



Heavy metal concentrations in deciduous tree rings reflects changes in temporal dynamic of industrial air pollution

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ABSTRACT

Urban expansion, industrialization, and increased traffic intensity are major global threats to human health, well-being, and forest ecosystems due to their contribution to air, soil, and water pollution. A striking example of such environmental degradation is the dieback of hardwood forests in Eastern Europe, particularly in the heavily polluted regions of Transylvania, Romania, such as Baia Mare and Copșa Mică.

This study investigates whether trees growing in industrially polluted areas accumulate higher concentrations of heavy metals in their wood compared to those in unpolluted areas. We analysed the concentrations of manganese (Mn), lead (Pb), zinc (Zn), and copper (Cu) in tree-rings of two broad-leaved species-European beech (*Fagus sylvatica*) and sessile oak (*Quercus petraea*), in two regions heavily impacted by industrial pollution. To assess the dynamics of heavy metal accumulation in wood, we used two analytical methods: inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry (XRF).

ICP-MS results showed significantly higher Mn concentrations in European beech wood from the intensively polluted site in Baia Mare. In contrast, XRF analyses revealed higher Mn levels in beech trees from unpolluted area, particularly in Copșa Mică. XRF also indicated high Zn levels in both tree species from intensively polluted site in Copșa Mică, and higher Cu concentrations in sessile oak from the same region. Pb was detected in Baia Mare samples, and its concentrations did not significantly differ between polluted and unpolluted sites.

These findings highlight species- and site-specific patterns of heavy metal accumulation and underscore the complexity of tree responses to long-term industrial pollution.

1. Introduction

Climate change, air pollution, urbanization, and demographic shifts are exerting profound effects on forests, altering their social, cultural, ecological, and economic roles. These disturbances have significant negative consequences for the social value of forests, as well as for livelihoods, public health, and overall quality of life. The impacts are particularly severe in regions where communities depend directly on forest resources. Moreover, urban populations, which are growing rapidly, also depend on forests and trees for resilience, human health, and welfare. However, urban expansion, industrialization, and increased traffic intensity pose significant global threats to both human well-being and forest ecosystem services, contributing to pollution of the air, soil, and water (Pulatoglu et al., 2025; Öztürk Pulatoğlu, 2024). This pollution adversely affects forest ecosystems and the organisms that

depend on them (Khosropour et al., 2019).

Heavy metals, which are among the most harmful pollutants, originate from sources such as industrial plants, non-ferrous metal processing, mining activities, and traffic emissions (Turkyilmaz et al., 2018; El-Hasan et al., 2002). While certain chemical elements (e.g., N, P, K, Mg, Zn, Fe, Ca, Na, Mn) are essential for tree growth and development, their high concentrations due to pollution pose a substantial threat to the health and the productivity of forests (Sevik et al., 2020).

Trees play a crucial role in mitigating pollution, particularly in urban environments, by filtering airborne contaminants and reducing the harmful effects of pollution (Alahabadi et al., 2017). Additionally, dendrochemistry, the study of the chemical composition of annual rings, provides valuable retrospective data on historical changes in environmental pollution levels (Sensula et al., 2017; Sawidis et al., 2011; Binda et al., 2021). For instance, imbalances in Mn and Ca concentrations in

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wood have been identified as early warning indicators of tree dieback, as observed in silver fir (*Abies alba* Mill.) and Scots pine (*Pinus sylvestris* L.) (Hevia et al., 2019). While leaves are commonly analysed to assess current heavy metal concentrations in trees, tree rings offer long-term insights into pollution history and fluctuations over time (Turkyilmaz et al., 2019). This has been demonstrated in studies of heavy metal accumulation in oak (*Quercus robur* L.) and maple (*Acer platanoides* L.) in Ankara, Turkey, a city significantly affected by industrial and vehicular pollution (Turkyilmaz et al., 2018, 2019). Similarly, research in Lithuania has revealed that heavy metals accumulate at much lower levels in wood compared to soil, highlighting the relationship between soil contamination and the chemical composition of tree rings in birch (*Betula pendula* L.) and Scots pine (Butkus and Baltrėnaitė-Gedienė, 2007). However, trees are not passive recorders of environmental conditions; ontogenetic and physiological processes, such as growth dynamics, preferential accumulation, and translocation of elements, can influence or obscure dendrochemical signals (Durand et al., 2020).

A striking example of forest decline linked to heavy metal pollution is found in Eastern Europe, particularly in Romania's Transylvanian regions of Baia Mare and Copșa Mică (Fig. 1). In these regions, symptoms such as growth decline and reduced productivity have been observed since the 1970s (Leșan, 2003). The Baia Mare industrial complex, operational since 1907, initially specialized in sulfuric acid production before expanding into copper processing and precious metal smelting in 1942 (Boros et al., 2015). During the communist era (1948–1980), the smelter processed approximately five million tons of ore annually. However, after 1990, mining and smelting activities declined significantly, reducing production to 1.4 million tons per year (Manoiu and Spiridon, 2017).

Similarly, in Copșa Mică, extensive heavy metal and carbon black pollution have severely impacted forests and soils. High concentrations

of heavy metals (Pb, Cu, Zn, and Cd) have been detected in regional soils (Ianculescu and Budu, 2007; 2010). The carbon black production facility, operational since 1936, expanded to an annual capacity of 63,000 tons by 1974 (Păucean and Gabor, 2015). Another major source of pollution was the non-ferrous metal processing plant, established in 1939, which produced metallurgical Zn and Pb. By the 1970s, its output had reached 50,000 tons of Zn and 20,000 tons of Pb annually. Following 1990, industrial activity in Copșa Mică, like in Baia Mare, declined sharply (Păucean and Gabor, 2015). These two heavily industrialized Romanian regions, Baia Mare and Copșa Mică, provide ideal settings for studying long-term changes in the concentration of chemical elements in tree rings through dendrochemistry (Binda et al., 2021). Copșa Mică and Baia Mare were the two most polluted cities in Romania. Due to extremely high levels of pollutant emissions during this period, Copșa Mică was considered the most polluted city in Europe (Păucean and Gabor, 2015).

Analysing heavy metal concentrations in tree rings over a 60-year period offers valuable insights into the historical evolution of local pollution. Previous research has indicated that pollution negatively affects broad-leaved trees in Baia Mare, as trees in polluted areas exhibited smaller increases in basal area compared to those in unpolluted regions (Sidor et al., 2022).

This study aims to determine whether trees in intensively polluted areas accumulate higher concentrations of heavy metals in their wood compared to those in unpolluted areas. We hypothesize that trees in polluted areas contain significantly higher levels of heavy metals in tree-rings than those in unpolluted areas.

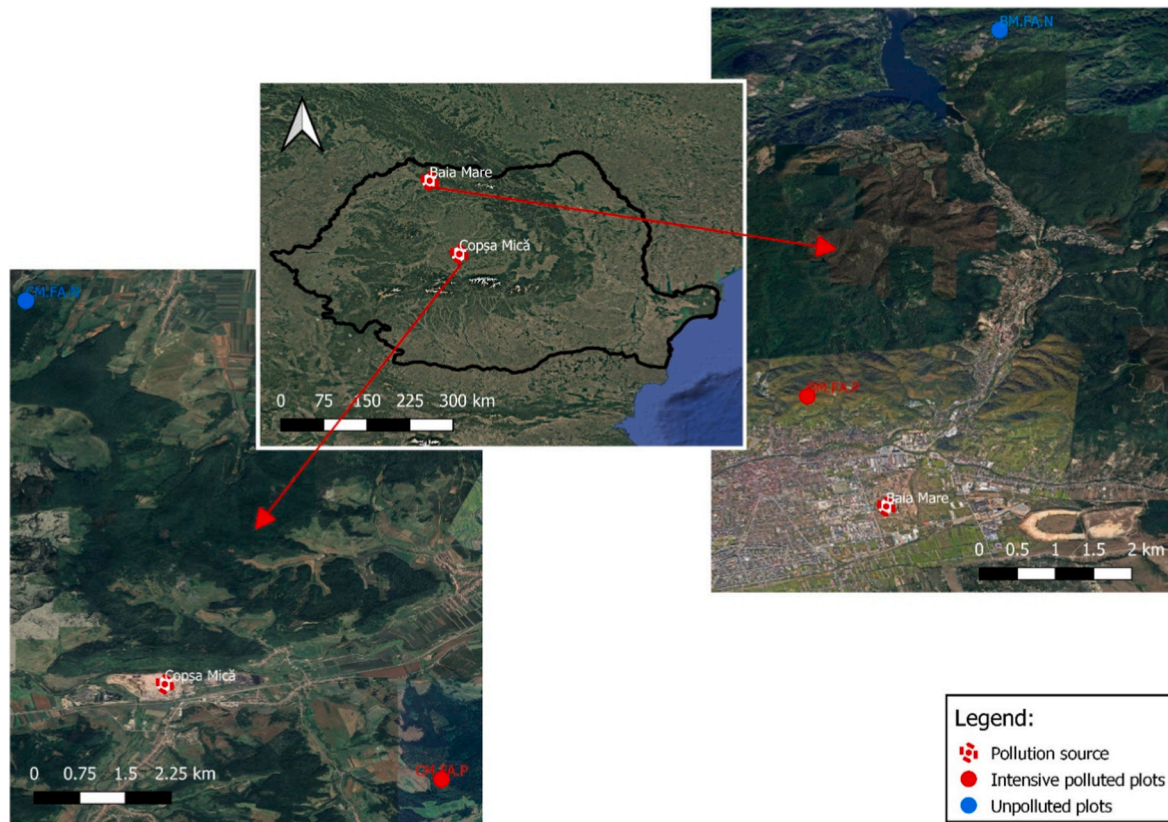


Fig. 1. Location of the two study areas in Romania. Baia Mare beech in polluted area - BM.FA.P; Baia Mare beech in unpolluted area - BM.FA.N; Copșa Mică beech in polluted area - CM.FA.P; Copșa Mică beech in unpolluted area - CM. FA.N; Copșa Mică sessile oak in polluted area - CM.GO.P; Copșa Mică sessile oak in unpolluted area - CM.GO.N.

2. Material and methods

2.1. Study areas

The Baia Mare (47° 39' N, 23° 34' E, 228 m a.s.l.) and Copșa Mică (46° 6' 45" N, 24° 13' 5" E, 287 m a.s.l.) study areas are located in Transylvanian region (northern and central Romania, respectively) (Fig. 1). In the two regions studied, experimental plots were systematically established in order to include both stands that had been severely affected by local industrial pollution and those that had not. Therefore, plots located near (2.7–3.0 km) or far (9–11 km) from pollution sources were sampled in each region assuming they corresponded to intensively polluted and unpolluted areas, respectively (Table 1). Based on previous research that examined multiple forest stands situated at varying distances from the primary pollution source, it was determined that pollution intensity in this region tends to shift approximately every 2 km (Ianculescu, 1978; Ianculescu et al., 2009). Moreover, this pattern is subject to significant variation depending on factors such as prevailing wind direction and speed, topography, and the characteristics of the forest stands themselves, including their capacity to buffer and mitigate pollution effects (Sidor et al., 2021).

When establishing the plots, it was taken into account that they should contain broad-leaved, mature trees (older than 60 years) in order to compare the dynamics of the chemical elements accumulated in the annual rings of the intensively polluted and unpolluted areas. The two studied species were European beech (*Fagus sylvatica* L.) in Baia Mare and European beech and sessile oak (*Quercus petraea* L.) in Copșa Mică.

2.2. Field sampling and core pre-processing

Five cores were taken from five trees in each plot using a 12-mm Pressler increment borer. The cores were air dried for 30 days in the laboratory before being sectioned with a cutter. Initially, they were cut transversely to highlight ring boundaries, which were identified using a binocular. Further processing involved dividing the samples into sections of five tree rings, starting from the most recent year of growth (2020) and covering a total period of 60 years (1961–2020). Analysing this 60-year series was essential for visually cross-dating the samples (Fritts, 1976) and examining the dynamics of chemical elements during both periods of intense pollution and times of significantly reduced industrial activity.

2.3. Dendrochemical analyses

A set of 12 five-ring samples was taken from each core, covering a 60-year period, resulting in a total of 336 samples. Each sample was sealed in a plastic container and labelled according to its area of origin, tree species, pollution intensity, and specific years.

Table 1
Characteristics of experimental plots.

Species	Number of cores	Period covered	Location	Distance from the polluting source (km)	Air pollution intensity
European beech	5	1961–2020	Copșa Mică	3	Intensive polluted
European beech	5	1961–2020	Copșa Mică	11	Unpolluted
Sessile oak	5	1961–2020	Copșa Mică	3	Intensive polluted
Sessile oak	5	1961–2020	Copșa Mică	11	Unpolluted
European beech	5	1961–2020	Baia Mare	2.7	Intensive polluted
European beech	5	1961–2020	Baia Mare	9.5	Unpolluted

Two dendrochemical methods—inductively coupled plasma mass spectrometry (ICP-MS) and X-ray spectrofluorometry (XRF)—were used to analyse chemical elements in the wood. ICP-MS is the most widely used method for elemental analysis worldwide due to its high precision and low detection limits (Aries et al., 2000). In contrast, XRF provides rapid results at a relatively low cost and is effective for quickly analysing large sample sets (Al Maliki et al., 2017).

For ICP-MS analysis, wood samples were dried at 105 °C. Then, 0.5–1 g of material was taken from the tree rings and completely dissolved in a 5:1 mixture of nitric acid and hydrogen peroxide. Sample preparation involved microwave digestion following EN 13657 standards, followed by filtration and dilution. The resulting solution was analysed using a PerkinElmer Elan DRC II instrument. To remove interferences, a two-channel Dynamic Reaction Cell (DRC) was used, pressurized with reaction gases such as methane and oxygen, depending on the specific isotope and type of interference. Calibration was performed using a Multi-Element Standard 3 stock solution from PerkinElmer, diluted to create a four-point calibration curve (10 ppb, 20 ppb, 50 ppb, 100 ppb). Samples exceeding 100 ppb were diluted to fit within the calibration range. This method is known for its high accuracy and extremely low detection limits (Aries et al., 2000). The instrumental parameters used for ICP-MS analysis are detailed in Table S1.

Due to the high cost and time-consuming nature of ICP-MS, only 48 samples were analysed using this method, four cores (two from each tree species), with one core from an intensively polluted area and one from unpolluted area. The selection included 24 samples from each region, evenly split between polluted and unpolluted sites. Specifically, European beech samples from the Baia Mare region and sessile oak samples from the Copșa Mică region were analysed.

For XRF analysis, a Bruker Tracer 5i X-ray fluorescence instrument (50 kV, 4 W, Rh target, SDD detector with graphene window, 8 mm collimator) was used. The instrument was factory-calibrated using the manufacturer's proprietary method. Analyses were conducted under standard atmospheric conditions without the use of filters. This portable instrument enables non-destructive, direct elemental analysis without the need for sample preprocessing (Konstantakopoulou et al., 2024). XRF analysis converts characteristic radiation intensities into element concentrations (Markowicz, 2011). Compared to ICP-MS, XRF provides rapid, cost-effective results, making it ideal for fast elemental analysis (Al Maliki et al., 2017), although it has a higher detection limit.

Sample preparation for XRF involved first grinding the wood samples into a fine powder to minimize natural variation in density that occur at the tree-ring level. The powdered material was then thoroughly mixed, and placed into ring dies. Using a hydraulic press, the mixture was compacted under medium pressure (115–300 MPa), forming solid, stable pellets. This pressing step not only produces a uniform sample suitable for XRF analysis but also further reduces the effects of density variation by tightly compacting the powder into a consistent matrix. All settings and measurements were adjusted directly on the handheld analyser and processed using Artax™ advanced spectral analysis software, which synchronizes power, function, precision, and accuracy for dynamic, field-capable, laboratory-grade elemental analysis. Data storage and empirical calibration were managed using EasyCal PC software.

Since XRF is a lower-cost method that allows for high-throughput analysis, 288 samples were analysed using this technique: 96 samples from beech trees in Baia Mare and 192 samples from Copșa Mică (96 from beech and 96 from sessile oak). In all cases, 48 samples were from intensively polluted areas and 48 from unpolluted areas.

All heavy metals were analysed using both methods; however, only four elements (Mn, Zn, Pb and Cu) were consistently identified in the chemical composition of the samples. Different samples were analysed using ICP-MS and XRF. Each method was used to identify trends and patterns in heavy metals accumulation, rather than validate one against the other.

2.4. Statistical analyses

The Shapiro-Wilk test was used to assess the normality of the data. Since some variables did not follow a normal distribution, the non-parametric Kruskal-Wallis H test was applied to determine whether there were significant differences ($p < 0.05$) in chemical element concentrations between polluted and unpolluted areas. The Mann-Kendall test (tau statistic) was also used to detect significant trends in element concentrations over time. Additionally, ANCOVA was applied to assess differences in trend slopes of element concentrations in relation to pollution levels. Data processing and graphical visualization were conducted using RStudio (R Core Team, 2023).

3. Results

3.1. ICP-MS analyses

The main heavy metals identified in the growth rings of broadleaved trees in both regions were Mn, Pb and Zn, which accumulated in different concentrations depending on the species and the pollution intensity.

Manganese was the most prominent heavy metal identified in tree-rings, with concentrations varying by species and pollution level. The highest Mn levels were recorded in European beech from the intensively polluted Baia Mare site, peaking 46 mg kg^{-1} in 1970 (Fig. 2A). Concentrations declined until 1985, then rose again to 43.8 mg kg^{-1} in 1995, before declining once more. In contrast, beech trees from the unpolluted Baia Mare site showed relatively stable and significant lower

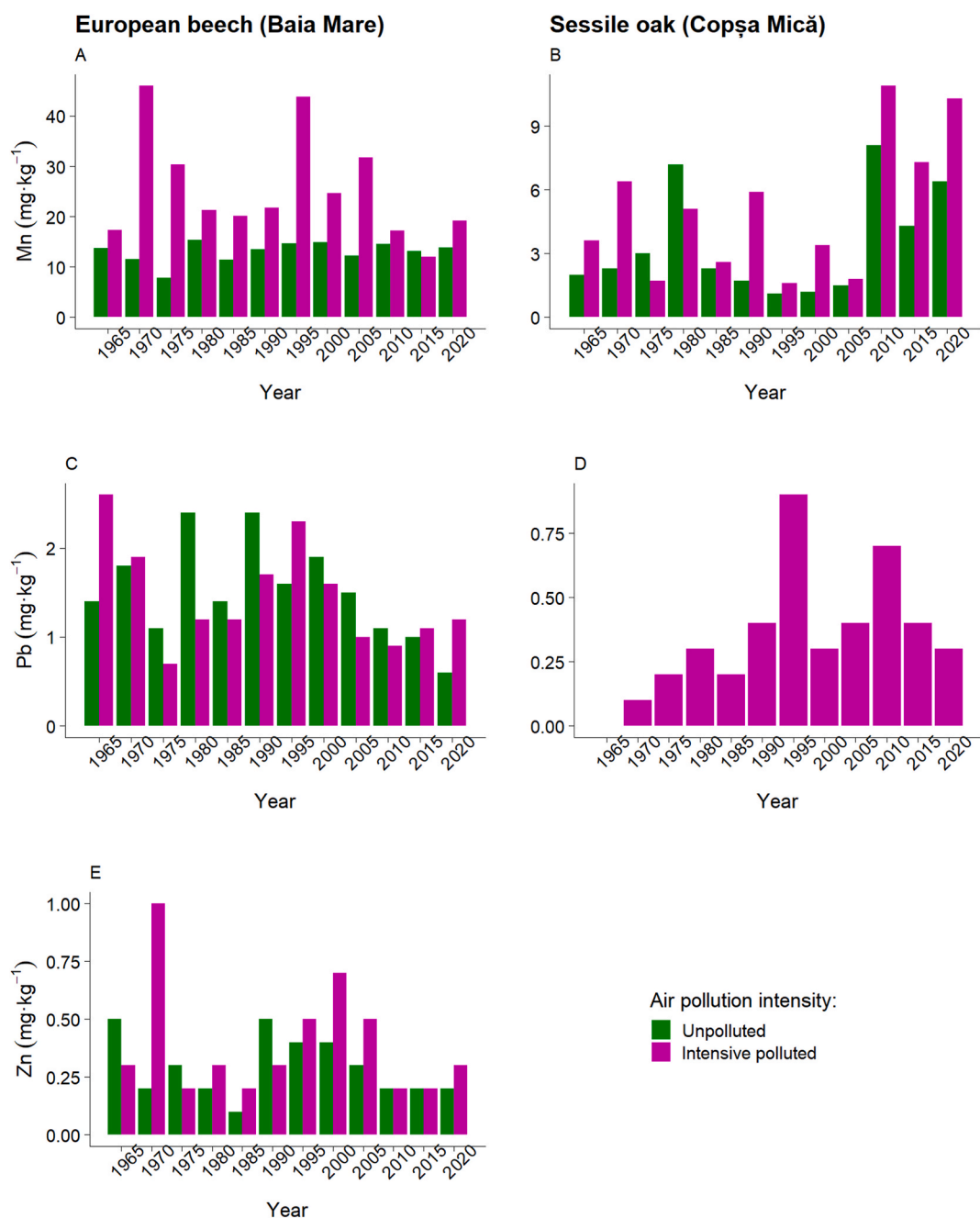


Fig. 2. Variation of heavy metals concentration in the deciduous tree rings according to the ICP-MS method.

Mn concentrations ($p < 0.01$).

In sessile oak from Copșa Mică region, Mn concentrations remained relatively constant over time in both polluted and unpolluted sites. While levels were slightly higher in the intensively polluted site (with a maximum of 10.9 mg kg^{-1} in 2010), the differences were not statistically significant ($p = 0.165$; Fig. 2B).

The highest Pb concentrations were found in beech trees from Baia Mare, reaching 2.6 mg kg^{-1} in 1965, followed by a constant increase until 1995 and a subsequent decline (Fig. 2C). In the unpolluted Baia Mare site, Pb concentrations showed a more irregular pattern until 1995, then decreased steadily until 2020. However, no significant differences in Pb concentration were observed between the polluted and unpolluted sites ($p = 0.706$).

In Copșa Mică, Pb was detected only in sessile oak from the polluted site, with a peak of 1 mg kg^{-1} in 1995 (Fig. 2D). No Pb accumulation was identified in sessile oak trees from the unpolluted site.

Zinc was identified only in beech trees from Baia Mare region. In the polluted site, Zn concentrations peaked at 1 mg kg^{-1} in 1970 and 0.75 mg kg^{-1} in 2000 (Fig. 2E). In the unpolluted area, Zn levels declined from 1965 to 1985, peaked at 0.50 mg kg^{-1} in 1990, and then decreased gradually, stabilizing after 2010. There were no significant differences in Zn concentrations between polluted and unpolluted areas ($p = 0.337$).

3.2. XRF analyses

As mentioned above, three statistical tests were applied to the datasets obtained from the XRF analysis, and the results are presented in Table 2.

Beech trees from Copșa Mică accumulated significantly higher Mn concentrations in the unpolluted area compared to the polluted one ($150\text{--}400$ vs $75\text{--}200 \text{ mg kg}^{-1}$; $p < 0.01$; Fig. 3; Table 2). In both areas, Mn concentrations declined over time, with a steeper decrease in the unpolluted site. In sessile oak, no significant differences in Mn concentrations were found between the polluted and unpolluted areas ($p = 0.62$). Similarly, in Baia Mare, Mn concentrations in beech trees did not differ significantly between polluted and unpolluted areas (Fig. 3; Table 2).

Lead was detected only in beech trees from Baia Mare (Fig. 4). No significant differences in Pb concentrations were observed between polluted and unpolluted areas ($p = 0.29$). In Copșa Mică, Pb was not detected in any tree samples, as concentrations were below the detection limit of the XRF method.

Beech trees from Copșa Mică accumulated high levels of Zn, especially in the intensively polluted area, where concentrations ranged

from 17 to 87 mg kg^{-1} , peaking between 1965 and 1995. In the unpolluted area, the maximum Zn concentrations reached 55 mg kg^{-1} in 1980. Over time, Zn concentration declined in both areas, with a more pronounced decrease in the intensively polluted site (Fig. 5; Table 2).

In sessile oak from Copșa Mică, Zn concentrations reached up to 60 mg kg^{-1} in the polluted area, while in the unpolluted area, values remained below 27 mg kg^{-1} . Zn levels were significantly higher in the polluted site for both sessile oak ($p = 0.02$) and beech ($p < 0.01$). Notably, an increasing trend in Zn concentration over time was observed in the unpolluted area.

In Baia Mare, beech trees also showed higher Zn concentrations in the polluted compared to the unpolluted one, with a significant decreasing trend over time in the polluted site.

In Baia Mare, beech trees exhibited an increasing trend in Cu concentrations over time, with higher values in the intensively polluted area than in the unpolluted one (Fig. 6; Table 2). For sessile oak in Copșa Mică region, Cu concentrations showed a negative trend over time in the polluted site, while remaining stable in the unpolluted area. Overall, Cu concentrations were higher in the polluted area.

4. Discussion

Our study analyses the accumulation of heavy metal concentrations in the tree rings of two hardwood species over a 60-year period in historically polluted regions of Romania. For several analysed elements, significant differences were observed between trees from intensively polluted areas and those from unpolluted regions. This confirms our main hypothesis that trees in intensively polluted areas accumulate higher quantities of heavy metals in their growth rings than those in unpolluted areas. Similar patterns have been observed in Norway spruce and silver fir in other industrially polluted areas of Romania, including regions affected by lime and cement dust pollution or mining activities (Cuciurean et al., 2024).

Notable examples include elevated Mn concentrations in beech from Baia Mare, as determined using the ICP-MS method, and high Zn concentrations in beech from Copșa Mică, as identified via the XRF method. However, exceptions to the expected pattern were also found, such as Mn concentrations in beech from Copșa Mică (XRF method), which were unexpectedly higher in unpolluted areas. This suggests that pollution may reduce Mn accumulation in beech wood from Copșa Mică, but this does not align with ICP-MS analyses from Baia Mare, indicating possible differences in pollution impact or analytical discrepancies. One possible explanation is that ICP-MS analyses only one sample at a time, and element concentration can vary significantly from tree to tree, as observed with the XRF method. Overall, our findings are consistent with

Tabel 2
Results of statistical tests applied to detect trends (Mann-Kendall), compare polluted and unpolluted areas (Kruskal-Wallis) and compare trend slopes of elements in polluted and unpolluted areas.

Region	Species	Element	Area	Mann Kendall		Kruskal-Wallis H	ANCOVA
Copșa Mică	European beech	Mn	Intensively polluted	tau = -0.303	p = 0.192	p < 0.01	p = 0.026
			Unpolluted	tau = -0.727	p = 0.001		
		Zn	Intensively polluted	tau = -0.626	p = 0.005	p < 0.01	p < 0.01
			Unpolluted	tau = -0.394	p = 0.086		
	Sessile oak	Mn	Intensively polluted	tau = 0.364	p = 0.114	p = 0.622	p = 0.786
			Unpolluted	tau = 0.481	p = 0.945		
		Zn	Intensively polluted	tau = 0.045	p = 0.890	p = 0.024	p < 0.01
			Unpolluted	tau = 0.481	p = 0.037		
Baia Mare	European Beech	Cu	Intensively polluted	tau = -0.431	p = 0.062	p < 0.01	p = 0.013
			Unpolluted	tau = 0.06	p = 0.834		
		Mn	Intensively polluted	tau = -0.303	p = 0.192	p = 0.395	p = 0.320
			Unpolluted	tau = 0.273	p = 0.243		
		Zn	Intensively polluted	tau = -0.565	p = 0.013	p < 0.01	p < 0.01
			Unpolluted	tau = -0.351	p = 0.130		
		Cu	Intensively polluted	tau = 0.362	p = 0.126	p = 0.155	p = 0.043
			Unpolluted	tau = 0.185	p = 0.448		
		Pb	Intensively polluted	tau = 0.092	p = 0.730	p = 0.288	p = 0.346
			Unpolluted	tau = -0.44	p = 0.072		

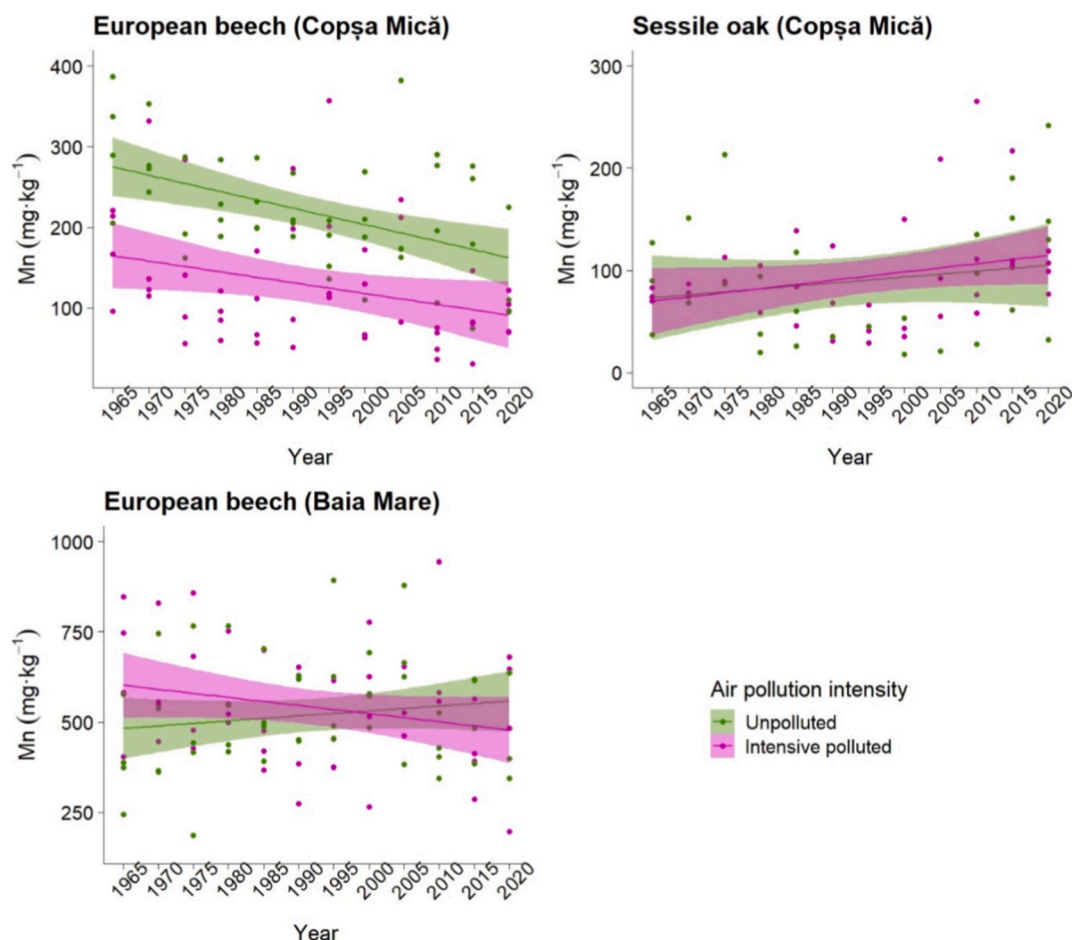


Fig. 3. Variation of Mn concentration in the deciduous tree rings analysed by the XRF method. Lines represent linear regressions fitted to the data set, and areas show 95 % confidence intervals.

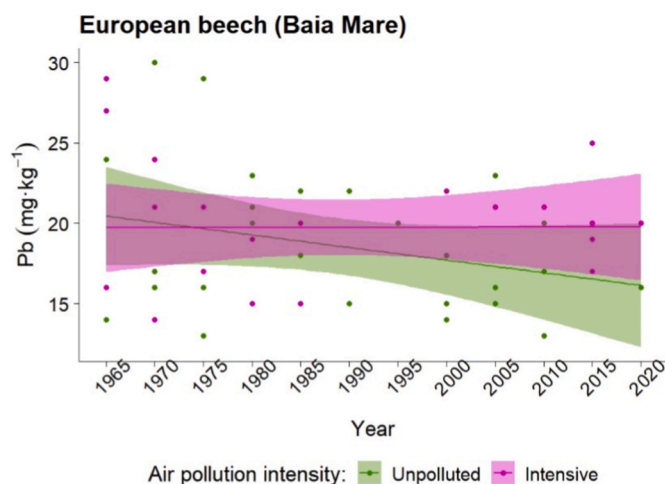


Fig. 4. Variation of Pb concentration in the beech tree rings from Baia Mare analysed by the XRF method. Lines represent linear regressions fitted to the data set, and areas show 95 % confidence intervals.

previous studies on similar elements. For instance, sapwood Mn concentrations have been reported to range between 40 and 1220 mg kg⁻¹ in various angiosperm and gymnosperm species (Meerts, 2002).

Pb concentrations were detected in beech trees from Baia Mare, regardless of pollution intensity. Even though there are studies highlighting the presence of Pb in soils in the Baia Mare region, these studies

were only conducted in areas affected by pollution (Damian et al., 2008; Lăcătușu et al., 1996; Big et al., 2012; Mihali et al., 2013). The presence of lead in unpolluted areas may be attributed to natural sources, particularly the geochemical composition of soils. Lead can occur naturally in soils as a result of the mineral composition of the parent rock from which the soil is derived (Tidball, 1976).

Pb was detected in sessile oak trees only in the intensively polluted area of Copșa Mică using the ICP-MS method, but in lower concentrations than in beech from Baia Mare. A comparable study in the Călimani Mountains found that Norway spruce trees affected by mining accumulated Pb up to 0.16 mg kg⁻¹ (Tichavský et al., 2021). The critical threshold for Pb is 10 mg kg⁻¹ (Yilmaz and Zengin, 2004), suggesting that beech trees in Baia Mare accumulated potentially harmful amounts of Pb. Similar findings were reported in Iran, where Pb concentrations reached up to 110 mg kg⁻¹ in leaves and 75 mg kg⁻¹ in bark from polluted urban parks (Solgi et al., 2020). The Pb concentrations identified through ICP-MS method in our study are comparable to those reported in the tree-rings of *Magnolia champaca* exposed to pollution in Mizoram, northeast India, where levels reached 3.173 mg kg⁻¹ (Balraju et al., 2025).

Mn concentrations in sessile oak trees from Copșa Mică were lower than those in beech from Baia Mare. The decline in Pb concentrations after 1995 likely reflects the significant reduction in industrial activity after 1990. The minimum values recorded since 1975 may be explained by the fact that our analysis only included trees that survived prolonged pollution exposure. This suggests that trees persisting in highly polluted areas are more resistant than those that succumbed to pollution stress over time.

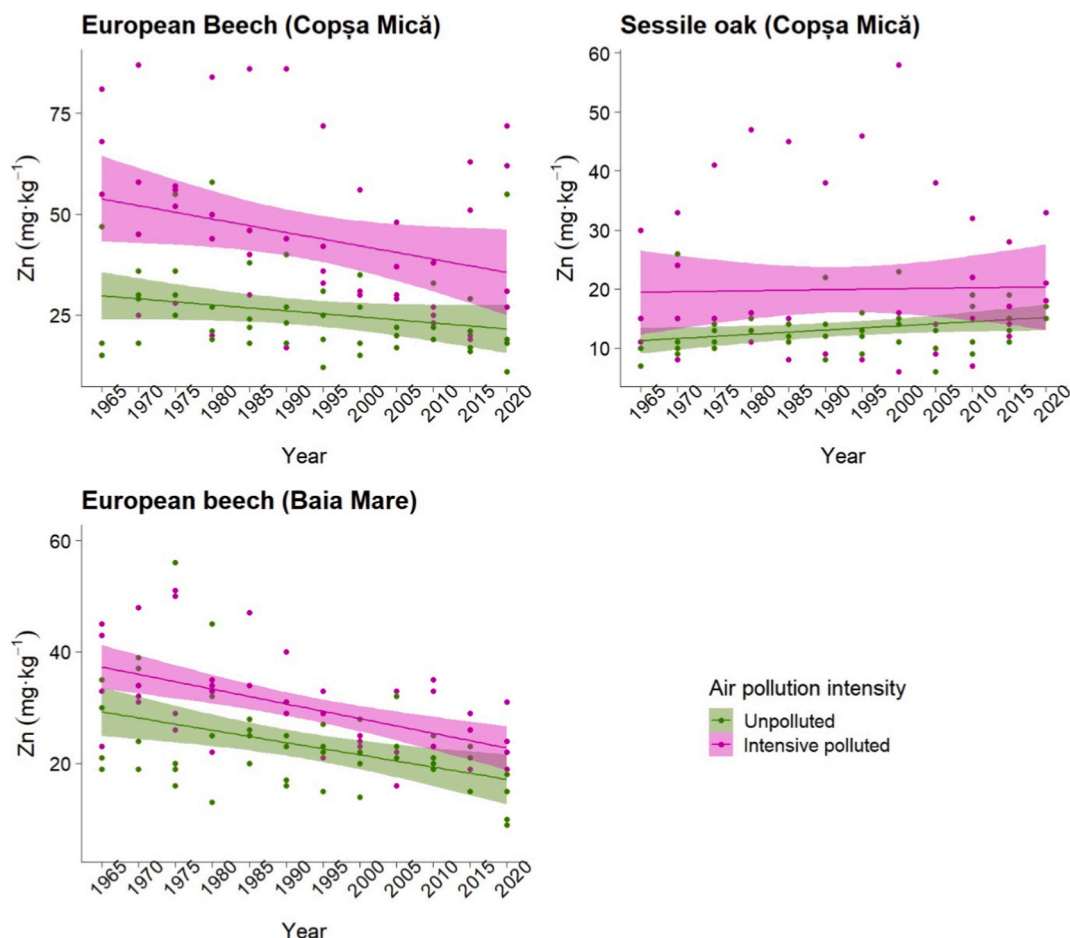


Fig. 5. Variation of Zn concentration in the deciduous tree rings analysed by the XRF method. Lines represent linear regressions fitted to the data set, and areas show 95 % confidence intervals.

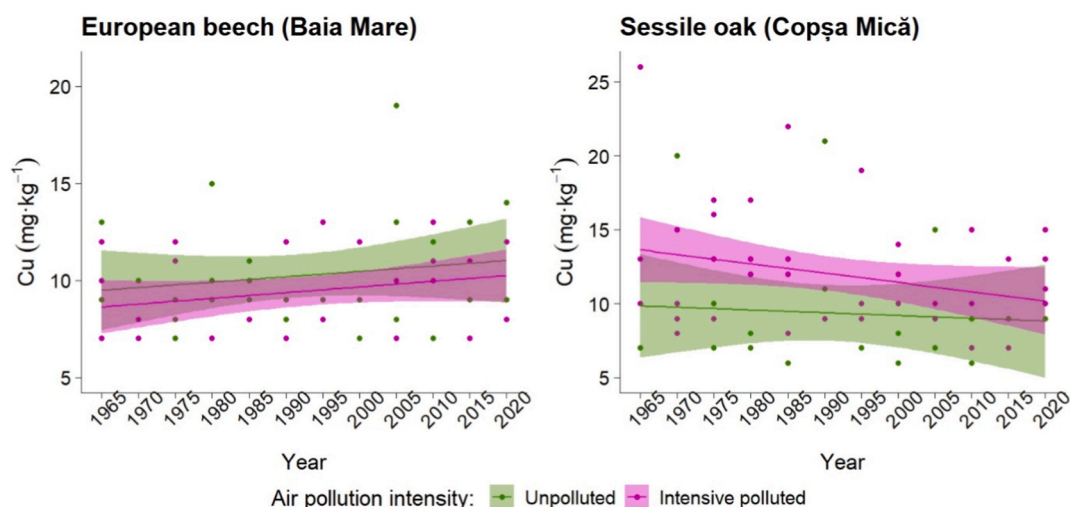


Fig. 6. Variation of Cu concentration in the deciduous tree rings by the XRF method. Lines represent linear regressions fitted to the data set, and areas show 95 % confidence intervals.

Zn concentrations indicated a stronger accumulation in trees from intensively polluted areas. To meet physiological needs, Zn concentrations in leaves should range between 15 and 30 mg kg⁻¹, and should not exceed 70 mg kg⁻¹ in the absence of pollution (Kabata-Pendias and Pendias, 1992). In our study, the highest Zn concentration (85 mg kg⁻¹) was found in beech wood from Copșa Mică, suggesting a strong pollution

load. When compared to previous studies, for instance, 4.7 mg kg⁻¹ in *Pinus sylvestris* from Lithuania (Baltreinaite et al., 2010) and 26.43 mg kg⁻¹ in *Cinnamomum camphora* from Shanghai, China (Xu et al., 2017), our findings reveal notable differences. These discrepancies can be attributed to species-specific uptake capacities, differing environmental contexts, and the intensity of pollution exposure in each region.

Regarding Cu accumulation, significant differences were observed only in sessile oaks from Copșa Mică, where higher concentrations were found in polluted areas. Previous studies have reported Cu (14–28 mg kg⁻¹) and Zn (54–92 mg kg⁻¹) concentrations in ash leaves, with higher values than those detected in bark from the same trees (Solgi et al., 2020). These Zn and Cu concentrations are comparable to those in our study, though Cu levels are typically lower in wood than in leaves (Cocozza et al., 2016). Also, our results regarding Cu concentration are comparable with those observed in the tree rings of *Magnolia champaca* in Mizoram, north-east India, where an average of 10.28 mg kg⁻¹ was found (Balraju et al., 2025).

The highest Mn concentrations were recorded in beech from Baia Mare's intensively polluted area. In contrast, although Mn levels in Copșa Mică beech were lower than those in Baia Mare, trees from unpolluted areas accumulated more Mn than those in polluted areas. A possible explanation could be the nature of pollution, as carbon black also has a mechanical effect by blocking stomata and limiting photosynthesis processes (Ianculescu et al., 1989), effects that can also lead to the limitation of the uptake of some soil elements. Under stress conditions, plants may increase Mn concentrations in their tissues to prevent phosphorus (P) mobilization and loss (Lambers et al., 2015). However, excessive Mn in soil can be toxic to trees, inhibiting the uptake of essential elements such as Ca, K, Mg, Fe, and P (Marschner, 2012; Millaleo et al., 2013). Similar trends have been reported in beech from Brussels (Belgium), where Mn concentrations declined from 200 to 60 mg kg⁻¹ over 90 years due to reduced dust emissions and decreased soil Mn availability (Penninckx et al., 1999). The concentrations identified in our study are higher than the 160 mg kg⁻¹, concentrations identified in the tree rings of *Pinus massoniana* from the Fuzhou area of the Taiwan Strait in eastern China (Chen et al., 2021). High Mn concentrations have also been found in leaves of deciduous trees in southern China, sometimes exceeding 450 mg kg⁻¹ (Liu et al., 2007).

Trees have been widely used as bioindicators of long-term heavy metal pollution across various regions. Some studies have focused on heavy metal accumulation in tree leaves and bark (e.g., Sawidis et al., 2011). A study in Tehran (Iran) found that sycamore (*Platanus orientalis* L.) trees in urban areas had significantly higher Cd, Pb, Ni, and Cr concentrations in their leaves than trees growing 15 km outside the city (Khosropour et al., 2019). Similarly, research on maple (*Acer platanoides* L.) in Ankara (Turkey) found that heavy metal concentrations (e.g., Zn, Cu, Co, Fe, Mn, Cr) were higher in bark than in wood (Turkyilmaz et al., 2018, 2019). This study also indicated that heavy metal concentrations in growth rings varied with tree age but did not show a linear correlation with traffic intensity. However, these studies lacked a retrospective temporal analysis. In contrast, a study in Valencia (Spain) compared heavy metal concentrations (Cd, Cr, Ni) in oak leaves sampled in 1941 (herbarium specimens) and 2012, finding that levels increased 10–16 times, whereas Pb and Zn concentrations declined (Martín et al., 2015). This approach aligns with dendrochemical studies that incorporate a historical perspective.

In our study, fewer samples from Baia Mare beech and Copșa Mică sessile oak were analysed using ICP-MS due to the high cost and time required for dendrochemical analyses with this method. While this limitation may affect the robustness of our findings, it is partially mitigated by complementary XRF analyses.

Although ICP-MS is a highly precise and sensitive method that enables qualitative assessments of heavy metal concentration in tree-rings, a critical limitation of this study is the very small sample size (only one specimen per species and site). This severely restricts the ability to generalize the findings or draw robust conclusions about spatial or temporal trends. The observed concentrations may reflect individual variability rather than broader environmental patterns, especially given the known heterogeneity, in metal uptake and retention between individual tree, even within the same stand (Scharnweber et al., 2016). Furthermore, the high variability in metal accumulation within a single tree-ring series, resulting from complex processes of uptake, transport,

incorporation, and remobilization, makes it difficult to interpret dendrochemical trends from such limited data. While XRF provided a broader overview, its results also showed variability among trees from the same region, underscoring the influence of individual-specific responses and site conditions. To validate and expand upon this findings, a significantly larger and more representative sample set is required.

5. Conclusions

ICP-MS analyses indicated elevated Mn concentrations in European beech wood from intensively polluted areas of the Baia Mare region, while XRF analyses revealed higher Zn concentrations in both European beech and sessile oak wood from intensively polluted areas in Copșa Mică. Copper concentrations were also elevated in sessile oaks from Copșa Mică polluted sites. Interestingly, manganese concentrations were unexpectedly higher in beech trees from unpolluted areas of Copșa Mică, as shown by XRF analyses.

It is important to interpret the ICP-MS results with caution, as only one tree per species was analysed from each region, each exposed to varying pollution levels. Despite the higher accuracy of ICP-MS in detecting trace metals in tree rings, the lack of replication limits the generalizability of the findings.

The highest Mn concentrations overall were found in beech trees from Baia Mare, where Pb was also detected; however, Pb levels did not differ significantly between polluted and unpolluted sites. Similar patterns were observed for Mn and Cu, even though prior studies have linked these elements to forest decline. Notably, the concentrations of the analysed elements in all sampled trees remain below toxicity thresholds.

These findings suggest that trees in polluted areas accumulate higher levels of certain heavy metals, and the extent of accumulation is influenced by species and site conditions. This highlights the importance of integrating long-term impact assessments to better understand how exposure to sub-toxic levels of heavy metals affects tree physiology, forest health, and ecosystem resilience. Assessing such impacts is essential for forest management strategies and environmental policies in historically and currently industrialized areas.

CRedit authorship contribution statement

Cristian Gheorghe Sidor: Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Conceptualization. **Cosmin Ilie Cuciurean:** Writing – review & editing, Writing – original draft, Visualization, Software, Resources, Formal analysis, Data curation. **Jesus Julio Camarero:** Writing – review & editing, Visualization, Validation. **Ovidiu Badea:** Writing – review & editing, Validation, Supervision.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apr.2025.102716>.

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