If Trees Could Talk - Dendrochemistry, a Promising Method for Understanding Pollution History

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Degree of Master of Science (120 credits)
with a major in Earth Sciences
60 hec

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2023 B1248

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ISSN 1400-3821

B1248
Master of Science (120 credits) thesis
Göteborg 2023

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Abstract

Heavy metal pollution presents a significant environmental challenge in the Anthropocene era, and understanding pollution history is crucial to address historical pollution and implementing effective mitigation measures. This study stands among a few comprehensive dendrochemical investigations that utilized an extensive dataset and energy dispersive X-ray fluorescence (ED-XRF) technique to reconstruct the contamination history of As, Cd, Cu, Ni, Pb, and Zn, with a focus on Cu. Twenty-two samples from European aspen (*Populus tremula*) and 15 soil samples were collected from an abandoned copper mine in Åtvidabergs municipality, with the aim to evaluate dendrochemistry as a method to investigate contamination history.

Soil samples exhibit high variability in contamination levels and pH over short distances, revealing a complex soil pollution picture and a poor correlation between heavy metal concentration in soil and tree-ring concentration. Concurrently, significantly higher tree-ring concentrations and variances are observed in the averaged dendrochemical profile and in individual samples, in the following order: Cu > Ni > As > Zn > Pb > Cd . Correlations with first difference and detrended data show a weak relationship with short-term climatic variations. However, a collective signal of increased dendrochemical anomalies during climatic conditions favoring high water flow is evident, suggesting dendrochemistry as a potential alternative for the reconstruction of past hydrological variations. Dendrochemical methods and European aspen demonstrates potential for recording environmental changes. Nevertheless, lower trace element concentrations in samples from the mines compared to the unpolluted site highlight limitations. For dendrochemistry to become a reliable tool for environmental investigations, future research should refine approaches for grouping climatic variables, understand the effects of different water sources on trace element uptake, and explore various plant parts to obtain a more accurate picture of historical contamination events. It is also essential to examine the high variability within the Populus genus.

Addressing these challenges will contribute to establishing dendrochemistry as a valuable tool for understanding historical pollution events and their ecological impacts. Ultimately, this research will shape future mitigation and restoration efforts for ecosystems impacted by anthropogenic activities and pollution.

Acknowledgements

I would like to begin by expressing my gratitude to my supervisor, Hans Linderholm. In my first year of the Geoscience program at the University of Gothenburg, Hans mentioned dendrochemistry in passing during a lecture. Since then, my time at the university has led me toward dendrochemistry, resulting in both a bachelor's thesis and now a master's thesis on the subject. I am extremely grateful for the opportunity to dive into this new and exciting research area, and for all the time, support, and guidance that has been provided by him, starting from my bachelor's thesis up until today. I would also like to thank Björn Gunnarson at the Dendrolab at Stockholm University for granting access to the dendro laboratory, all his help with analyses, support, and his genuine interest in my work.

Special thanks also go to Mauricio Fuentes. You have been a tremendous support throughout this work and have always taken the time to assist me and answer my questions on everything from dating tree samples and statistical analyses to thoughts on music and philosophy. I would also like to express my gratitude to Kristina Seftigen, Jesper Björklund, and Petter Stridbeck at the GULD Laboratory. Your input and demonstrated interest are very much appreciated and have been of great assistance. Extra thanks go to Petter Stridbeck for all his help with data management and processing.

Last but not least, I want to thank my partner, Frida Ekström, and our two cats, Ozzy and Mikkel-räv. This project has been fun, but it has also taken a lot of time and been stressful from time to time. My cats have taken this seriously and assumed the role of emotional support animals without me having to ask. The greatest thanks though, goes to Frida. You are always there for me and have been an enormous support during times of stress. Without you, this project would not be possible. All my love is directed to you.

Contents

1 Introduction

Since the onset of the Industrial Revolution, human impact on Earth's systems has accelerated. In early 2000s Crutzen coind the term Anthropocene, a geological era marked by significant human influence on Earth's systems, leading to various environmental consequences, including heavy metal pollution (Crutzen, 2016; Nachana'a Timothy, 2019). Heavy metals naturally occur in soil pedogenic processes. However, human activities related to urbanization and industrialization have increased their circulation in ecosystems (Sarkar, 2002). Ecological heavy metal pollution involves both essential and non-essential elements, some of which pose high ecotoxicological risks (Desideri et al., 2010; Kabata-Pendias & Szteke, 2015) The occurrence, transport, and toxicity of heavy metals are primarily determined by the properties of the element, although soil properties like texture, temperature, moisture, pH, redox conditions, and salinity also play a key role (Alloway, 2012). Increased greenhouse gas emissions predicted to alter hydrological patterns, raise temperatures, and increase extreme events' frequency (IPCC, 2014), risk exacerbating heavy metal pollution and its ecotoxic consequences (Alloway, 2012; Biswas et al., 2018). Making Sweden vulnerable with over 90,000 polluted sites identified, many related to mining and metallurgy (SGI, 2022).

Continuous environmental monitoring is crucial for understanding the long-term impact of polluted sites and the influence of a changing climate (Biswas et al., 2018; Nachana'a Timothy, 2019; Owen et al., 2020). Dendroecological methods, such as dendrochemistry, can provide long-term proxy data for pollution history by analyzing the chemical composition of annually formed tree rings to create a chemical profile reflecting the tree's living environment (Lepp, 1975; Watmough, 1999). The studies are few; however, dendrochemical methods have been shown to successfully identify dendrochemical signals related to mining and metallurgy activities (Cui et al., 2013; Guyette et al., 1991; Zyskowski et al., 2021).

1.2 Aim of Study

Heavy metal pollution presents a significant environmental challenge in the Anthropocene era (Briffa et al., 2020). Ever-increasing economic growth and the expansion of human civilization have resulted in an unprecedented release of anthropogenic pollutants (Biswas et al., 2018) with the mining industry alone producing billions of tons of toxic waste annually (Owen et al., 2020). As the "Green" energy revolution heavily relies on non-renewable raw materials, mining and its waste production are predicted to increase in the near future (Herrington, 2021).

Despite the strengthening of environmental legislation in recent decades (Michanek & Zetterberg, 2012) the effects of historical contamination may continue to impact ecosystems and humans for years to come (Alloway, 2012; Nachana'a Timothy, 2019). Acquiring knowledge of pollution history is crucial for developing strategies to address historic pollution and implement effective mitigation measures for the future (Chen et al., 2021). Dendrochemistry is emerging as a promising tool for providing high-resolution temporal and spatial pollution histories, which can help in understanding pollution dynamics and monitoring the effectiveness of environmental regulation and mitigation programs (Binda et al., 2021). As a relatively young field of research, dendrochemistry has seen limited studies. Most are based on relatively few trees (3-7 trees), and studies on larger sample sets are rare (Muñoz et al., 2019; Odabasi et al., 2016). Further investigation is therefore required for dendrochemistry to become a commonly used approach as an environmental forensic tool.

This study aims to evaluate dendrochemistry as a method to describe the contamination history at Närstads mining field, a abandoned copper (Cu) mine located in Åtvidaberg municipality. This will be achieved by investigating dendrochemical signals in 22 European aspen (*Populus tremula*) using Energy Dispersive X-Ray Fluorescence (ED XRF) (19 from the mine site and three from a control site). By revealing dendrochemical signals' responses to climatic variations, soil metal concentration, and pH, this study aims to contribute relevant knowledge to drive further the development of dendrochemical approaches for better understanding and management of historical and future heavy metal pollution.

1.3 Trace Elements or Heavy Metals:

1.3.1 Definitions and Implications

Heavy metals naturally occur in soils, originating from parent materials through pedogenetic processes, with varying concentrations, some in trace amounts below certain analytical detection limits (Alloway, 2012). Understanding their distribution and impact is crucial, as human activities have significantly altered their circulation, posing risks to ecosystems and health (Crutzen, 2002; Nachana'a Timothy, 2019). Heavy metals are commonly referred to as elements with a specific density greater than 5g cm-3 or a relative atomic mass above 20 (Barceló & Poschenrieder, 1990) or 40 (Nachana'a Timothy, 2019). They encompass essential, beneficial, and directly toxic elements with no known vital biological function. Although all nutrients can become toxic in excess, that alone is not a criterion for classifying an element as a heavy metal. The terms "trace element" and "heavy metal" are often used interchangeably; however, in this context, i will use "trace element", TE for short. As it refers to the element's natural occurrence in soil, instead of its toxic properties, and is the preferred term among authors (Barceló & Poschenrieder, 1990).

1.4 Soil Characteristics Affecting Trace Element Uptake

TE can be divided into total and bioavailable concentrations. Total concentration encompasses all forms of TE in the soil, including ions bound to minerals, organic and inorganic complexes, organic matter, clays, oxides, carbonates, and free ions. Bioavailable TE is the fraction of total soil concentration potentially available for plants to absorb. This includes hydrated, ionized, free ionic, soluble inorganic ion pair, and low molecular weight organometallic chelate species. The Bioavalibile TE are strongly influenced by soil characteristics, such as pH, redox potential, clay content, and soil organic matter (SOM), influence the availability and uptake of TE (Antoniadis et al., 2017).

1.4.1 Role of pH in Trace Element Bioavailability

pH is considered the primary factor affecting TE bioavailability. Low pH influences the strength of cationic absorption by soil colloids, organic matter, clay minerals, and particles, as well as Fe/Al oxides and thereby increase the bioavailability. While higher pH promotes TE hydrolysis. In soil, hydrated TE species require electrostatic attraction to form reversible outer-sphere complexes. Hydrolysis collapses the hydration "pillow," allowing less reversible inner-sphere complexes on colloid surfaces, reducing bioavailable TE (Alloway, 2012).

1.4.2 Influence of Redox Potential on Trace Element Solubility

Redox potential refers to electron activity that affects the solubility of TE in soil (ibid) High redox potential can increase oxidation and solubility, making TE more available to plants. In contrast, low redox potential can lead to TE reduction by binding to soil particles, and thereby decreased availability. Factors that influence redox potential include the presence of oxygen, pH, SOM, chemical nature of TE, and the dissolution of Fe-Mn oxyhydroxides (Chuan et al., 1996; Wiklander, 1976).

1.4.3 Impacts of Clay, CEC, and SOM on Trace Element Availability

The availability of TE in soil are further depend on factors like clay content, cation exchange capacity (CEC), and SOM. Soils with high clay content can retain more TE than exemple sandy soils due to clay particles' negative charge, which arises from isomorphic replacement of Si4+ with Al3+ and Al3+ with Mg2+ (Wiklander, 1976). Different clay minerals have varying CEC, affecting TE sorption and availability to plants (Antoniadis et al., 2017). CEC measures the maximum amount of positively charged particles a soil can hold, with high clay content soils often having higher CEC values. Particle size also plays a role in determining TE availability. In addition to clay, SOM also plays a crucial role in TE availability. SOM influences bioavalibilty in two ways: by increasing CEC and improving plant growth and soil conditions, such as water-holding capacity and soil structure in light-textured soils, while reduces micropores, decreasing capillary forces that limit plant access to water (Antoniadis et al., 2017; Wiklander, 1976).

1.5 Plant-Soil Interactions in Trace Element Uptake

Plants have developed remarkable strategies to grow and survive in contaminated soils, despite the toxic effects excess TE can have on their physiology and survival. These strategies can be roughly divided into exclusion, accumulation, and translocation, with exclusion occurring in the rhizosphere and accumulation and translocation occurring within the tree (Antoniadis et al., 2017).

1.5.1 Exclusion: Plant Strategies in the Rhizosphere

The rhizosphere, characterized by complex interactions between root systems, soil substrate, and microorganisms, is the primary site for TE uptake. Plants can manipulate the rhizosphere's characteristics through root exudates and microbial interactions, which affect TE bioavailability, uptake, and tolerance. Plants exposed to TE have developed TE-tolerant ecotypes that include mechanisms to avoid and exclude TEs (Guerra et al., 2011). One such mechanism involves redistributing root biomass to "search" for areas with lower TE content (Kahle, 1993). Additionally, plants can modulate the soil's mechanical and hydrological properties by secreting root exudates, which act as a defense mechanism by excluding TEs (Vannoppen et al., 2015).

1.5.2 Root Exudates, Microorganisms, and Trace Element Bioavailability

Root exudates, primarily composed of low molecular weight compounds like organic acids (OAs), can alter the soil's chemical environment and consequently affect TE bioavailability (Antoniadis et al., 2017). Symbiotic relationships between plants and microorganisms also play a significant role in plant adaptation to contaminated soils. The mutualistic symbiosis between plants and ectomycorrhiza (ECM) fungi, such as those found in European Aspen growing on heavily contaminated soil (Krpata et al., 2008) have been shown to significantly impact how plants respond to heavy metals by storing TE in fungal hyphae vesicles within their roots, inhibiting uptake by the tree (Bano & Ashfaq, 2013). Non-mycorrhizal fungi, such as endophytes in shrubs and herbs growing on mine wastelands, have been shown to influence adaptation to divalent ions of Zn and Pb (Li et al., 2012). Furthermore, rhizobacteria can promote root growth and increase TE bioavailability, thus affecting plant uptake of heavy metals (Antoniadis et al., 2017).

1.5.3 Accumulation and Translocation: Intra-Plant Trace Element Movement

Translocation is a crucial process for transporting TEs and ensuring tree survival. TEs are absorbed through soil water and transported toward the foliage, where elements such as copper (Cu) and zinc (Zn) play essential roles in photosynthesis (Taiz et al., 2015). However, translocation can introduce challenges in dendrochemistry, as the transport and storage of TEs in trees are highly variable and species-dependent (Liu et al., 2013; Stoltz & Greger, 2002). Different Populus clonal variations have shown varying ratios of translocation between plant parts, often with a more extensive accumulation in roots or shoots (Baldantoni et al., 2014; Guerra et al., 2009; Hassinen et al., 2009).

Antoniadis and Levizou et al., (2017) broadly categorized sequestration/compartmentalization and binding/chelation as key mechanisms for translocation and TE accumulation. The former occurs in the cell (cell wall, vacuole), which regulates TE influx and prevents metabolic disruption. The abundance of polysaccharides containing carboxyl groups in the cell wall acts as an important site for accumulation. The latter employs various ligands to decrease TE toxicity in the cytoplasm. Chelation with various ligands dictates TE transport and storage in plants for specific processes or sequestration in different plant parts. These mechanisms determine where TEs are transported and stored within the plant (Guerra et al., 2011).

1.5.4 Interpreting Dendrochemical Analyses

Despite these adaptations, the high variability in TE accumulation and concentration within tree rings and between individual trees presents challenges in dendrochemical analyses. This variability can make it difficult to interpret data, potentially impacting the result (Binda et al., 2021). Nonetheless, understanding plant-soil interactions and the uptake, defense, and translocation mechanisms plants employ in contaminated soils remains crucial for advancing scientific knowledge and developing Dendrochemical methods.

1.6 Dendroecology

Dendroecology refers to various dendrochronological techniques applied to ecological problems (Fritts & Swetnam, 1989). The use of tree-ring to monitor environmental changes was established by the American astronomer A.E Douglass in early 1900s and is credited as the founder of dendrochronology. Since then, dendrochronology has become a useful tool to study climate variations (Fritts, 2012), extreme events (Hevia et al., 2018), dating archeological and historical structures (Bernabei et al., 2019). Using tree-ring as a monitor of temporal environmental changes is possible due to trees' annual growth pattern. Trees growing in temperate regions produce annual growth rings characterized by light-colored early-wood formed during rapid growth in spring, and dark-colored late-wood formed during slower growth in summer and fall. The variation in tree-rings width (TRW) is affected by both biotic and abiotic factors. Biotic factors include genetic variations between species and between individual trees, as well as aging. Abiotic factors cover a wide range of environmental factors such as temperature, precipitation, soil moisture, wind, nutrient availability, light. These factors are usually common for all trees at a specific site. Making it possible to establish a relationship between variation in TRW and abiotic factors (ibid). Since the mid 1970s the field of dedrochemistry has evolved from dendrochronology as a way to reconstruct changes in the chemical environment (Lepp, 1975).

1.7 Dendrochemistry

Dendrochemistry is the analysis of the chemical components present in tree rings, with the assumption that the chemical composition of a tree-ring at least partly reflects the chemical environment the tree grew in during the year of formation (Watmough, 1999). Dendrochemical studies can therefore be utilized to gain insights into how environmental changes, such as pollution, affect ecosystems over time.

An important aspect of dendrochemistry is understanding how trees absorb and accumulate TE. Lepp (1975) identified foliage, bark, and roots as the main uptake pathways for TE, with root uptake being the primary pathway. Absorption and translocation of TE from bark to xylem have been shown to be minimal when radioisotopes of Mn and Zn were applied to the bark (Lin et al., 1995), consistent with the core function of bark (Binda et al., 2021). Studies on atmospheric uptake have shown rapid uptake and accumulation of TE in the most recent tree rings, as opposed to uptake via roots, which can exhibit a delay between deposition, uptake of heavy metals, and appearance in tree rings (Peckham et al., 2019). This highlights a complex relationship between root systems, soil properties, and TE uptake and storage in tree rings (Antoniadis et al., 2017; Balouet et al., 2012).

This complexity is further exacerbated by significant intra-tree variation of TE concentration between individual trees growing at the same site. Microsite variations in soil properties, soil chemistry, hydrology, etc., influence the uptake and immobilization of TE from soil to tree, along with genetic variations, both between species and individual trees (Baldantoni et al., 2014) and different wood cell characteristics (Watmough, 1997).

When using dendrochemical methods as a forensic tool, there are limitations that can affect the representativeness and reliability of the analysis or interpretation of the results. Limitations include tree availability, distance from contamination, recent releases affecting sapwood, and challenges with inappropriate tree types and alternative sources for elemental markers (Binda et al., 2021). Species identification and possible retranslocation mechanisms of elemental markers can also add complexity (Balouet et al., 2007). Many dendrochemical studies have used a small number of trees, and further research is needed to better understand inter-tree variability. By analyzing a higher number of trees, the method can become more reliable and easier to understand, reducing variance and assessing the sample size effect on contamination patterns (Muñoz et al., 2019).

Accuracy and precision of dendrochemical analysis could also aggravate the end product of the research. Early dendrochemical studies were limited by analytical techniques, often resulting in low resolution and Limit Of Detection (LOD) by bulking several tree rings into sections (Watmough, 1999). As analytical techniques have developed since early dendrochemical research (Barnes et al., 1976), several techniques (e.g., ED-XRF, ICP-MS, or LA-ICP-MS) are used with differences in LOD, resolution, cost, and time effectiveness. ED-XRF is a non-destructive technique, typically used to detect first transition row metals, such as Mn, Fe, Cu, and Zn. However, the appropriate technique should be based on the research objectives and the elements of interest (Binda et al., 2021).

1.8 Populus tremula

Populus tremula, commonly known as European aspen, is a deciduous tree species found throughout Europe, Asia, and tropical Africa. It is known for its adaptability to various habitats, including boreal ecosystems, mountainous regions, and riparian areas. Aspen prefers well-drained, loamy soils with a high water table, and can reproduce on rock outcrops, shallow soils, and mine waste dumps (Jansson et al., 2010). It has an extensive and shallow root system capable of producing root suckers up to 40 meters from the mother tree, allowing it to form clonal colonies (Myking et al., 2011). The species is fast-growing, reaching heights of up to 40 meters within 20 years, making it an opportunistic "pioneer" species in disturbed sites (Guerra et al., 2011). However, Populus trees are generally shade and drought intolerant, requiring high water and light levels, which is why they often colonize riparian areas and wetlands (Dickmann & Kuzovkina, 2014). The flowering and seed production among Populus are temperature-dependent processes, with seed production in large numbers (DeBell, 1990). Vegetative reproduction through root suckers is the most important form of asexual reproduction, and Populus trees exhibit high levels of adaptive genetic variation within and among populations. Genetic variation is an essential aspect of the evolutionary process, allowing a species to adapt to changing environmental conditions and increasing survival in diverse environments (Hall et al., 2007; Sebastiani et al., 2014).

2 Method

2.1 Preliminary Investigation and Risk Classification: Basis for Site Selection

In 2004, Östergötlands County Administrative Board conducted a preliminary study on 23 abandoned mines in Östergötland to identify the environmental impact of mining waste and risk-classify sites using the Swedish Environmental Protection Agency's MIFO model (Länsstyrelsen, 2004). This study lays the groundwork for selecting the location of this study (*See section 2.2 - Study site: Explanation of the different mines mentioned below*).

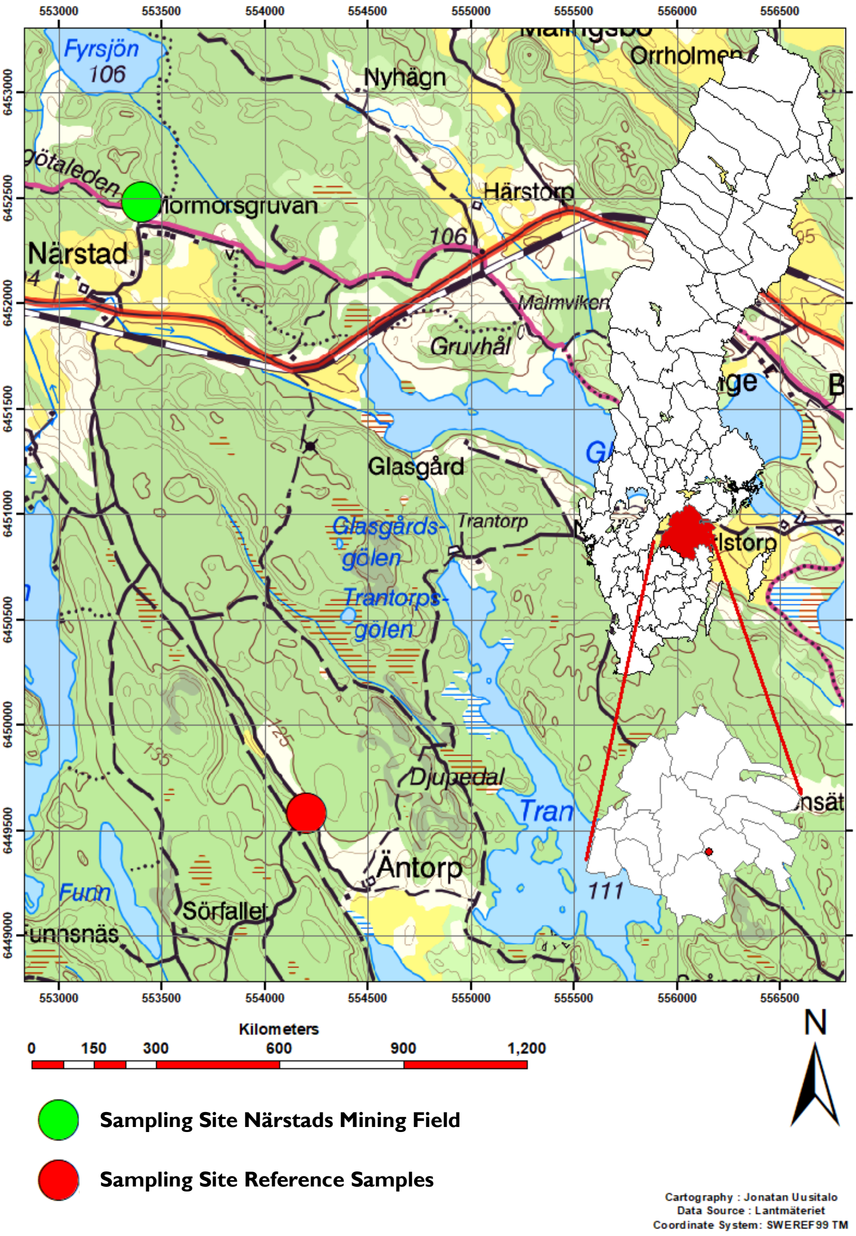
The MIFO model uses a four-step scale to classify sites based on their risk to human and environmental health. The pre-study involved collecting surface water samples, tailing samples, sediment samples, and measuring surface water pH from mine tailings. Surface water samples revealed that the leachate from Varpgruvan is highly acidic, with a pH slightly above 3, while the pH of surface water from Mormorgruvan and a drainage ditch was close to 7. No surface water sample from Haggruvan was obtained.

The County administrative board classified the area surrounding the three mines as a 2 on the 4-degree scale, signifying "a major risk to human and environmental health today and in the future". Cu concentrations at Varpgruvan and Mormorgruvan are considered very serious. Zn levels at Mormorgruvan are moderately serious, while Nickel (Ni) concentrations at Varpgruvan are very serious. Lead (Pb) and Cadmium (Cd) levels at Mormorgruvan and Varpgruvan are deemed moderately serious. A sediment sample taken from the drainage ditch exhibited high concentrations of Cu, Ni, and Arsenic (As), which decreased closer to the lake.

2.2 Study site

With over 500 known ore deposits, Östergötland county has a rich mining history dating back to the 13th century. The oldest preserved document related to Närstads mining field is from 1413, during King Erik of Pomerania's reign. The mining field reached peak copper production in the 18th and 19th centuries, becoming Sweden's second-largest copper producer until the discovery of the Skellefteå mining field in 1920 (Länsstyrelsen, 2004). The focus of this study is Närstads mining field (58°12'36"N 15°54'32"E), located approximately 5 km W-N-W of Åtvidaberg city (*Fig 1*). While the mining field comprises of various mines, this study primarily focuses on the mines and tailings of Mormorgruvan, Haggruvan, and Varpgruvan and its surroundings.

The three mines lie in an approximately W-E cardinal direction (*Fig 2*), with elevations ranging from 110-130 meters above sea level. A drainage ditch (*Fig 2)* runs from the mines in the SE-NW direction towards lake Fyrsjön, approximately 800 meters downstream, with all mines draining into it. North of the mines, the vegetation comprises a mosaic of mixed forest and open land with shrub, dominated by coniferous trees such as spruce and pine, and deciduous trees like birch, oak, and aspen. South of the mines, agricultural land prevails. Forested areas are mainly found around the mines and the tailings, with shrubland and young trees in between (*Fig 2*). A 200-meter-long and 40-meter-wide forested area is centered around the drainage ditch. Soil types in the area include sandy till, postglacial clay, and fen peat, with postglacial clay dominating around the mines.



Cartography : Jonatan Uusitalo
Data Source : Lantmäteriet
Coordinate System: SWEREF99 TM

Figure 1: Overview of the sampling sites. Östergötland county marked in red on the Sweden map and red point marks the location of Närstads mining field in Åtvidaberg municipality.

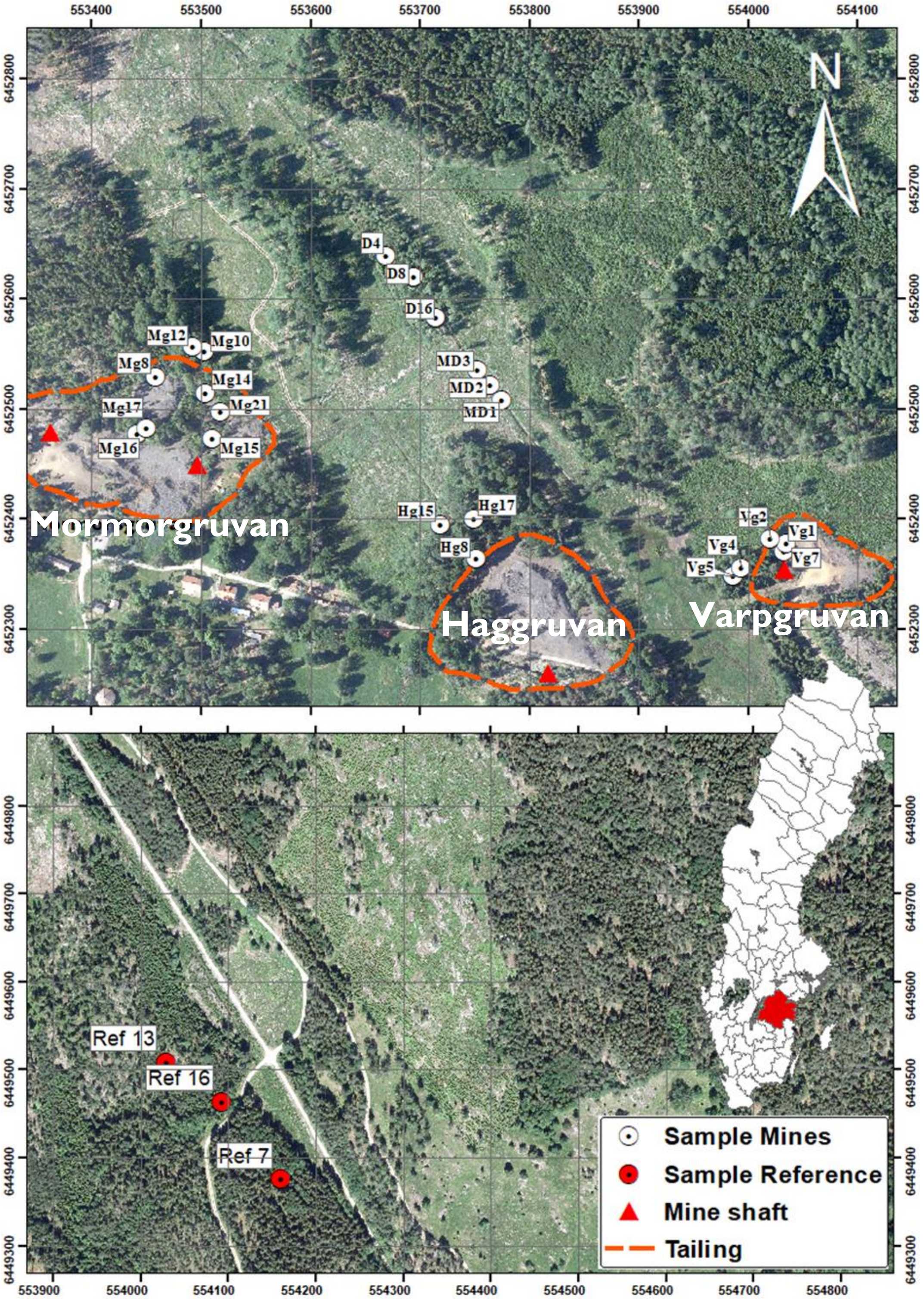


Figure 2: Overwiev of the sampling locations at Närstads mining field (top image) and reference site (bottom image). Fyrsjön is located to the north, outside the image. Grid size in the map is 100x100. Coordinate system: Sweref 99TM

Samples for ED-XR analysis are taken from five sub-locations, Mormorgruvan, Haggruvan, Varpgruvan, the forested area along the drainage ditch, as well as a reference site (*Fig 2*). Samples from Mormorgruvan are named Mg followed by a number, Haggruvan = Hg, Varpgruvan = Vg, the drainage ditch = D, and the reference site = Ref

2.2.1 General Climate

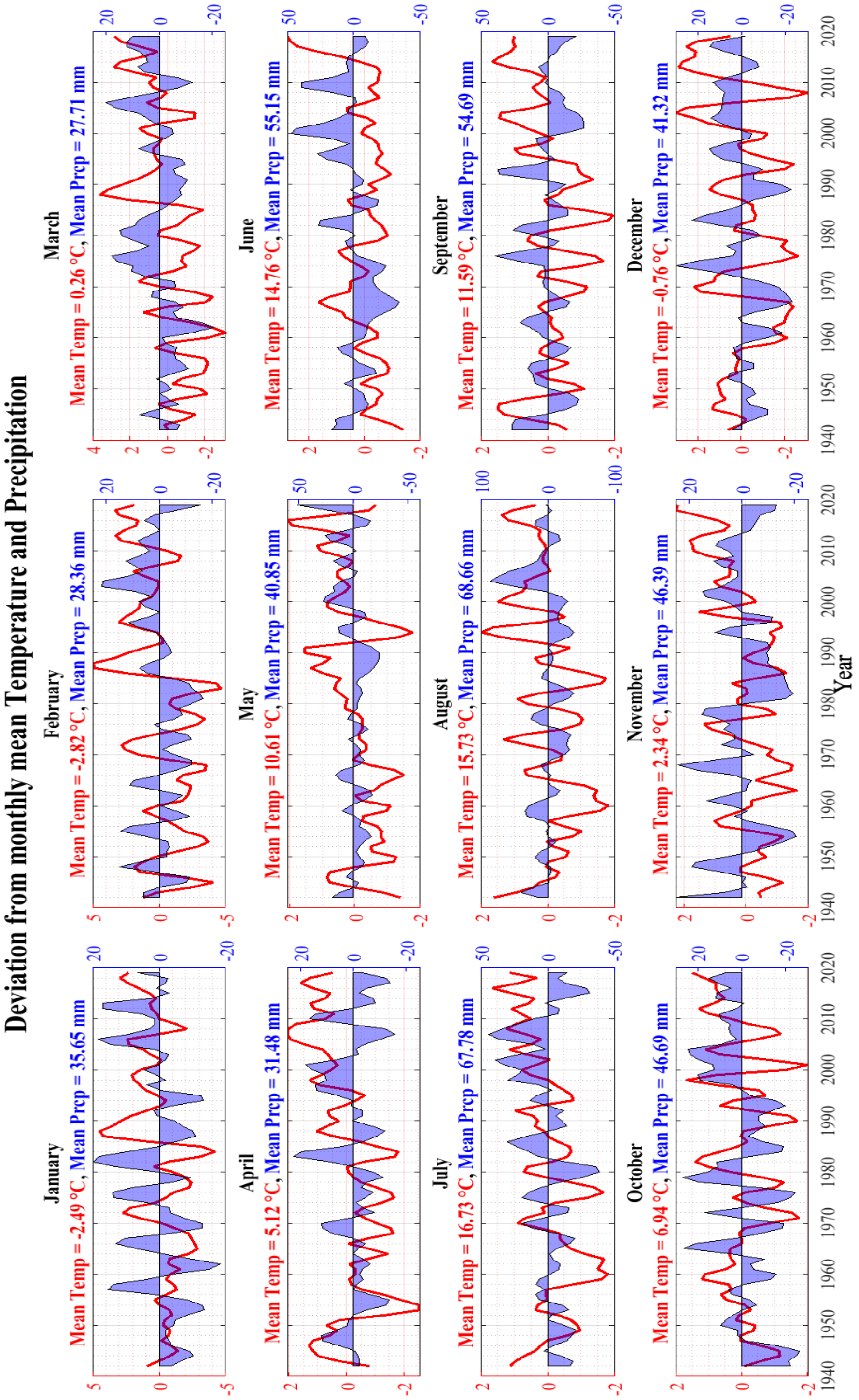


Figure 3: Deviation from monthly mean precipitation in blue on the right y-axis, and temperature in red on the left y-axia. 0 on the Y-axis represent the average value during the whole timeseries (1944-2021). The data are filtred with a gaussian curve with a 5 year window for clearer visualization.

Östergötland County's climate is classified as warm-temperate, with deciduous forests as the predominant vegetation (SMHI, 2022). The study site experiences an average annual temperature of 7°C and 580 mm of precipitation (Normal period 1991-2020). The highest average temperature and precipitation occur in July (17°C and 74 mm), while the lowest temperature is in January and February (-1.5°C), and the lowest precipitation is recorded in March. August sees the maximum precipitation with 273 mm, and April has the minimum with 0.8 mm. The maximum monthly average temperature is in July at 21.3°C, and the minimum is in January at -9°C (The whole climatic period, 1944-2021) (*Fig 3*).

2.2.2 Mormorgruvan

Mormorgruvan is the largest mine in the Närstads mining field. The mineralization is dominated by Chalcopyrite ($CuFeS2$), Bornite ($Cu3FeS4$), and Pyrite ($FeS2$), with Magnetite ($Fe3O4$) and Malachite ($Cu2CO3(OH)2$) in red quartz-rich biotite schist host rock. The complex landscape around Mormorgruvan features mixed forest, drainage ditches, and soil ranging from postglacial clay to 30x20 cm tailing rocks (*Fig 4a-e*). The tailing has a volume of 40,000-80,000 m3 and is 8-10 meters high (Länsstyrelsen, 2004), separated into three distinct tailings with wooded areas seperates them. The majority of the tailing are located east of the mine shaft, with two smaller tailings to the northeast. Mg8 grows at the base of a smaller tailing, with a forest to the north and the tailing to the south. The soil in the forested area exhibits similarities to boreal forest soil with elements of tailing rock. Ditches mark a clear boundary between the clay-rich shrubland and the tailings. Mg14 and Mg10 grow along a ditch respectively towards the shrubland, while Mg12 is situated 5 meters on the opposite side of Mg10.

Figure 4: *a) Sample Mg15 is behind the camera. Nygruvan is located 10 meters behind the truck (back of the truck is seen to the left in the image). b) An uprooted tree showing soil characteristic close to the tailings. c) Sample Mg14 with a ditch between the small tailing in the background and the tree. d) Sample Mg10 is located on the right-hand side of the image. The tailing at sample Mg8 can be seen in the center of the picture. e) Sample Mg8 is growing at a smaller tailing to the east of the Mormorgruvan mine shaft.*

Nygruvan located east of Mormorgruvan collects runoff from the tailing. The mine shafts are typically water-filled, and a small channel drains Nygruvan northward along a small forest road (*Fig 4d*). Mg15 grows near the water channel, while Mg16 and Mg17 grow between the tailing and Nygruvan. Mg21 is found 50 meters north. The soil in this area has low organic content and minimal topsoil, dominated by tailing stones.

2.2.3 Haggruvan

Haggruvan is located 300 meters east of Mormorgruvan and has a mine shaft south of the tailing and similar ore mineralization with less pyrite. The 2-8-meter-high tailing has a volume of 20,000-40,000 m3. A crescent-shaped forest strip of oak and aspen grows west to north of the tailing. The soil is primarily clay, with a depth of at least 2 meters. Hg8, Hg15, and Hg17 grow in this area, with Hg8 at the tailing base similar to Mg8, Hg15 by the ditch, and Hg17 in between (*Fig 6a-d*).

Figure 4*: a) Sample Hg15 seen closest to the camera. b) Sample Hg8 seen center in the image growing at the tailings. c) View over the tailings with Haggruvan's mine shaft located 60 meters behind the camera. d) A ditch running from Haggruvan's tailings located behind the camera. D4, D8, and D16 were collected from the forested area on the right-hand side of the image, and Mormorgruvan is located outside of the image on the left. The ditch in the image runs parallel to the main ditch on the right-hand side of the image and connects to the main ditch 120 meters ahead.*

2.2.4 Varpgruvan

Located in the eastern part of Närstads mining field. Its mineralization differs from the other mines, with abundant pyrite and the presence of chalcopyrite, arsenopyrite, and magnetite. The tailing has a volume of 6,000-10,000 m3 and a 2-3 meter depth. Varpgruvan's mine shaft lies between the tailing to the east and a wooded area to the west. A ditch runs from the side of the mine shaft through the wooded area. Vg5 grows approximately 20 meters from the mine shaft along the ditch, while Vg4 grows about 5 meters north of Vg5 near a sinkhole. Vg1, Vg2, and Vg7 grow north of the wooded area in a more open landscape. Vg1 and Vg7 grow in close proximity to the tailing, and Vg2 located 20 meters west (*Fig 7a-d*). The soil at Vg4 and Vg5 has high organic content, while Vg1, Vg2, and Vg7 grow on clay and sand-rich soil with a large proportion of tailing rocks.

Figure 5: a) Varpgruvan mine shaft. b) Vg4 is located behind the fence with the sinkhole. c) View over Varpgruvan's tailings with the mine shaft located behind the car. Sample Vg7 is located with Varpgruvan's tailings in the background.

2.2.5 Ditch

An 800-meter-long ditch running from Varpgruvan to Lake Fyrsjön, with several parallel ditches contributing water. A wooded area dominated by aspen lies 200 meters northeast of MG10 and Mg12. The wooded area, measuring 160x40 meters, is divided by the ditch and consists of peat. Trees are similar in age, with D16 growing nearest the mines, D4 nearest the lake, and D8 in between. The samples grow between the ditch and Mormorgruvan (*Fig 8a-d*).

Figure 6: a) Sample D4. b) The wooded area where the tree samples are collected is seen in an image taken in the northeast cardinal direction. c) The main ditch. The image is taken in height with Haggruvan, looking towards Fyrsjön. d) Sample D8

2.2.6 Reference

Reference samples were obtained from a coniferous forest with oak and birch as the primary deciduous species within a topographic depression. A rarely traveled forest road (Trafikverket, n.d) runs through the center of the depression, close to the samples. The area west of the reference samples remains unlogged, while a smaller section between the road and Ref 7 experienced logging 3-10 years ago (Skogsstyrelsen, 2023). Signs of forest thinning are evident around Ref 7. Ref 16 and Ref 13 are located 70 and 100 meters northwest of Ref 7, respectively, with no visible indications of logging or thinning nearby. The soil in this region exhibits characteristics typical of coniferous forests, consisting of a high concentration of coarse stones and boulders (*Fig 9a-d*).

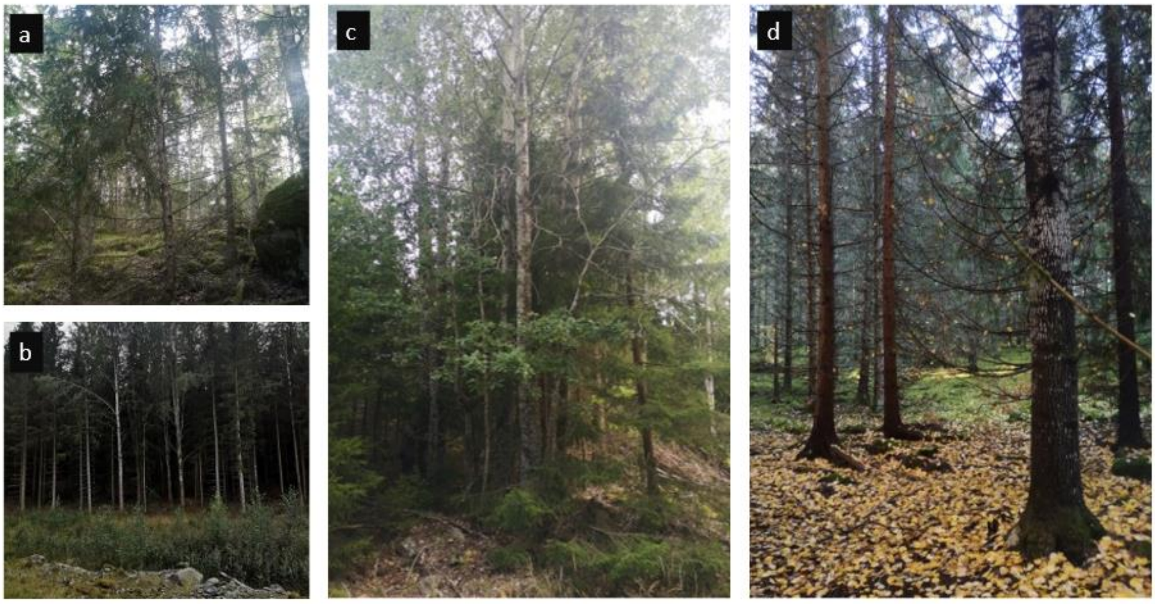


Figure 7: a) Image of the ground that is representative for the area. b) Image taken from the road towards west-southwest, looking over the logged area. c) Reference sample 16. d) Reference sample 7

2.3 Sampling and analysis

2.3.1 Soil Trace Element Concentration

15 Soil samples were obtained using a Russian corer at a depth of approximately 20 cm. The complex topography and soil properties occasionally hindered the acquisition of a sufficient amount of soil in direct proximity to the sampled trees. In the vicinity of the tailings, a high proportion of waste rock and low levels of mineral and organic soil material characterize the soil. Consequently, soils from beneath all trees were not obtained, and the distance between the tree and the soil sample may vary by up to approximately 15 meters. Three samples were taken

from the main ditch between the mines and the sampling location for the ditch (named MD – Main Ditch). The samples were stored in zip-lock bags.

The samples were air-dried at room temperature (20 degrees Celsius) in a well-ventilated room (*Fig 10a*). They were then homogenized using a ceramic mortar and pestle. While visibly large organic materials were removed, efforts were made to retain as much of the soil's original composition as possible. The homogenized soil was compacted to eliminate soil pores, and a thin plastic film was subsequently placed over each sample. The soil samples were analyzed with a Portable X-ray fluorescence spectrometry (pXRF) of model Olympus X Delta, equipped with an Rh tube and soil mode setting for 60 seconds. This method is suitable for determining element concentrations below 1%, including Al, As, Ba, Bi, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hf, Hg, K, Mn, Mo, Nb, Ni, P, Pb, Rb, S, Sb, Se, Sr, Sn, Ti, Th, U, V, W, Y, Zn, and Zr (Knight et al., 2021).

2.3.2 Soil pH

To measure soil pH-$_{H_2O}$, five grams of soil were weighed and placed into 50 mL plastic tubes. Subsequently, 25 mL of deionized water was added to the tubes, and they were shaken to suspend the soil particles (*Fig 10b*). After allowing the suspended material to settle for approximately 24 hours (Nilsson et al., 2015)the pH levels in the water solution were measured using a Metrohm 691 pH Meter calibrated for a pH range of 4-7.

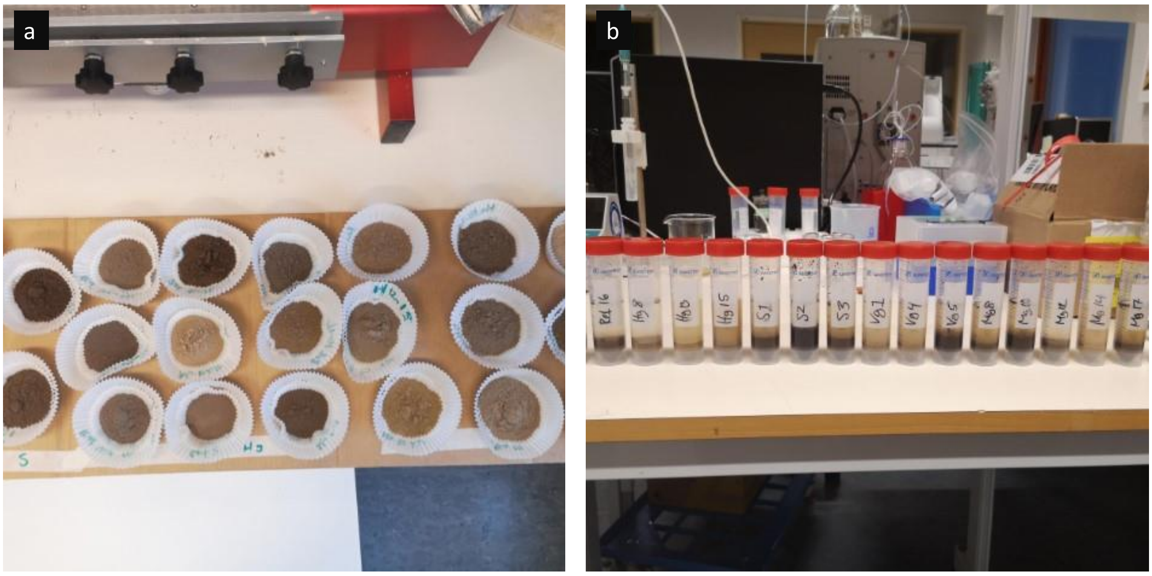


Figure 8: a) Drying of Soil samples. b) Prepared soil samples for pH measurement.

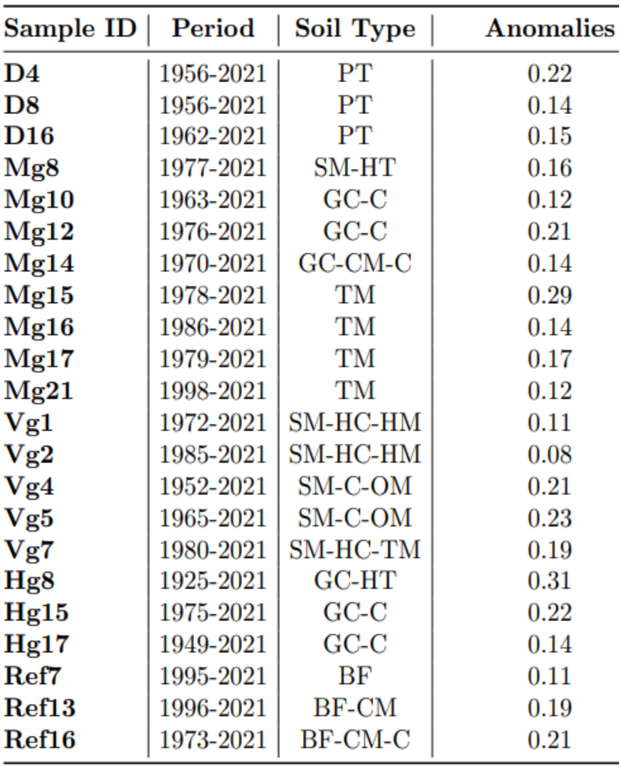
2.3.3 Tree sampling

In 2021/2022 I conducted a preliminary study at Närstads mining field to identify suitable tree species for this project. Out of six species, Aspen showed the highest Dendrochemical potential. Given its abundant presence relative to the mines, and that Europea Aspen have successfully been used to identify dendrochmical signals (Rocha et al., 2020), and the fact that the Populus genus and Aspen species are often used in phytoremediation and considered hyperaccumulators of pollutants (Kozlov & Zverev, 2022; Laureysens et al., 2004). In September 2022, samples from 87 trees were collected, growing around Mormorgruvan, Haggruvan, Varpgruvan, Ditch, and the Reference site, with 2 radii obtained per tree. Varpgruvan provided samples from only 7 trees, as the availability of viable Aspen individuals was limited (*Fig 2*). A 10 mm increment borer was used at breast height (approximately 130 cm) to extract amples from healthy European Aspen trees, free of visible scarring or damage.

2.3.4 Tree- ring preparation and dating

To ensure accurate identification of individual tree rings, all samples were glued to a wooden core mount, with the transverse wood surfaces oriented upright (*Fig 11a*). To further facilitate identification, the samples were polished using a razor blade and sandpaper with progressively finer grit. Polishing with sandpaper was minimized. Heat generated during the process could volatile organic compounds (Balouet et al., 2007), and wood dust can fill the vessel lumen, which could complicate measurements (Locosselli et al., 2019). The rings were identified and dated with a precision of 1 µm using a stereomicroscope, Tsap-Win software, and Lintab 6 measuring table. Average TRW was calculated using both radii from each tree, with both statistical

Table 1: Tree samples analyzed with ED-XRF. This table contains the following columns:
***Sample ID** – Sample name*
***Periods** - Analyzed time period.*
***Soil Type** - Descriptions of soil types: PT = Peat, SM = Sandy Moraine, HT = High content of tailing material, C = Clay, GC = Glacial Clay, CM = Coarse Material, TM = Primarily tailing material, OM = Organic Material, BF = Boreal forest soil.*
***Anomalies** - The average number of anomalies per year (Average nr of anomalies/ Sample length).*



Sample ID	Period	Soil Type	Anomalies
D4	1956-2021	PT	0.22
D8	1956-2021	PT	0.14
D16	1962-2021	PT	0.15
Mg8	1977-2021	SM-HT	0.16
Mg10	1963-2021	GC-C	0.12
Mg12	1976-2021	GC-C	0.21
Mg14	1970-2021	GC-CM-C	0.14
Mg15	1978-2021	TM	0.29
Mg16	1986-2021	TM	0.14
Mg17	1979-2021	TM	0.17
Mg21	1998-2021	TM	0.12
Vg1	1972-2021	SM-HC-HM	0.11
Vg2	1985-2021	SM-HC-HM	0.08
Vg4	1952-2021	SM-C-OM	0.21
Vg5	1965-2021	SM-C-OM	0.23
Vg7	1980-2021	SM-HC-TM	0.19
Hg8	1925-2021	GC-HT	0.31
Hg15	1975-2021	GC-C	0.22
Hg17	1949-2021	GC-C	0.14
Ref7	1995-2021	BF	0.11
Ref13	1996-2021	BF-CM	0.19
Ref16	1973-2021	BF-CM-C	0.21

and visual verification for false or missing rings. The quality of the cross-dating was validated with COFECHA (Holmes, 1983).

2.4 Dendrochemical Analysis

2.4.1 ED-XRF

The energy-dispersive X-ray fluorescence (ED-XRF) technique is a non-destructive (*Fig 11*), high-resolution method for simultaneously analyzing multiple elements. By directing X-rays at a sample, the atoms' inner-shell electrons excite. This causes a vacancy, which is replaced by an outer-shell electron. As a result of this process, energy is released in the form of a photon, which can be detected and analyzed to determine the elemental composition of the sample (Smith et al., 2008).

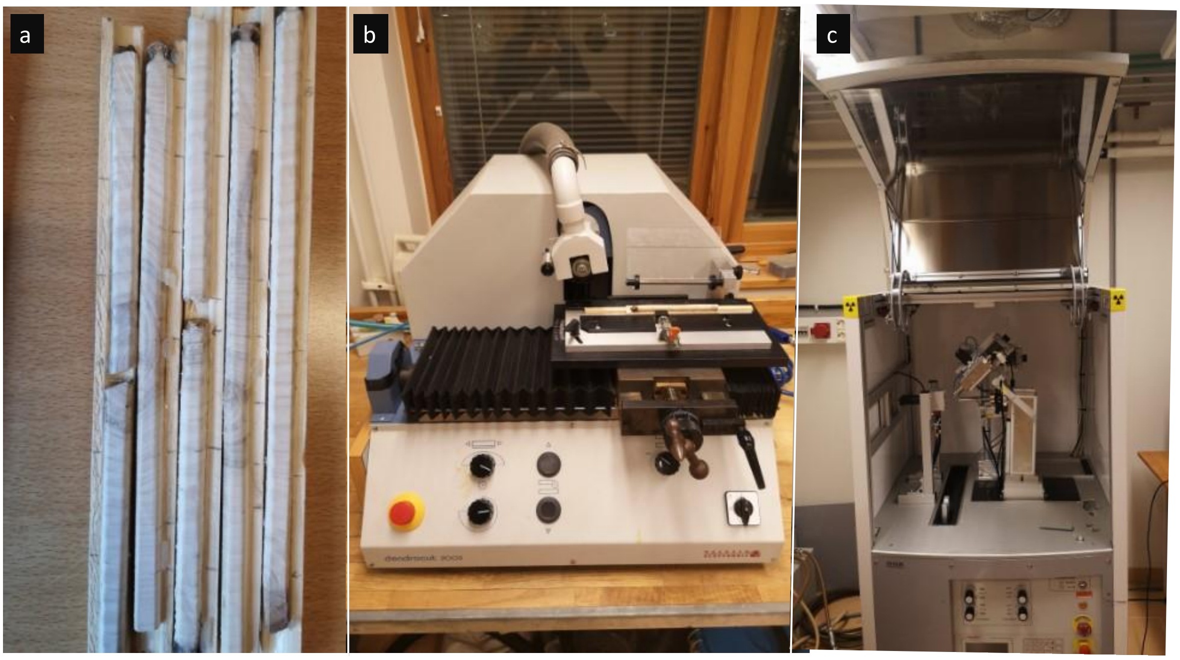


Figure 11: Four tree samples glued onto wooden core mount. b) The dual-blade circular saw used for cutting the laths. c) ITRAX ED-XRF multi-scanner used for dendrochemical analysis in the Dendrolab at Stockholm University.

2.4.2 Sample Selection for Dendrochemical analysis

Out of the 87 collected samples, 22 were selected for chemical analysis, including 19 from the mining field and 3 from the reference site (*Fig 2; Table 1*). The selection criteriwere based on:

- The pollution history and sulfide content in the tailings (Länsstyrelsen, 2004).
- The catchment analysis derived from the preliminary study that preceded this research.
- The chemical and pH analyses of the collected soil samples.

Considering the significant influence of the tailings' sulfide content on the mobility of metals (Barceló & Poschenrieder, 1990), a combination of the sulfur content in the tailings, the pollution history as described by the Östergötlands County Administration Board (Länsstyrelsen, 2004), and the catchment analysis from the preliminary study were used to identify areas around the mines where the trees exhibit increased potential for pollutant uptake. Additionally, soil samples were employed to confirm the pollution status and level, and to identify trees growing in proximity to areas with high soil concentrations of Cu.

The Swedish Geological Survey (SGU) carries out geochemical measurements aimed at determining the natural occurrence, or background levels, of trace elements. Soil samples exhibiting significantly higher TE concentrations than the background levels provided by SGU (SGU, n.d) were prioritized (*Fig 12*).

To ensure a more comprehensive representation of the area, additional samples that were not grown near locations with high metal content were selected. All samples underwent a consistent analytical method for assessment.

2.4.3 Methodology

Thin wooden laths (1.2 mm) were cut from the samples using a dual-blade circular saw (*Fig 11b*). The laths were cut as far from the sanded surface as possible to minimize the risk of sanding-dust filling the vessel's lumen and obscuring the analysis. The chemical composition of the samples was analyzed using an ITRAX Multiscanner from Cox Analytical Systems (www.coxsys.se) at the Dendrolab of Stockholm University (*Fig 11c*).
An exposure time of 3 seconds with a line scanning step of 50 microns were used with a Cr tube regulated at 30 kV and 50 m A. The ITRAX Multiscanner produces chemical profiles for the elements Al, Ar, As, Ba, Br, Ca, Cd, Cl, Co, Cs, Cu, Fe, Ge, Hg, K, Mg, Mn, Mo, Ni, P, Pb, Rb, Sc, Se, Si, Sr, S, Ti, V, Zn and Zr, together with a radiographic and optical image of the samples.

2.4.4 Data Processing

The radiographic images were used in the WinDendro program (Régent instruments Canada Inc., version 2012a) to produce pixel-based TRW data to link the annual rings with the ED-XRF profiles. Wood Matrix Effect can manifest in samples exhibiting a heterogeneous structure or structural differences, such as density variations between spring and summer wood or within an annual ring. This is adjusted through Compton correction (Smith et al., 2008). This correction process entails dividing the results by coherent scattering (Garivait et al., 1997) to prevent any negative impact on the accuracy of the ED-XRF results. The average value for each element is then calculated for the annual rings. Both the first and last year of each chemical profile were removed to avoid potential edge or pith bias effects (Rocha et al., 2020).

2.5 Data Sources and Statistical Analysis

2.5.1 Climate data

The climate data are provided by the Swedish Meteorological Institute (SMHI, n.d.). Monthly average temperature data are from station number 85240, Linköping-Malmslätt, located approximately 30 km N-N-W of the study site. The monthly average precipitation data are from the same station up to 2002. Due to some missing years of precipitation data, the period 2002-2021 was retrieved from station 86260 – Gustorp D, located approximately 30 km N-N-E of the study site.

2.5.2 Regional pH data

Regional pH data spanning from 1995 to 2020 were utilized to identify potential correlations between shifts in regional pH and trace element uptake within the tree samples. The pH data, provided by the Swedish University of Agricultural Sciences (SLU, 2021), represents the average pH of measurements taken from humus layers. These measurements were carried out within a 20 km radius surrounding the Mormorgruvan mining field. The quantity of measurements varied from 19 to 44 samples annually, with an average of 34 measurements being conducted per year.

2.5.3 Methodological Approaches in Statistical Analysis

The Shapiro-Wilk test for normality was utilized to assess the distribution of dendrochemical data, revealing that most samples exhibited a non-normal distribution. Consequently, the non-parametric Wilcoxon signed-rank test was employed to identify significant differences between samples, while Spearman rank correlation was applied to discern similarities between dendrochemical profiles, climate variables, TRW, and regional pH measurements. To avoid scale differences to influence the correlation, z-score is applied to normalize the data. First-order differences eliminates potential autocorrelations in the time series, focusing on consecutive observation changes to reveal short-term relationships and emphasize immediate responses to climatic variations. Meanwhile, correlations with detrended data—achieved by removing polynomial trends—allowed for the investigation of long-term similarities without trends in the raw data obscuring underlying patterns (Fritts, 2012).

Spearman correlations with raw data were performed to explore similarities between variables with preserved trends. Bonferroni correction was applied to mitigate type 1 errors during multiple comparisons, such as those between climate variables and dendrochemical profiles. Bonferroni correction is a simple and conservative method that may increase the risk of Type II errors and result in overly conservative p-values (Weisstein, 2004).

High frequencies were filtered out using a Gaussian filter with a window comprising 10% of the time series length to aid in the identification of long-term trends and anomalies, ensuring a scientifically accurate description. Anomalies were defined as variations exceeding or falling below 30% of the time series average, following the methodology used by Balouet, Burken et al. (2012) and Rocha, Gunnarson et al. (2020). All statistical analysis is applied to As, Cd, Cu, Ni, Pb, and Zn. Main focus will be on Cu as it is the main pollutant (Länsstyrelsen, 2004).

2.5.4 Detrending Techniques: The Use of Polynomial Fit

A common method to detrend dendrochronical data is to fit a negative exponential or straight line to remove age or climatic trends in the data. While a negative exponential or straight line can satisfactorily remove these trends in many coniferous species, a polynomial fit is a more versatile option for detrending data from deciduous trees or in cases where factors such as growth disturbances or contamination need to be considered. The polynomial curve is commonly used in dendroclimatological studies where an exponential function may not be sufficient due to changes in a tree's environment throughout its lifetime, such as stand disturbances and changing forest conditions (Fritts, 2012). A polynomial fit curve is applied, where the degree is determined by calculating the sum of squares of residuals for each trendline and selecting the degree that gives the smallest sum of squares of residuals. This method is used to detrend the TRW and dendrochemical profiles for each sample. Z-score is applied to the data before detrending.

3 Result

3.1 Soil Sample

3.1.1 Trace Element Concentration

Cu concentrations exhibit significant variability between the samples (*Fig 12*). Concentrations exceeding background levels from SGU are observed in soil from Varpgruvan (*Vg4 and Vg5*), Mormorgruvan (*Mg17, Mg10, Mg15, Mg8, Mg21*), and from the drainage ditch (*MD1, MD2, MD3*). These samples exhibited Cu concentrations 11-443 times higher than the reference samples (*Ref7, Ref13, Ref16*) and 2-42 times higher than SGU background levels from the area. All three reference sample exhibit Cu concentration lower than the SGU background levels. Soil samples from Mg12, Mg14, Vg1, Hg8, and Hg15 show copper concentrations ranging between background levels at the mines and reference site. Among all soil samples, Mg21 (Cu = 6244 ppb) displayed exceptionally high concentration, with the next highest concentration found in Vg5 (*Cu = 2917 ppb*). MD1 (*Cu = 882 ppb*) (*nearest the mines*) and MD3 (*Cu = 923 ppm*) (furthest from the mines) exhibited similar concentrations, while MD2 (*Cu = 2019 ppm*), positioned between them, had more than twice the concentration. Ni (*not shown*) was only observed in Vg5 and along the drainage ditch. Only Mg15 (*Zn = 354 ppm*) and Mg21 (*Zn = 123 ppm*) demonstrated significantly higher zinc concentrations than SGU's background levels (*Zn = 61 ppm*) (*not shown*). Pb concentrations varied with concentrations around background levels, Arsenic was only found at the mines, and Cd was not detected in any of the samples.

3.1.2 Soil pH

The pH-$_{H2O}$ levels showed considerable variability, ranging from 4.37 to 6.80 (*Fig 12*). The lowest pH values were observed in soil samples from the reference site, with pH values ranging from 4.37 to 5.00. In contrast, the highest pH values were observed along the ditch (*5.61-6.80*), showing a decrease in pH towards Fyrsjön. The largest variation in pH was observed in samples from Varpgruvan and Haggruvan, although only a few samples were taken from these sites. At Haggruvan, a difference of 1.29 in pH is observed between Hg8 (*pH=5.19*), taken near the tailings, and Hg15 (*pH=6.49*), taken from a ditch located 50 meters from Hg8. Similarly, samples from Varpgruvan also exhibited relatively high variation in pH, with Vg5 (*pH=4.71*) having a pH value more than one pH unit lower than Vg1 (*pH=5.75*). The samples from Mormorgruvan showed less variability in pH values, with an average pH of 5.59, with the lowest value observed at Mg14 (*pH=5.18*) and the highest at Mg17(*pH=5.83*). Neither high or low frequency correlation between dendrochmical profiles and regional pH show any significant relationship.

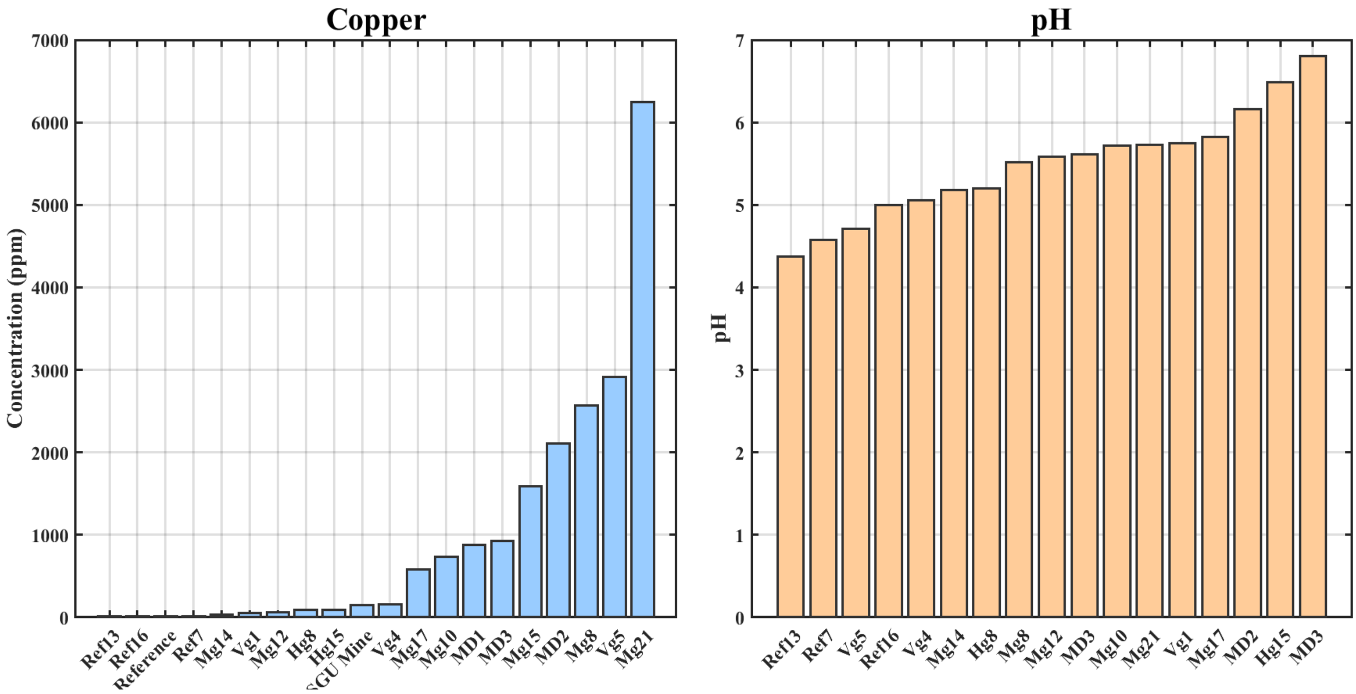


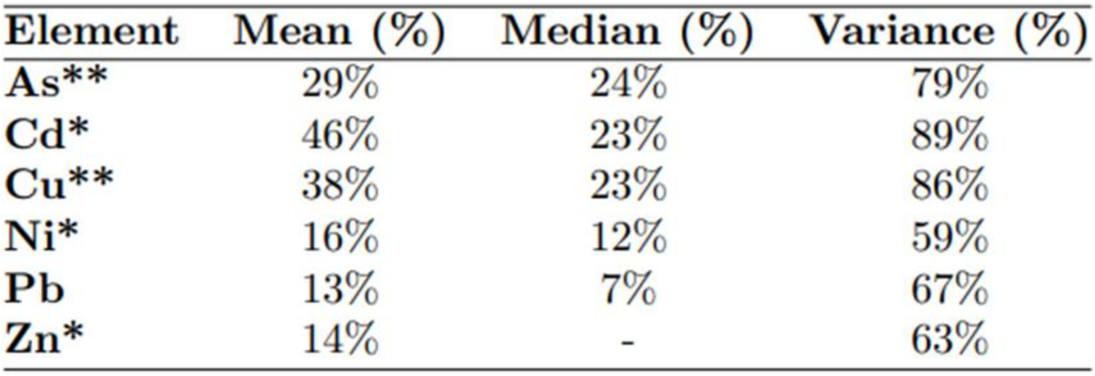
Figure 12: Left figure show Cu concentration in the soil samples ordered from lowest to highest concentration. "Reference" and "SGU Mine" are background levels of Cu from SGU (See 2.4.2 Sample Selection for Dendrochemical analysis)(SGU, n.d) . "Reference" are representing background levels at the reference site and "SGU Mine" represent background levels at the mines. Samples named MD referes to Main Ditch. MD1 is located towards the mines and MD3 towards Fyrsjön. The right figure show pH values ordered from lowest to highest pH.

3.2 Dendrochemistry

3.2.1 Comparison of Trace Element Concentrations Between Mines and Reference Site

By calculating the average of all samples from the mines for each TE, a generalized comparison between the contaminated and reference sites is facilitated. When comparing the mines with the reference site, the Mann-Whitney U-test reveals significant differences in TE content for Ni, Cu, Zn, As, and Cd. The contaminated site exhibits elevated mean (13%-46%), median (7%-24%), and variance (59%-89%) for all TEs except Zn, which displays a median lower than the reference site (*Table 2*). No significant differences are observed for Pb. Mean, median, and variance do, however, surpass those of the reference site.

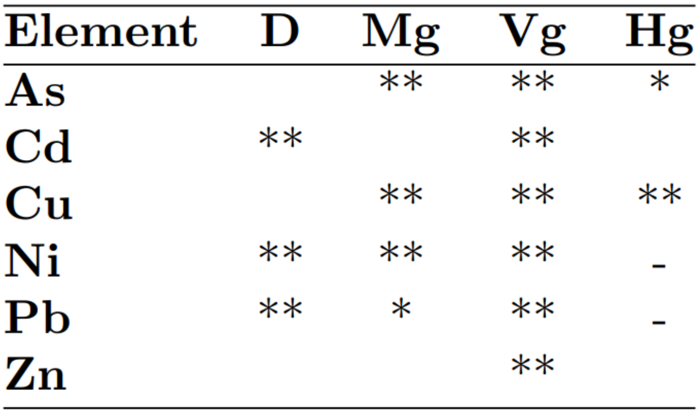
*Table 2: Percentage differences in mean, median, and variance between the average dendrochemical profile for samples from the mines and the average profile from the reference site. * = p<0.05, indicating a significant difference using the Mann-Whitney U-test. ** = p<0.01, indicating a highly significant difference using the Mann-Whitney U-test. No * = no significant difference observed. - = reference site show higher values than contaminated sites.*



Element	Mean (%)	Median (%)	Variance (%)
As**	29%	24%	79%
Cd*	46%	23%	89%
Cu**	38%	23%	86%
Ni*	16%	12%	59%
Pb	13%	7%	67%
Zn*	14%	-	63%

3.2.2 Variation in Trace Elements Across Sublocations Relative to Reference Site

*Table 3: Significant difference using Mann-Whitney U-test between sublocation D (Ditch), Mg (Mormorgruvan), Vg (Varpgruvan), Hg (Haggruvan) and Ref (Reference site). . * = p<0.05, ** = p<0.01, No * = no significant difference. - = reference site show higher mean values than contaminated sites.*



Element	D	Mg	Vg	Hg
As		**	**	*
Cd	**		**	
Cu		**	**	**
Ni	**	**	**	-
Pb	**	*	**	-
Zn			**	

By calculating the mean values for each sublocation (*Mormorgruvan, Haggruvan, Varpgruvan, Ditch, and Reference*), the Mann-Whitney U-test reveals significant differences in TE content between the sublocations and the reference site. Nonetheless, not all sublocations exhibit statistically significant differences for every trace element. Varpgruvan consistently displays elevated content across all TEs (*Table 3*). In general, sublocations exhibit increased mean TE concentrations and variance, even when statistical differences are not apparent. Haggruvan is the sole sublocation with a lower mean concentration (Ni and Pb) than the reference site. For Zn, significant differences are lacking, except in the case of Varpgruvan. Furthermore, Ditch and Varpgruvan demonstrate significantly higher maximum concentrations for all TEs compared to the reference site, with maximum concentrations ranging from 2 to 5 times higher than the reference site. Minimum concentrations are comparable among all TEs and sublocations.

3.2.3 Analysis of Individual Samples Relative to Reference Site

The individual samples exhibit considerable variation in central tendencies (*Fig 13*). Generally, 44% of the samples can be statistically distinguished from the reference samples in the following order: Cu > Ni > As > Zn > Pb > Cd (Only Cu is shown). A few samples display significantly higher concentrations and variations across all TEs. Four of the samples (D4, Mg15, Vg4, Vg5) are notable for exhibiting significantly elevated central tendencies among all TEs and maximum values 2-4 times higher, except for Cd, where Vg5 shows no significant difference.

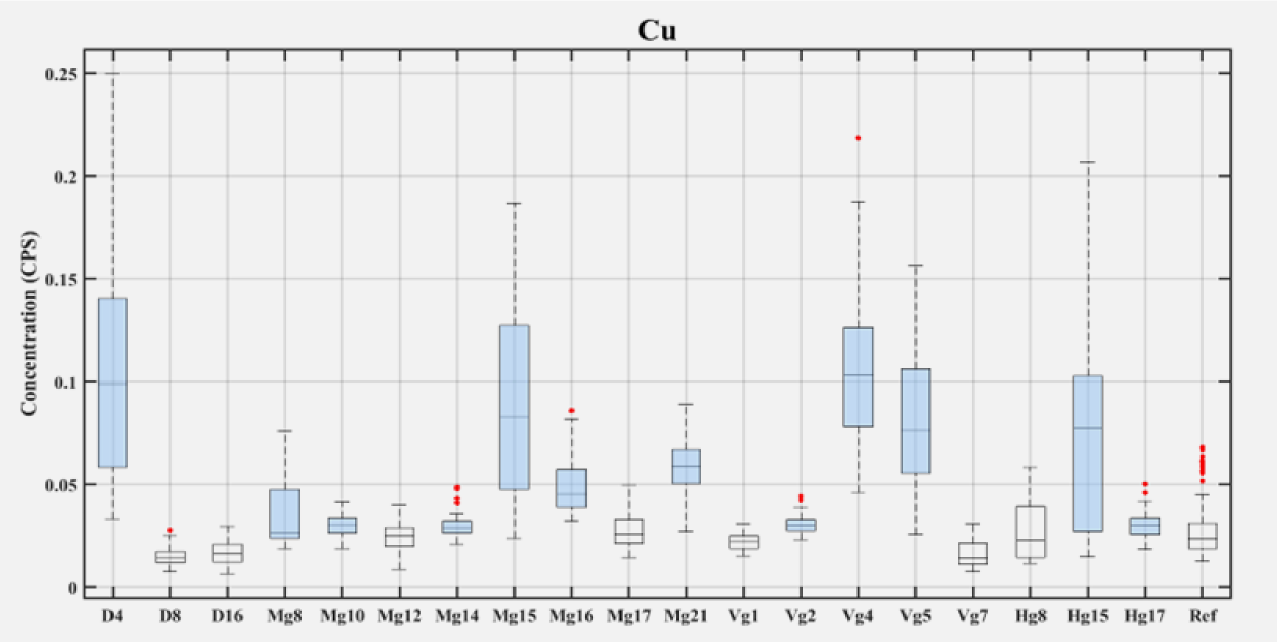


Figure 13: Box plot of Cu concentrations in individual samples. Colored boxes represent samples that show significant differences from the reference samples. The reference samples are grouped together instead of being shown as three separate samples and the Y-axis shows concentrations in counts per second (CPS). The red dots represent data points that are 1.5 times the interquartile range and are considered outliers. (MathWorks, 2021).

3.3 Trace Element Anomalies in Dendrochemistry

All TE exhibit well-defined anomalies during two primary periods: the mid-1970s to the mid-1980s and the late 2000s to early 2010s (*Fig 14*). In contrast, the time between these periods, centered around 1990, displays low to non-existent anomalies and reduced TE concentrations. Of the 17 samples predating 1980, seven (*D4, D16, Mg12, Mg14, Mg17, Vg5, Vg7*) reveal anomalies in TE concentration during the first period, while three samples (*Mg8, Mg10, Vg1*) show local maxima within the same timeframe (*similar pattern is seen through all TE*). The 1990s are marked by minimal anomalies, with absolute or local minimum concentrations varying among the trace elements. Subsequently, an increase in uptake from the early to late 2000s is observed, characterized by multiple anomalies across various samples. This pattern highlights the distinct periods of higher anomaly frequency in the mid-1970s to the mid-1980s and the late 2000s, with a contrasting period of low anomalies centered around 1990.

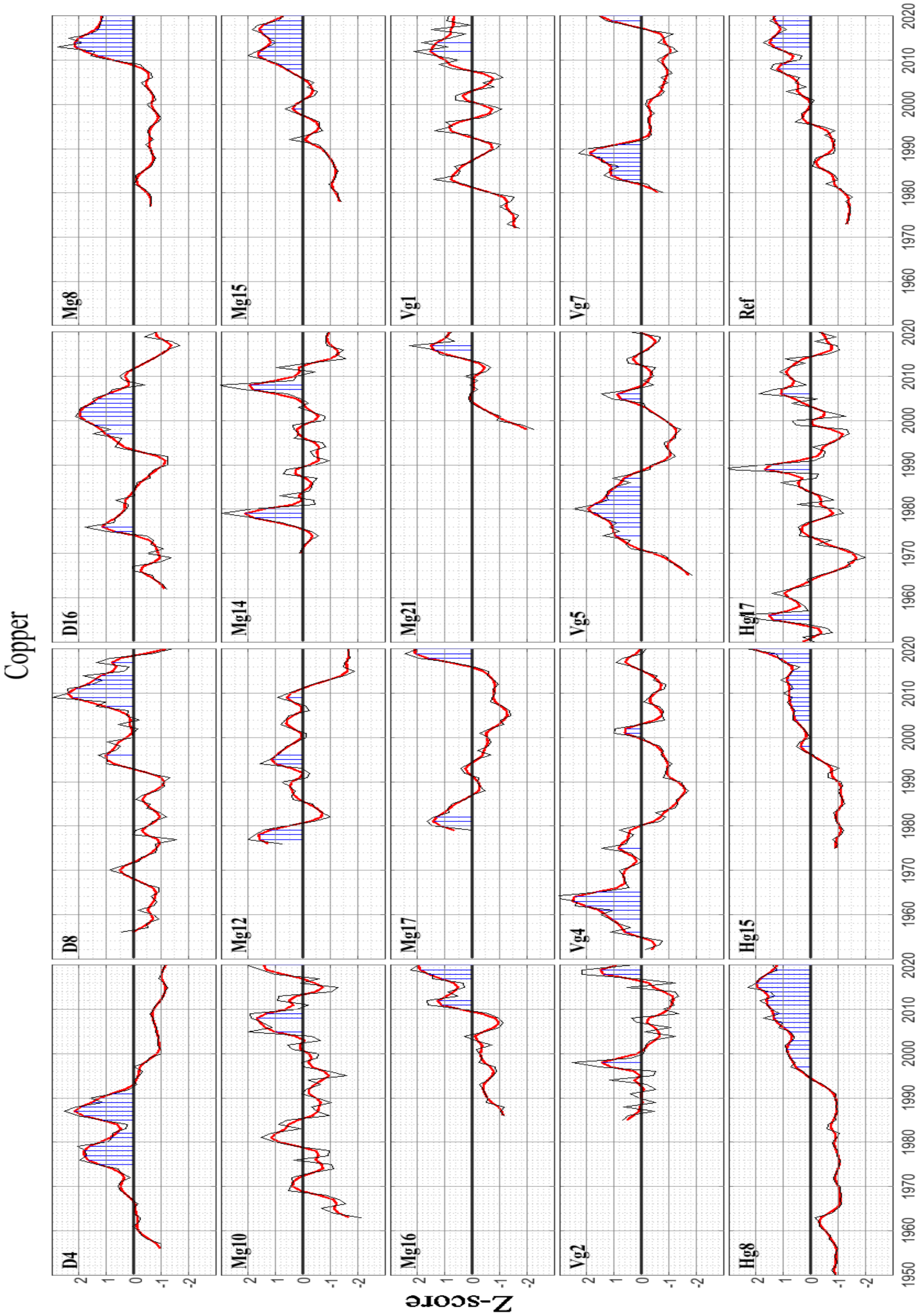
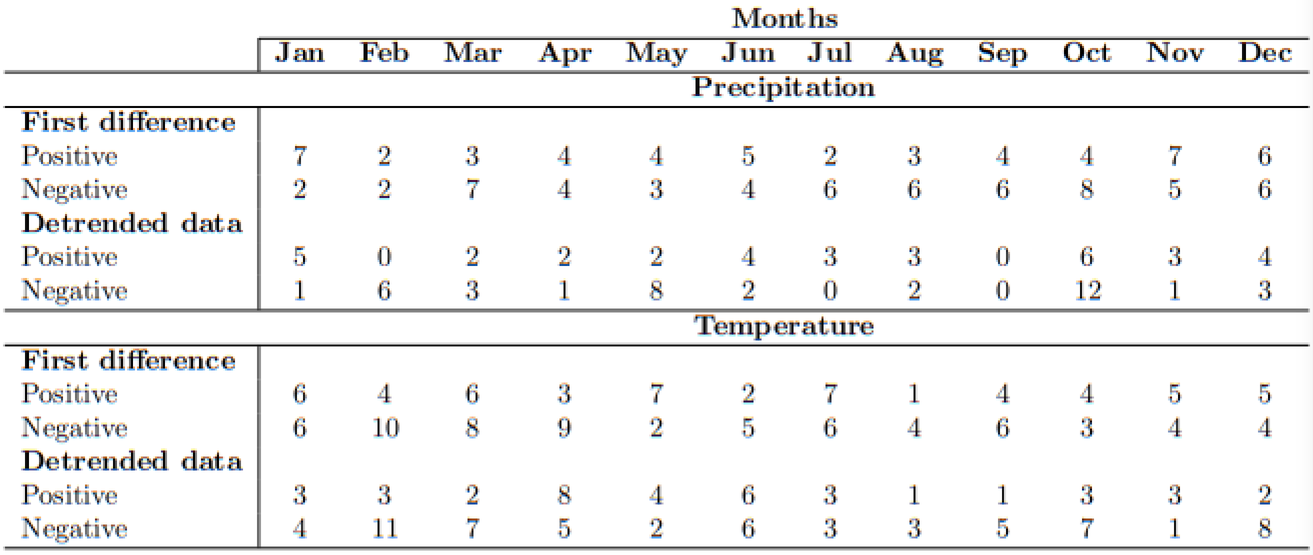


Figure 14: Dendrochemical profile for all samples. Anomalous years are marked with the blue vertical line. The black line shows raw dendrochemical data for Cu, while the red line represents data filtered using 10% of the sample length and fitted with a Gaussian curve. The Y-axis displays z-scores. "Ref" represents the average dendrochemical profile. Reference sample 13 exhibits anomalies during the years 1996-1998, while Reference sample 7 shows no anomalies.

3.4 Climatic Influence on Dendrochemical Signals

Spearman correlation of first differences revealed a low correlation on an interannual level (*$p<0.05$*). Approximately 7% of all chemical profiles have a significant correlation (*$p<0.05$*) with temperature and precipitation, independent of direction (*Table 4*). Arsenic and Cd showed a greater tendency to correlate with temperature, while Ni, Cu, and Zn have higher correlations with precipitation. Pb exhibited an equal number of correlations with both temperature and precipitation. The relationship between temperature and precipitation and the TEs is highly variable in direction, as indicated by the low average correlation coefficient (r-bar) values across all TEs *(-0.059 – 0.066)* (*not shown*). Correlations between climate and polynomial residuals also revealed few significant correlations (*$p<0.05$*), with temperature showing 40% more correlations than precipitation. Correlation with raw data revealed a more robust pattern between TE uptake and climate, especially for temperature. Temperature exhibited twice the number of significant correlations as precipitation at $p<0.05$. Upon correcting for type-1 error, the number of significant correlations was nearly eliminated. Temperature showed one significant correlation for first differences and two for residuals, while precipitation showed one for first differences and none for residuals. Raw data analysis yielded similar results, with precipitation showing no significant correlations and temperature revealing six.

Table 4: The number of significant correlations for First Difference and detrended data with p<0.05 (Result without type-1 error correction). Positive = positive r-value. Negative = negative r-value. The significant correlations refer to the total number of significant correlations for all TE (As, Cd, Cu, Ni, Pb, and Zn).



	Months											
	Jan	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**
	Precipitation											
First difference												
Positive	7	2	3	4	4	5	2	3	4	4	7	6
Negative	2	2	7	4	3	4	6	6	6	8	5	6
Detrended data												
Positive	5	0	2	2	2	4	3	3	0	6	3	4
Negative	1	6	3	1	8	2	0	2	0	12	1	3
	Temperature											
First difference												
Positive	6	4	6	3	7	2	7	1	4	4	5	5
Negative	6	10	8	9	2	5	6	4	6	3	4	4
Detrended data												
Positive	3	3	2	8	4	6	3	1	1	3	3	2
Negative	4	11	7	5	2	6	3	3	5	7	1	8

4 Discussion

4.1 Soil Samples

4.1.1 Spatial Distribution and Uptake of Trace Element

The spatial distribution of TE displays significant heterogeneity frequently observed on a local scale at industrial sites (Austruy et al., 2019). Cu is the primary pollutant in the area, as confirmed by the high total Cu concentrations found in the soil samples (*Fig 12*) and corroborated by the findings of the County administrative board (Länsstyrelsen, 2004). The Cu distribution is highly variable between samples, with differences of up to 200 times observed at Mormorgruvan. The channel with water running from Nygruvan passes near where Mg21 samples are collected. Since Nygruvan receives runoff water from Mormorgruvans tailings, higher concentrations of TE due to leaching could be possible in the vicinity of the water (Höglund et al., 2003). The significant differences between Mg21 and Mg14 demonstrate mining areas' highly complex and variable soil chemistry. Despite their absence in the soil samples, Cd and Ni were recorded in the dendrochemical profile for all samples (*not shown*). Several samples do however show years without a dendrochemical signal for Cd and As, which aligns with the soil samples' low Cd and As concentrations.

Total TE concentration provides a variable and generally poor indication of tree-ring TE concentration, and using a soil sample to confirm the contaminating status (Watmough, 1999) has its constraints and should be considered a sampling strategy with limitations. As demonstrated in other studies (Kabata-Pendias & Pendias, 1992; Mandre, 2014), there is a weak relationship between total TE concentration and root-uptake. Furthermore, the results of this study reaffirm the findings of previous research, highlighting the need for caution when interpreting the relationship between total soil concentration and tree TE uptake (*Fig 12; Fig 13).*

The weak penetration depth of the X-rays and small beam diameter (8 mm) limit the measured soil volume to around 0.01 cm^3 - 0.02 cm^3, resulting in sample masses in the tens of milligrams range (Laperche & Lemière, 2020). Additionally, Sanden et al. (1988) found that TE concentration and pH at the Bersbo mining field, 10 km northeast of Närstads mining field, highly depend on mass water flow. During a single season, pH changes by several units, and Cu concentration varies tenfold. Consequently, soil samples are merely a snapshot of soil chemistry at the collection site.

Along with the extensive root system and massive volume of root-soil interaction compared to the analyzed soil, a poor relationship between soil samples and tree-ring could therefore be expected, making soil samples a poor indicator for identifying trees affected or influenced by pollution. However, detecting total concentration indicates potential TE availability (Antoniadis et al., 2017).

4.1.2 Soil pH

The pH measurements, spanning 2.5 units over short distances, indicate a highly heterogeneous distribution of bioavailable TE (Kabata-Pendias & Szteke, 2015). This finding emphasizes the complexity at industrial sites and supports the observed limitations in predicting TE uptake by trees based on soil chemistry. Considering pH as the primary factor controlling bioavailability (ibid), the generally low pH at the reference site, including seasonal variations (Sandén, 1988) could explain higher TE uptake despite low total TE concentrations. The lower pH at the reference site is likely due to the naturally low pH in coniferous forest soils (Nilsson et al., 2015), which would increase bioavailability compared to the more alkaline soil at the mining field (Kabata-Pendias & Szteke, 2015).

No significant relationship was found between regional pH and individual samples. However, the decreasing pH trend of 0.01 units per year (*not shown*) aligns with the increase of TE in several samples over the same period (*1995-2020*). The dominant effect of soil pH on TE solubility and bioavailability would favor free metal cations, increasing TE uptake (Rengel, 2011). Therefore, the lack of a statistical relationship between regional pH change and TE uptake should not be interpreted as a lack of influence. The acidification trend is likely one of many factors affecting dendrochemical signals in the area.

4.2 Dendrochemistry

4.2.1 Contaminated and Reference Sites: A Comparison

The observed significant differences in metal content between the contaminated and reference sites imply that historical mining activities continue to influence chemical soil properties 150 years after the mine's closure (*Table 2*). Earlier studies have attributed higher mean concentrations and more significant variances to greater variations in pollutant concentrations (Austruy et al., 2019; Odabasi et al., 2016). These studies suggest that diverse pollution sources and their varying intensities in contaminated areas could contribute to the increased variance in tree rings. High variations observed in tree rings and among different sites have been attributed to industrial activity in various tree species (Baldantoni, Cicatelli et al. 2014, Xu, Tong et al. 2014). Although the mean is more significant for all TE, the result raises questions about the method of averaging multiple samples. Averaging provides a composite picture of the dendrochemical signals across a larger area but may not accurately represent the variation and severity of pollution.

Furthermore, averaging samples with varying lengths or TE concentrations may result in a poor representation of the pollution history. While averaging is commonly used in dendrochemical studies (Chen et al., 2021; Muñoz et al., 2019; Nechita et al., 2021), it does not adequately reflect the contamination levels (*Fig 12*). Cu levels are several thousand percent higher than the reference site. In contrast, the average dendrochemical data reveals a 48% increase compared to individual samples showing up to 300% higher concentrations (*Table 2; Fig 13*).

4.2.2 Differences within and between Samples

At the sub-location level, Varpgruvan is the only location showing a significant difference across all TE. This aligns with the Länstyrelsen. (2004) calculations of sulfide content (*Varpgruvan: 40-60% sulfide-rich waste; Mormorgruvan: 10-20%; Haggruvan: "Waste dominated by bedrock without extensive sulfide mineralization or weathering")* in the tailings and weathering grades on waste rocks. Higher amounts of sulfide-bearing waste lead to increased acid mine drainage, resulting in greater mobility of free ions and increased bioavailability (Barceló & Poschenrieder, 1990).

The individual samples (*Fig 13*; *Fig 14*) show high variation within and between samples. Unexpectedly, reference samples demonstrate higher TE uptake than several contaminated samples. Earlier dendrochemical studies have attributed variability between and within samples to differences or changes in micro-climate and environmental conditions (Austruy, Yung, et al. 2019), soil chemical properties (Rocha, Gunnarson, et al. 2020), or physiological mechanisms related to allocation and sequestration (Smith, Balouet, et al. 2014), highlights the complex interactions between TE pollution and uptake. In light of the complexity, mineralization shows an uneven distribution in the bedrock (Länsstyrelsen, 2004), and soil properties are highly variable over short distances (*Table 1; Fig 12*). Aspen's extensive root system and the defense mechanism to exclude trace elements by redistributing root biomass (Kahle, 1993) and altering rhizosphere characteristics (Guerra et al., 2011) could result in low tree-ring concentrations.

Furthermore, the Populus genus displays high inter- and intraspecific variability, which can influence plant growth and adaptation to different environments (Sebastiani et al., 2014). Specific genes involved in internal processes for managing harmful substances can be expressed differently depending on the root environment (Hassinen et al., 2009; Kohler et al., 2004). The high spatial variation in soil TE (*Fig 12*) might lead to changes in the compartmentalization and translocation of TEs towards roots or shoots, as seen in several studies (Laureysens, Blust, et al. 2004, Hassinen, Vallinkoski, et al. 2009, Baldantoni, Cicatelli, et al. 2014). Which could manifest as relatively low concentrations when sampled at chest height.

4.3 Dendrochemical Anomalies and Their Response to Climatic Variations

Two periods of well-defined TE anomalies are evident in the dendrochemical records: the mid-1970s to the mid-1980s and the late 2000s. In contrast, a period centered around 1990 displays low to non-existent anomalies and reduced TE concentrations. Despite a weak year-to-year relationship between dendrochemical signals and climate variables, long-term trends and peaks can be identified between samples and climate variables (Fig 3; *Fig 14*).

During the 1960s to the 1980s, industrial emissions and vehicle exhaust of SOx and NOx peaked in Sweden, leading to challenges with acid deposition, TE leaching, and mobilization across the country. Since 1980, regulations have reduced national emissions by 90% and European emissions by 70% (Wilson & Bell, 1996), mitigating acid rain and its environmental impacts (Havs- och vattenmyndigheten, n.d). Boreal ecosystems display sensitivity to acid deposition during snowmelt events, as precipitation accumulates over several months and rapidly enters streams and soil within just a few weeks (Laudon et al., 2004). Both high amounts of snow during winter, and rain during snowmelt contribute to the significant impact on water flow observed during these events (SMHI, 2023). Sandén. (1988), found that a significant part of the annual metal transport occurs during spring and autumn, while low metal transport results from low runoff. High water flow and floods can increase TE bioavailability by causing variations in biogeochemical processes, such as denitrification, manganese and iron oxide reduction, and sulfate reduction (Antoniadis et al., 2017).

The climate data (*Fig 3*) show that the 1970s-1980s experienced high precipitation, particularly in early spring, whereas the 1990s saw below-average precipitation for almost all months. Consecutive years of dendrochmical anomalies or local maxima during climatic conditions favoring high water flows and the reversed patterns during low, suggest higher transport and bioavailability of TE during wet periods recorded in the trees. The dendrochemical records also reveal increased TE uptake and anomalies during the 2000s, a period with higher precipitation and temperature than in the 1970s-1980s. Although statistical evidence for this relationship still needs to be provided., the collective signals across different locations reveal a dendrochemical response to changes in hydrological conditions which are expected to increase TE transport and bioavailability (Antoniadis et al., 2017). Further research is necessary to draw definitive conclusions on how climatic variations can modulate tree-ring TE concentrations.

4. 4 Climate Variations, Dendrochmical Signals, and Trace Element Uptake

When examining high-frequency data, a limited relationship between temperature and precipitation variations and metal content in tree rings becomes evident (*Table 4*). Only a few significant correlations with first- differences and detrended data suggest that variations in monthly precipitation or temperature do not substantially impact uptake. However, more significant correlations indicate that temperature might influence trace element uptake more than precipitation over short-term variations. Elevated soil temperatures can enhance the bioavailability of TE by altering pH and redox potential and promoting microbial activity and metabolism, which in turn leads to increased mobility (Biswas et al., 2018). In contrast, some dendrochemical studies have identified associations between both factors, indicating an immediate response in metal uptake following precipitation events (Chen et al., 2021; Cui et al., 2013).

Grouping climatic variations by calendar month may not accurately represent dendrochemical signals, as anomalies suggest TE absorption resulting from the accumulated effects of multiple climatic variables (*Section 4. - Dendrochmical Anomalies*). Investigating alternative approaches for grouping climatic variables could enhance correlations. Moreover, trees with roots accessing groundwater, in addition to soil water, may be less sensitive to monthly fluctuations or display delayed dendrological responses with several years (Balouet et al., 2012). Populus hybrids have been demonstrated to absorb aromatic hydrocarbon pollution from fractured bedrock (BenIsrael et al., 2019; BenIsrael et al., 2020). Furthermore, the soil layers are thin, particularly at Mormorgruvan and Varpgruvan, and mining-induced fractures affecting groundwater flow are expected (Länsstyrelsen, 2004). Historical records on production reveal that high water flow in the mines slowed down or halted production during "bad" years (Åtvidaberg, 2009). Thus, facilitated access to groundwater is plausible.

Additional research is necessary to draw definitive conclusions on how climatic variations influence tree-ring TE concentrations and how different water sources affect dendrochemical signals.

4.5 Assessing the Potential and Limitations of Dendrochemical Analysis for Reconstructing Historical Pollution

Dendrochemistry offers a promising method for providing high-resolution temporal and spatial pollution histories; however, more research is needed to establish it as a common environmental forensic tool. This study emphasizes some of the limitations in the method.

4.5.1 Limitations

Many dendrochemical studies investigate pollution events, such as oil spills (Balouet et al., 2007) or industrial operations (Chen et al., 2021), that occur during the lifetime of the studied tree. The year preceding the contamination event is used to establish background values (Balouet, Oudijk et al. 2007). However, due to mining activities spanning centuries and the essential role of trees and charcoal in early mining (Bernes & Lundgren, 2009), finding trees that can provide background values or enable longer reconstructions around older industries can be challenging (Rocha et al., 2020). The generally weak associations between soil TE concentration, soil pH, and tree-ring concentration indicate complex soil-root relationships, which can make it difficult to identify suitable trees for dendrochemical analysis that accurately record pollution events. This emphasizes the limitations of using a single soil sample as an indicator of tree-ring concentration and as a mean to confirm contamination status. A deeper understanding of how soil properties affect TE uptake is needed to overcome these challenges.

4.5.2 Potential

The low correlation between dendrochemical profiles and climate factors, combined with the fact that anomalies appear during periods of high precipitation and wet conditions (*Fig 3; Fig 14*), suggests that TE anomalies are more closely related to hydrological conditions than monthly variations or specific events. High water flow are associated with an increase in metal movement and these conditions can create an environment that facilitates the uptake and transport of TE (Sandén, 1988). Occurens of anomalies when climatic conditions favours TE movement indicates that this method can potentially reveal historical pollution changes in relation to climate variations. To draw conclusions, statistical evidence is needed, and identifying the primary water source is essential for accurately interpreting dendrochemical variations in relation to climatic and environmental changes.

4.5.3 Aspen as a Model Species

European aspen presents certain advantages and challenges for investigating pollution variations. Aspen have an extensive root systems with various defense mechanisms, which could influence trace element uptake and make interpretations more difficult (Binda et al., 2021; Guerra et al., 2011). High variability within the Populus genus may also affect growth and adaptation, impacting TE allocation in plant parts. Several studies show a higher accumulation of TE in roots and shoots, suggesting that a more accurate picture of historical variations could be achieved with samples taken at different heights or by sampling other plant parts, such as roots (Baldantoni et al., 2014; Guerra et al., 2009; Hassinen et al., 2009).

Despite challenges, aspen is widely distributed, capable of growing in contaminated areas, and often used in phytoremediation (Baldantoni et al., 2014; Kozlov & Zverev, 2022). European aspen have demonstrated suitability of for environmental investigations (Rocha et al., 2020), and this study aligns with prior research. Future studies focusing on how different plant parts record contamination events would be a crucial aspect to further develop dendrochmical methods.

5 Conclusion

This research stands as one of the most extensive dendrochemical investigations conducted using ED-XRF, highlighting the potential of European Aspen for reconstructing contamination history. The enduring impacts of anthropogenic activity are revealed by the significantly higher trace element concentrations in trees from mining sites. Nevertheless, samples from these sites showed lower concentrations than the unpolluted site, indicating complex soil-root interactions and tree defense mechanisms influencing the dendrochemical signals. The inherent heterogeneity in contamination and observed variations in trace element uptake underscore the necessity for a larger sample size in future studies to ensure a more accurate interpretation of the data. This underlines the need for further research, focusing on the influence of soil characteristics, including the observed high variability in contamination levels and pH on TE uptake, the exploration of various plant parts for a more comprehensive depiction of historical contamination, and an investigation into the high variability within the Populus genus and its impact on trace element allocation.

While the samples display a low correlation with short-term climate variations, a collective signal identifies a relationship between high water flows and trace element uptake. Notably, pronounced TE anomalies during the mid-1970s to mid-1980s and late 2000s coincided with climatic conditions favoring high water flows. This suggests that hydrological variations could modulate trace elements in tree rings, potentially positioning dendrochemistry as an alternative proxy for reconstructing past hydrological variations. Despite the promising results, addressing the mentioned challenges can further elevate dendrochemistry as an innovative approach to understanding historical pollution events, their spread, and ecosystemic impacts. Ultimately, dendrochemistry could be an essential tool for understanding the fate of existing polluted sites in a changing climate and for shaping future mitigation and restoration efforts for ecosystems impacted by anthropogenic activities.

If trees could talk, they might tell tales of their environmental past. Through dendrochemical analyses, we are beginning to decipher their language and listen to their stories.

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