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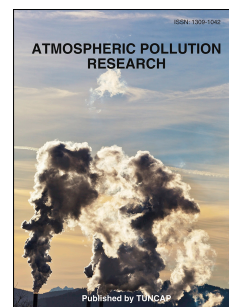
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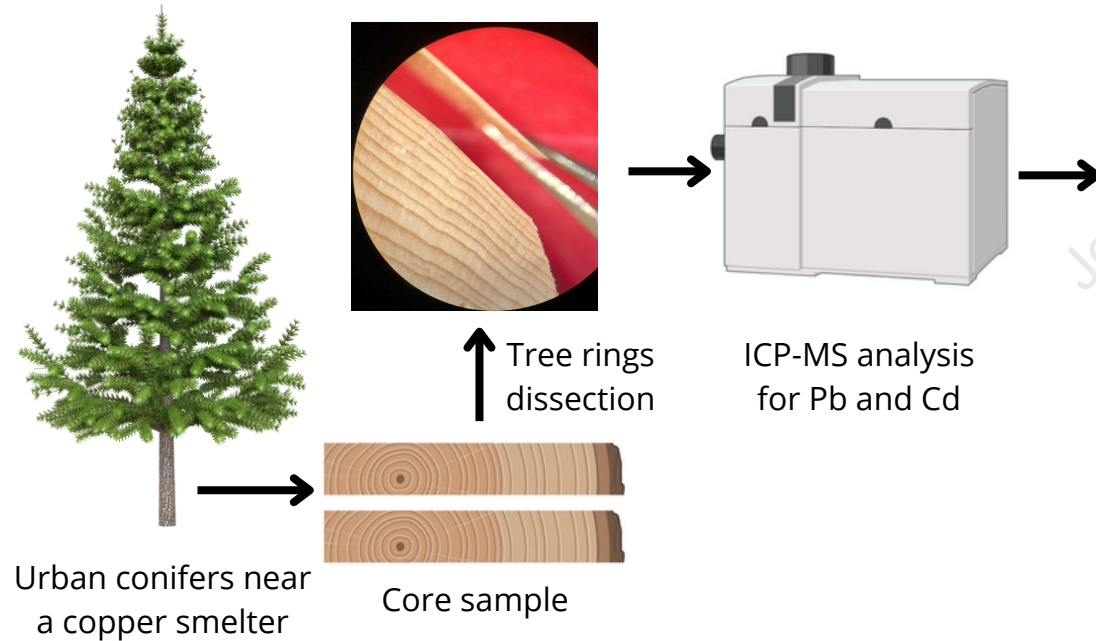


Spatiotemporal assessment of lead (Pb) and cadmium (Cd) contamination in tree rings of urban trees near an industrial smelter

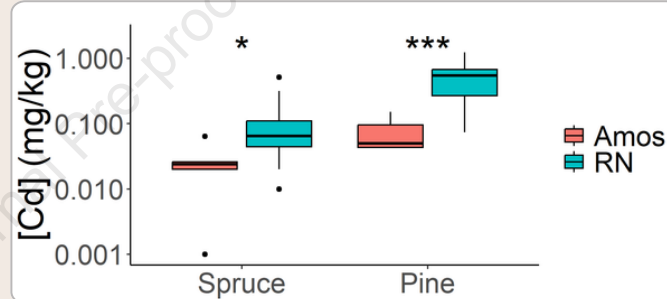
Sampling process

Analysis

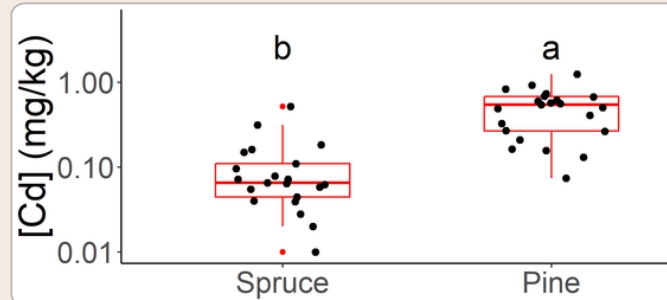
Main results



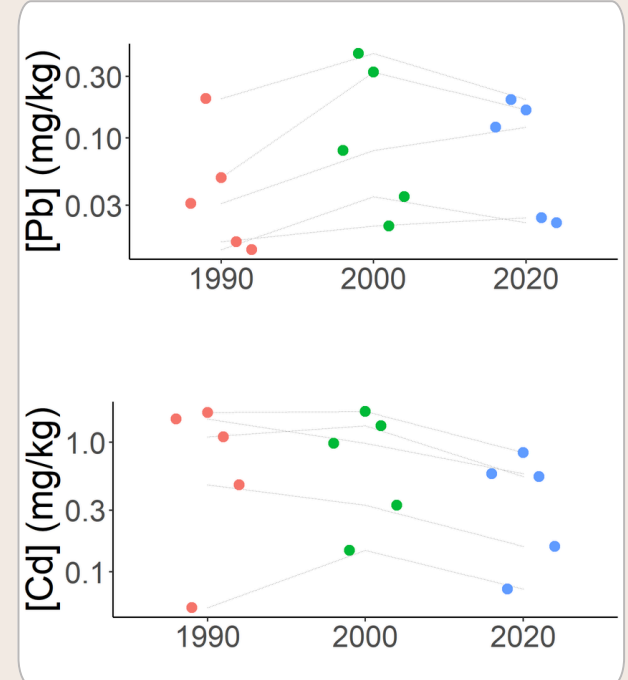
Comparison with a distant city



Species differences



Temporal evolution



Spatiotemporal assessment of lead (Pb) and cadmium (Cd) contamination in urban tree rings near an industrial smelter: high intraspecific variability but limited spatial differentiation.

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Abstract

Assessing lead (Pb) and cadmium (Cd) concentration in tree rings may provide historical records of environmental contamination, capturing temporal changes and spatial distribution. This study examined heavy metal (HM) bioaccumulation in tree rings to assess the impact of smelting activities using urban trees. Tree rings from urban conifers were collected within a 5 km radius of the smelter to estimate spatiotemporal trends of Pb and Cd concentrations, evaluating the outcomes of contamination reduction measures and interspecies bioaccumulation patterns. Pb isotopic ratios ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$) were also measured to evaluate the Pb origin. Results showed no clear spatial pattern in relation to distance to the smelter, which may be due to the small sampling area. However, Cd bioaccumulation in urban pine was 4 to 7 times higher than in the distant site, 80 km away, indicating a local impact of industrial contamination in the urban area. Temporal analysis for pine showed a decrease of 0.27 mg/kg Cd (47%) between 1990 and 2020, reflecting the potential influence of contamination-reducing measures, while Pb concentrations in pine were 2.7 times higher (increased by 0.06 mg/kg) for the same period. Pine bioaccumulated more Cd than spruce, while spruce accumulated higher levels of Pb compared to pine. Isotope measurement confirmed that the copper smelter is the primary source of Pb. These findings underscore the complex nature of HM uptake in urban trees and suggest that further research is needed to understand the spatiotemporal effects on HM bioaccumulation patterns and which species are best suited for phytoremediation.

Keywords: Heavy metals, contamination, tree rings, smelter, urban trees.

1. Introduction

Urban environments are affected by airborne heavy metal (HM) contamination, primarily from anthropogenic sources (Kumar et al., 2017). HM are found in particularly high concentrations in industrial cities associated with metallurgy, mining operations, and waste incineration facilities (De Silva et al., 2016; Perone et al., 2018; Bi et al., 2020; Briffa et al., 2020). The presence of HM in urban environments poses risks to human health and ecological systems, as soil, water, and vegetation have the ability to accumulate these metals (Li et al., 2001; Binner et al., 2023), leading to chronic exposure and potential toxicity for both residents and wildlife (Jadaa and Mohammed, 2023; Devi, 2024; Edo et al., 2024). Lead (Pb) and cadmium (Cd) are toxic heavy metals with serious health and environmental impacts. Pb affects the nervous system, especially in children (Wang et al., 2009) and is linked to cardiovascular and kidney diseases. Cd is a known carcinogen that accumulates in the kidneys and weakens bones (Järup et al., 1998). In plants, HM can cause disruptions in nutrient uptake, oxidative stress, transcriptomic and enzymatic damage, impaired photosynthesis, and a reduction in biomass and overall development (Zulfiqar et al., 2019; Haider et al., 2021; Matei et al., 2025).

Heavy metals can adhere to fine particulate matter (PM), allowing them to remain suspended in the air and be transported over long distances by wind. The extent of their dispersion depends on particle size, atmospheric conditions, and emission sources (Daggupaty et al., 2006; Soriano et al., 2012), as well as the wind direction in which PM are often more concentrated in the downwind direction from the emission source (Žibret and Šajn, 2008; Khaniabadi et al., 2018). Larger particles tend to settle closer to the source, while smaller ones ($< 2.5 \mu\text{m}$) can travel hundreds of kilometers before deposition (Daggupaty et al., 2006; Hou et al., 2006; Zhang et al., 2018). PM can carry HM directly onto leaves and stems, but only smaller ones can enter ($< 0.1 \mu\text{m}$). Heavy metals in soil dissolve into bioavailable forms influenced by pH and organic matter, then enter roots via passive diffusion or active transport. Once absorbed, they move through the xylem to stems and leaves or are sequestered in root tissues limiting toxicity (Clemens et al., 2002; Matei et al., 2025).

To assess HM dispersion patterns in the environment, airborne pollution monitoring networks are needed, which can include sensors that integrate average exposure conditions. In this context, analyzing tree rings as indicators of environmental contamination offers several advantages, including the ability to reveal pollutant spatial distribution and temporal changes in contamination levels through the absorption of HM by root water uptake (Nabais et al., 1999; Martinelli, 2004; Savard et al., 2006b; Kiss et al., 2019). HM are then translocated from the roots to the trunk and shoots, where they can be retained (Sumiahadi and Acar, 2018). HM are primarily stored in woody tissues of tree species (Li et al., 2020). The mobility of HM in the soil and plant tissues is a key factor to be considered for using tree rings to monitor historical pollution, as it determines the reliability of these indicators for reconstructing metal deposition in the environment (Lepp, 1975). Numerous studies have highlighted the potential of tree ring Pb and Cd concentrations as effective indicators to reconstruct historic metal deposition (Cutter and Guyette, 1993; Savard et al., 2006a; Doucet et al., 2012; Chen et al., 2021) as they exhibit limited radial mobility, particularly in conifers, which have an even wood structure across rings (Watmough et al., 1999; Doucet et al., 2012). However, the potential mobility of HM in xylem tissue varies between tree species, which may have distinct abilities to uptake and accumulate metals in their tissues (Li-qiang et al., 2004; Alahabadi et al., 2017).

In addition, contamination sources can be identified and confirmed using environmental indicators such as Pb isotopes ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$), which help distinguish between natural, industrial, and other anthropogenic emissions such as mining (Savard et al., 2006b; Novak et al., 2010). For example, Savard et al. used Pb isotopes to trace pollution sources in forest trees located outside the city of Rouyn-

Noranda, which differ from urban trees in terms of environmental exposure (Savard et al., 2006b). Acute levels of emissions from complex, heterogeneous contamination sources, including local traffic, construction activities, and multiple industrial processes, can be found in urban areas, leading to specific HM concentrations and isotopic ratios (Yu et al., 2016; Widory et al., 2018).

The use of tree rings in the context of smelter emissions can provide valuable insights for evaluating the evolution of emissions over the years. In this paper, we aim to assess the spatial and temporal patterns of HM contamination in Rouyn-Noranda by quantifying metals bioaccumulated in the tree rings of urban trees. Rouyn-Noranda, located in western Québec, Canada, has a history closely tied to the in-town Horne copper smelter that initiated its activity in 1927 (GLENCORE, 2022). We hypothesized that (1) HM concentrations in tree rings would decrease with distance from the smelter and (2) will vary across the tree species considered. Additionally, we hypothesized that (3) HM concentrations would be higher in earlier tree rings compared to recent rings due to the implementation of pollution-reducing regulations affecting smelter operations. Finally, we expected that (4) the Pb isotopic ratios in the analyzed tree rings would clearly fingerprint smelter emissions.

2. Methods

2.1. Study area

The Horne smelter has been a significant source of HM emissions in the region of Rouyn-Noranda (RN) since its beginning. Operating since 1927, the smelter has released various pollutants into the surrounding environment, including HM and metalloids such as cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), and arsenic (As) (Bonham-Carter, 2005; Canada Government, 2021). In the Rouyn-Noranda area, tree rings have shown high concentrations of heavy metals beginning in the 1940s, with a significant rise after 1960 (Savard et al., 2005). Additionally, isotopic analysis of lead identified the smelter as the primary source of contamination in the nearby natural forest ecosystems (Savard et al., 2006b). The dispersion of these pollutants is also influenced by the prevailing winds. These winds carry the emitted particles across the region, leading to higher concentrations of pollutants in soils and trees in downwind areas (Hou et al., 2006). An assessment of the dispersion pattern, however, has yet to be attempted within the Rouyn-Noranda urban area using trees from private gardens and public parks.

2.2. Tree selection and wood sampling

Trees were selected after a public call for participative science on social media. A total of 63 residents from Rouyn-Noranda expressed interest, alongside participation from the municipal administration. 53 coniferous trees were selected within the urban area limit, including 32 trees from private yards and 21 trees from public parks. The sampled tree species includes 21 white spruce (*Picea glauca* (Moench) Voss), 19 red pines (*Pinus resinosa* Aiton), 4 white pines (*Pinus strobus* L.), 5 larch (*Larix laricina* (Du Roi) K. Koch), and 4 cedars (*Thuja occidentalis* L.) (Fig. 1, Table S1). White and red pines were considered together for the analyses because they are within the same genus and display similar functional traits (Motley, 1949; Wetzell and Burgess, 1994). We chose to focus our analysis on the two most extensively sampled species (Spruce and Pine) to ensure consistency in sampling structure and enhance the robustness and comparability of our results. The other species had too few samples, making meaningful comparisons impossible and rendering the data difficult to interpret. However, the complete data are available in Supplementary materials (Appendix A). Pine and spruce are effective biomonitors for HM due to their long lifespan and ability to accumulate pollutants in both needles and wood over time, providing a reliable record of contamination (Sawidis et al., 2011; Godek et al., 2015).

All 53 trees were located within a 5 km radius of the Horne smelter, but only four trees were located north of the smelter because of limited urban development in this direction. For comparison purposes, ten additional “distant” trees (5 white spruce and 5 red pines) were chosen in Amos, Québec, Canada, a city located roughly 80 km northeast of Rouyn-Noranda, where the influence of the smelter should be low (Henderson and Knight, 2005) but not nonexistent since the fingerprint of the Horne smelter is measured in the air more than 100 km (Daggupaty et al., 2006). Metadata on the maintenance practices of private yards was collected through a survey proposed to the owners to know if additional factors could explain HM concentrations (ex. soil restructuration around the tree, major renovation work of the house or use of pesticides in the garden); however, none of the management variables was significant in our analysis (Appendix A).

For each tree, a 1.2 cm diameter wood core was extracted at breast height (around 1.3 m) with an increment borer. A single core was sampled from each tree to minimize damage, particularly because many trees were located on private properties. This approach was the only feasible option that provided more than enough wood material while remaining acceptable to the property owners. Tree cores were selected for sampling because the trunk, as the largest and most stable organ of the tree, offers a reliable and continuous archive of metal accumulation over time (Aznar et al., 2008; Sevik et al., 2019). Unlike needles, which are responsive to short-term environmental fluctuations, wood tissue allows for reconstruction of long-term contamination patterns (Turkyilmaz et al., 2018; Chen et al., 2021). In the lab, each wood core was processed to obtain two flat, polished faces using a sliding microtome (WSL Core-Microtome, Gärtner and Nievergelt, 2010). This method facilitated tree ring measurement and counting while preventing contamination by wood dust. Cores then underwent oven-drying at 60°C for 3 hours before being stored at room temperature. Manual counting of growth rings was performed under a binocular microscope. Using a steel blade, the last five complete growth rings of each core (44 trees in Rouyn-Noranda and 10 trees in Amos), corresponding to the years 2018-2022, were dissected under a binocular microscope. In addition, the oldest trees from Rouyn-Noranda (5 white spruce and 5 red pines) were also sampled for growth rings corresponding to two other time frames: 1998-2002 and 1989-1993 (Fig S1). Subsequently, around 200 mg of material from each dissected period (2020s, 2000s and 1990s) was obtained with equal weight for each tree ring, and the pooled samples were stored in Eppendorf tubes waiting for metal analysis. In our study, when we refer to 2020, we are specifically considering the tree rings from that year and have not accounted for the lag in pollutant uptake. When interpreting the results, readers should consider that the metals found in the 2020 ring may have originated from emissions occurring over the previous 10–15 years.

In addition, 5 white spruce trees from various directions around the smelter among the 21 sampled, were selected for an exploratory lead isotope characterization (Table S2). The distinct isotopic ratios of lead can help trace its origin, whether it is from natural, industrial, or other anthropogenic emissions (Savard et al., 2006b).

2.3. Lead and cadmium analyses

Pb and Cd are known for their limited translocation, often remaining localized in the growth layers where they are initially absorbed (Cutter and Guyette, 1993). Moreover, studies have shown that conifers, including species such as spruce and pine, are effective biomonitors due to their ability to retain metal signals over time and their widespread distribution in polluted and remote areas (Saladin, 2015; Aleksandrova et al., 2020).

All analyses, including metal concentrations and lead isotopes, were conducted at the INRS-ETE Geochemistry Laboratory, Québec, Canada. The composite wood samples underwent a digestion

process using nitric and hydrofluoric acid within polytetrafluoroethylene containers, followed by gentle heating to concentrate metals. Subsequently, digested samples were treated with ultrapure water and nitric acid. Pb and Cd concentrations within tree rings were determined using Inductively Coupled Plasma Mass Spectrometer (ICP-MS Thermo XSeries) (U.S. E.P.A, 1994; Poupon, 2021). Quality assessment of the heavy metal concentration analyses was ensured by incorporating blank solutions (ultrapure water) and certified reference materials (pine needles 1575a, Mackey et al. (2004) and citrus leaves 1572, Alvarez and Alvarez (1982)) in each batch of samples analyzed. The detection limits were 0.002 and 0.004 mg/kg for Cd and Pb respectively, and the analytical precision for metal concentration measurements varied depending on the tree species and metal analyzed. For Cd, the precision was 3.0% in pine and 10.3% in spruce. For Pb, the precision was 20.4% for pine and 15.2% spruce (10% replicates). The precision for certified reference materials ranged from 3 to 8%.

The isotopic ratios of Pb ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$) were analyzed using a Thermo iCAP Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Samples were filtered in a solution of 0.2% HNO₃. Correction for mass bias during the determination of the isotopic ratios was performed using analyses of SRM 981 (Common lead NIST, USA) after every two samples.

2.4. Prevailing wind direction

The direction of the prevailing winds was integrated as a key parameter for studying the dispersion of HM. This factor was considered in the interpretation of our data, even though no samples were collected from the northeastern zone, a non-urban area directly influenced by the prevailing winds. Wind direction and speed from a meteorological station located in Rouyn-Noranda (Environment Canada ROUYN station, ID number: 10849, latitude: 48°14'45" N ; longitude: 79°02'03" W), were acquired from Environment and Natural Resources Canada's historical data covering the period from 1994 to 2023 (Environment Canada, 2023). The wind direction was measured in tens of degrees and represents the direction from which the wind is blowing. This value represents the average direction at the time of observation aggregated to an hourly interval. To extract the prevailing wind directions from the data, “polarFreq” function from “openair” package (Carslaw and Ropkins, 2012) was used in RStudio environment. This function is designed to generate a polar diagram illustrating the frequency of winds in various directions and speeds.

To create a variable indicating the relative exposure of the sampled trees to the prevailing winds, the Beers’ transformation (Eq. 1) was used (Beers et al., 1966).

$$\text{Aspect} = \cos(\theta_{\max} - \theta) + 1 \quad (\text{Eq. 1})$$

Here, θ is the angle between the smelter and a tree and $\theta_{\max}$ is the angle which is to be assigned the highest numerical value on the transform scale corresponding to the prevailing wind axis (20°, angle obtained from x-axis in the counterclockwise (trigonometric) direction). This approach yields a value between 0 and 2. The closer the value is to 2, the closer the tree is to the prevailing wind axis relative to the smelter; conversely, the closer the value is to 0, the farther the point is. In theory, higher values therefore indicate a higher likelihood of receiving contamination from the smelter.

2.5. Statistical analysis

All statistical analyses and computations were performed using the RStudio software (R Core Team, 2021).

Linear models were used to evaluate how the (log-transformed) metal concentration in the wood of the sampled trees over the period 2018-2022 was affected by exposure to the prevailing winds (Aspect; winds passing over the smelter), by the distance to the smelter (km), by their interaction and by tree species identity. All possible combinations of variables, ranging from the simplest (one variable) to the most complete, including (Eq. 2) and excluding interaction terms, were systematically tested, with models ranked according to the lowest Akaike Information Criterion (AIC corrected for small samples: AICc). We used model averaging to evaluate the relative support for each model. When no single model has an Akaike weight above 0.9, model averaging provides more robust parameter estimates (Burnham and Anderson, 2002; Grueber et al., 2011).

$$\log_{10}[\text{Metal}] = \beta_0 + \text{Species} + \text{Aspect} * \text{Distance} \quad (\text{Eq. 2})$$

where Metal could be either Pb or Cd. β_0 represents the baseline value of the log-transformed metal concentration when all other variables are at their reference levels.

Additionally, the Kruskal-Wallis test was used to further assess significant differences in log-transformed metal concentrations between the studied tree species. The test is adapted to small sample sizes and heterogeneous variance between groups. Subsequently, Dunn's post-hoc test was applied to identify the specific species showing significant differences in metal concentrations.

A Wilcoxon rank-sum test was performed to compare metal concentrations between samples from Rouyn-Noranda and the distant group in Amos. This non-parametric method is appropriate for comparing two groups from small and heterogeneous samples.

To analyze the temporal evolution of pollutant concentrations (Pb and Cd) in tree rings, linear mixed-effect models were used. Year was considered as a fixed effect to assess the general trend in metal concentrations over time, and individual tree identity was included as a random effect since measurements were repeated on the same trees.

3. Results

3.1. Spatial distribution of sampled trees

All trees were located between 0.3 and 4.5 km from the smelter, with the majority located in the southwest direction (Fig. 1). This spatial distribution is due to the location of the city of Rouyn-Noranda relative to the smelter, as well as the presence of Osisko Lake to the east of the smelter and tailings ponds to the north. Prevailing winds in the city also originate from the southwest and northwest. However, for the following analyses, the prevailing winds with the highest frequency were selected, which come from the southwest (Figs. S2 and S3). This aligns with the dominant summer winds, which is also the main growing season for trees. Due to the location of the sampled trees and the direction of the prevailing wind, most of the trees had mid to low exposure to wind passing over the smelter (Fig. S5).

3.2. Lead and cadmium concentration in present tree rings (2018-2022)

Model averaging based on Akaike weights indicated that species identity was the only significant variable explaining metal accumulation patterns in tree rings, suggesting that tree species accumulated metals differently. White spruce had higher Pb concentrations and lower Cd concentrations than pine (Table 1, Fig. 2). Other factors, such as wind and distance, did not significantly affect Cd or Pb concentrations in tree rings (Table 1, Table S3 and S4). The Kruskal-Wallis test confirmed these

differences between species in metal accumulation, with p-values < 0.0001 for both Pb and Cd (chi-squared = 14.951 and 24.699 for Pb and Cd respectively). The Dunn's test indicated that pine trees accumulated significantly lower levels of Pb than spruce (Fig. 2). On the other hand, spruce accumulated lower levels of Cd than pine (Fig. 2).

Table 1: Model-averaged parameter estimates with their 95% confidence intervals for the models for Pb and Cd concentrations (log-transformed) in relation to environmental variables and species identity. These results apply only to trees sampled in Rouyn-Noranda. Each row presents the estimates for each independent variable in the sets of candidate models retained by model averaging. The 95% CI estimates in bold do not include 0 and are significant.

Metal	Parameter	Estimate	Upper CI	Lower CI
Pb	Wind	0.05	-0.23	0.33
	Distance	0.02	-0.13	0.17
	Wind:Distance	-0.16	-0.49	0.18
	Species_Pine	-0.59	-0.84	-0.34
	Species_Spruce	0.59	-0.34	0.84
Cd	Wind	0.00	-0.23	0.24
	Distance	-0.06	-0.18	0.06
	Wind:Distance	-0.02	-0.30	0.26
	Species_Pine	0.76	0.55	0.97
	Species_Spruce	-0.76	-0.97	-0.55

A Wilcoxon rank-sum test indicated that Pb concentrations were similar between trees from Rouyn-Noranda and the distant sites, with p-values of 0.093 for pine and 0.398 for spruce (Fig. 3A, Table S5). In contrast, Cd concentrations in distant pines had levels 4 to 7 times lower than pines from Rouyn-Noranda (Fig. 3B, Table S5). This suggests that while Pb contamination may not differ markedly between the two cities, Cd levels remained significantly elevated in Rouyn-Noranda compared to Amos.

3.3. Lead and cadmium concentration in past tree rings

There was a significant decrease in Cd concentrations in pine between 1990 and 2020 (p-value = 0.02) while Cd concentrations between 1990 and 2000 were similar (p = 0.688). Cd concentrations in 2020 were 0.27 mg/kg lower than in 1990, representing a 47% decrease. In spruce, no significant change in Cd concentrations was observed between 1990 and 2020 and between 1990 and 2000 (p = 0.129 and 0.68 respectively). However, the analysis suggests a slight downward trend in metal accumulation over this period (Fig. S6). The Pb concentrations in pine trees were higher in 2020 and 2000 compared to 1990 (p = 0.026 and 0.005 respectively). There was an increase of 0.04 mg/kg in 2000 and 0.06 mg/kg in 2020 compared to 1990, representing concentrations 2 to 2.7 times higher than those in 1990. No significant change in Pb concentrations was observed in spruce trees over time (Table 2).

Table 2: Temporal variations in Pb and Cd concentrations in Rouyn-Noranda tree rings using linear mixed-effect models: $\log_{10}(\text{Metal}) = \text{Year} + (1|\text{tree})$. "Year" is included as factor and "tree" is specified as a random effect, which accounts for individual differences among the sampled trees (n = 5). The estimate column reports the estimates of the periods in the original unit (mg/kg) obtained as $10^{\wedge}(Y)$. p-values indicate difference between a specific period and Year 1990 (** = p-value < 0.01, * = p-value < 0.05).

Estimate (mg/kg)

Pb	Spruce	Year 1990	0.13 (***)
		Year 2000	0.11
		Year 2020	0.14
	Pine	Year 1990	0.03 (**)
		Year 2000	0.10 (**)
		Year 2020	0.07 (*)
Cd	Spruce	Year 1990	0.15 (**)
		Year 2000	0.14
		Year 2020	0.06
	Pine	Year 1990	0.59
		Year 2000	0.65
		Year 2020	0.32 (*)

3.4. Lead origin

Isotopic contents of Pb in tree rings were compared with values reported by Savard et al. (2006) and Hou et al. (2006) to identify possible pollutant origins. These studies established the isotopic ranges characteristic of smelter-derived Pb contamination (Table 3). Three of the five analyzed trees fall within the isotopic ranges of the smelter origin for both the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. For the South 1 and Osisko Lake sites, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was approximately 1.1 and the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio was around 2.15 (Table 3). These values are in between the smelter signature and the normal Canadian urban air signature (Sturges and Barrie, 1987). Finally, the $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratios recorded for all specimens were remarkably consistent, ranging from 0.99 to 1.10.

Table 3: Measurements of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in the last tree rings of the five selected white spruce trees, in Rouyn-Noranda. The reported signatures from different Pb sources are also indicated for Horne (Hou et al., 2006; Savard et al., 2006b; Widory et al., 2018) and Sudbury (Widory et al., 2018) smelters, along with Canadian (Carignan and Gariépy, 1995) and American (Simonetti et al., 2000) urban air signature.

Tree	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
West	1.01	2.30
North	1.03	2.29
Osisko Lake	1.10	2.17
South 1	1.10	2.18
South 2	1.02	2.33
Horne smelter signature	0.92 to 1.03	2.20 to 2.50
Sudbury smelter signature	1.15	2.15
Canadian urban air signature	1.15 to 1.17	2.05 to 2.10
American urban air signature	1.17 to 1.23	2.00 to 2.07

4. Discussion

4.1. Metal contamination in the city of Rouyn-Noranda

Higher Cd concentration was detected on studied trees in Rouyn-Noranda in comparison to those in Amos. Values in Amos were comparable but higher than those at unpolluted sites located 800 km north of the Horne smelter, which showed Pb and Cd concentrations ranging from 0.01 to 0.03 mg/kg (Savard

et al., 2005). The values from these unpolluted sites are three times lower than the median Pb concentrations and nine times lower than Cd levels found in this study near the Horne smelter, with more than 73% of Pb data and 94% of Cd data exceeding 0.03 mg/kg (Fig. 2). Historical data measured in past tree rings in Rouyn-Noranda region before 1930 indicated that average concentrations of Pb were below 0.1 mg/kg and Cd below 0.2 mg/kg (Savard et al., 2005). Such values are similar to those of natural reserves or parks, where anthropogenic impact is minimal and Pb concentrations are typically below 0.1 mg/kg (Bindler et al., 2004). In our case, 53% of our Pb data and 70% of our Cd data exceeded these levels of past concentrations (Savard et al., 2005, Fig. 2). These comparisons strongly suggest that emissions from the Horne smelter could have contributed to heavy metal accumulation on the trees of Rouyn-Noranda. These elevated values show that urban areas, particularly sites close to the smelter and other industrial sources, experience significantly higher levels of metal contamination compared to forested regions. However, typical concentrations of heavy metals in plants are not well documented, particularly for urban trees. There could be considerable variation due to differences in study conditions such as soil characteristics, plant species, and analytical methods. All these aspects can impact reported thresholds for normal and toxic heavy metal concentrations (Table 4).

The isotopic values of Pb, when compared with established ranges in the literature (Savard et al., 2006b; Komárek et al., 2008; Widory et al., 2018), confirm the smelter as the primary source of this HM concentrations.

Table 4: Summary of reported Pb levels in tree rings across various contexts found in the literature, documented in mining areas, regions near copper smelters, and natural reserves. It summarizes both background or historical concentrations and the maximum levels recorded.

Context	Location	Past/Background	Maximum concentration	References
Mining	Duparquet, Québec, Canada	Past: 0.05 mg/kg	0.25 mg/kg	(Arteau et al., 2020)
Mining	Murdochville, Gaspé, Canada	Past: 0.05 mg/kg	0.55 mg/kg	(Aznar et al., 2008)
Copper smelter	San Luis Potosi, Mexico	Background: 0.35 mg/kg	Up to 1.4 mg/kg	(Beramendi-Orosco et al., 2013)
Copper smelter	Příbram, Czech Republic	0.02 mg/kg	Up to 0.8 mg/kg	(Mihaljevič et al., 2008)
Copper smelter	Rouyn-Noranda, Québec, Canada	Background: 0.03 mg/kg Past: <0.1 mg/kg	Up to 1 mg/kg	(Savard et al., 2006b)
Reserves and parks	Sweden	< 0.1 mg/kg	-	(Bindler et al., 2004)

According to Savard et al. (2004), the highest concentrations of Pb and Cd found in forest ecosystems near the Horne smelter were 1 mg/kg and 0.6 mg/kg, respectively, for sites that were more than 9 km away from the smelter. Arteau et al. (2020) reported a maximum value of [Pb] of 0.25 mg/kg in Abitibi region, while Aznar et al. (2008) indicated that concentrations remain below 0.55 mg/kg in Eastern Canada contaminated sites. Regarding Cd, few studies have specifically focused on this metal. However, we found that concentrations near a copper smelter in China were reported to be less than 0.6 mg/kg, which is lower than the values observed in our study (Cui et al., 2023). In our study, the maximum concentrations observed in the urban environment of Rouyn Noranda are notably higher, reaching 2.29 mg/kg for Pb and 1.24 mg/kg for Cd (Table S6). Urban areas might experience additional sources of HM contamination such as road dust or past leaded gasoline (Duzgoren-Aydin, 2007; Yang

et al., 2024). While the smelter is a significant source of pollution, it is important to consider that these other urban background sources may also contribute to the elevated Pb and Cd levels observed in the urban trees (Savard et al., 2006b). Road traffic can generate significant Pb contamination through the resuspension of historically deposited lead from gasoline, while construction activities and deteriorating infrastructure (e.g., lead-based paints, corroding pipes) may also release other metals into the environment (Thornton, 1992; Zwolak et al., 2019; Yang et al., 2024). Urban areas might also experience soil decontamination over time, which could further complicate the interpretation of our results. In the 1990s, a large-scale soil decontamination effort took place in the Notre-Dame neighbourhood of Rouyn-Noranda, the nearest to the Horne smelter. This intervention involved the removal of 6 inches of soil across more than 580 affected properties. After 1990, soil decontamination was carried out if the owners accepted the decontamination offer (Gagné, 2007; Bilodeau et al., 2020). A survey conducted on decontamination processes did not allow us to establish a link between these practices and any potential impact on our samples (Appendix B). Indeed, none of our respondents reported having carried out soil decontamination, which may be due to their recent residence in the house and their lack of awareness regarding the property's history. Additionally, 7 respondents (30%) indicated that they had performed soil addition when planting the sampled tree (Appendix B).

4.2. Metal concentration in relation to distance from the smelter within the urban perimeter

Our study reveals that distance from the HM source was not a relevant parameter in our analysis, despite our initial hypothesis that increasing distance from the pollution source would lead to a corresponding decrease in these concentrations. One plausible explanation for this outcome is the proximity of all sampled sites to the smelter, which may have constrained our ability to detect distance-related effects. Studies have shown that soil contamination originating from the Horne smelter can extend up to 100 km (Daggupaty et al., 2006; Hou et al., 2006). In addition, other studies have also demonstrated that metal concentrations often follow a clear gradient within a 5 km radius, similar to our study area, with urban sites closer to the smelter exhibiting significantly higher soil metal concentrations (Gagné, 2007; Bilodeau et al., 2020). These results suggest that distance-related patterns might still be expected in the range of our study. Additionally, the height of the chimneys plays a critical role in determining the distance over which heavy metals can be dispersed. Higher chimneys release pollutants at greater altitudes, allowing the particles to travel longer distances before settling (Romeiro et al., 2020). For certain heavy pollutants like Pb, faster deposition is expected, while finer and lighter particles have longer atmospheric lifetimes and can be transported over greater distances (Fergusson and Stewart, 1992; Daggupaty et al., 2006). The deposition of Cd particles occurs within 10-20 km from the emission source, which means that the 5 km perimeter of this study may not allow for precise understanding of Cd attenuation with distance (Fergusson and Stewart, 1992). Additionally, the smelter's operational practices determine the optimal time for emission by considering the direction of wind and its potential impact on dispersion. Consequently, it has been shown that Mount Powell, in the northwest of the city center of Rouyn-Noranda, had higher contamination levels compared to the urban area (Bilodeau et al., 2020).

As shown in Figure 1, the sampling distribution is uneven, with only four trees located north of the smelter and a small number of trees sampled windward from the smelter, an area where Osisko Lake creates a natural barrier. This spatial imbalance may affect our ability to detect directional pollution trends. Future studies with a broader and more evenly distributed sampling design would improve this directional evaluation and provide a clearer understanding of pollution dispersion patterns. However, such studies should focus on natural forests rather than urban environments, in order not to be constrained by specific urban geography. In addition, the direction from which the wood sample is taken could be important, as some metals, such as Nickel and Cobalt, tend to accumulate more in the

direction of pollution (Key et al., 2023), although this has not been observed for Chromium (Pulatoglu et al., 2025). To date, no such evidence exists for Pb and Cd. In our study, we were unable to assess this aspect because only one core sample per tree was collected, in order to minimize damage to trees located in private yards and to encourage owner participation. We acknowledge that collecting multiple cores on selected trees could represent a valuable improvement for future analyses.

4.3. Temporal variation of heavy metal in tree rings

The temporal differences observed in metal concentrations in pines, particularly the decrease in concentration of Cd between 1990 and 2020, provide insights into the evolution of environmental contamination in urban areas. The increase in Pb concentrations indicates that Pb contamination remains a persistent issue despite regulatory efforts aimed at reducing emissions. Several factors can contribute to this trend. First, historical industrial activities and leaded gasoline have left significant lead deposits in urban soils, which can continue to affect vegetation (Duzgoren-Aydin, 2007; Nazari Heris et al., 2020; Wade et al., 2021). Unlike Pb, Cd has fewer prominent sources in urban environments. Its primary sources include industrial activities such as mining and battery production (Thornton, 1992). The observed decrease in Cd concentrations in recently formed growth rings, in contrast to the persistent levels of Pb, can also be explained by the differences in emission patterns and regulatory measures over time. The smelter emitted Pb at levels reaching thousands of tons until 1995, followed by hundreds of tons, thereafter. In contrast, Cd emissions were significantly lower, amounting to only tens of tons after 1995 (Fig. 4) (Bonham-Carter, 2005; Savard et al., 2006a). This suggests that, unlike Cd, whose levels have shown a more marked decrease due to fewer residual sources, Pb contamination remains persistent in the urban environment. The analyzed tree rings do not seem to effectively reflect the historical reduction trends in emissions from the Horne smelter, at least for Pb. This may be due to the time span being too short or because plants tend to absorb more metals in their roots and shoots with increasing contamination (Kahle, 1993).

It is important to highlight that the limited number of samples for the temporal analysis (only five individuals per species) may have affected the robustness of the results, which increases the risk of Type II errors, where actual trends in heavy metal accumulation may go undetected due to limited statistical power. This small sample size is partly due to the relatively young age of trees in urban areas, which limits the amount of growth rings available for analysis. In forests, trees can provide a longer historical record of metal accumulation, allowing for a more comprehensive study of temporal trends. Expanding the study to include more trees or spanning a greater range of years would likely improve the ability to detect finer trends in both Cd and Pb concentrations.

Interestingly, past studies have found a temporal lag of approximately 13 to 15 years between the emission of pollutants and their possible absorption into tree rings (Savard et al., 2006b; Aznar et al., 2008; Arteau et al., 2020), due to the time required for HM to migrate in the soil-root-trunk continuum (Sumiahadi and Acar, 2018). However, it could present a challenge if we want to compare our tree ring data to emission records from the smelter, as it is difficult to account for the temporal lag between metal emissions and absorption in the trees. In our case, this means that tree rings from 1990 may contain metals emitted over the previous 10–15 years rather than 1990 conditions (Fig. 4). Therefore, when interpreting the data and assessing the timeline of contamination events, this lag must be carefully accounted for to accurately evaluate the impact of the smelter and the effectiveness of environmental regulations.

4.4. Species differences

In this study, we observed that pine trees accumulated more Cd than spruce, while spruce showed higher concentrations of Pb compared to pine. Heavy metals can enter plants through multiple pathways, including root uptake from soil, foliar absorption via stomatal gas exchange, and direct deposition of airborne particles on leaves or bark (Clemens et al., 2002). Disentangling the relative contribution of each mechanism to metal uptake in our trees remains challenging. One hypothesis is that root uptake dominates in the absorption of HM in our study. Indeed, foliar absorption through stomatal gas exchange could play a role in metal absorption in urban environments, but it is mainly relevant for ultrafine particles ($< 0.1\mu\text{m}$). Heavy metal bioaccumulation varies by species due to differences in metal uptake, storage, and detoxification mechanisms according to the tree anatomical structure (Koç et al., 2024; Pulatoglu et al., 2025). Some species accumulate more metals due to their tissue affinity for certain metal ions and their ability to store them in specific compartments, such as vacuoles or cell walls, thereby reducing their toxicity (Peng and Gong, 2014). Currently, the specific differences in metal bioaccumulation between pine and spruce species have not been examined in depth. These differences in bioaccumulation may be related to each species' unique characteristics and their distinct metal uptake mechanisms (Li-qiang et al., 2004).

Spruce, with a slower growth rate and a superficial root system, may differ in its metal uptake capacity compared to pine, which has a faster growth rate and deeper taproots (Puhe, 2003). These differences in root architecture could influence the efficiency with which each species absorbs metals from the soil (Lilles and Astrup, 2012; Swidrak et al., 2013; Li et al., 2020). Conversely, bark properties do not appear to influence the accumulation of Pb and Cd, as these metals are primarily absorbed through the cambium and fixed to the cell walls during growth (Catinon et al., 2008). Furthermore, each species may develop unique adaptations to cope with environmental stress, such as the production of intracellular chelators or the storage of metals in root vacuoles, which limits their translocation to aerial parts (Clemens et al., 2002) and could explain the observed differences between pine and spruce (Saladin, 2015; Pajević et al., 2016). For example, pine trees have shown greater resistance to Pb compared to spruce (Seiler and Paganelli, 1987), which may explain the relatively low Pb accumulation observed in the sampled tissue of pine. The variability in analytical precision for Pb and Cd concentrations may affect the interpretation of the data. We report a maximum precision variability of 20.4% for Pb and 10.3% for Cd. With [Pb] mean values of 0.07 and 0.31 mg/kg for both pine and spruce, a difference lower than 0.01 and 0.06 mg/kg may just be due to analytical precision. With [Cd] mean values of 0.50 and 0.11 mg/kg for both pine and spruce, a difference lower than 0.05 and 0.01 mg/kg may just be due to analytical precision. However, the standards used in our analyses underwent a much more rigorous homogenization process compared to our wood samples, and the variability range was from 3% to 8%. As a result, this number represents both intra-sample variability and analytical error.

Tree species capable of accumulating heavy metals in their wood are particularly important for phytoremediation studies, as they can help assess long-term pollution trends and contribute to environmental remediation efforts (Tangahu et al., 2011). Wood, as the largest organ of the tree, offers substantial storage capacity for contaminants over time. However, it generally accumulates lower concentrations of heavy metals compared to needles or bark (Koç et al., 2024; Koç et al., 2025). Our results indicated that pine accumulates significant levels of Cd and spruce accumulates more levels of Pb, suggesting their potential specific role in monitoring and mitigating heavy metal contamination. They can help stabilize contaminants and reduce their bioavailability in soils.

Tree ring analysis presents several methodological challenges, particularly regarding the uptake of heavy metals by trees. Heavy metals can enter tree rings through various routes, including leaves, the root system, and bark. However, the relative importance of these pathways can vary depending on

species and local conditions (Lepp, 1975). While the uptake of heavy metals through roots is generally considered the most significant route (Padmavathiamma and Li, 2007; Ali et al., 2013; Sumiahadi and Acar, 2018), variability in metal absorption and accumulation is influenced by factors such as root exposure, selective uptake, and fixation mechanisms, which differ among species, contamination types, and soil conditions (Balouet et al., 2007; Beramendi-Orosco et al., 2013). Ideally, each tree species must be assessed individually for precise analysis, an aspect which was not targeted by our study.

5. Conclusion

The analysis of urban tree rings provided insights into HM bioaccumulation, showing that pine trees accumulated more Cd than spruce, while spruce trees exhibited higher concentrations of Pb compared to pine. The results highlight the importance of considering species-specific traits when analyzing environmental contaminants. The study highlights that species differ in their capacity to accumulate heavy metals, indicating that only certain species may be suitable candidates for phytoremediation purposes. Contrary to expectations, no clear reduction in HM concentrations within the 5 km distance from the smelter was observed in our study. However, it was established that Cd bioaccumulation in Rouyn-Noranda is 4 to 7 times higher than in Amos, suggesting a localized impact of Horne smelter contamination in the urban area. Additionally, a decrease in Cd bioaccumulation over time was observed in pine, likely reflecting the effects of pollution-reducing measures implemented by the smelter. In contrast, Pb bioaccumulation in pine increased across the years, indicating a more persistent presence of Pb in the environment despite regulatory changes. Nevertheless, the smelter isotopic signature of the Pb in tree rings was confirmed by the measured $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ values. Future research is needed, particularly over different time scales, to better understand temporal patterns of heavy metal bioaccumulation in the study area. Additionally, given the ability of certain tree species to accumulate heavy metals in their wood, further studies should explore their potential role in phytoremediation. Understanding species-specific accumulation capacities could provide valuable insights for developing nature-based solutions to mitigate soil and atmospheric contamination.

6. Glossary

Cd: Cadmium

HM: Heavy metal

Pb: Lead

7. Conflict of Interest

The authors declare that the Horne smelter contributed in part to the financing of the study but did not interfere in any phase of the analyses or interpretation of results.

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9. Author Statement

Elsa Dejoie: Writing – review & editing, Writing – original draft, Conceptualization, Methodology, Formal analysis, Visualization. **Marc-André Lemay:** Writing – review & editing, Formal analysis. **Annie DesRochers:** Writing – review & editing, Conceptualization, Supervision, Funding acquisition. **Nicole J. Fenton:** Writing – review & editing, Conceptualization, Supervision, Funding acquisition. **Joëlle Marion:** Writing – review & editing, Methodology. **Martine M. Savard:** Writing – review & editing. **Trevor J. Porter:** Writing – review & editing. **Daniel Proulx:** Writing – review & editing, Methodology. **Fabio Gennaretti:** Writing – review & editing, Writing – original draft, Conceptualization, Supervision, Project administration, Funding acquisition.

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11. Data availability

All data used in this paper is available in dataset S1.

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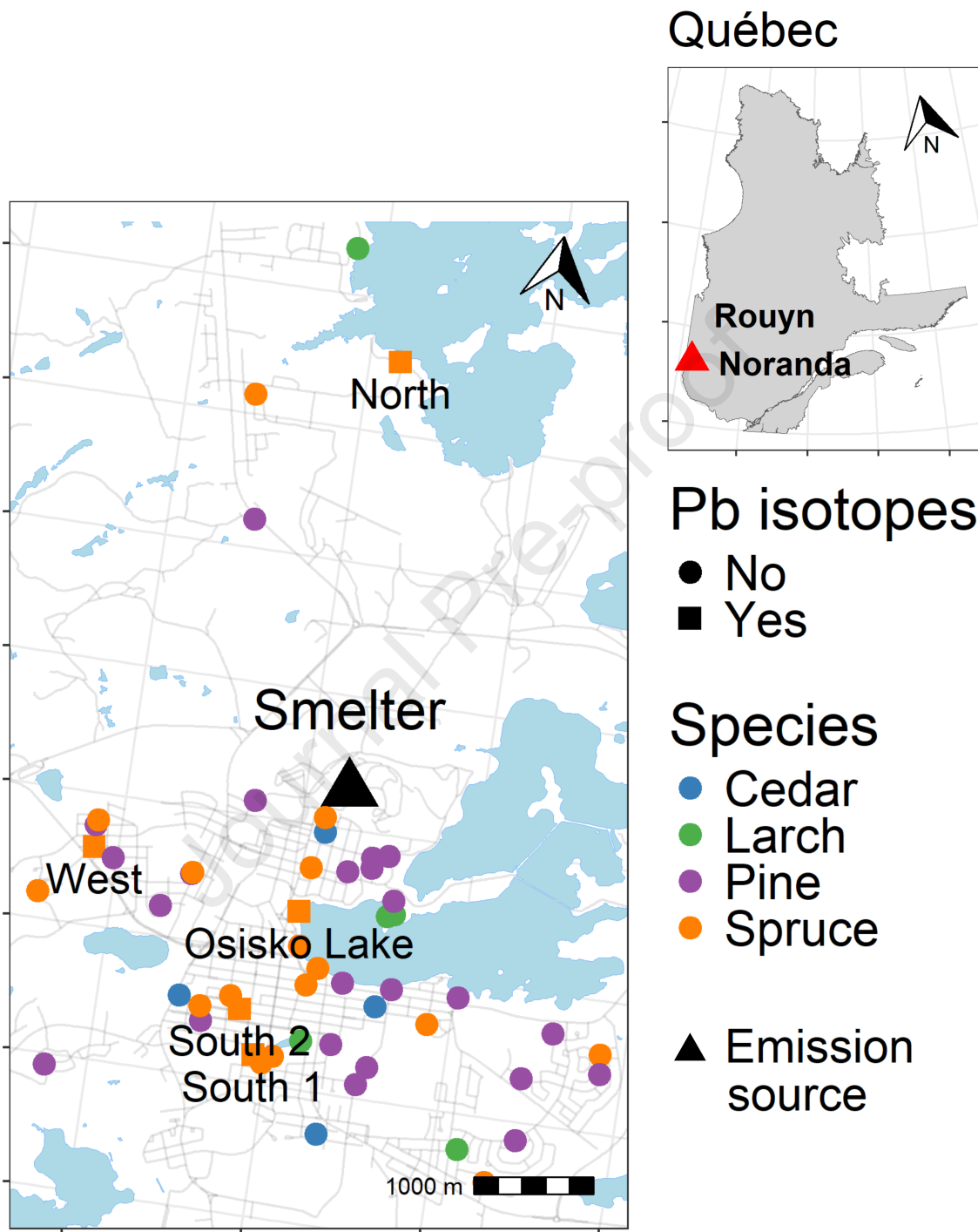
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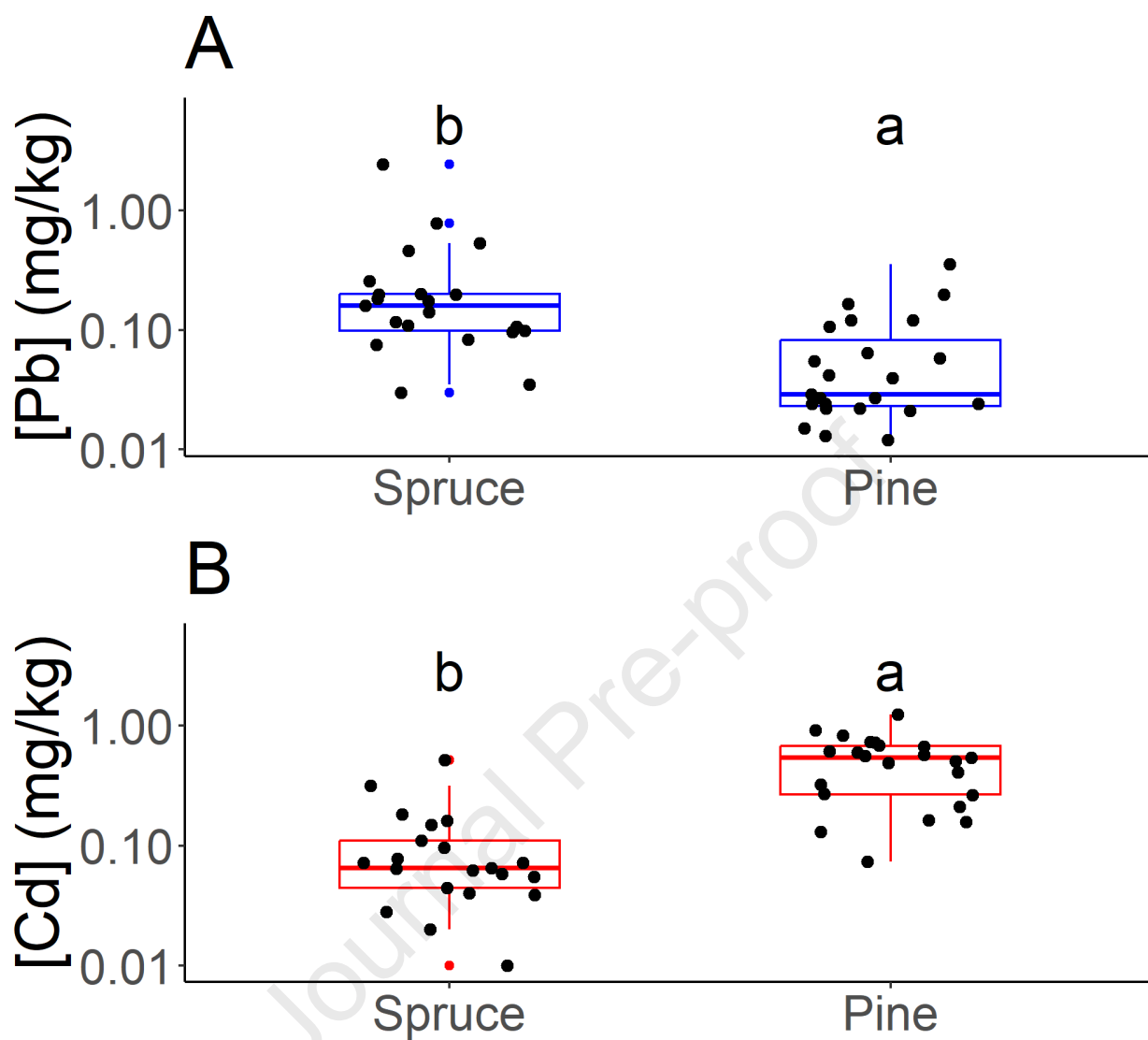
Figure 1: Species and spatial distribution of the selected trees in the urban area limit of the Horne smelter, Rouyn-Noranda (Québec, Canada). Heavy metal concentration was measured from all trees, and only some trees analyzed for lead isotopes (refer to legend). Streets (represented with black lines) and lakes (shaded polygons with blue lines) are displayed as background features to provide geographical context.

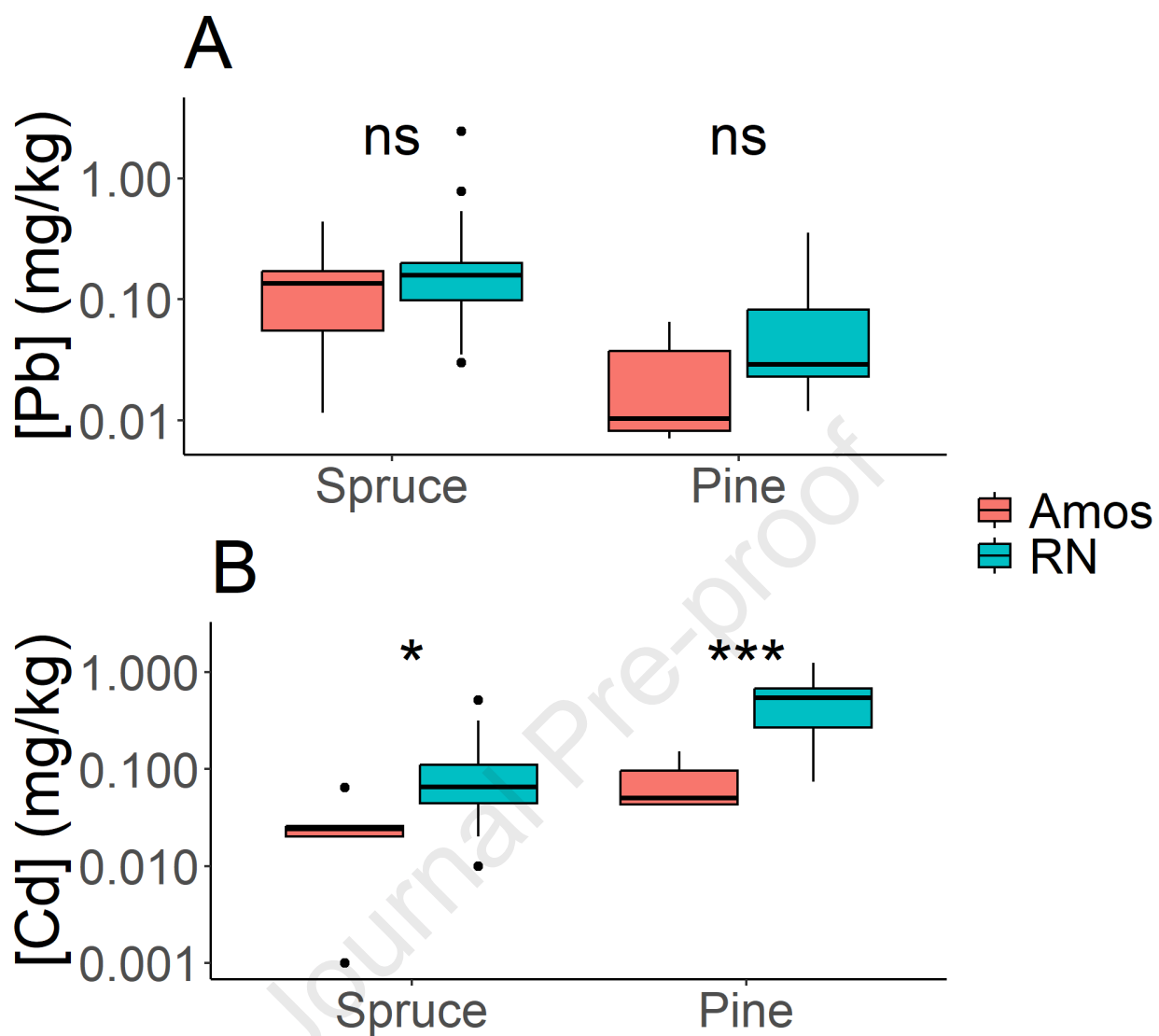
Figure 2. Concentration of (A) lead and (B) cadmium by species in Rouyn-Noranda samples. Boxes represent the interquartile range (Q1 to Q3), horizontal middle line are the median, and bars extend to the most distant data points that are not considered as outliers (values exceeding 1.5 times the interquartile range from the quartiles). Y-axes are all mg/kg but use a log10 scale. Letters show the results of Dunn's post-hoc test to identify which species exhibited significant differences in their medians (Table S6). Boxes sharing the same letters are not significantly different from each other.

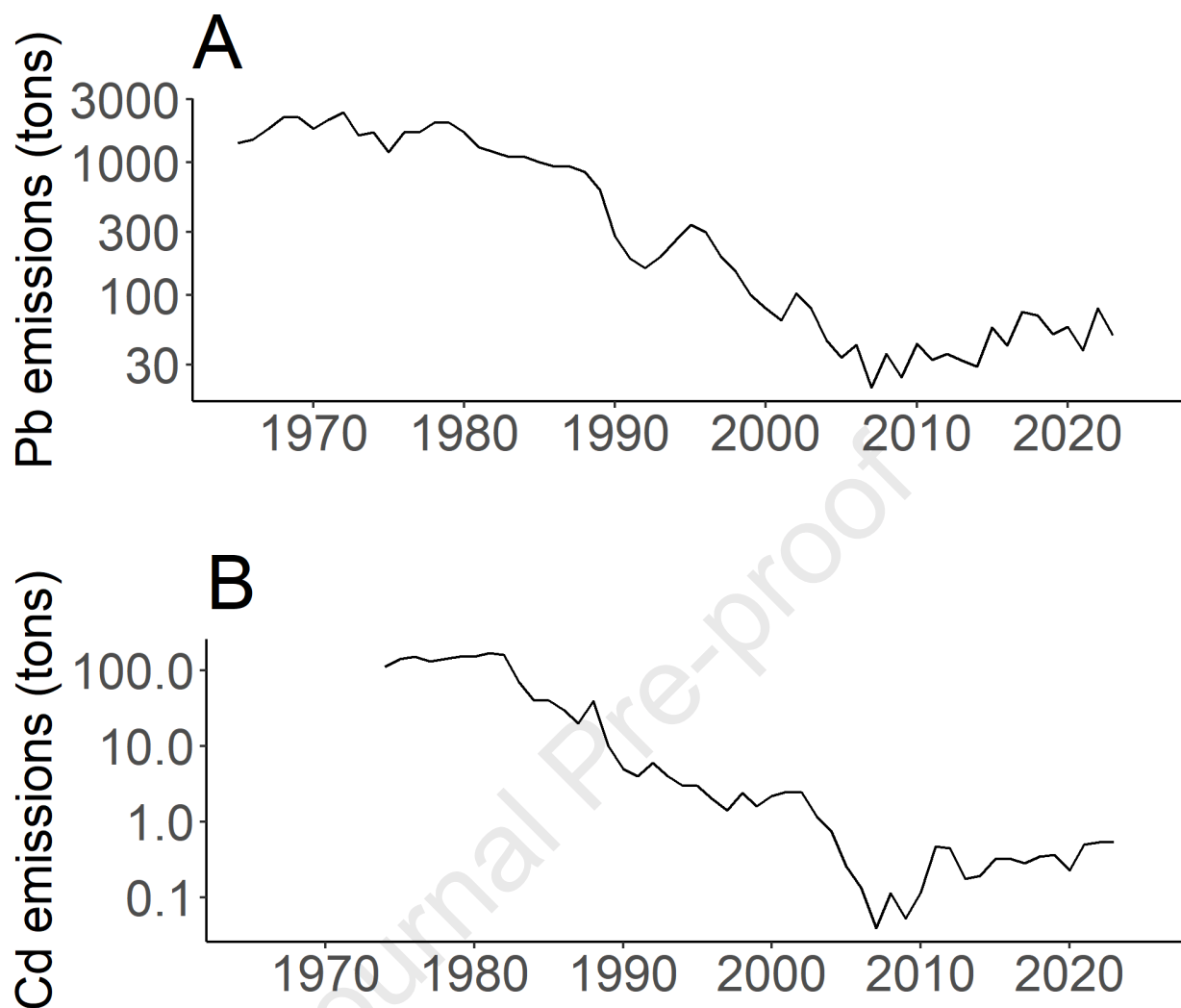
Figure 3: Concentrations of (A) Pb and (B) Cd by species and location (distant (Amos) vs. Rouyn-Noranda (RN)). Y-axes are all mg/kg but use a log10 scale. Statistical significance determined by Wilcoxon test is indicated as follows: ns = not significant, *** = p-value < 0.001, * = p-value < 0.05.

Figure 4: Data on atmospheric emissions processed by the Horne Smelter per year from (A) 1965 to 2023 for Pb and from (B) 1975 to 2023 for Cd. The data from 1965 or 1975 to 2001 originate from the GSC MITE Point Sources Project of the Geological Survey of Canada (Bonham-Carter, 2005). The data from 2002 to 2023 come from the National Pollutant Release Inventory, which compiles pollutant emissions and transfers reported by industrial facilities across Canada.









Highlights

- Tree rings are used for spatiotemporal quantification of heavy metals in the urban area
- No spatial pattern was observed in a 5 km area around the copper smelter
- Cd concentration is 4 to 7 times higher in the urban pines than in distant city (80km)
- Pine bioaccumulated more Cd and spruce bioaccumulated more Pb
- Cd in tree rings was lower in 2020 compared to 1990 for both pine and spruce

Declaration of Interest Statement

The authors declare that the Horne smelter contributed in part to the financing of the study but did not interfere in any phase of the analyses or interpretation of results.