taken up by the roots and transported to the aerial parts but reduce the risk of phytotoxicity to the food chain (toxic to plants and the original contents and nontoxic for humans and animals) (Zn, Cu, Ni). Natural and anthropogenic sources [43] can contribute to the accumulation of metals in the ecosystem where trees are grown. It is complex to assess the toxic effect of trace elements on plants, as it depends on several factors that cannot be measured on a linear scale [11,44].

Some scientists have reported a migration of some elements within trees (for example, P, K, Ca), while some other elements (for example, Zn, Al, Cu) have a constant concentration in all parts of the xylem [44]. Comparing the fluctuation in the amplitude of median concentration of the elements, it can be seen that dynamics of these fluctuations are different in different periods of time for both samples. The concentration of some elements can be nearly constant, with just some increase during a short period of time of about 2–3 years (for example, Zn, Ni, Cu) in both samples of wood. In our research, Zn is at the same level in both samples, with just two episodes of higher concentrations observed in HKF2 in the 1980s. More fluctuations in the median concentration are observed in OLE than in HKF2. A strong increase in Na concentration since the 1980s is observed only for HKF2. In both samples, the fluctuation in Cu amplitude shows some similarities to the changes in Cu of the rainfall load.

Limitation of the Study

In Poland, the number of monitoring stations was limited during the industrial period. Future studies should focus on trees located close to monitoring stations. These results suggest that a higher concentration of elements has been found in wood collected away from the industrialized region. The impact of the transport of pollution by wind cannot by omitted. It is also questionable whether the forest near Olesno can be taken as a natural reference site.

5. Conclusions

This study describes geochemical differences in the trees that grow in the Silesia region. The impact of pollution on plant tissue is evident. The element concentrations in trunks reflect the sum of different effects, explaining why, in annual tree rings, there is no direct linear correlation between rainfall load and concentration of these elements in wood of the annual rings. However, additional data collection would help to confirm the observations and determine the link between trees and rainfall load. Even wood samples (tree-ring width chronology) do not show reduction of the size of annual tree rings from 1960–1980, and the concentration of the elements is higher than in the site next to the steelwork. Future research should consider the potential effects of pollution sources and local point sources, immission and rainfall load over a longer period of time, and plant physiology.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Median contents of elements (Na, Mg, Cr, Fe, Ni, Cu, Zn, Pb) in wood of pines growing in industrialized area (HKF2).

Site	**Hutki-Kanki**							
	Concentration of the Element in Wood, mg/kg (Median)							
Year	**Na**	**Mg**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**Pb**
1965	9.2	50.9	1.0	3.0	<LD	0.6	10.2	0.5
1966	9.1	82.4	0.9	1.1	<LD	0.7	13.5	0.7
1967	5.5	59.7	0.9	0.7	3.6	0.5	11.6	0.6
1968	3.0	95.0	0.9	0.4	<LD	0.6	11.0	0.6
1969	4.9	52.9	0.9	0.9	<LD	0.4	11.5	0.6
1970	4.1	46.8	0.9	0.9	<LD	0.5	10.2	0.4
1971	3.1	45.8	0.9	1.0	<LD	0.5	10.9	0.5
1972	26.7	48.4	1.2	10.4	<LD	2.5	13.7	0.7
1973	30.6	107.8	1.2	18.7	<LD	2.6	19.0	1.1
1974	52.4	81.4	1.3	37.5	<LD	1.0	13.7	0.6
1975	75.1	80.5	1.0	2.9	0.8	0.9	13.0	0.6
1976	21.2	47.4	1.0	3.3	4.1	0.8	12.6	0.5

1977	28.1	51.8	1.0	7.0	0.8	1.4	13.0	0.6
1978	25.7	46.1	1.0	4.8	0.7	1.2	11.4	0.3
1979	25.2	45.6	1.0	4.5	2.3	1.1	11.2	0.3
1980	214.4	55.9	1.7	53.1	1.1	11.2	32.7	1.4
1981	35.9	42.9	1.4	18.0	1.0	3.0	15.1	0.5
1982	16.8	42.7	1.1	9.3	1.0	1.2	11.3	0.4
1983	27.9	126.4	0.9	3.4	2.0	1.5	17.5	0.5
1984	21.7	49.1	1.1	5.7	0.8	1.7	13.6	0.4
1985	20.1	51.8	1.0	5.1	0.6	1.0	12.3	0.6
1986	16.8	45.1	1.0	2.6	<LD	0.9	11.8	0.4
1987	37.0	95.2	1.0	5.1	<LD	2.2	25.4	0.7
1988	33.2	52.6	0.9	4.2	1.0	1.0	13.9	0.4
1989	23.8	45.6	1.0	3.0	0.7	0.9	12.7	0.4
1990	18.6	54.2	0.9	2.2	0.8	0.9	12.1	0.4
1991	53.1	41.2	1.0	22.8	<LD	2.3	11.1	0.4
1992	20.7	50.8	1.0	4.4	0.7	1.0	12.3	0.5
1993	14.0	44.0	0.9	2.2	1.1	0.7	10.3	0.3
1994	16.6	44.2	0.9	1.6	1.3	0.6	9.9	0.3
1995	24.0	37.4	0.9	1.2	1.0	0.4	7.4	0.2
1996	18.9	48.8	1.1	11.0	0.6	0.6	7.5	0.2
1997	25.1	38.1	1.0	2.7	<LD	0.9	9.0	0.2
1998	18.8	27.5	1.0	2.2	<LD	0.6	7.0	0.2
1999	47.1	36.7	1.1	6.6	0.7	1.5	9.2	0.3
2000	33.3	44.8	1.1	5.9	1.4	1.2	10.6	0.3
2001	11.9	46.2	0.9	1.7	0.6	0.8	9.2	0.2
2002	50.5	54.2	1.5	21.4	0.7	3.9	14.6	0.5
2003	45.8	69.0	1.0	3.2	0.7	1.3	13.1	0.3
2004	73.8	99.4	1.7	31.3	1.1	2.0	17.3	0.6
2005	26.9	63.8	1.1	10.8	0.7	1.0	13.2	0.3
2006	54.5	59.7	1.9	72.9	<LD	12.7	19.5	0.7
2007	42.7	57.0	1.1	8.6	0.7	2.1	11.9	0.2
2008	31.9	71.3	1.0	8.7	0.9	1.8	12.7	0.3
2009	26.1	48.0	0.9	1.7	1.7	1.3	9.8	0.1
2010	30.7	68.1	0.9	4.0	0.7	1.6	13.2	0.2

Table A2. Median contents of elements (Na, Mg, Cr, Fe, Ni, Cu, Zn, Pb) in wood of pines growing in comparative site (OLE).

Site:	**OLESNO**							
	Concentration of the Element in Wood, mg/kg (Median)							
Year	**Na**	**Mg**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**Pb**
1967	25.0	109.0	1.7	11.8	0.9	2.3	8.4	0.2
1968	25.4	118.4	3.2	40.6	0.7	3.8	11.6	0.7
1969	23.9	117.2	2.4	29.9	1.1	2.7	11.3	0.6
1970	22.8	98.6	2.1	24.2	0.9	5.5	9.3	0.5
1971	29.9	99.1	2.5	126.4	1.3	4.5	11.8	1.1
1972	25.0	104.0	1.9	44.7	1.0	7.8	12.6	1.1
1973	21.3	93.7	1.9	33.0	1.3	3.3	11.5	0.6
1974	26.3	103.0	2.9	108.4	1.4	6.5	13.4	1.7
1975	15.4	108.9	1.7	11.0	2.0	1.8	10.4	0.4
1976	17.7	102.3	3.2	61.8	1.0	7.6	10.3	1.8
1977	15.1	96.4	2.3	55.4	1.0	4.1	10.8	1.2

1978	13.9	93.5	2.1	31.7	0.8	3.8	11.1	0.8
1979	19.4	98.9	2.9	63.7	1.2	19.1	13.0	1.4
1980	17.8	85.5	2.8	62.8	0.9	3.5	9.9	1.0
1981	38.4	110.5	3.7	83.1	1.1	7.2	13.8	1.8
1982	57.7	112.2	1.8	13.7	0.9	2.7	10.2	0.5
1983	110.9	113.0	2.9	67.1	0.9	6.1	12.7	1.8
1984	90.7	142.5	5.3	51.7	1.2	7.6	14.2	1.7
1985	136.3	104.7	1.7	10.0	0.8	1.7	9.4	0.3
1986	131.8	103.2	1.7	11.8	0.8	1.7	10.4	0.3
1987	122.8	112.6	3.1	23.8	0.8	2.7	9.9	0.7
1988	77.7	83.2	1.7	10.9	1.0	1.1	7.6	0.2
1989	98.5	118.5	3.7	72.7	1.1	5.4	10.9	1.4
1990	102.5	120.1	2.7	29.3	1.0	2.6	10.8	0.4
1991	93.1	113.1	4.3	64.5	0.9	3.9	11.3	1.2
1992	131.1	102.3	2.2	13.2	0.8	1.8	9.2	0.3
1993	187.4	102.7	2.8	23.9	1.1	3.5	13.1	0.6
1994	167.3	99.0	2.7	37.0	1.1	3.3	9.3	0.7
1995	171.6	133.7	5.0	71.9	1.1	4.5	10.1	1.5
1996	163.0	134.8	5.1	77.7	1.2	5.0	11.2	1.6
1997	165.9	92.4	5.0	84.1	1.4	5.2	12.2	1.7
1998	165.4	92.4	5.0	84.8	1.4	4.5	12.3	1.7
1999	155.6	108.2	4.7	39.0	0.8	4.7	10.9	0.8
2000	164.3	121.4	5.8	112.4	1.1	10.0	12.4	2.0
2001	211.0	136.7	5.3	123.8	1.2	12.7	14.0	2.7
2002	134.6	109.3	3.2	45.1	1.4	3.5	10.1	1.3
2003	116.6	87.6	2.7	27.2	3.9	3.0	7.2	0.7
2004	97.5	67.4	3.3	74.7	1.0	4.2	6.1	1.2
2005	45.4	86.5	4.7	119.6	0.9	14.3	7.0	2.0
2006	31.4	74.5	3.3	73.8	1.0	8.6	7.3	1.9
2007	29.8	79.0	2.9	50.2	0.9	4.9	6.9	0.9
2008	28.6	76.8	3.7	81.9	1.0	7.0	7.2	1.8
2009	33.6	84.2	1.6	20.7	0.7	3.5	6.5	0.4
2010	29.8	89.3	1.7	27.7	0.9	4.9	6.6	0.5

References

1. Schweingruber, F.H. *Tree Rings and Environment. Dendroecology*; Swiss Federal Institute for Forest, Snow and Landscape Research, and Paul Haupt Verlag: 1996; pp. 609.
2. McLaughlin, S.B.; Shortle, W.C.; Smith, K.T. Dendroecological applications in air pollution and environmental chemistry: Research needs. *Dendrochronologia* **2002**, *20*, 133–157.
3. Sensula, B.M.; Pazdur, A.; Bickerton, J.; Derrick, P.J. Probing palaeoclimatology through quantitation by mass spectrometry of the products of enzyme hydrolysis of alpha-cellulose. *Cellulose* **2011**, *18*, 461–468. https://doi.org/10.1007/s10570-010-9490-y.
4. Nechita, C.; Iordache, A.M.; Lemr, K.; Levanič, T.; Pluhacek, T. Evidence of declining trees resilience under long term heavy metal stress combined with climate change heating. *J. Clean. Prod.* **2021**, *317*, 128428.
5. Key, K.; Kulaç, Ş.; Koç, İ.; Sevik, H. Determining the 180-year change of Cd, Fe, and Al concentrations in the air by using annual rings of *Corylus colurna* L. *Water Air Soil Pollut.* **2022**, *233*, 244.
6. Budzyńska, S.; Budka, A.; Roszyk, E.; Niedzielski, P.; Mleczek, M. Trace of negative changes in environment recorded in cores of trees growing near busy city roads in Poznań, Poland–dendromonitoring of urban pollution. *Ecol. Indic.* **2023**, *149*, 110198.
7. Dobrzańska, J.; Lochyński, P.; Kalbarczyk, R.; Ziemiańska, M. Challenges in the Application of dendrochemistry in research on historical environmental pollution in an old copper mining area. *Forests* **2021**, *12*, 1505.
8. Kabata-Pendias, A. *Trace Elements in Soils and Plants*, 4th ed.; CRC Press: Boca Raton, FL, 2011.
9. Pearson, C.L.; Manning, S.W.; Coleman, M.; Jarvis, K. A dendrochemical study of *Pinus sylvestris* from Siljansfors Experimental Forest, central Sweden. *Appl. Geochem.* **2006**, *21*, 1681–1691.

10. Malik, I.; Wistuba, M.; Danek, M.; Danek, T.; Krapiec, M. The influence of atmospheric pollution emitted by the Chemical Plants in Tarnowskie Gory (the northern part of the Silesian Upland) on the width of Scots pine tree rings (*Pinus sylvestris* L.). *Ochr. Środowiska I Zasobów Nat.* **2011**, *47*, 9–21.
11. Danek, M. The influence of industry on scots pine stands in the south-eastern part of the Silesia-Kraków Upland (Poland) on the basis of dendrochronological analysis. *Water Air Soil Pollut*. **2007**, *18*, 265–277.
12. Danesino, C. Environmental indicators for heavy metals pollution: Soils and higher plants Cecilia *Sci. Acta* **2009**, *3*, 23–26.
13. Lukaszewski, Z.; Siwecki, R.; Opydo, J.; Zembrzuski, W. The effect of industrial pollution on zinc, cadmium and copper concentration in the xylem rings of Scot's pine (*Pinus sylvestris* L.) and in the soil. *Trees* **1988**, *2*, 1–6.
14. Juknys, R.; Vencloviene, J.; Stravinskiene, V.; Augustaitis, A.; Bertkevicius, E. Scots pine (*Pinus sylvestris*) growth and condition in polluted environment: From decline to recovery. *Environ. Pollut.* **2003**, *125*, 205–212.
15. Savard, M. Tree-ring stable isotopes and historical perspectives on pollution—An overview. *Environ. Pollut.* **2010**, *158*, 2007–2013.
16. Białobok, S.; Boratynski, A.; Bugała, W. (Eds.) *Biologia Sosny Zwyczajnej*; Polska Akademia Nauk: Poznań-Kórnik, Poland, 1993; p. 624.
17. Sensuła, B.; Fagel, N.; Michczyński, A. Radiocarbon, trace elements and Pb isotope composition of pine needles from a highly industrialized region in southern Poland. *Radiocarbon* **2021**, *63*, 713–726. https://doi.org/10.1017/RDC.2020.132.
18. Sensuła, B.; Piotrowska, N.; Nowińska, K.; Koruszowic, M.; Lazaj, D.; Osadnik, R.; Paluch, R.; Stasiak, A.; Strączek, B. Characteristics of pine needles exposed to pollution in Silesia, Poland: Carbon isotopes, iWUE, and trace element concentrations in pine needles. *Radiocarbon* **2023**, *65*, 233–246. https://doi.org/10.1017/RDC.2023.1.
19. Sensuła, B.; Toroń, B.; Rocznik, J.; Sasiela, A.; Świątkowski, J.; Tomaszowska, A. Characteristics of pine needles exposed to multi-source pollution in Silesia: Radiocarbon concentration in pine needles and elemental analysis of the needles' surface deposits. *Radiocarbon* **2022**, *64*, 1333–1344. https://doi.org/10.1017/RDC.2022.85.
20. Sensuła, B.; Opala, M.; Wilczyński, S.; Pawełczyk, S. Long-and short-term incremental response of *Pinus sylvestris* L. from industrial area nearby steelworks in Silesian Upland, Poland. *Dendrochronologia* **2015**, *36*, 1–12.
21. Sensuła, B.; Wilczyński, S.; Opała, M. Tree Growth and Climate Relationship: Dynamics of Scots Pine (*Pinus Sylvestris* L.) Growing in the Near-Source Region of the Combined Heat and Power Plant During the Development of the Pro-Ecological Strategy in Poland. *Water Air Soil Pollut.* **2015**, *226*, 220. https://doi.org/10.1007/s11270-015-2477-4.
22. Sensuła, B.; Wilczyński, S.; Monin, L.; Allan, M.; Pazdur, A.; Fagel, N. Variations of tree ring width and chemical composition of wood of pine growing in the area nearby chemical factories. *Geochronometria* **2017**, *44*, 226–239. https://doi.org/10.1515/geochr-2015-0064.
23. Sensuła, B.; Wilczyński, S. Dynamics Changes in Basal Area Increment, Carbon Isotopes Composition and Water Use Efficiency in Pine as Response to Water and Heat Stress in Silesia, Poland. *Plants* **2022**, *11*, 3569.
24. Rinn, F. *TSAP—Reference Manual*; Frank Rinn: Heidelberg, Germany, 2010.
25. Holmes, R.L. Computer-assisted quality control in treering dating and measurement. *Tree-Ring Bull.* **1983**, *43*, 69–78.
26. Holmes, R.L.; Lough, J.M. *RESPO—Response and Correlation Function*; Laboratory of Tree-Ring Research, University of Arizona: Tucson, AZ, USA, 1999.
27. Hall, G.S.; Yamaguchi, D.K.; Rettberg, T.M. Multielemental Analyses of Tree Rings By Inductively Coupled Plasma Mass Spectrometry. *J. Radioanal. Nucl. Chem.* **1990**, *146*, 255–265. https://doi.org/10.1007/BF02164193.
28. Hoffmann, E.; Lüdke, C.; Scholze, H.; Stephanowitz, H.Analytical investigations of tree rings by laser ablation ICP-MS. *Fresenius' J. Anal. Chem.* **1994**, *350*, 253–259. https://doi.org/10.1007/BF00322478.
29. *JASP*, version 0.17.1; JASP Team: https://jasp-stats.org/download/ (accessed on 5 March 2023)
30. Available online: https://easystats.github.io/parameters/reference/principal_components.html (accessed on 5 March 2023).
31. Wołkowicz, S.; Strzelecki, R. Geochemistry of post-Chernobyl caesium in soils and plants in Opole region. *Przegląd Geol.* **2002**, *50*, 941—944.
32. Sobecka, L.E.; Protasowicki, M. Effect of sublethal poisoning with nickel on the selected tissues of sheat-fish Silurus Glanis. *Zesz. Probl. Postep. Nauk Rol.* **1997**, *448*, 307–310
33. Opała, M. (The University of Silesia, Katowice, Poland). Report Personal communication, 2012.
34. Said, I. Nickel pollution pathways in small ecosystem, Egypt. *Arab J. Geosci.* **2022**, *15*, 988. https://doi.org/10.1007/s12517-022-10259-3.
35. Lombardo, M.; Melatia, R.M.; Orecchio, S. Assessment of the quality of the air in the city of Palermo through chemical and cell analyses on Pinus needles. *Atmos. Environ.* **2001,** *35*, 6435–6445. https://doi.org/10.1016/S1352-2310(01)00348-X.
36. Yin, R.; Wang, D.; Deng, H.; Shi, R.; Chen, Z. Heavy metal contamination and assessment of roadside and foliar dust along the Outer-Ring Highway of Shanghai, China. *J. Environ. Qual.* **2013,** *42*, 1724–1732.
37. Steinnes, E.; Grodzińska, K.; Szarek-Łukaszewska, G.; Nygárd, T. Stężenie ośmiu metali śladowych w powierzchniowej warstwie gleb: Porownanie między Polską i Norwegią, *Chem. Inz. Ekol.* **2005**, *12*, 603–609.

38. De Vleeschouwer, F.; Gérard, L.; Goormaghtigh, C.; Mattielli, N.; Le Roux, G.; Fagel, N. Atmospheric lead and heavy metal pollution records from a Belgian peat bog spanning the last two millenia: Human impact on a regional to global scale. *Sci. Total Environ.* **2007**, *377*, 282–295.
39. Yu, S.; Zhu, Y.G.; Li, X.D. Trace metal contamination in urban soils of China. *Sci. Total Environ.* **2012**, *421–422*, 17–30.
40. Dąbkowska-Naskręt, H.; Różański, S.; Bartkowiak, A. Forms and mobility of trace elements in soils of park areas from the city of Bydgoszcz, north Poland. *Soil Sci. Annu.* **2016**, *67*, 73–78.
41. Chaney, R.L.; Brown, S.L.; Stuczynski, T.I.; Daniels, W.L.; Henry, C.L.; Li, Y.; Siebielec, G.; Malik, M.; Angle, J.S.; Ryan, J.A.; et al. Risk assessment and remediation of soils contaminated by mining and smelting of lead, zinc, and cadmium. *Rev. Int. Contam. Ambient.* **2000**, *16*, 175–192.
42. Chaney, R.L.; Oliver, D.P. Sources, potential adverse effects and remediation of agricultural soil contaminants. *Contam. Soil Environ. Australas. Pac. Reg.* **1996**, 323–359. https://doi.org/10.1007/978-94-009-1626-5_11
43. Cutter, B.E.; Guyette, R.P. Factors affecting species choice for dendrochemistry studies. *J. Environ. Qual.* **1993**, *22*, 611–619.
44. Kabata-Pendias, A.; Pendias, H. *Biogeochemia Pierwiastków Śladowych (Biogeochemistry of Trace Elements)*; PWN: Warszawa, Poland, 1993.