

Article

Challenges in the Application of Dendrochemistry in Research on Historical Environmental Pollution in an Old Copper Mining Area

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Abstract: This research investigates the long-term environmental impact and historical temporal pollution patterns caused by a former copper mine in Iwiny (south-western Poland) using a dendrochemical approach. An additional aspect of this research was considering the possibility of using the inductively coupled plasma-optical emission spectrometry (ICP-OES) measurement technique as a cheaper alternative to inductively coupled plasma mass spectrometry (ICP-MS) in dendrochemical analyses conducted in copper mining areas. In the study area, a tailings storage facility (TSF) dam failure (1967) took place and the alkaline flotation waste containing high concentration of Cu and Pb are stored. Tree cores from pedunculate oak (*Quercus robur* L.) were analysed for the content of 11 trace elements (TEs) (Cd, Mn, Ni, Zn, Cr, Co, Pb, Cu, Fe, Al, Ag) using the ICP-OES technique, while tree rings' widths (TRWs) were also measured. Samples that were most significant in the context of the research goals were verified with the ICP-MS method. The results revealed the strong long-term impact of the copper industry as reflected in a substantial increase in the mean contents of: (1) Mn, Ni, Zn, Cr, Pb, Cu and Fe in industrial vs. control trees, (2) TRWs for control vs. industrial trees. However, the observed patterns of TEs and TRWs did not correspond to the known timing of pollution inputs (mining activity, tailings spill). Peak levels were observed for Zn and Fe after the mine was closed. The lack of new sources of pollution and the temporal relationship strongly suggests that the tree rings recorded the chemical signal of the TSF reclamation (the use of fertilizers and agrotechnical interventions). Patterns of 7 elements were detected in most of the samples by ICP-OES (Co and Cd were not detected, Al and Ag were partly detected), while ICP-MS detected all of the elements. Significant differences were obtained for Ag, Cd, and Co. Despite challenges with the application of dendrochemistry in research on old mining areas (e.g., lack of old trees), it has proved to be a useful tool for investigating the aggregate environmental impact.

Keywords: tree rings; ICP-OES; ICP-MS; trace elements; tailings storage facility



Citation: 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. <https://doi.org/10.3390/f12111505>

Academic Editor: František Kačík

Received: 9 September 2021

Accepted: 27 October 2021

Published: 31 October 2021

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1. Introduction

Over the years, Europe has made great strides towards becoming a sustainable industrial system, striving to be the first climate-neutral continent [1]. These efforts have raised awareness of environmental problems, leading to restrictive government regulations that increasingly affect the mining industry [2]. The aggregate environmental impact, even of medium-scale mining, can be significant as a result of considerable cumulative volumes and slow chemical processes [3]. In particular, the accumulation of mine tailings is considered a key problem, because every year billions of tons of waste are generated globally by processing plants [4–6]. They are often disposed in tailings storage facilities (TSF) using the hydrotransport method. Waste streams often contain hazardous contaminants such

as heavy metals, sulfur compounds, and process reagents [7,8]. Therefore, dam failure poses a great risk to TSFs. There is still a lack of data concerning the impact of TSFs on the environment, especially forest ecosystems [9,10]. Studies conducted in areas affected by tailings leakages have focused mainly on the analysis of water [11,12], soil [13], and leaves and fruits [14], because direct monitoring of environmental chemistry often does not cover long periods of time. This poses a problem for conducting environmental studies, because mining impact analysis must take into account historical time scales to evaluate the temporal patterns of pollution [5].

1.1. Application of Dendrochemistry in Environmental Monitoring

The chemical analysis of tree rings, which have been used to monitor historical changes in soil and atmospheric chemistry since the early 1970s [15], is considered to be a powerful approach to monitoring environmental quality [16]. However, the limitations of dendrochemistry need to be considered, namely: tree species-specific physiological responses, age and species differences between trees, a small number of old trees in industrial areas and a shortage of control sites, mobility of chemicals in the xylem, uptake mechanism (root, foliar, bark), and bioavailability depending on soil pH [17–22]. For these reasons, it is extremely difficult to directly transfer all the principles underlying dendrochronology to dendrochemistry. The principle of site selection [23] combined with widespread deforestation in industrial areas plus a lack of sufficiently old trees means that the principle of replication [23] can be very difficult to apply here fully. The standard number assumed in dendrochronological studies, i.e., about 20 trees sampled on various sites [22,24], may not be achievable in many industrial areas. Dendrochemical studies usually involve an analysis of two or more cores per tree and more than one tree of a given species per site [17,21,25]. However, due to the specificity of the research area and the research questions posed, published papers also tend to include studies in which a relatively small number of trees were used (several meticulously selected cores) [17,26–29]. An additional limitation concerns issues related to the suitability of individual tree species for dendrochemical research [19,30–34], long a focus of scientific interest. These challenges notwithstanding, many dendrochemical studies have successfully provided new environmental data concerning various industrial sectors [21,25,29,35,36], many of which were focused on mining [21,34,37–39], including the exploitation of copper ores [18,40,41].

1.2. Pollution in Old Copper Basin

Poland is the leading copper producer in the EU [42]. In the post-mining area of the so-called Old Copper Basin (south-western Poland), a total of over 174 million Mg of mining waste is deposited in TSFs over an area of more than 1000 hectares [43,44]. Moreover, in 1967 a tragic accident occurred there. In the village of Iwiny in TSF1 the dam burst, resulting in the leakage of alkaline Cu-mine tailings that flooded the Bobrzyca River Valley at a length of about 19 km and width of 50 to 220 m. Eighteen residents of the surrounding villages lost their lives as a result [44]. The authorities kept secret the results of chemical analyses of the water made immediately after the incident [45,46], and only a few publications have focused on the subject. In the area of the Old Copper Basin, high contents of heavy metals, mainly Cu and Pb, were found in the mining waste, which may have posed a threat to the environment and to the health of the population [47–49]. Researchers have shown that although Cu and Pb remain in post-flotation sediments in very poorly soluble forms, there is a risk of increasing their bioavailability, e.g., as a result of some agrotechnical treatments [47].

To fill the indicated research gap, chemical analysis of tree rings was conducted to interpret the temporal patterns of pollution in the Old Copper Basin using measurements of selected chemical elements (Cd, Mn, Ni, Zn, Cr, Co, Pb, Cu, Fe, Al, Ag) in wood. The main objective of this study was: (i) to investigate the long-term effects of copper mining on trees growing in the Old Copper Basin. Two specific objectives were also set: (ii) to ascertain whether the 1967 TSF1 failure had been recorded by changes in the concentrations

of TEs in tree rings; and (iii) to analyse the effect of TSF reclamation on tree growth. Additionally, the technical aspect of the measurements was investigated. Inductively coupled plasma mass spectrometry (ICP-MS) is a widely used technique in dendrochemical studies, but inductively coupled plasma-optical emission spectrometry (ICP-OES, also known as ICP-AES) is more readily available and a less expensive measurement technique. This research tested whether the ICP-OES can be an alternative to ICP-MS in dendrochemical studies conducted in copper mining areas (iv).

2. Materials and Methods

2.1. Study Area and Tailings' Characteristics

The Old Copper Basin is located in the Lower Silesian Voivodeship (south-western Poland) (Figure 1). The Konrad mine was established in 1950, TSF1 in Iwiny (51°12'23.5'' N, 15°43'57.3'' E) (Figure 1) was commissioned in 1953. On 13 December 1967, 4.6 million m³ of tailings leaked from it and flooded the surrounding area. Low negative temperatures were recorded on December 12 (−8 °C) and December 13 (−2.78 °C) [50]. Due to the extent of the damage, the sediment layer was removed from the soil surface mainly in built-up areas. In agricultural and forest areas, it has been left largely unchanged in many cases [47]. During the reconstruction of the dam, the waste was deposited in a newly created TSF2 (emergency), built on the forebay of the existing tailing pond embankment. TSF1 was decommissioned in 1971 and TSF3 was commissioned at the same time and only closed for copper ore mining at the Konrad mine in 1989 [51]. As a result of the post-flotation tailings' treatment using technology, the Old Copper Basin areas are very difficult to remediate [43,48,49]. In 1991, TSF1 and 2 were reclaimed by planting poplars, birches, black locust, pines and larches [51]. However, a field inspection conducted during the 2020 fieldwork revealed that it was still not possible to introduce vegetation over the entire area occupied by the TSFs. The unfavourable conditions for plant growth are due to poor physical characteristics (a high share of very fine particles and low content of skeletal fraction and organic matter) and chemical characteristics (low biological activity, high Ca, Cu and Pb contents, and pH of the sediment at about 7.7) [47–49], which is characteristic of many forms of waste generated by copper mining [52]. Due to the physical properties of post-flotation tailings, the windblown dust from the beaches of the tailings' ponds is virtually non-existent. Thus, the main potential route for pollutant uptake is through tree roots.

Archival Research

Due to the scarcity of publications on the study area, particularly on the 1967 accident in terms of the exact extent of the leakage and detailed chemical composition of the waste, an archival search was necessary. The archival materials were searched both directly in the State Archive in Wrocław and by means of the 'Search the Archives' archival resources on-line service (<https://www.szukajwarchiwach.gov.pl>, accessed on 5 March 2021), entries: "Iwiny" "Katastrofa w Iwinach" ("The disaster in Iwiny"), "Kopalnia Konrad" ("Konrad mine"). At the State Archives in Wrocław, access to research carried out immediately after the dam failure was obtained.

2.2. Tree-Ring Sampling and Ring-Width Measurements

Based on archival materials [53], the area of the leakage was plotted on a contemporary map (Figure 1), before the sampling locations were determined. For this purpose, trees over 80 years old were selected (allowing for results from years prior to the accident) that were located in the area of the leakage, known as Industrial (Ind.) sites. The only trees meeting the above conditions were two pedunculate oaks (Ind. 1 and 2) growing close to the site of the breach formation, between TSF2 (built after the failure) and TSF1 (from which the leakage occurred) (Figure 1). Taking into account habitat compatibility (fresh mixed broadleaved forest), species and the appropriate age, a reference tree was selected from the control site (Control) located at a distance of 3 km from the tailings pond in the direction opposite to the course of the Bobrzyca River. The prevailing wind directions, W

and WSW, were also considered by selecting the control site location from the windward side of TSF1.

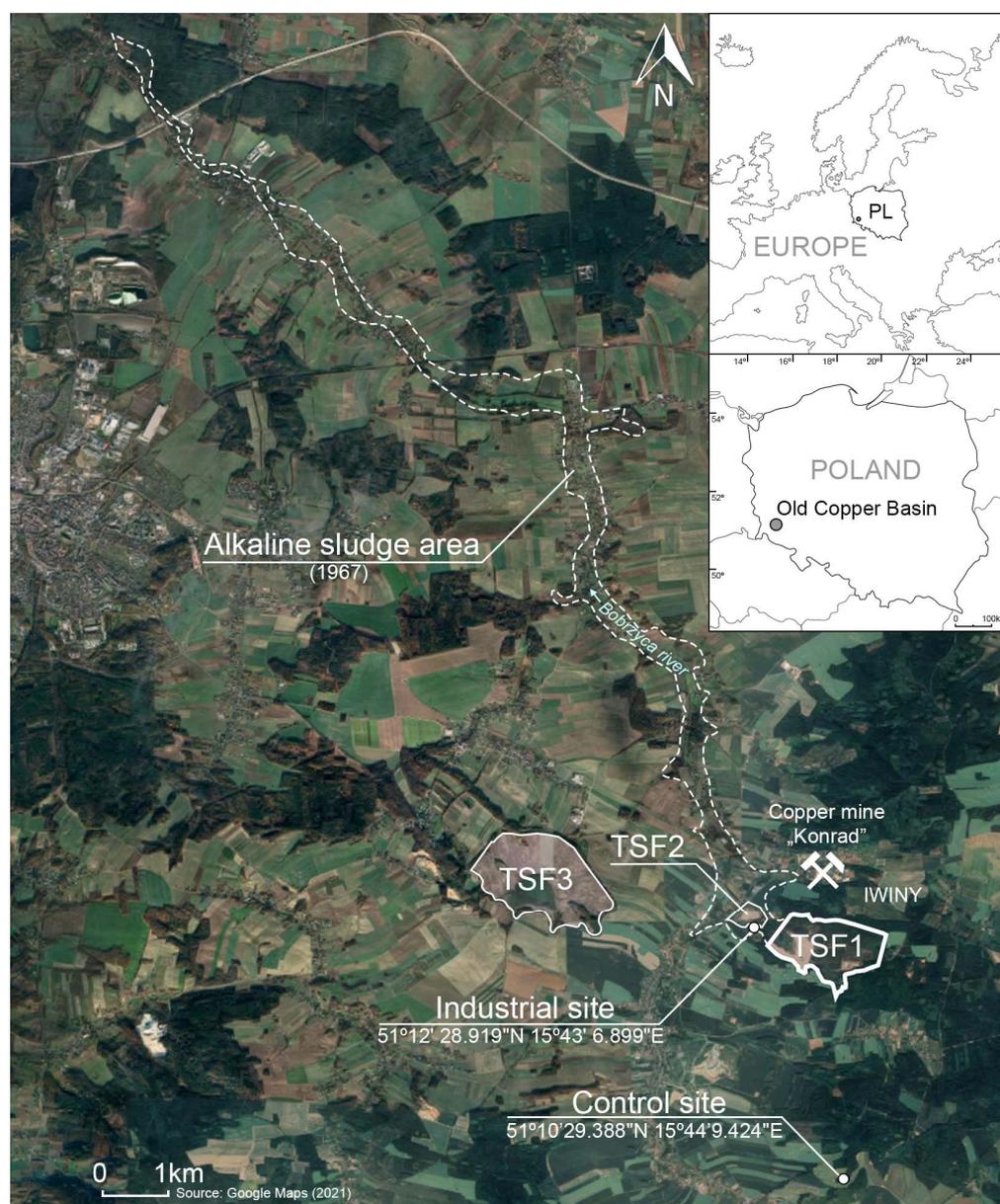


Figure 1. Location of study plot: Industrial (Ind.) and Control site and tailings storage facilities (TSFs) in so-called Old Copper District, Poland. The 1967 leakage area is presented on the basis of materials from the State Archive in Wrocław, Bolesławiec Branch [53].

Field work was conducted in June 2020. Three 5 mm diameter tree-ring samples were collected at breast height from the northern side of each tree using a Pressler increment borer. To avoid contaminating the cores, latex gloves were worn and the increment borer was rinsed with isopropyl alcohol between each core [22]. The samples were then secured in clean polypropylene containers. After being brought to the laboratory, samples were placed in a core clamp [22] and pre-dried. All cores were dated; however, in order to avoid contamination of the samples, only one of the three cores taken per tree was sanded (for better visibility of the tree rings). For this reason, it was a reference point for the dating of the other cores. The tree-ring's width (TRW) was measured using the LINTAB™ 6 with a precision of 0.01 mm. For each tree, two samples for each four-year period were used for dendrochemical analyses. Surfaces that came in contact with the sanding tools

and increment borer were removed from two cores with diamond tools. After that, cores were cut into 4-year sections with a ceramic knife [18]. A time interval of 1959–2014 was designated to allow for analysis in the context of the long-term impact of copper mining (began 8 years prior to TSF1 dam failure and ended 23 years after reclamation of TSF1 and TSF2).

The next stage was drying the wood samples in a drier at a temperature of 60 °C for 24 h and weighing them to determine the dry weight of the samples. They were then pre-digested in 3 mL of 69% HNO₃ acid (Merck KGaA, Darmstadt, Germany, Suprapur[®]) for 24 h at room temperature, before the temperature was raised to 90 °C for 2 h [18]. The process was continued as long as the solids were not completely dissolved. Thus, another 3 mL of 69% HNO₃ acid (Merck, Darmstadt, Germany, Suprapur[®]) was added for 2 h at 90 °C. The blank solution (HNO₃ and H₂O₂) was prepared in the same way. The samples were then allowed to cool to room temperature and diluted to 50 mL using LiChrosolv[®] solvents for liquid chromatography (Merck KGaA, Darmstadt, Germany) and filtered through a 0.45-µm PTFE filter (Merck KGaA, Darmstadt, Germany, Millipore) immediately before further analyses. Continuous quality control procedures were followed during sample preparation and analysis.

The analysis of 11 chemical elements (Cd, Mn, Ni, Zn, Cr, Co, Pb, Cu, Fe, Al, and Ag) was performed using ICP-OES (Thermo Scientific iCAP 7000 Series ICP-OES analyser, Thermo Fisher Scientific Inc. Waltham, MA, USA). ICP Multi-element standard IV (Merck KGaA, Darmstadt, Germany, Certipur[®]) was used to validate the constant quality assessment of the calibration curve during analyses. The certified reference material of Apple leaves NIST Standard Reference Material 1515 (Merck KGaA, Darmstadt, Germany) was used to validate the analytical procedures. Machine blanks and reference samples were included every 20 samples.

2.3. Verification of Results

The most significant samples in terms of the research goals were re-examined: from the period of the TSF1 dam failure (1967–1970) and from the time intervals during which the most significant changes in the contents of analysed TEs were recorded using the ICP-OES method. They were measured using the ICP-MS technique (Agilent 7900 ICP-MS, Agilent Technologies, Inc., Santa Clara, CA, USA) and the same chemical reagents. For subsequent verification of the results obtained via the ICP-MS measurement technique, the following time intervals were selected:

- A (1967–1970), in which the dam failure occurred.
- B (1995–1998), in which Zn and Fe content reached a peak in the tree rings from the Ind. site. The Zn content at the Ind. site is more than 10 times higher than the result obtained at the Control site and nearly three times higher than the average Zn content at the Ind. site during 1959–2014. Moreover, Fe in the Ind. site represents the highest result of all measurements made in this study. It was nearly 48 times the result obtained at the Control site and more than 2 times the average Fe content in the Ind. site from 1959 to 2014.
- C (1999–2000), in which the Al content reached a peak at the tree rings from the Ind. site. Furthermore, the Zn content at the Ind. site was more than 18 times higher than the Control site result and more than two times higher than the average Zn content at the Ind. site from 1959 to 2014. Fe also maintained a high level, its content in the Ind. site was more than six times the Control site result and less than two times the average content in the Ind. site from 1959 to 2014.
- D (2011–2014), in which the Mn content in the Ind. site was the highest of all the samples analysed. It was nearly 32 times higher than the result obtained at the Control site and almost two times higher than the average Mn content at the Ind. site during 1959–2014. Moreover, the Fe content at the Ind. site was more than 172 times higher than the result at the Control site and more than 1.5 times higher than the average Fe content of the Ind. site from 1959 to 2014.

2.4. Statistical Analysis

All statistical analyses and graphical representations of the results were performed in Statistica 13.3 statistical software and the Adobe Photoshop graphic program. If the content of an element in the sample was below the limit of detection (LOD), it was marked as not detected (nd). These results were always treated as zero in statistical analyses. Given the number of samples, the results were mainly analysed using the mean (\bar{x}) and standard deviation (\pm SD). Similarity measures (— Gleichläufigkeit coefficient of convergence (GLK, %), TVBP—t value according to Baillie and Pilcher, TVH—t value according to Hollstein) were calculated using TSAP-Win Scientific software (version 4.69f (c)), Rinntech-Metriwerk GmbH & Co. KG, Heidelberg, Germany. The ARSTAN software program [54] was used for detrending and indexing (standardising) tree-ring series (Industrial (Ind.) and Control). Due to normal data distribution, the parametric t-test was used to determine any significant statistical difference between the mean TRW for Industrial vs. Control site (significant at $p < 0.05$). Due to non-normal data distribution, the non-parametric Mann–Whitney U test was used to determine any significant statistical difference between the mean TEs values for Industrial vs. Control site and ICP-MS vs. ICP-OES measurement technique (significant at $p < 0.05$).

3. Results

3.1. Cumulative Impact of Copper Mining on Trees in the Old Copper Basin

The results of this study have provided insight into the long-term impact of copper mining on trees growing in the Old Copper Basin. Comparison of the TEs contents (Figure 2a) illustrates differences between the mean results obtained at the Ind. site and the Control site. The control site for each analysed TE showed lower values than the Ind. site: Mn and Zn almost five times, Pb almost seven times, Fe more than three times, Cu more than two times. For Cd and Co, all values obtained were below the LOD, while Ag and Al were detected only in trees growing at the Ind. site. Significant differences (at $p < 0.05$) were obtained for Mn, Ni, Zn, Cr, Pb, Cu, and Fe (Figure 2a, Supplementary Materials Table S1). Also, TRW measurements show differences between tree growth at these two sites (Figure 2b). The mean TRW over the entire period analysed (1959–2014) was significantly greater at the Control site ($t = 4.4$, $p < 0.001$), a difference of 0.7 mm.

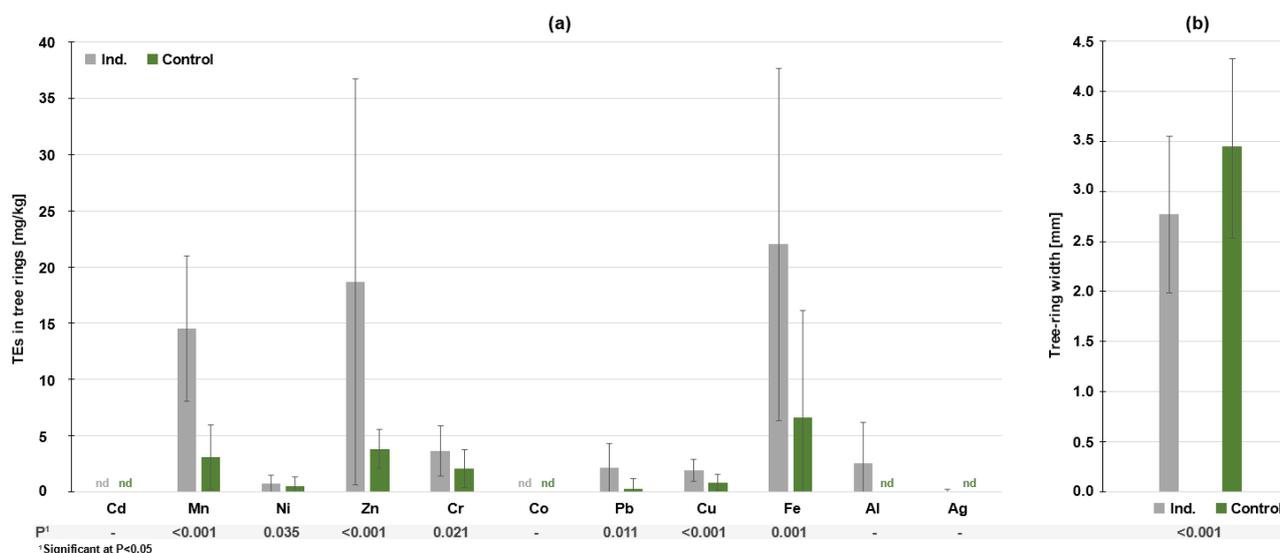


Figure 2. (a) Mean trace element (TE) contents [mg/kg] in the tree rings of pedunculate oak in different study sites (Control vs. Industrial (Ind.)) between 1959 and 2014 (with standard deviation (\pm SD) error bars). Values below the limit of detection (LOD) were marked as nd (not detected); (b) Mean tree rings' widths (TRWs) of trees growing at the Iwiny Industrial and Control site between 1959 and 2014 (with standard deviation (\pm SD) error bars).

3.2. Temporal Patterns of Pollution in the Old Copper Basin

The results of analyses performed with the ICP-OES technique have made it possible to understand the historical changes in the TE content at the Ind. and Control site in the years 1959–2014 (Figure 3). Mn, Ni, Zn, Cr, Cu and Fe were detected in each tree at all time intervals analysed. For Pb, Ni, Cu, Ag and Al, some results below the LOD were recorded. The tree from the Control site showed lower TE content than the trees from the Ind. site in most cases. The exception here was Fe from 1979 to 1982 and from 1999 to 2006. Short-term fluctuations are visible for most of the elements, but generally their contents remain at comparable levels.

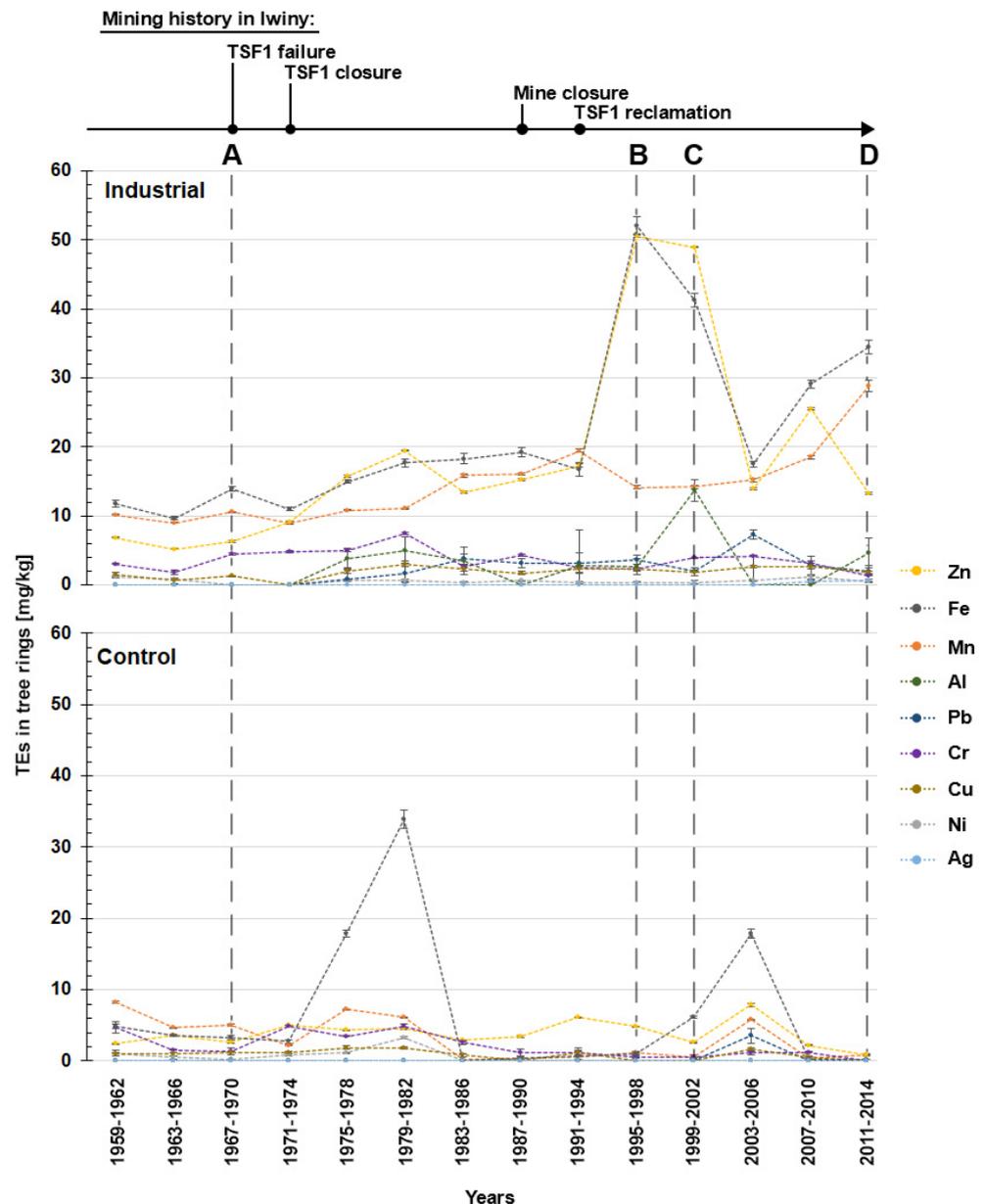


Figure 3. Historical variations of selected trace elements (TEs) in the tree rings of pedunculate oak in different study sites (Control vs. Industrial (Ind.)) between 1959 and 2014. Vertical dashed lines indicate the time intervals (A–D) that have been selected for verification by inductively coupled plasma mass spectrometry (ICP-MS).

Figure 3 highlights the events relevant to the purpose of the study area’s copper mining history: 1967 accident, 1971 closure of TSF1, 1989 mine closure, and the 1991 reclamation of TSF1 and TSF2. These are important reference points for the results obtained, for they

show that the content of the analysed TEs did not increase after the 1967 leakage, nor did they decrease after the closure of either TSF1 or the entire mine. Peak levels were observed for Zn and Fe in 1995–2002, i.e., after completion of mining activities in the study area and reclamation of TSF1 and TSF2.

Historical variations of selected TEs in the tree rings of each of the analysed trees are presented in Figure 4. In the mid-1990s and early 2000s, there was a peak in Zn (Ind. 1), Fe (Ind. 1 and Ind. 2 but with a four-year time lag) and Al content (Ind. 2). In the remaining years, Fe and Zn stabilised at a much lower level with concomitant low contents in the Control trees throughout the analysed period (except for Fe in 1979–1982). Al, on the other hand, was only detected in the Ind. 2 tree starting from the time interval 1975–1978. Several short-term Al content fluctuations can be observed. In the case of Mn, a gradual increase can be observed throughout the analysed period (Ind. 1 and Ind. 2), in contrast to the results obtained for the Control tree. Pb was not detected in the 1960s (in the Ind. 1 since the mid-1970s and in the Ind. 2 since the early 1980s). At that time, Pb stabilises at a similarly low level except for the peak in the time interval 2003–2006 (Ind. 2).

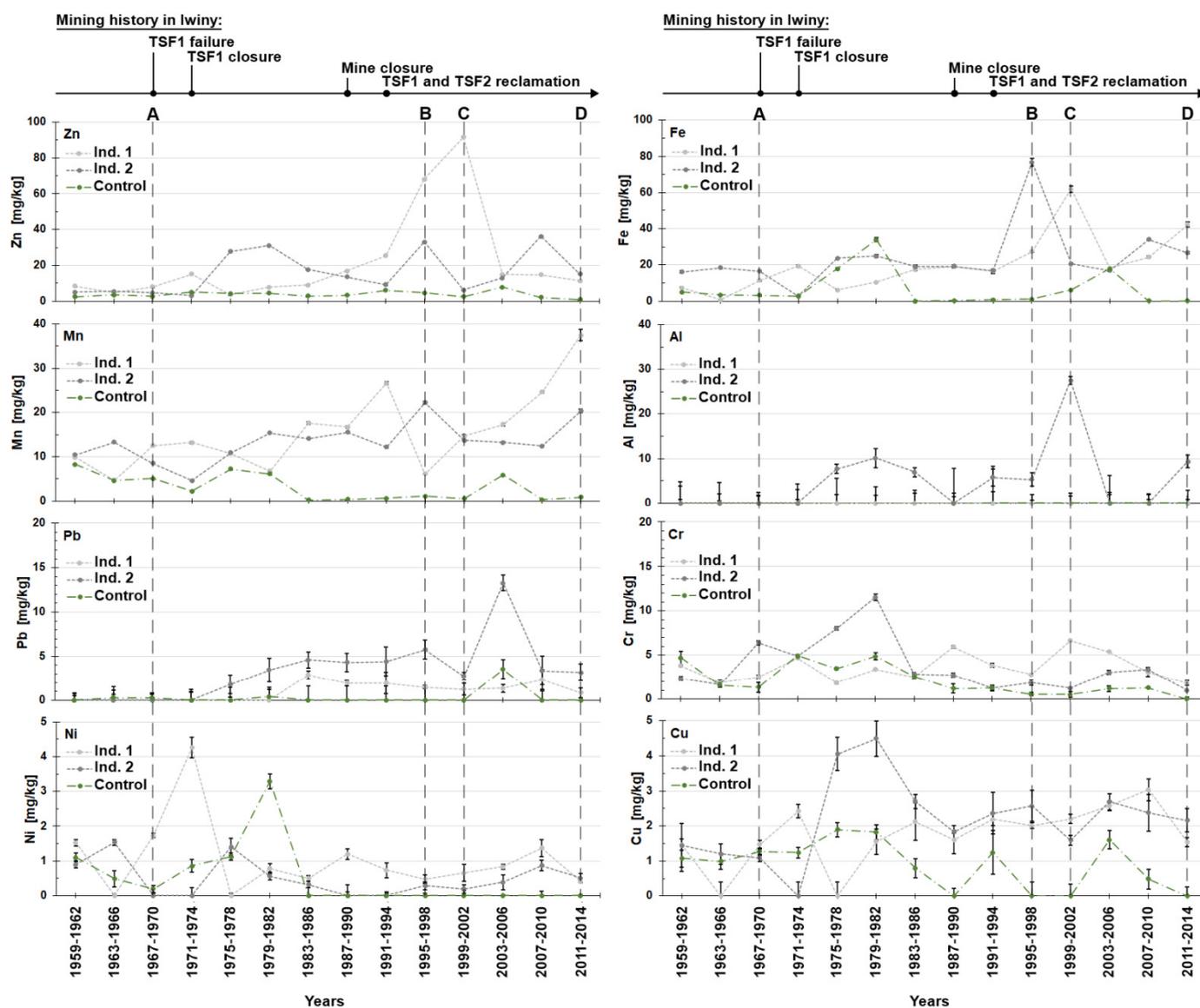


Figure 4. Trace elements (TEs) contents [mg/kg] in tree rings of all studied trees: Industrial 1 (Ind. 1), Industrial 2 (Ind. 2), and Control from 1959 to 2014. Vertical dashed lines indicate the time intervals (A–D) verified by inductively coupled plasma-mass spectrometry (ICP-MS).

Temporal patterns of Cr and Cu are characterised by the presence of short-term fluctuations and differences in the directions of changes (increase/decrease) between Ind. 1 and Ind. 2 trees. In the late 1970s and early 1980s, it is possible to notice a slight increase in Cu content (Ind. 2), in which values decrease and stabilise at a similar level (both Ind. 1 and Ind. 2) from the beginning of the 1990s until the end of the studied period. Short-term increases in Ni (Ind. 1 with a 4-year lag), Cu (Ind. 2 with an 8-year lag), and Cr (Ind. 2 with an 8-year lag) were recorded after the TSF1 dam failure. However, these increases were by no means recorded in both Ind. 1 and Ind. 2. All other steep increases in concentrations of the studied TEs occurred after the reclamation of TSF1 and TSF2. In the vast majority of the samples, the control tree exhibited significantly lower elemental contents compared to the Ind. area trees. The exceptions were abrupt increases in Ni and Fe contents (1979–1982). However, their contents were generally and substantially lower than in trees of Ind. 1 and Ind. 2.

3.3. Measurements of Tree-Rings' Width throughout the Period 1959–2014

The samples extracted from pedunculate oaks ranged from 81 to 100 years (Table 1). In order to assess the degree of similarity in the course of compared growth curves, the GLK index was calculated (ranged from 80% to 83%). The accuracy of the measurements was also assessed using the t-value index (ranged from 11.7 to 19.7). Therefore, the course of the increments of all the studied trees revealed high consistency. Due to the small number of trees that met the study criteria, it was not possible to create a local chronology (a master chronology has never been developed for this area). In subsequent studies, samples were analysed only in the designated time interval of 1959–2014. Similarity measures were lower, but still quite high for Ind. and Control site (GLK-63 %, TVBP-3.8, TVH-3.9). A different response between sites occurred only in 1981–1983 and 1969 (Figure 5 -increases in TRW at the Control site are accompanied by concomitant decreases in TRW at the Ind. site and vice versa). Moreover, no sustained release of Ind. trees' growth was observed after closure of the mine or TSF1. Additionally, there was no reduction in TRW after the leakage of mine tailings (time interval A).

Table 1. Assessment of the quality of the analysed individual sequences based on the characteristics.

Tree	Years	GLK (%)	TVBP	TVH
Ind. 1	1921–2020	80	13.6	13.4
Ind. 2	1939–2020	82	11.7	11.8
Control	1923–2020	81	17.3	19.7

Notes: GLK—Gleichläufigkeit coefficient of convergence (%), TVBP—t value according to Baillie and Pilcher, TVH—t value according to Hollstein.

3.4. Results' Verification

Measurements by the ICP-MS technique off all samples for periods A–D obtained roughly 10–100 times lower LOD compared to ICP-OES (Table 2). The exceptions were Fe and Zn. However, it should be noted that the contents of Fe and Zn in wood were the highest in the analysed samples. The ICP-MS technique was sufficient for TEs the content of which was too low to be detected with the ICP-OES technique (Cd, Co and some results of Pb, Ni, Cu, Ag, and Al) (Table 3). Only in the case of Ag were some values below the LOD (also for ICP-MS). The results obtained by the ICP-MS technique showed less variation compared to the ICP-OES technique, as reflected by the lower standard deviation (Table 3). Significant differences (at $p < 0.05$) were obtained for Ag, Cd, and Co (Table 4). It should be noted that the results obtained with both methods are convergent for most of the TEs: Al, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The contents not detected with the ICP-OES technique, as a result of verification with the ICP-MS technique, usually obtained very low values.

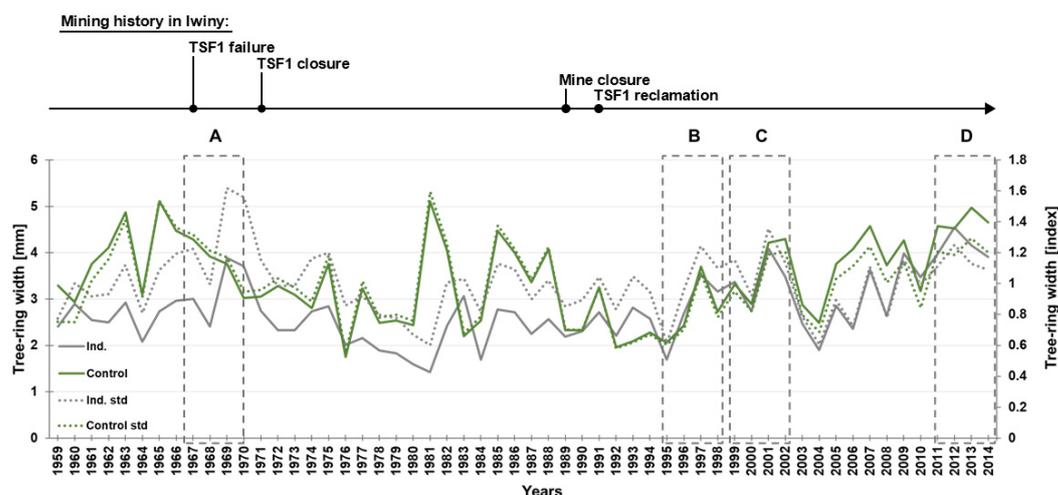


Figure 5. Raw and standardised tree rings’ widths (TRWs) measurements for Ind. and Control site. The vertical dotted lines indicate the time intervals (A–D).

Table 2. Comparison of limit of detection (LOD) levels [ppm] for trace elements (TEs) from selected periods A–D analysed by both inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) techniques.

Table	LOD	
	ICP-MS	ICP-OES
Ag	1.8×10^{-5}	3.0×10^{-3}
Al	2.3×10^{-3}	1.4×10^{-2}
Cd	2.1×10^{-5}	1.0×10^{-3}
Co	5.3×10^{-5}	2.3×10^{-3}
Cr	1.7×10^{-4}	1.0×10^{-3}
Cu	1.6×10^{-4}	1.0×10^{-3}
Fe	2.6×10^{-3}	1.0×10^{-3}
Mn	1.3×10^{-4}	9.0×10^{-4}
Ni	9.6×10^{-5}	1.0×10^{-3}
Pb	2.1×10^{-4}	2.0×10^{-3}
Zn	3.6×10^{-3}	3.0×10^{-4}

Table 3. TEs contents in mineralised solutions. Comparison of results obtained by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectrometry (ICP-OES) measurement techniques [ppm] and standard deviation (\pm SD) at selected time intervals A–D.

		A (1967–1970)			B (1995–1998)			C (1999–2002)			D (2011–2014)		
		Ind. ¹ 1	Ind. ¹ 2	Control	Ind. ¹ 1	Ind. 1 2	Control	Ind. 1 1	Ind. 1 2	Control	Ind. 1 1	Ind. 1 2	Control
Ag	ICP-MS	3.8×10^{-3}	3.3×10^{-3}	4.0×10^{-3}	3.3×10^{-4}	3.4×10^{-3}	1.6×10^{-4}	8.7×10^{-4}	1.9×10^{-3}	1.3×10^{-3}	2.9×10^{-4}	9.2×10^{-3}	5.6×10^{-5}
	\pm SD	1.6×10^{-4}	9.2×10^{-5}	1.8×10^{-4}	9.0×10^{-6}	4.1×10^{-5}	3.0×10^{-6}	1.0×10^{-5}	1.8×10^{-5}	1.4×10^{-5}	1.0×10^{-5}	6.9×10^{-5}	2.0×10^{-3}
Ag	ICP-OES	nd ²	7.8×10^{-3}	nd ²									
	\pm SD	-	-	-	-	-	-	-	-	-	-	1.5×10^{-3}	-
Al	ICP-MS	7.2×10^{-3}	2.3×10^{-3}	nd ²	6.4×10^{-1}	2.9×10^{-2}	nd ²	7.4×10^{-2}	2.4×10^{-1}	nd ²	9.3×10^{-2}	1.1×10^{-1}	nd ²
	\pm SD	2.2×10^{-4}	8.4×10^{-5}	-	1.8×10^{-3}	6.0×10^{-4}	-	1.1×10^{-3}	3.3×10^{-3}	-	1.1×10^{-3}	1.0×10^{-3}	-
Al	ICP-OES	nd ²	nd ²	nd ²	nd ²	1.8×10^{-2}	nd ²	nd ²	1.5×10^{-1}	nd ²	nd ²	6.1×10^{-2}	nd ²
	\pm SD	-	-	-	-	7.1×10^{-3}	-	-	5.5×10^{-3}	-	-	8.5×10^{-3}	-
Cd	ICP-MS	2.3×10^{-4}	1.9×10^{-4}	1.7×10^{-4}	3.4×10^{-4}	4.1×10^{-4}	1.2×10^{-4}	4.0×10^{-4}	3.1×10^{-4}	4.9×10^{-5}	3.6×10^{-4}	6.7×10^{-4}	3.9×10^{-5}
	\pm SD	1.1×10^{-5}	1.2×10^{-5}	7.0×10^{-6}	1.4×10^{-5}	1.3×10^{-5}	5.0×10^{-6}	1.6×10^{-5}	9.0×10^{-6}	4.0×10^{-6}	8.0×10^{-6}	1.6×10^{-5}	1.0×10^{-6}
Cd	ICP-OES	nd ²											
	\pm SD	-	-	-	-	-	-	-	-	-	-	-	-
Co	ICP-MS	1.3×10^{-3}	6.5×10^{-3}	1.8×10^{-3}	4.6×10^{-4}	1.1×10^{-3}	1.8×10^{-3}	3.5×10^{-4}	1.5×10^{-3}	2.3×10^{-3}	5.2×10^{-4}	nd ²	5.2×10^{-4}
	\pm SD	4.7×10^{-5}	3.2×10^{-4}	5.8×10^{-5}	3.7×10^{-5}	5.4×10^{-5}	4.0×10^{-6}	1.5×10^{-5}	2.9×10^{-5}	3.0×10^{-6}	1.8×10^{-5}	-	1.2×10^{-5}
Co	ICP-OES	nd ²	nd ²	nd ²	nd ²	2.3×10^{-3}	nd ²						
	\pm SD	-	-	-	-	8.3×10^{-4}	-	-	-	-	-	-	-
Cr	ICP-MS	1.3×10^{-2}	3.0×10^{-2}	6.9×10^{-3}	1.3×10^{-2}	7.1×10^{-3}	3.3×10^{-3}	4.4×10^{-2}	6.7×10^{-3}	2.3×10^{-3}	1.2×10^{-2}	5.5×10^{-3}	1.4×10^{-3}
	\pm SD	3.3×10^{-4}	5.4×10^{-4}	2.3×10^{-4}	3.5×10^{-4}	1.3×10^{-4}	3.4×10^{-5}	6.1×10^{-4}	7.2×10^{-5}	4.6×10^{-5}	1.2×10^{-4}	6.7×10^{-5}	2.2×10^{-5}
Cr	ICP-OES	1.3×10^{-2}	2.9×10^{-2}	7.4×10^{-3}	1.3×10^{-2}	6.4×10^{-3}	2.4×10^{-3}	4.3×10^{-2}	6.8×10^{-3}	2.6×10^{-3}	1.1×10^{-2}	6.5×10^{-3}	nd ²
	\pm SD	1.0×10^{-3}	1.1×10^{-3}	2.7×10^{-3}	4.4×10^{-4}	1.4×10^{-3}	9.0×10^{-4}	4.2×10^{-4}	3.9×10^{-4}	2.1×10^{-3}	1.6×10^{-3}	2.3×10^{-4}	-
Cu	ICP-MS	6.6×10^{-3}	2.0×10^{-3}	2.8×10^{-3}	1.2×10^{-2}	9.6×10^{-3}	4.9×10^{-3}	1.6×10^{-2}	9.7×10^{-3}	3.5×10^{-3}	1.2×10^{-2}	1.7×10^{-2}	2.4×10^{-3}
	\pm SD	1.9×10^{-4}	1.0×10^{-4}	7.1×10^{-5}	2.8×10^{-4}	1.3×10^{-4}	5.3×10^{-5}	3.4×10^{-4}	5.3×10^{-5}	2.3×10^{-5}	1.4×10^{-4}	6.0×10^{-5}	3.3×10^{-5}
Cu	ICP-OES	7.7×10^{-3}	5.0×10^{-3}	7.0×10^{-3}	9.4×10^{-3}	8.9×10^{-3}	nd ²	1.4×10^{-2}	8.8×10^{-3}	nd ²	9.2×10^{-3}	1.4×10^{-2}	nd ²
	\pm SD	6.1×10^{-4}	4.9×10^{-4}	5.1×10^{-4}	3.5×10^{-4}	2.1×10^{-3}	-	8.1×10^{-4}	9.1×10^{-4}	-	7.6×10^{-4}	2.0×10^{-3}	-

Table 3. Cont.

		A (1967–1970)			B (1995–1998)			C (1999–2002)			D (2011–2014)		
		Ind. ¹ 1	Ind. ¹ 2	Control	Ind. ¹ 1	Ind. ¹ 2	Control	Ind. ¹ 1	Ind. ¹ 2	Control	Ind. ¹ 1	Ind. ¹ 2	Control
Fe	ICP-MS	1.6×10^{-1}	6.2×10^{-2}	9.1×10^{-3}	2.9×10^{-1}	4.0×10^{-1}	4.8×10^{-2}	6.5×10^{-1}	2.0×10^{-1}	6.3×10^{-2}	4.1×10^{-1}	3.1×10^{-1}	3.2×10^{-2}
	±SD	3.1×10^{-3}	7.4×10^{-4}	1.9×10^{-4}	8.9×10^{-3}	5.7×10^{-3}	1.0×10^{-3}	1.1×10^{-2}	3.3×10^{-3}	7.8×10^{-4}	3.6×10^{-3}	9.0×10^{-4}	5.8×10^{-4}
Fe	ICP-OES	6.0×10^{-2}	7.5×10^{-2}	1.8×10^{-2}	1.3×10^{-1}	2.7×10^{-1}	4.7×10^{-3}	4.0×10^{-1}	1.1×10^{-1}	3.2×10^{-2}	2.5×10^{-1}	1.7×10^{-1}	1.4×10^{-3}
	±SD	2.1×10^{-3}	1.0×10^{-3}	1.9×10^{-3}	1.8×10^{-3}	1.1×10^{-2}	2.8×10^{-3}	1.0×10^{-2}	2.1×10^{-3}	2.1×10^{-3}	8.0×10^{-3}	3.0v	1.6×10^{-3}
Mn	ICP-MS	6.5×10^{-2}	3.8×10^{-2}	2.5×10^{-2}	3.0×10^{-2}	7.8×10^{-2}	5.5×10^{-3}	9.8×10^{-2}	7.9×10^{-2}	3.8×10^{-3}	2.9×10^{-1}	1.7×10^{-1}	7.6×10^{-3}
	±SD	1.3×10^{-3}	8.0×10^{-4}	2.7×10^{-4}	8.1×10^{-4}	1.0×10^{-3}	7.6×10^{-5}	1.6×10^{-3}	5.7×10^{-4}	3.9×10^{-5}	2.1×10^{-3}	1.2×10^{-3}	1.3×10^{-4}
Mn	ICP-OES	6.6×10^{-2}	3.9×10^{-2}	2.8×10^{-2}	2.9×10^{-2}	7.7×10^{-2}	4.9×10^{-3}	9.4×10^{-2}	7.6×10^{-2}	3.0×10^{-3}	2.2×10^{-1}	1.3×10^{-1}	6.2×10^{-3}
	±SD	2.6×10^{-4}	5.9×10^{-4}	6.3×10^{-4}	4.9×10^{-4}	1.2×10^{-3}	1.5×10^{-4}	1.8×10^{-3}	1.1×10^{-3}	2.0×10^{-4}	7.6×10^{-3}	2.4×10^{-3}	1.9×10^{-4}
Ni	ICP-MS	1.3×10^{-2}	1.1×10^{-3}	6.9×10^{-3}	6.1×10^{-3}	3.1×10^{-3}	8.8×10^{-4}	7.8×10^{-3}	3.4×10^{-3}	8.6×10^{-4}	6.5×10^{-3}	6.5×10^{-3}	7.9×10^{-4}
	±SD	2.7×10^{-4}	3.7×10^{-5}	9.0×10^{-5}	1.7×10^{-4}	7.0×10^{-5}	1.7×10^{-5}	8.1×10^{-5}	4.9×10^{-5}	2.8×10^{-5}	7.3×10^{-5}	4.6×10^{-5}	1.1×10^{-5}
Ni	ICP-OES	9.1×10^{-3}	nd ²	1.1×10^{-3}	2.2×10^{-3}	9.7×10^{-4}	nd ²	4.2×10^{-3}	1.1×10^{-3}	nd ²	2.4×10^{-3}	3.3×10^{-3}	nd ²
	±SD	3.2×10^{-4}	-	5.4×10^{-4}	5.3×10^{-4}	5.4×10^{-4}	-	1.6×10^{-3}	8.0×10^{-4}	-	4.7×10^{-5}	8.2×10^{-4}	-
Pb	ICP-MS	2.1×10^{-3}	2.0×10^{-3}	1.7×10^{-3}	1.2×10^{-2}	2.1×10^{-2}	1.4×10^{-3}	1.2×10^{-2}	1.7×10^{-2}	2.2×10^{-3}	1.1×10^{-2}	2.0×10^{-2}	1.5×10^{-3}
	±SD	4.0×10^{-5}	5.6×10^{-5}	4.5×10^{-5}	9.6×10^{-4}	2.5×10^{-4}	1.5×10^{-5}	1.6×10^{-4}	1.3×10^{-4}	1.6×10^{-5}	1.3×10^{-4}	1.1×10^{-4}	3.7×10^{-5}
Pb	ICP-OES	nd ²	nd ²	nd ²	6.9×10^{-3}	2.0×10^{-2}	nd ²	7.8×10^{-3}	1.5×10^{-2}	nd ²	4.9×10^{-3}	2.1×10^{-2}	nd ²
	±SD	-	-	-	9.5×10^{-4}	5.0×10^{-3}	-	4.4×10^{-3}	2.9×10^{-3}	-	3.2×10^{-3}	5.7×10^{-3}	-
Zn	ICP-MS	5.2×10^{-2}	2.1×10^{-1}	1.1×10^{-2}	4.0×10^{-1}	1.7×10^{-1}	4.6×10^{-2}	7.1×10^{-1}	6.9×10^{-2}	2.7×10^{-2}	1.0×10^{-1}	1.3×10^{-1}	2.7×10^{-2}
	±SD	1.2×10^{-3}	5.9×10^{-3}	3.4×10^{-4}	8.2×10^{-3}	2.1×10^{-3}	4.5×10^{-4}	1.3×10^{-2}	5.8×10^{-4}	1.3×10^{-4}	1.0×10^{-3}	1.4×10^{-3}	4.7×10^{-4}
Zn	ICP-OES	4.2×10^{-2}	2.1×10^{-2}	1.5×10^{-2}	3.2×10^{-1}	1.2×10^{-1}	2.1×10^{-2}	5.9×10^{-1}	3.5×10^{-2}	1.3×10^{-2}	6.9×10^{-2}	9.9×10^{-2}	6.3×10^{-3}
	±SD	4.5×10^{-4}	6.7×10^{-4}	9.6×10^{-4}	1.2×10^{-3}	5.5×10^{-4}	4.4×10^{-4}	1.4×10^{-3}	5.6×10^{-4}	4.0×10^{-4}	7.4×10^{-4}	1.1×10^{-3}	3.8×10^{-4}

¹ Industrial. ² Not detected.

Table 4. Evaluation of the significant difference between the mean values of the analysed TEs calculated using inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) measurement techniques from selected periods A–D ($N = 12$).

TEs	Technique	Sum of ranks	U ¹	p^2
Ag	ICP-MS	211	11	<0.001
	ICP-OES	89		
Al	ICP-MS	180	42	0.089
	ICP-OES	120		
Cd	ICP-MS	222	0.01	<0.001
	ICP-OES	78		
Co	ICP-MS	207	16	<0.001
	ICP-OES	94		
Cr	ICP-MS	151	71	0.977
	ICP-OES	149		
Cu	ICP-MS	161	61	0.551
	ICP-OES	139		
Fe	ICP-MS	173	49	0.198
	ICP-OES	127		
Mn	ICP-MS	154	68	0.843
	ICP-OES	146		
Ni	ICP-MS	183	39	0.060
	ICP-OES	117		
Pb	ICP-MS	173	49	0.198
	ICP-OES	127		
Zn	ICP-MS	173	49	0.198
	ICP-OES	127		

¹ U—Mann–Whitney U test. ² Significant at $p < 0.05$ (bold font).

4. Discussion

4.1. History of Changes in the Environmental Chemistry of the Old Copper Basin

The conducted dendrochemical analyses and TRW measurements demonstrated the long-term impact of the copper mining industry on trees in the Old Copper Basin (objective i). This was reflected in a substantial increase in mean contents of all TEs in industrial vs. control trees (significant differences were obtained for Mn, Ni, Zn, Cr, Pb, Cu, and Fe) as well as a significantly lower mean TRW of industrial vs. control trees (mean TRW lower by over 0.7 mm).

Research into the impact of the 1967 post-flotation tailings leakage showed that it did not cause significant increases in the content of selected TEs in tree rings or decreases in their width between 1967 and 1970 (objective ii). Some increases were observed for Ni, Cu, and Cr, but none for the second Ind. site tree, and the differences were not as significant as the results from the mid-1990s and early 2000s. Moreover, they occurred with different delays (from 4 to 12 years). The failure to record a strong chemical signal associated with the leakage is most likely due to the very low phytoavailability of heavy metals in the sediments. Additionally, this effect may have been amplified due to the timing of the TSF1 dam failure, which happened in December (tree dormancy in winter combined with seasonally frozen soils). However, no significant increase in the TE content was recorded, even assuming a long delay in recording, and no significant changes in

the contents of the studied TEs lasted until the 1990s. During this time, the content of Zn and Fe reached their highest levels in periods B and C. The mining activity in the area was terminated 6 years earlier (with a significant decrease in mining from the 1980s until closure), and no new sources of contamination appeared in the vicinity. Therefore, attention was drawn to the temporal relationship between the reclamation carried out and an increase in the contents of Zn and Fe, as well as a gradual increase in Mn. These significant changes occurred only among elements necessary for the proper functioning of plants, with relatively low toxicity, commonly used in fertilizers [55–57] and regulating plant uptake of TEs, that pose a greater ecological risk, i.e., Pb, Cr, Cu, and Ni [56]. The above information substantiates the statement that the uptake of Zn, Fe, and Mn by tree roots occurred after their deliberate, professional application in the form of fertilizers and plant preparations as part of reclamation efforts. Also, the resulting improvement in the soil's physical and chemical properties may have increased the phytoavailability of elements (Fe, Zn, and Mn show limited solubility in alkaline and carbonate soils) [56]. Fe is an immobile nutrient whose deficiency symptoms (chlorosis) show up in new growth [56]. Moreover, Fe, Mn, and Zn are not easily translocated across ring boundaries [58], therefore the dating is not subject to high uncertainty. Although the environmental data alone cannot indisputably link the significant increase in Fe, Zn, and Mn directly to the agrotechnical interventions and fertilization of TSF1, we may speculate that we might have obtained a chemical signal delayed by approximately 4 years describing the impact of TSF1 and TSF2 reclamation (objective iii). Moreover, the results obtained in period D for Mn suggest a progressive decrease in sediment pH, most likely due to the impact of treatments carried out during reclamation. These results, combined with lack of activation of Cu and Pb stored in the tailings, may be the premise for a partial improvement of the soil's physical and chemical properties (lowering of pH, increasing the proportion of sand and skeletal fractions, supplementation of nutrients).

Many studies have successfully used dendrochemical methods to detect TE contamination in soil [17,21,26,36]. The presented results from Iwiny showed that the tree rings did not register a strong signal of contaminants we know were introduced into the environment as a consequence of the leakage, and most likely recorded the impact of reclamation with a four-year lag. Results of chemical measurements of water samples from the Bobrzyca River made between 6. 12. 1967 and 2. 01. 1968. [mg/l]: Fe between 1. 2–100, Cu between not detected (nd)-1. 4, Pb nd, Zn between 0. 10–0. 15, Phenols between nd-10. 02. They confirmed that anthropogenic activities introduced considerable amounts of heavy metals into the environment [45]. Furthermore, the results of the radioactivity measurements showed that the post-flotation tailing slurries carried large amounts of ground minerals containing possibly radioactive elements. The highest recorded results in samples from the Bobrzyca River obtained on consecutive days after the event were the following: (15. 12. 1967), 01:00 h = 752. 6 pCi/l, (16. 12. 1967) 01:00 h = 107. 6 pCi/l. (at that time, the Soviet standard for surface waters was 30 pCi/l) [46]. The analysis of the study results indicates the occurrence of environmental contamination that can potentially be recorded in tree rings. The State Archive in Wrocław, Bolesławiec Branch, provided access to a map made immediately after the accident, which shows the exact extent of the leakage [53]. However, the obtained data proved the existence of a cumulative multi-year environmental impact of the copper industry. The research findings are consistent with many previous studies. Those studies proved that higher concentrations of trace elements are definitely present in rings of trees exposed to pollution than from reference sites. At the same time, they admitted that the known date of entry for the contaminant into the environment was not properly recorded in the tree rings. The above conclusions were reached as a result of the analysis of the content of Cd and Zn in Scots pine wood 12 years after contamination [37], as well as research investigating changes in the trace element content in Norway spruce rings following soil amendment with Cd and Zn [59]. The study on N, P, K, Ca, and Mg concentrations in oak rings in the context of a fertilization experiment reported that a change in element composition was registered by the trees, albeit spread over the entire

radial profile (20 years before and 38 years after the known timing of nutrition inputs) [60]. A research project carried out in Zhengzhou, China proved that dendrochemical methods are an effective part of any environmental monitoring programme, even though at the same time the temporal patterns in tree rings of elements Zn, Cu, and Pb were only roughly consistent with the contamination history [61]. In the case of air pollutants, a delay by at least 13 years has been noted between atmospheric emissions from metallurgical activities and when they were recorded by rings [38].

4.2. Verification of Results

An additional aspect of the research was considering the possibility of using the ICP-OES measurement technique as a cheaper alternative to ICP-MS in dendrochemical analyses conducted in copper mining areas. A key advantage of using ICP-MS over ICP-OES is the higher sensitivity of this technique, which allows it to achieve LOD as low as parts per trillion (ppt) [62,63]. ICP-MS therefore offers the possibility of very high sample throughput in the laboratory, but with the consequence that laboratory set-up costs (multiple high purity gases requirement, HEPA filters, dust reduction measures) and operating costs are higher than for ICP-OES [63]. ICP-OES is used in environmental monitoring for analyses, including elemental concentrations in deposited dust on leaves [64], TE content measured in tree bark [65] or leaves and fruits using a combined approach, i.e., using more than one technique, e.g., ICP-MS for TE analyses and ICP-OES for mineral element measurements [65]. Multiple dendrochemical studies have also been published showing the successful use of ICP-OES [26,60,66–69] or a mixed approach: ICP-OES (Ca, Mg, Cu, Fe) combined with GFAAS (K, Pb, Cd) [66]. The LOD was sufficient to address the research questions posed, but it was not always possible to detect all the elements analysed. For example, concentrations of 17 elements (Mn, P, Ba, B, Cu, Co, Ca, Mg, Na, Cd, Cr, Ni, Al, Fe, As, Mn, and Zn) measured in the rings of oak trees using ICP-OES showed that only the results for Ni were below the detection limits [69]. In the conducted ICP-OES analyses of tree rings from the Old Copper Basin, Co, Cd, and partly Al and Ag were not detected. For Pb, Ni, and Cu, single results below LOD were recorded (Figure 4). Essentially, all verified results were detected by ICP-MS. Only for Ag did some results not exceed the LOD at all on both ICP-MS and ICP-OES. The ICP-OES technique can, therefore, be an affordable alternative to ICP-MS, but with lower TE values, the required adequate LOD of the analytes will also dictate the technique of choice. Depending on the requirements of the study, the mass of the samples can be increased [60], a combined approach can be used [65], or the repeat control measurement of selected samples proposed in this paper can be performed using a measurement technique with a lower LOD. Although the studies carried out in Iwiny did not allow for the detection of all elements, performing verification on ICP-MS for key years gave us confirmation of the results obtained (objective iv). In particular, when taking into account the research objectives, the key role was played by TEs, which generally occur in wood in higher amounts (Fe, Zn, Mn). Moreover, the content of these trace metals showed the greatest changes in the analysed period.

4.3. Challenges in the Application of Dendrochemistry to the Old Copper Basin

The research attempted to reconstruct contamination in an area that is special in terms of its history as well as being the subject of very little research work to date. It is an example of an area where environmental problems related to the consequences of mining activities, such as TSF failures, storing a large amount of mining waste characterised by a high content of heavy metals that is difficult to reclaim, are common in Europe and globally. In this investigation, the main difficulties concerned the lack of consistent long-term instrumental records (which at the same time constituted a premise for the application of dendrochemical analyses), field constraints (small number of trees fulfilling the research criteria), tree species conditions (ring-porous wood structure), and contamination characteristics.

Due to the characteristics of the research area and site selection criteria, two trees growing on the Ind. site and one tree growing on the Control site were analysed in

this study (three cores were collected from each). According to many studies, in such a situation a cautionary approach is recommended. If possible, all arguments favour the use of multiple cores from multiple trees in various sites to reduce uncertainty in dendrochemical research [15,17,18,70]. However, published work in dendrochemistry also presents results for only two cores from two different trees, e.g.: Scots pine [29], Horse chestnut [17], Chinese pine [26]. Due to site conditions and lack of availability of other species (especially conifers), pedunculate oak cores were used. Despite the ring-porous wood structure, oaks have found applicability in dendrochemical studies [30,60,66,71–73]. Some studies have concluded that oak rings did not passively record certain soil nutrient concentrations [72]. Other researchers point to some potential for the white oak species, but emphasize that the size of the sapwood zone of this species renders analyses difficult (the smaller the number of rings in the sapwood, the lower the mobility of elements in the xylem) [19,30,60,74]. High concentrations of mineral elements in sapwood and low levels in heartwood are characteristic of oaks [71]. In addition, at the sapwood/heartwood boundary a sudden increase in the concentration of mineral element is observed due to resorption from senescing sapwood rings. However, this does not apply when it comes to explaining the observed peaks in the Mn, Fe, and Zn content in Iwiny for time intervals B (1995–1998) and C (1999–2002), because in the analysed trees the sapwood zone ends in later years: Ind. 1 in 2007 (13 rings), Ind. 2 and Control in 2009 (11 rings). This represents the standard score for pedunculate oaks in Central Europe [75].

In order to carry out a correct interpretation of the results obtained, it is necessary to take into account the characteristics of the pollutants (high pH, low phytoavailability of Cu, Pb). The interpretation of the results adopted in the present work is supported by other studies who claimed that the Mn content in rings is inversely proportional to the soil pH whose changes are well-documented [72,76]. Moreover, acidic soils at the sampling site are essential for the efficient uptake of Pb [76]. At the Ind. site, Pb was not detected until after TSF1 closure. In general, higher Pb contents were observed in the period after the mine closure (including its peak in 2003–2006). Moreover, the Cu content is higher after TSF1 closure. Taking into account the way Cu and Pb behave in carbonate soils when planning agrotechnical procedures, and especially when choosing the forms of nitrogen fertilizers, reduces the risk of formation of soluble complexes of these metals with ammonium ions or low-molecular organic acids [47,77,78]. The reclamation carried out avoided this threat related to the increased bioavailability of large amounts of Cu and Pb in areas adjacent to TSF 1 and TSF2, resulting in its uptake by trees. The cessation of mining activity, combined with the absence of new sources of pollution in the area, renders the reclamation carried out as the most probable reason for the increase in Fe, Zn, and Mn contents. This is supported by the temporal consistency and widespread use of these elements in fertilizers and plant protection products [55–57].

In this study, we were able to follow the guidelines for minimizing any uncertainty in dendrochemical measurements [17,30,70] to the following extent: more than one core was taken from each tree, trees were of similar age, all grew in the same forest habitat, and in the immediate vicinity of the pollution source (except for the Control tree). Additionally, the multidecadal period was investigated. The definite and prevailing problem in the area is soil contamination (limiting factor).

The dendrochemical analyses carried out should be considered as an important stage in monitoring the condition of the environment, especially in areas where environmental health risks for the population have been identified [16,25,79]. Thanks to dendrochemical analyses carried out, it was possible to demonstrate the environmental load caused by earlier long-term exploitation of copper ores. Furthermore, evidence was provided that the reclamation of TSF1 and TSF2 was carried out, despite difficulties resulting from the specific nature of the contamination, under the supervision of the Złotoryja Forestry District in a professional and responsible manner. This avoided the existing real risk of mobilising large amounts of Cu and Pb stored in sediments and mining waste in the area. Also thanks to the results obtained, a signal from tree rings was detected indicating most probably an

increase in the bioavailability of Zn, Fe, and Mn. These TEs are essential for plants and, moreover, have relatively low toxicity [56]. The obtained results provide a rationale for monitoring the bioavailability of heavy metals in sediments and soils in the vicinity of TSF1 and TSF2, as well as for research into factors that could potentially cause their activation in the Old Copper Basin. It is also advisable to continue dendrochemical analyses using different species on more trees in this area.

5. Conclusions

Dendrochemistry has proven to be a useful tool for studying the long-term impact of pollution in the Old Copper District, even though an abrupt, short-term environmental event was not recorded. Some limitations and challenges must be kept in mind as a direct result of the study area's characteristics and the type of contaminants analysed.

1. The main aim of the research (i) was achieved, i.e., the long-term impact of copper mining in Iwiny was proved by comparing the average content of TEs in tree rings (significant differences were obtained for Mn, Ni, Zn, Cr, Pb, Cu and Fe) and the average TRW from the Ind. and Control site. At the Control site significantly lower element contents were recorded than at the Ind. site. The average width of TRW throughout the analysis period was significantly greater for the Control position, the difference being 0.7 mm.
2. The 1967 TSF1 dam failure was not recorded in tree rings as a strong chemical signal or TRW reduction (ii). In Iwiny, soil contamination prevailed, and the main limiting factor was the low bioavailability of the dominant contaminants (Cu, Pb) found in mining wastes and sediments deposited on soils. This was most likely the reason for the lack of a significant increase in TEs content after 1967.
3. The factors listed in point 2 were partially modified in 1991 as a result of the remediation of TSF1 and TSF2 through the use of fertilizers and agrotechnical treatments aimed at improving the physical and chemical properties of soils. The lack of new sources of pollution on the Ind. site along with the temporal relationship strongly suggests that the tree rings recorded the chemical signal of the TSF reclamation. Fe and Zn content reached a peak in the 1990s and early 2000s, i.e., already after the end of mining activities in the study area. Additionally, a gradual increase in Mn between 1959 and 2014 was observed. These are essential plant elements of relatively low toxicity. It should be stated that thanks to proper reclamation, a real threat was avoided, i.e., the risk of mobilising large amounts of Cu and Pb deposited in mining waste and sediments on the surrounding soil.
4. ICP-OES is an effective measurement technique for dendrochemical studies of the environmental impact of old copper mining and can be a low-cost alternative to ICP-MS (significant differences were obtained only for Ag, Cd, and Co). However, it has to be considered, that in the case of lower TEs values, the required adequate LOD of the analytes will also dictate the technique of choice.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/f12111505/s1>, Table S1: Evaluation of the significant difference between the mean values of the analysed trace elements (TEs) calculated for Industrial (Ind.) and Control site (n = 28).

Author Contributions: Conceptualization, J.D.; methodology, J.D. and P.L.; software, J.D. and P.L.; validation, P.L. and R.K.; formal analysis, J.D.; investigation, J.D.; resources, J.D. and P.L.; data curation, J.D. and P.L.; writing—original draft preparation, J.D.; writing—review and editing, R.K., P.L. and M.Z.; visualization, J.D.; supervision, R.K.; project administration, J.D.; funding acquisition, J.D. field work: J.D., R.K. and M.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the WROCLAW UNIVERSITY OF ENVIRONMENTAL AND LIFE SCIENCES (Poland), the Ph.D. research program "Innowacyjny Doktorat", grant number N070/0004/20.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank the Złotoryja Forest District for authorizing sampling. Our acknowledgements are also directed to the Laboratory for Environmental Research (Wrocław University of Environmental and Life Sciences) for their support during the study.

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

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