A study of the behavior of selected metals in affected environments using an isotopic approach

Studium chování vybranych kovů v ovlivněném prostředí
s využitím izotopů

Mgr. Rafael Santos Baieta

Ph.D. thesis

Supervised by prof. RNDr. Martin Mihaljevič, CSc.

Institute of Geochemistry, Mineralogy and Mineral Resources
Faculty of Science
Charles University

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Dedication

I dedicate this thesis to my grandmother Zélia, whom I lost during my time in Prague, for her love of education and my love for her. She had the will to see me finish my Ph.D. I failed her in that regard. I engrave her name here, hoping that she might forgive me and that I did make her proud in the end.

Desculpa-me avó. Obrigado por tudo.

Declaration of the author/Prohlášení autora:

I declare that this Ph.D. thesis was written by myself and that all the literary sources were appropriately cited. Neither this work nor the substantial part was used to reach the same or any other academic degree.

Prohlašuji, že jsem předkládanou disertační práci vypracoval samostatně a že všechny použité literární zdroje jsou řádně uvedeny. Dále prohlašuji, že tato práce ani její podstatná část nebyla předložena k získání stejného či jiného akademického titulu.

In Prague, October 2022
V Praze, říjen 2022

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Rafael Santos Baieta

Abstract

Metals of anthropogenic origin have consistently polluted the environment. This thesis focuses mainly on highly contaminated soils or tree rings near mines and smelters in Sub-Saharan Africa. However, Portuguese soils were also assessed to study Pb isotopes in post-fire soils. The tracing capabilities of Pb isotopic ratios were employed to determine contamination sources and to evaluate the potential of pine trees as an environmental archive.

Several analytical methods were applied, such as catalytic oxidation, Q-ICP-MS, ICP-OES, FEG-SEM/EDS, EPMA, XRD, etc.

Soils near smelters located in three different cities [Kabwe (Pb-Zn), Luanshya (Cu, Co), and Selebi Phikwe (Ni, Pb)] exhibited concentrations of metals greatly exceeding those deemed acceptable by the competent authorities. In Kabwe, for example, concentrations of Pb exceeded 16 000 mg kg^{-1}. In all sites, contamination was shown to be significant only in the upper ±15 cm of soil. Samples of soils taken in remote locations were always clear of contamination.

In Luanshya, metal(oid) bearing particles found in the soils were typically spherical and composed of rapidly cooled sulfides and oxides in the flue gas chambers of the local smelter. These were present only in the topsoil.

The tree ring record of pine trees in Kabwe was shown to mimic the historical production record of the local smelter within a shift of 5 − 7 years. Carbon isotopes were also used to predict stress in the trees. These moments were concurrent with peaks in smelter production.

Forest fires were shown to alter the Pb isotopic makeup of soils depending on burning temperature. We suggested that the Pb isotopic ratios of soils may be used to determine burning temperature, but more study is needed.

Additionally, Pb originating in the legacy of leaded gasoline burning was found in all studied systems, as shown by its isotopic signature.

Abstrakt

Antropogenní zdroje trvale znečišťují životní prostředí řadou kovů. Tato práce se věnuje studiu chování vybraných kovů především ve vysoce kontaminovaných půdách a letokruzích stromů v blízkosti dolů a hutí subsaharské Afriky. Ke studiu portugalských půd po požárech, hledání zdrojů kontaminace a k zhodnocení letokruhů borovice coby geochemického archívu byly využity izotopové poměry Pb.

Pro tento účel bylo využito řady analytických metod (např. Q-ICP-MS, ICP-OES, FEG-SEM/EDS, EPMA, XRD).

Studované vzorky půd byly odebrány v blízkosti hutí, které se nacházely ve třech městech [Kabwe (Pb-Zn), Luanshya (Cu, Co) a Selebi Phikwe (Ni, Pb)]. Ve všech případech obsahovaly takové koncentrace kovů, které značně překračují hodnoty považované příslušnými orgány za přijatelné. Kupříkladu obsahy Pb na lokalitě Kabwe přesahovaly 16 000 mg kg^{-1}. Na všech lokalitách byla kontaminace významná jen v povrchové části půdy (hloubka ± 15 cm). Vzorky odebrané ve vzdálenějších místech od hutí byly vždy bez kontaminace.

Na lokalitě Luanshya byly kovy a polokovy v půdách vázány na kulovité částice, které byly tvořeny rychle ochlazenými sulfidy a oxidy pocházející z huti. Tyto částice se nacházely pouze v povrchových částech půd.

Podařilo se prokázat, že obsahy kovů v letokruzích borovic na lokalitě Kabwe korespondují s historickou produkcí místní huti s posunem 5 – 7 let. Studium izotopů uhlíku ukázalo, že se zvýšenou produkcí huti a vstupu kovů do letokruhů docházelo ke zvýšenému stresu studovaných stromů.

Studie o lesních požárech odhalila, že izotopové poměry Pb v postižených půdách jsou ovlivněny teplotou hoření. Po dalším detailním studiu by tedy pravděpodobně šlo využít izotopových poměrů Pb k určení teploty hoření.

Izotopové signatury Pb ukázaly, že ve všech studovaných systémech se také nacházelo Pb pocházející ze spalování olovnatého benzínu.

Index

List of Annexes

1.   Introduction

1.1.   Metals polluting soils

Soils play a significant role in the sustainability of the environment and human civilization due to their productivity. Therefore, the maintenance and management of this resource are of utmost importance and fall under society's responsibility (Kabata-Pendias, 2010).

Before any discussion on soil pollution is to be had, It is essential to understand the difference between soil contamination and pollution. Knox et al. (2015) defined soil contamination as soil whose chemical composition deviates from the normal composition but does not negatively impact organisms. Soil pollution, however, occurs when human activities cause the increase of specific elements or compounds compared to background levels and negatively impact the environment.

The main contributors to local and regional inorganic atmospheric contamination are metals, metalloids, and sulfur dioxide (SO_2) released during smelting. They subsequently reduce soil and water quality and harm human and animal life due to the inhalable nature of the emitted nano-sized particles (Biswas et al., 2007; Vespa et al., 2010). They reach the surface of the soils, and their impact depends

on the soils' chemical and physical properties and the speciation of polluting particles.

Researchers have applied several methods to understanding the consequences of these particles' presence in different environments. For example, some scientists use air samplers to capture and study smelter-derived atmospheric pollution (Dye et al., 2000). The collected particles can then be examined for their properties. Leaching tests using acids mimicking the digestive capabilities of the lungs and stomach to determine the extractability of the metals present within consumed or breathed particles (Ettler et al., 2019, 2018, 2014b, 2012). A more direct approach may also be adequate. For example, Yabe and his team have extensively studied the biology of people and creatures in a site heavily polluted by a Pb-Zn smelter: Kabwe, Zambia. They have found increased levels of Pb in the blood (Yabe et al., 2015), urine, and feces (Bose-O'Reilly et al., 2018; Yabe et al., 2018) of local children and in the tissues of animals: liver and kidneys of cattle (Yabe et al., 2011) and chickens (Yabe et al., 2013). Lead is the primary pollutant worldwide, but local and regional pollution always depends on which metals are extracted locally. For example, up to 65 % of anthropogenic Cu atmospheric emissions happen due to smelting (Nriagu and Pacyna, 1988). As later discussed in this work, the surrounding soils of smelters and mines working with this metal are heavily impacted. For example, people intoxicated

by Cu can present various health issues like liver and kidney disease (Gaetke and Chow, 2003).

Humanity has long since started smelting ores for their metals to be used in various ways. Of course, this led to some pollution. Smelted amounts were minimal for most of human history, so pollution was never widespread. The first primitive smelting techniques are believed to have been invented around 8000 years ago, which would have caused the first man-caused Pb emissions (Goodwin and Ponikvar, 2013). Any age of cultural development led to some metal pollution stored in sediments, soil, and ice (Kabata-Pendias, 2010). Through the past 1000 years, however, Pb concentrations in soils have consistently risen due to increased anthropogenic activities. Today this development is recorded in polar ice cores, which we can study (Dickson et al., 1972).

The most significant propagation of Pb in the environment has been observed throughout the last century, precisely due to the advent of leaded gasoline. Fortunately, this practice has declined over the past few decades due to the increased awareness of its negative impact on the environment. Countries and institutions had continuously banned this fuel, culminating in August 2021 when Algeria stopped producing it, the last country to do so (Lobet, 2021). Studies have reported that atmospheric Pb has declined since the banning movement started (Bollhöfer and Rosman, 2002, 1997, 2001). Soil Pb

concentrations worldwide are now decreasing, a first in recorded history (Friedland et al., 1992; Trefry et al., 1985).

These developments are cause for celebration, but one must be aware that Pb is still present in soils or at sites like Kabwe, which still suffer from active pollution. The immobile nature of Pb in soils implies a high retention time, meaning that the return to pre-anthropogenic concentrations can take a long time (Harrison et al., 1981). Hence, studying and understanding the Pb remains is still vital (Figure 1).

Figure 1 Slag dump magnitude compared to the active smelter facilities in Selebi Phikwe.

1.2.   Smelter-surrounding soils in sub-Saharan Africa

Continental sub-Saharan Africa has been the stage for exploration and exploitation of natural resources without regard for the environment till the present day. Due to the disinterest, ignorance, or incapability of governing bodies and mining companies to act, mining and smelting have remained among

4

the most polluting activities in Africa (Durand, 2012; Edwards et al., 2014). Historically (and still to this day), resource exploitation has not been universally regulated, or enforcement has not taken place (Dong et al., 2013), allowing high metal concentrations to accumulate in the topsoils surrounding these locations (Dudka and Adriano, 1997; Merrington and Alloway, 1994). There are several examples of mining towns that, to this day, are constructed on highly contaminated soils.

The soils affected by these activities will remain contaminated due to the non-biodegradable nature of the metals (Li et al., 2004), so work must be done to understand their behavior and how to remediate the problem (Nakayama et al., 2011). Studying each site separately is essential, and not developing a general solution. That would not be optimal since the extent of smelter-derived metal contamination in soils is typically dependent on the chemical and physical characteristics of the polluting particles (Vera Castellano et al., 2004) and the soils themselves (Kříbek et al., 2019).

The work done on this thesis touches on Kabwe and Luanshya in Zambia and Selebi Phikwe in Botswana (Figure 1, 2). However, many others surrounding the Central African Copperbelt suffer the same fate. A few examples: Kombat (Mihaljevič et al., 2019) and Tsumeb (Ettler et al., 2016) in Namibia, Nkana, (Ettler et al., 2011), Kitwe (Ettler et al., 2011; Mihaljevič et al., 2018, 2011) in Zambia, among others.

Figure 2 View from the top of Selebi Phikwe's slag dump.

1.3. Mobilization of metals in soils

The presence of metals in large concentrations in soils is not, by itself, problematic. The negative impact arises when mobilization takes place. When mobilized from soils, Pb has been shown to contaminate water resources (Abraham et al., 2017; Ré et al., 2021; Trefry et al., 1985) and be transported elsewhere. Metal-bearing particles may be wind-blown and transport contaminants far away from the source (Csavina et al., 2014, 2011), or they can be pulverized. Direct and intentional soil ingestion is common in Africa and referred to as *pica* or *geophagia*. Indirect ingestion also occurs from hand-to-mouth or dermal contact. Dust inhalation may also happen (Zhao et al., 2021). Ingestion of contaminated crops or cattle is considered indirect ingestion. Plants can incorporate metals and metalloids by root uptake or deposition on bark and leaves (Bigalke et al., 2011; Jiang and Liu, 2010; Piechalak et al., 2002; Shahid et al., 2011). Mobilization can happen in many ways. The work done in this thesis partly focuses on the plant aspect of mobilization (Baieta et al.,

6

2021), mobilization occurring during wildfires (Baieta et al., 2022), and leaching from soil particles.

1.4. Wildfires affecting soils

Climate change is real. Temperatures have been rising yearly, causing many concerns for both populations and the environment (Figure 3). One of those concerns is the rise in wildfire frequency (IPCC, 2022).

A wildfire constitutes an accidental fire, including unauthorized human-caused fires, escaped prescribed fire projects, and fires caused by lightning (Hoover and Hanson, 2022). The US Congressional Research Service reported that the number of wildfires has decreased throughout the past 30 years while the number of acres burned has increased. The average number of acres burned yearly from 2000-present is doubled compared to the 1990s (Hoover and Hanson, 2022).

One of the most significant impacts of wildfires is how they affect the soils in the burned areas. Organic matter is one of the main soil components (especially in topsoils), and a portion or all of it is always lost during fires due to its combustible properties (Giovannini et al., 2001). High temperatures can cause the partial or total volatilization of some soil nutrients, like organic nitrogen (Fisher and Binkley, 2000). On the other hand, the combustion of the soil biomass and subsequent ash generation may concentrate other nutrients (potassium, phosphorus, Kutiel and Shaviv, 1992). Runoff and wind erosion are also concerns

in post-fire soils (Martin and Moody, 2001) due to decreased porosity when the soil structure is affected (Durgin and Vogelsand, 2011). The easy transport of the soil's finer fractions may cause the soil to become coarser (Mermut et al., 1997). In addition to altering its chemical and physical properties, soil firing may also significantly affect its biological component (Certini, 2005). Mobilization occurs furthermore when smoke particles are transported high up into the atmosphere (Tuhý et al. (2021), Figure 3).

Figure 3 Viral photo of a forest fire in Vieira, Leiria in Portugal (2017).

1.5.   Trace elements in plants

Our interest was mainly in plants' ability to store uptaken metals in their biomass. Plants accumulate trace elements, *heavy metals*[*] in particular, in or on their tissues while adapting to the chemical properties of the surrounding

*This term is increasingly frowned upon.

environment. Hence, plants are passive receptors of trace elements due to fallout on their leaves and bark and by root uptake while also controlling the uptake or rejecting some elements. Historically, this property of plants has been used as a geochemical indicator in prospecting for valuable ore metals (Vernadsky, 1998).

The metabolic fate and role of each trace element in plants have been summarized by Kabata-Pendias (2010) as follows:

1. Uptake (absorption) and transport within a plant,

2. Enzymatic processes,

3. Concentrations and forms of occurrence,

4. Deficiency and toxicity,

5. Ion competition and interaction.

There are three entry points for trace elements in plants: root uptake, foliar uptake, and, in the case of trees, absorption through the bark (Klaminder et al., 2005; Watmough and Hutchinson, 2003).

Metal uptake through the roots of a plant can be both a metabolic (active) and a nonmetabolic (passive) process. In either case, the concentration of metals in the available pool correlates positively with the uptake rate (Kabata-Pendias, 2010). Essentially, the diffusion of ions from the exterior to the interior of the roots classifies as passive uptake, while active uptake occurs against the natural gradient requiring energy. The relevant mechanism in root uptake

will depend on the characteristics of the solution present in the soil and which elements are involved. For example, Pb is preferably absorbed passively, while active processes preferably absorb Cu and Zn. If the elemental concentrations in the soil are greater than a certain threshold, all absorption processes become passive (Loneragan, 1975).

Leaves function as an entry point for airborne metals and other compounds. Foliar uptake occurs by metabolic mechanisms and nonmetabolic cuticular penetration, the most important route of entry. The first occurs when an element is accumulated against the natural gradient (Kabata-Pendias, 2010). Trace elements that enter the plants through the leaves can migrate to other tissues, even the roots. Studies have shown that Pb, Cd, and Zn are not likely to migrate to the roots, although Cu seems very mobile (Kabata-Pendias, 1979). Some plants, in particular, are much more susceptible to absorbing trace metals from the atmosphere, making them very suitable for the photoindication of atmospheric pollution.

1.6. Tree rings as an environmental archive

Common knowledge states that trees grow radially from a central point and form *rings* or layers that can be counted to determine the tree's age (Figure 4). As the tree grows, the rings become hardwood, locking in any uptaken metals. Like ice cores from the polar caps, or lake sediments previously mentioned, tree rings can be used to window into the past.

10

Figure 4 Tree section reveals its yearly growth rings and their asymmetry. @istock.com; credit: Mehmet Gokhan Bayhan.

Lepp (1975) wrote:

"The precise measurement of heavy metal levels within successive annual growth rings of trees presents, at first sight, an attractive and straightforward means for producing a detailed history of heavy metal pollution."

This single article gave rise to the field of dendrochronology, which today helps researchers composite a more accurate picture of past events. Tree rings have also been used as an approximate environmental archive (Mihaljevič et al., 2015, 2008; Tommasini et al., 2000; Watmough, 1999) specifically for Pb anthropogenic emissions, allowing for a detailed understanding of the human impact on the ecosystems. However, Lepp already understood that tree rings could not be used as an infallible source for detailed past atmospheric/soil composition modeling, writing:

"However, before serious consideration is given to such a technique, many processes relating to the uptake, transport, and deposition of heavy metals within trees must be understood."

Since then, studies have uncovered several factors that may hinder the reliability of tree rings as an environmental archive. These factors include climatic variations (Kirdyanov et al., 2007; Time et al., 2018), soil acidity (metal mobility) fluctuations not caused by pollution sources (Kabata-Pendias, 2010), radial mobility in the xylem (Cutter and Guyette, 1993; Prohaska et al., 1998), different elements having distinct roles in the tree and various species of trees behaving differently (Patrick and Farmer, 2006; Watmough, 1999).

Following the works of Satake et al. (1996), barks pockets instead of tree rings have started being used. Several works from the same group have shown that this approach may have advantages (Bellis et al., 2005, 2004, 2002a, 2002b). However, it is not always possible to obtain these samples. The most obvious disadvantage is that it implies that the tree must be cut instead of thinly drilled with the bore extractor used to obtain an entire tree ring core.

1.7. Lead isotopic ratios as a tracer for contamination

One can ascertain the condition of a chosen environment or material to be contaminated or polluted by simply determining if the concentration of a specific element or compound deviates from the established norm. However, this path alone is not adequate to unearth the source of said contaminants or pollutants.

12

Komárek et al. (2008) stated that the knowledge of Pb's chemical and mineralogical position in soils is not enough to ascertain the source of this metal. Hence, various methods have been studied to trace these foreign components to their origin. One of those methods implemented in this thesis is the usage of Pb isotopic ratios, specifically $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$.

The versatility of Pb isotopes as a tool for tracing sources of contamination should not be understated. The literature strongly supports its utility in several different fields, such as: determining migration velocities in sediments (Erel, 1998; Puchelt et al., 1993), chronological markers (Baieta et al., 2021; Renberg et al., 2001; Shirahata et al., 1980), direct contamination source determination: waste incineration (Monna et al., 1997), mining/smelting processes (Baieta et al., 2021), leaded gasoline-related deposition (Baieta et al., 2022; Hernandez et al., 2003), among others. A review by Komárek et al. (2008) extensively describes the usage of Pb isotopes in environmental sciences. That versatility was exploited during the works executed for this thesis.

1.8.   Aims and goals

The study of the environment and its pollutants is an essential field of study as populations grow increasingly aware of the preciosity and fragility of their surroundings. There is no question whether human activities have negatively impacted ecosystems; they have. So, during the work projected for this thesis, we set out to find ways of tracing our impact. For this purpose, we decided to use

the particular ability of stable isotopic ratio signatures as a sort of fingerprint. We wanted to understand how to use these ratios and how they behave in different environments that were somehow altered by non-usual forces.

We set out to answer the following questions:

- Where are metal contaminants stored in soils?

- Are excess metals in soils and tree biomass traceable to their source using their isotopic signatures?

- Are the isotopic signatures of individual tree rings helpful in mapping out nearby smelter historical activities?

- Are wildfires changing the isotopic signatures of burned soils? How exactly?

The first step to obtaining the sought-after answers was selecting appropriate locations affected by particular events.

2. Methodology

2.1. The chosen affected locations

There were five sites where samples were collected. A brief description of each follows.

Kabwe, Luanshya, Selebi Phikwe, and Kombat (Annexes II – V, Figure 5) are cities in sub-Saharan Africa where mining and smelting activities continuously and significantly impact the quality of surrounding soils. In all of these sites, we collected soil and slag samples to assess soil contamination and vertical movement, and we tried to trace the contamination to the aforementioned anthropogenic activities.

Luanhsya has been the site of extensive Cu mining and smelting (Aurélien et al., 2022) and Selebi Phikwe of Cu and Ni. Here, samples were taken only to assess the behavior of these metals in the soil.

Kabwe, the fourth largest city in Zambia, is a site for Pb and Zn mining. It is widely known to be one of the most contaminated inhabited places in the world due to these activities (United Nations, 2021). An associate children's rights director at Human Rights Watch recently said: "*Zambian political leaders and candidates should recognize the urgency of the Kabwe situation and commit in their election campaigns to cleaning up this toxic legacy*" (Human Rights Watch, 2021).

Main sampling sites
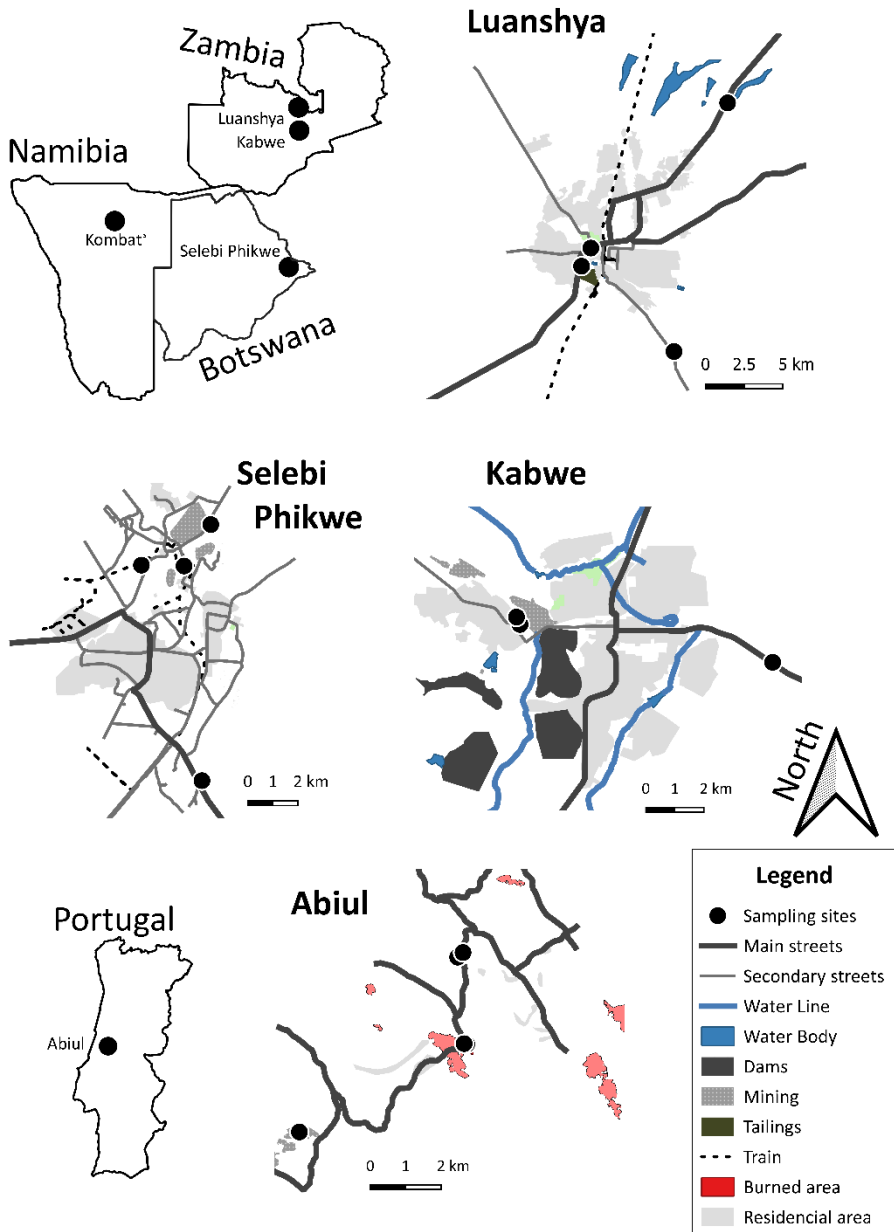
Figure 5 Schematic map of the sites that are discussed within the context of this thesis. Kombat was not addressed in this thesis.

Hence, we believed this to be the perfect site for testing our hypothesis that tree rings can be used to approximate historical smelter activity. From this site, we took samples from three separate pine trees (*Pinus montezumae,* Lamb).

To study the isotopic compositional changes and the variations in concentrations of Pb before and after wildfires, we selected Abiul, Portugal. While on a trip to the country, a fire broke out. We took this opportunity to collect samples from the freshly burned soils and brought them back to the lab for analysis.

See Annexes II to IV for more in-depth site descriptions.

2.2.   Sampling

Sampling was a necessity at every studied location. Different types of samples required other methods of sampling. However, sample types were always processed equally independently of location or schedule.

Soil sampling took place in all the studied locations. The sampling sites were chosen based on local environmental characteristics. Consistently, it took place in the highly affected areas (by the subject of the study: pollution, fires, smelter) and analogous non-affected sites (control). This approach was ideal for understanding the main differences between affected and non-affected soils. Soil profiles were collected to study vertical metal movement and isotopic shifts. A 1 m pit (or lower in cases where it was impossible to excavate that depth) was opened at each profile site (Figure 6a), and soil samples were taken at regular depth increments (5 or 10 cm). Sets of identified PE bags were used to store

the samples (Figure 6b). The O-horizons, when present, were collected at 1 cm and 5 cm and studied separately. Increments may have been smaller in deeper layers when the soil horizons were thinner than 5 cm. Ideally, we collected at least one sample per existing horizon.

Figure 6 Overview of sampling and sample handling. a) Example of an open pit from which soil samples were gathered. b) Soil samples left in the sun for air-drying to constant weight. c) A slag found in an open-air slag dump with a geological hammer for scale. d), e) extraction of a tree ring core using a Haglof incremental borer collected at cheat height. f) Granulometry determination using the sedimentation method.

Bedrock samples were collected from the bottom of the profiles (C-horizon) or at a local quarry if the pits were not penetrating deep enough. These, when available, served as the backing for the geogenic isotopic ratios (or signals), unaltered by natural soil-forming processes or others, and anthropogenic activity.

One primary objective in sites contaminated by mining and smelting was connecting these activities to the high concentrations of metals found in local soils and trees. Hence, representative slags were taken from open-air slag dumps to proxy for "smelting isotopic signature" (Figure 6c).

Tree rings, the samples needed for dendrochemical studies, were collected only in one site, Kabwe, and from three pine trees (*Pinus montezumae* L.). The ring cores were obtained using a Haglof incremental borer with a diameter of 5 mm used at chest height (Figure 6d, e). Each tree was drilled three times at relative angles of 120°. These essentially functioned as triplicates if a ring was missing or damaged.

In the sites affected by wildfires, ashes were collected from the surface of soils near the opened pits.

2.3. Treatment of samples

The soil samples were air-dried at room temperature to constant weight in situ (Figure 6b) or in the lab. The soil's reactive fraction was separated using a 2 mm mesh sieve. A portion of the sample was milled to analytical fineness

in a planetary agate mill (Fritsch, Pullverissette, Germany). The slag samples were crushed, milled to analytical fineness, and digested in mineral acids. The detailed digestion procedure is described elsewhere (Ettler et al., 2009). The tree ring cores were cut into segments representing three years of growth and dried to constant weight.

Digests of soils, ash, and bedrock were prepared for the elemental and isotopic analysis using HF and $HClO_4$. A weighted amount of 0.2 g of the sieved soil, ash, and bedrock was dissolved using 0.5 ml of $HClO_4$ (70–72 % v/v) and 10 ml HF (50% v/v). Later it was evaporated to dryness at 170 °C for two hours. The evaporated sample was then re-dissolved with 0.5 ml $HClO_4$ (70–72 % v/v) and 5 ml HF (50% v/v) and again evaporated. Finally, it was dissolved in 2 ml analytical grade HNO_3 (Merck, Germany, v/v) and purified by sub-boiling distillation. The individual tree ring segments were digested overnight in PTFE Savillex® beakers (Minnetonka, USA) in 10 ml of concentrated HNO_3 at 150 °C. The deionized water (DI) was obtained from a Milli-Q Academic purifying system (Millipore®, USA). The digests were transferred to a 100 ml volumetric flask.

The hydrometer method (Figure 6f) was used to determine the granulometry of the sieved soil (Gee and Or, 2002, 2018).

2.4. Bulk Chemistry

All soil samples underwent the same general procedure, although with minor differences when collected from different sites or at other times.

The soil pH was measured for the <2 mm soil fraction, both in H_2O and a 1 (or 2) M KCl solution, using a soil-to-extract ratio of 1:5 (or 2.5, v/v) after one-hour agitation (ISO 10390, 2005) using a Schott Handylab pH-meter (Schott, Germany).

The cation exchange capacity (CEC) was calculated as a sum of the extracted Al and basic cations using a 0.1 M $BaCl_2$ solution (Hendershot and Duquette, 1986) and buffered at a pH = 8.1 to saturate soil cation exchange sites. The extracts of $BaCl_2$ were analyzed for their components using an inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500 radial, Thermo Scientific, Germany) at the Czech University of Life Sciences under the conditions recommended by the manufacturer.

The crystalline Fe and Al oxides were determined by acid oxalate extraction using 0.2 M ammonium oxalate at a pH = 3. An ICP-OES (Agilent 5110, USA) was used to measure the resulting solution.

Total carbon (TC) and total sulfur (TS) concentrations were determined by catalytic oxidation using an ELTRA CS-500 element analyzer (ELTRA, Germany) at 1250 °C (or 1450 °C). The accuracy of the results was verified using reference materials (SRM) NIST 1635.

2.5. Trace element measurements

The variety of samples collected (slags, soils, and tree rings) needed to be analyzed for their contents, mainly Cu, Zn, and Pb but also others. Post-digestion, these samples were treated as a bundle, and all underwent similar procedures.

Trace element concentrations were determined using a quadrupole-based inductively coupled plasma mass spectrometer (Q-ICP MS, XSeries 2, Thermo Scientific, USA) under the recommended conditions and/or ICP OES under the conditions described elsewhere (Mihaljevič et al., 2011). The accuracy of the measurements was controlled using the following reference materials: SRM NIST 2711a - Montana II soil, NIST 1575, Pine needles, and NIST 1515, Apple leaves. The accuracy of the measurements was <5% RSD.

2.6. Lead isotopic determinations

The Pb isotopic composition of the studied materials was mainly used as a contamination tracer and therefore needed to be analyzed precisely. The dissolved stock solutions were diluted to a concentration <25 µg kg^{-1} Pb and then measured using a quadrupole-based inductively coupled plasma mass spectrometer (Q-ICP MS, XSeries 2, Thermo Scientific, USA) under the recommended conditions. The mass bias correction was executed by bracketing 1:1 a reference material, SRM NIST 981, Common Lead. The Pb concentration in the procedural blank was below 0.03 µg kg^{-1}. The accuracy of the measurements was determined using the certified reference material

22

BCR-2 (Basalt, Columbia River; USGS), and the standard errors of the ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios were <0.4% RSD and <0.5% RSD, respectively.

2.7.   Carbon isotopic determinations

We needed to assess the stress our tress had suffered in their history. To achieve this, we analyzed the stable C isotopic composition of the 3-year segments of tree rings. The isotopic determinations were done using a Thermo Flash 2000 elemental analyzer connected to a Thermo Delta V Advantage isotope ratio mass spectrometer in a Continuous Flow IV system (ThermoFisher Scientific, USA). Each sample's elemental C wt. % determined the minimum necessary sample weight. The released gases (CO_2) separated in a GC column were transferred to an MS source through a capillary.

Typically, C isotopic ratios are reported as delta (δ) values and expressed relative to Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}C$ (‰). The delta values are normalized to a calibration curve based on IAEA-CH-6, IAEA-CH-3, and IAEA 600 international standards.

The $\delta^{13}C$ is calculated using the following formula:

$$\delta^{13}C = \left(\frac{\left(\frac{\delta^{13}C}{\delta^{12}C}\right)_{sample}}{\left(\frac{\delta^{13}C}{\delta^{12}C}\right)_{standard}} - 1 \right) \times 1000 \text{ ‰}$$

where *sample* is the tree ring measured ratio, and *standard* (VPDB) is the reference material measured ratio.

2.8. Sequential extraction procedure (SEP)

When necessary to determine the chemical fractionation of metals or metalloids, a sequential extraction procedure, henceforth refered to as SEP, was done using the BCR scheme described by Rauret et al. (1999).

The SEP consisted of the following steps: Step 1 – exchangeable/acid extractable fraction (targeting soluble/exchangeable metals and carbonates), 0.11 M CH_3COOH; Step 2 – reducible (targeting Fe–Mn oxyhydroxides), 0.5 M $NH_2OH·HCl$ at pH 1.5; Step 3 – oxidizable (targeting organic matter and sulfides), H_2O_2 (85 ∘C) then 1 M CH_3COONH_4; Step 4 – residual, total digestion (targeting metals bound to silicates) (for a more detailed description of the preparation of the extraction solutions and procedure, see, e.g. (Bacon and Davidson, 2008; Rauret et al., 1999).

The extractions were duplicated in 100-ml PE reactors (P-lab, Czech Republic). These were centrifuged after each step, with washing steps (when necessary, Bacon and Davidson, 2008; Rauret et al., 1999), diluted to 2% (v/v) HNO_3. The extracted solutions were measured using a quadrupole-based inductively coupled plasma mass spectrometer (Q-ICP MS, XSeries 2, Thermo Scientific, USA) under the recommended conditions for the relevant elemental concentrations.

2.9. Mineralogical determinations

The mineralogical composition of the soils was determined by X-ray diffraction analysis (XRD) using a PANalytical X'Pert Pro diffractometer (PANalytical,

24

the Netherlands). The XRD was equipped with a diffracted-beam monochromator and X'Celerator multichannel detector, using CuK_{α} radiation (40 keV, 30 mA). The powdered samples were scanned from 3° to 70° 2θ, in steps of 0.02°, with a 200 s count time at each step. The diffraction data were analyzed using the X'Pert HighScore Plus software (version 1.0d).

In some cases, the mineralogical composition of the soils needed to be assessed to decipher the pollutant-bearing particles. The pollutants in question were metals; hence, most metal(loid) containing particles were believed to be heavier than the geogenic ones. The first undertaken step for the mineralogical determination was to separate this heavy mineral fraction of the topsoils. The obtained particles were analyzed for their structure in XRD and composition. The relevant soils' heavy mineral fractions (HMF) were obtained by centrifuging the 0.05 - 0.5 mm size fraction of the original samples in 1,1,2,2-tetrabromoethane diluted with 1,4-dioxane (specific gravity 2.70 g cm^{-3}). The heavy fraction was then washed using ethanol, dried, and fixed with epoxy resin in a standard polished section (Czech Geological Survey).

Polished sections of the HMF were prepared for qualitative chemical analyses of representing mineral phases to be measured by an electron probe microanalyzer (JEOL EPMA 8530F). The EPMA was equipped with a field emission gun electron source (FEG), an energy dispersion spectrometer (EDS; JEOL JED-2300F; 15 keV, 10 nA, and a beam diameter of 2 μm), five wave-dispersion spectrometers (WDS)

were used for the scanning electron microscopic (SEM) imaging, EDS analyses, and quantitative analyses in the energy-dispersive mode under the operating conditions detailed in Annex V.

A freeware software, Image J, courtesy of Schneider et al. (2012), was used to measure the diameter of selected particles from still pictures acquired while using the FEG-SEM/EDS and EPMA.

2.10.   Soil burn severity (SBS)

When studying soil affected by a fire, or some burning, it is crucial to assess its impact on the soil properties. Hence, said soils must be classified according to a soil burn severity scale (SBS) to be able to interpret and compare results with the published literature. Several published works have suggested variations of this scale. We opted for the version proposed by (Vega et al., 2013; Table 1).

Table 1 Soil Burned Severity classification table through the post-fire soil and visual characteristics. Table adapted from Vega et al. (2013).

SBS Level	Organic horizons (Oi, Oe, Oa)	Mineral horizon (Ah)
0	No evidence of fire	No evidence of fire.
1	Oa layer partially or totally intact.	Undisturbed.
2	Oa layer totally charred and overlapping the mineral soil. Possibility of ash.	Undisturbed.
3	Organic horizons completely consumed (bare soil). Possibility of ash.	Undisturbed. Soil structure unaffected. SOM not consumed. Surface fine roots not burned.
4	Organic horizons completely consumed (bare soil). No charred residue. A thick layer of ash.	Soil structure affected. SOM consumed in the top layer. Soil color altered (grey). Surface fine roots burned.
5	Organic horizons completely consumed (bare soil). No charred residue.	Soil structure affected. SOM consumed in the top layer. Soil color altered (reddish). Surface fine roots burned.

3. General findings

3.1. Soil contamination in mining and smelting environments

Here are some of the findings spanning Annexes I, II, IV, and V. The published and unpublished works focused on Zambian or Namibian cities highly impacted by mining and smelting activities. To better understand soil pollution, samples of topsoil, 1m deep (typically) soil profiles, and slags (smelting by-products) were collected.

3.1.1. Metal concentrations in the studied soils

In general, high concentrations of the metals processed in the local smelters were expected in soils close to the said smelters (Deng et al., 2016; Rieuwerts et al., 1999; Rieuwerts and Farago, 1995). All the while, in remote sites, pollution was expected to be minimal.

For contrast, context and classification, we used the guidelines on soil quality published by the World Health Organization (WHO, Cu 30 mg kg^{-1}, Zn 90 mg kg^{-1}, Pb 35 mg kg^{-1}, Tembo et al., 2006) and the Canadian Soil Quality Guidelines (residential: Cu 63 mg kg^{-1}, Zn 200 mg kg^{-1}, Pb 140 mg kg^{-1}, Canadian Council of Ministers of the Environment, 2007).

The highest concentrations were almost always found in the topsoil, not in deeper layers (Figure 7). Typically, only the top 10 - 15 cm was contaminated in all sites. Kříbek et al. (2019) found similar results in Kabwe.
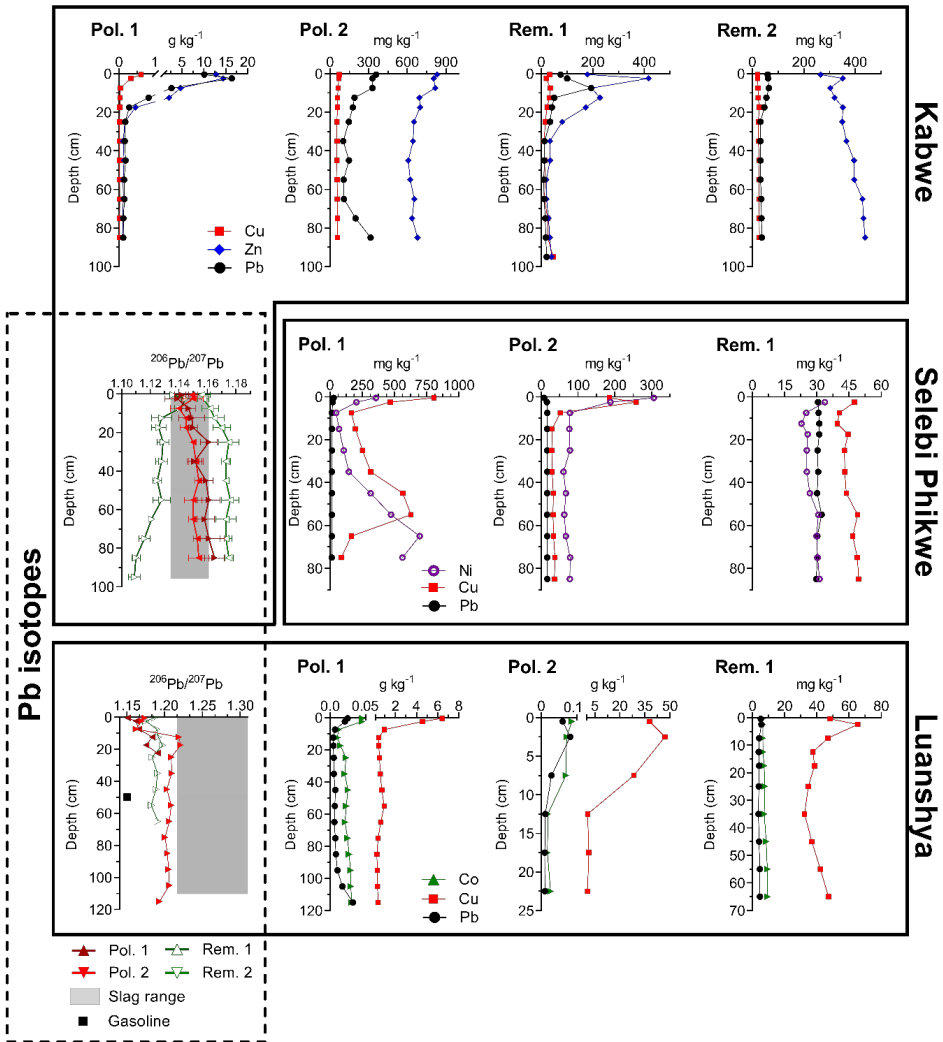
Figure 7 Elemental concentrations of local metal pollutants in the selected sites; Cu, Zn, and Pb in Kabwe; Ni, Cu, and Pb in Selebi Phikwe; Co, Cu, and Pb in Luanshya. Note the different scales on the x-axis (very high concentrations are shown as g kg^{-1} instead of mg kg^{-1}). Additionally, the isotopic ^{206}Pb/^{207}Pb ratios in all soil profiles and slags collected in Kabwe and Luanshya were plotted. Slag ratios were plotted as a shadow for better visualization. For the sake of simplicity, soil profiles were referred to as Pol. 1 and 2 (polluted) and Rem. 1 and 2 (remote).

Hence, metal concentrations below this depth were mostly geogenic and controlled by pedogenic processes. In a few cases, higher than background concentrations were found in lower layers, but these soils showed signs of either having been turned or placed artificially altogether. Other outliers were found and were addressed in the relevant Annexes.

In Kabwe (Annex II), the highest amounts of Pb, Zn, and Cu, the local contaminants, were found in the two profiles collected near the mine/smelter. The concentrations of these metals were as high as 16 000 mg kg^{-1} Pb, 14 0000 mg kg^{-1} Zn, and 600 mg kg^{-1} Cu, significantly exceeding the acceptable limits. The remote sites had much lower concentrations; up to 194 mg kg^{-1} Pb; 438 mg kg^{-1} Zn; 46 mg kg^{-1} Cu.

In Luanshya (Annex IV), Cu and Co were the most critical metals. Lead was also evaluated due to its potential as a source of pollution tracer. The maximum Cu and Co concentrations in the profiles near the smelter were 46 000 mg kg^{-1} and 86.0 mg kg^{-1}, respectively. Cobalt concentrations were much lower than expected. The remote site was uncontaminated (81.0 mg kg^{-1} Cu and 9.26 mg kg^{-1} Co). The highest concentration of Pb was 81.0 mg kg^{-1} in topsoil close to the smelter. This value was low but significantly contrasted with the remote soil (5.54 mg kg^{-1} Pb).

In Luanshya, samples of topsoils (0 – 3 cm) were collected in a general area and analyzed for their contents. These values were plotted to visualize the spatial

distribution of said contents (Figure 8). Sulfur (S), emitted by the smelter and present in sulfidic particles, and Cu, Co, and Pb had their epicenter at the smelter. The SE-NW yearly average wind direction was the main reason for the observed spatial pattern. It was especially noticeable for Cu and Co.
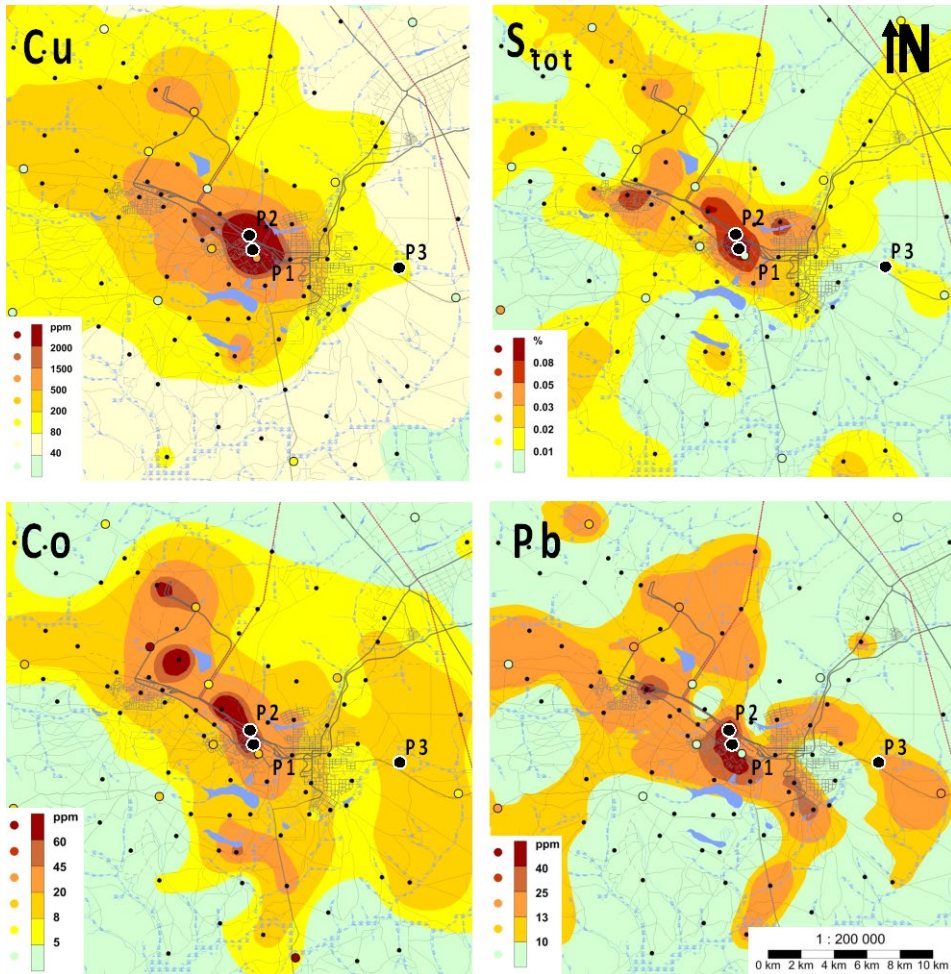
Figure 8 Contour maps of the TS (A), Cu (B), Pb (C), and Co (D) concentrations (in mg kg^{-1}) in topsoil (0–3 cm depth) in the Luanshya area, Zambia.

Selebi Phikwe (Annex I) is a Cu and Ni extraction and processing town. These were the most important metals to study on this site. The highest concentrations of Ni (696 mg kg^{-1}) were found in one of the profiles near the smelter at 60 – 70 cm of depth. The highest concentrations found in the topsoil were in the same profile at 356 mg kg^{-1} Ni. The other profile collected near the smelter had a similar topsoil concentration which immediately lowered to nominal values (around 70 mg kg^{-1} in deeper layers than 15 cm). The Ni concentrations in the remote profile were relatively constant at 30 mg kg^{-1} at all depths. Copper had its most significant presence in one of the topsoils at 800 mg kg^{-1}. In the same profile, Cu levels decreased in the first mineral layers and increased in deeper layers, maxing at 629 mg kg^{-1} at a depth of 50 – 60 cm. Like Ni, the other contaminated profile had no Cu increase in depth (at least not in the reached depths). The remote profile was uncontaminated, with Cu concentrations grasping 45 mg kg^{-1} throughout the profile. Lead had no significant presence on this site. All soils were uncontaminated, with concentrations ranging from 7.92 to 32.2 mg kg^{-1}.

3.1.2. *Speciation and availability of the pollutants*

A SEP assessed the chemical fractionation of the expected pollutants to determine metal availability. The importance of metal speciation in Luanshya is touched upon in the current Chapter, and the data from Selebi Phikwe is briefly described (Annex I). The data was plotted for both sites in Figure 9.
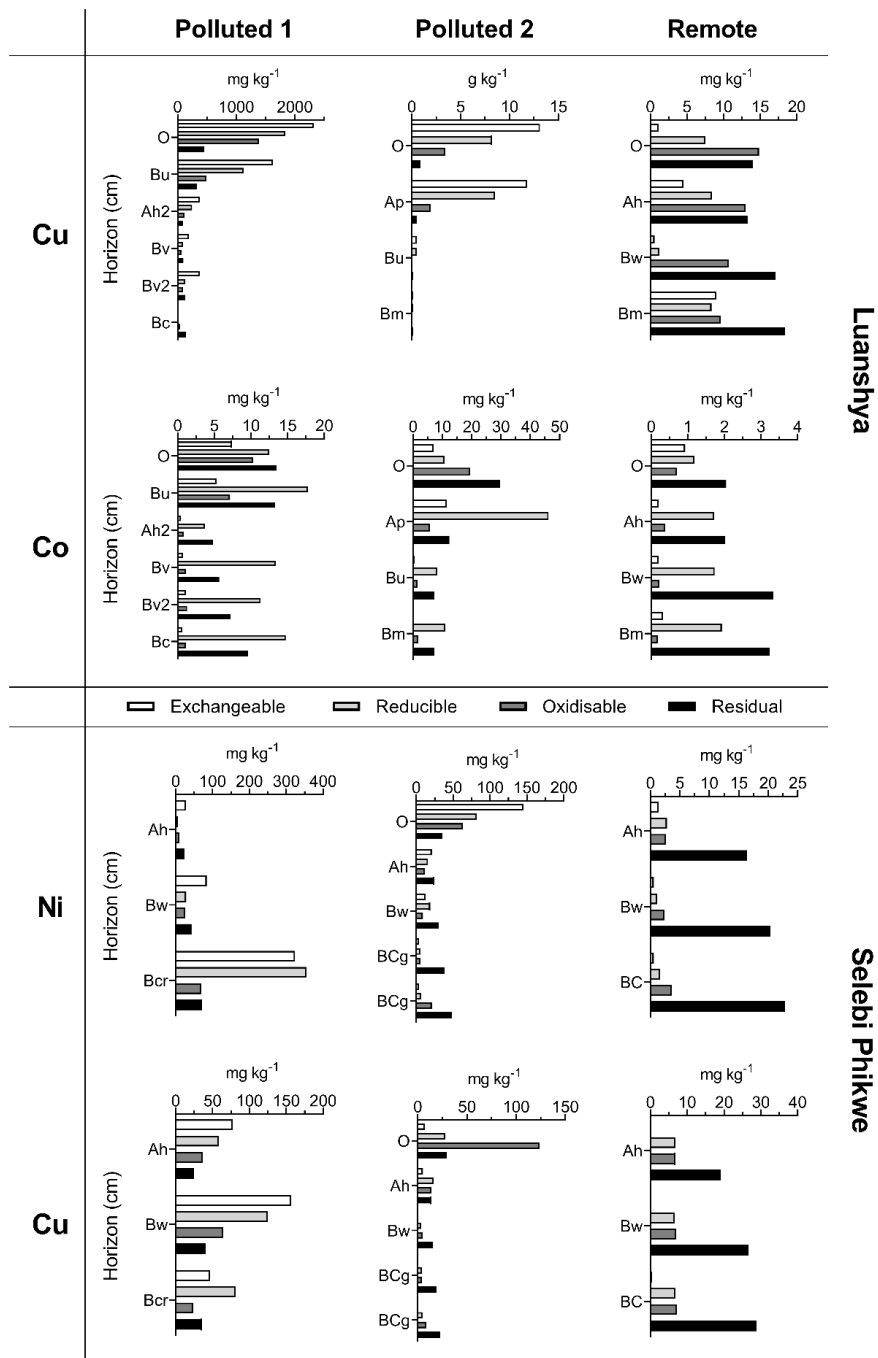
Figure 9 The concentrations Cu, Co, and Ni (horizontally) in the different SEP fractions for the selected samples of the polluted and remote soil profiles (vertically) collected in Luanshya and Selebi Phikwe.

In the published and unpublished works where this method was used, we considered that only metals released during the exchangeable step of the SEP were available or easily leached in situ.

Copper was found to be present in Luanshyan topsoils in incredible concentrations. Worryingly, up to 52.3 % was released in the exchangeable fraction of topsoils collected near the smelter. The high lability of (probably) anthropogenic Cu contrasts with the unavailability in the remote profile. Here, only 5.60 % of Cu was exchangeable. Cobalt concentrations were not as problematic, but considering this metal is one of the most extracted in Luanshya, it was deemed necessary also to determine its availability. Cobalt was most exchangeable near the surface of the soils, with 16.9 % and 15.1 % in contaminated soils and 19.1 % in the remote site. The low concentrations were combined with an unimpressive exchangeable rate.

In the case of Selebi Phikwe, the two main polluters were Cu and Ni. Nickle was highly labile in the contaminated soils, with up to 46.5 % released in the exchangeable fraction of both topsoils. One of the profiles verified this down to 65 cm of depth.

These high percentages, coupled with the previously described high concentrations of this metal in the soil, define a highly polluted soil with potential for leeching and plant uptake. The remote soil, however, did not have a significant proportion of exchangeable Ni (up to 6.00 %). Copper

in Selebi Phikwe was interesting. Copper was highly exchangeable in one of the contaminated soils (40.5 %), while in the other, it was not (up to 10.7 %). Barely any Cu in the remote soil was released during the exchangeable step of the SEP (0.91 %). The SEP results suggested that the metals of anthropogenic origin had greater polluting potential than those from natural pedogenic processes. But why was this?

In Luanshya, we tried to identify the source of Cu contamination by studying the Cu-bearing particles. Many spherical particles were found in the topsoils of the polluted soils but not in the remote soil (Figure 10). These particles were formed in the smelter flue gas chambers, where melt typically solidifies rapidly. These particles were then emitted into the atmosphere and deposited on surrounding topsoils. The spatial distribution of Cu and S_{tot} in the Luanshya contour map (Figure 8) may be seen as a heat map of the accumulation of these particles. Previous works have described them as mainly composed of oxides (spinels), sulfides or glass, and silicates (slag-like phases) as relics of melt emitted during the smelting processes (Adamo et al., 1996; Ettler et al., 2014a; Gregurek et al., 1999, 1998; Knight and Henderson, 2006). As expected, our results showed high percentages of Cu in these particles, usually in the form of sulfides and oxides.
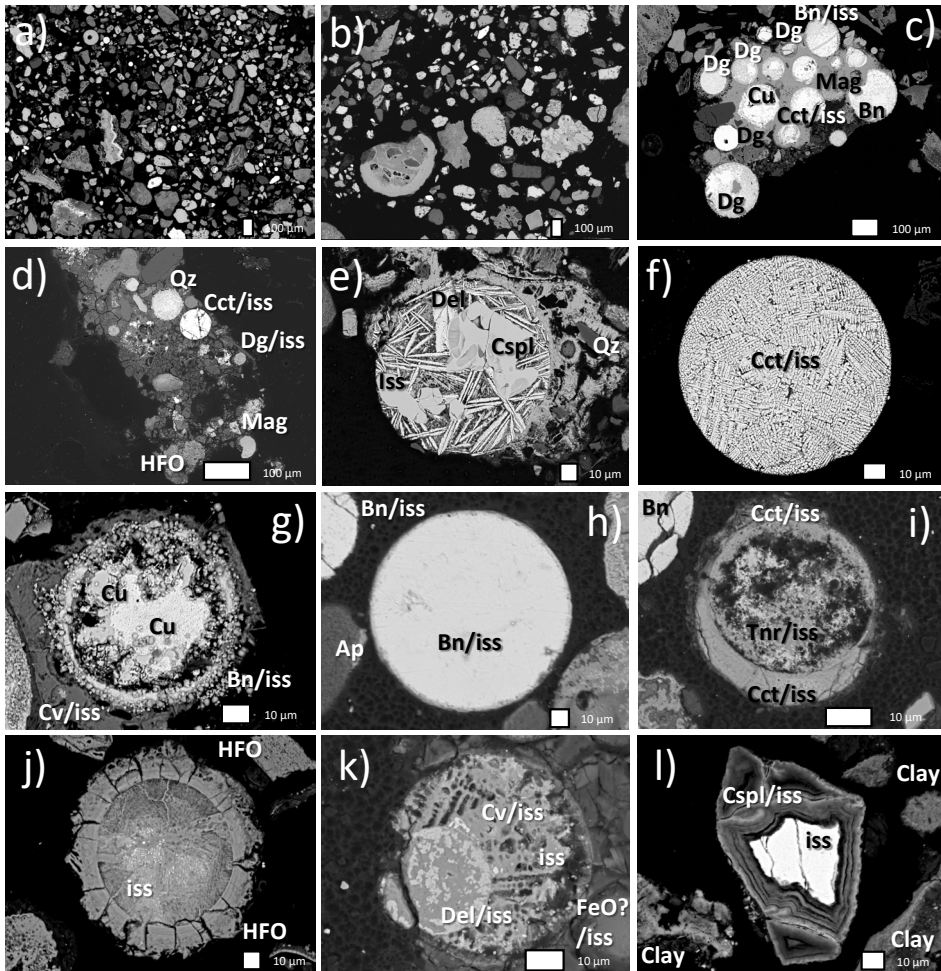
Figure 10 Depiction of particles separated in the HMF. a) An overview of a polished section of HMF from contaminated (P1: 0-1 cm), b) and uncontaminated (P3: 0-5 cm) soils. Many of the obtained particles were spherical anthropogenic and smelter-derived metal-rich droplets. c) Agglomerate of several Cu-bearing spherical particles (P1: 0-1 cm). d) The only observed particle in the remote topsoil HMF containing other small spherical smelter-originated Cu-bearing particles (P3: 0-1 cm). Examples of textures: e) dendritic (P1: 0-1 cm), f) skeletal (P1: 0-1 cm), g) porphyritic (P1: 0-1 cm), h) no texture (P2: 0-5 cm). i-k) Further examples of weathered anthropogenic particles (P2: 0-5 cm). l) Slag formed by a solid Fe, Cu, and S solution (P1: 0-1 cm). The mineral nomenclature abbreviations were defined as in Warr (2021): Ap – apatite [$Ca_5(PO_4)_3(OH,F,Cl)$], Bn – bornite [Cu_5FeS_4], Cct – chalcanthite [$Cu(SO_4).5(H_2O)$], Cspl – cuprospinel [$(Cu, Mg)Fe^{3+}_2O_4$], Cu – copper, Cv – covellite [CuS], Del – delafossite [$CuFeO_2$], Dg – digenite [Cu_9S_5], iss – intermediate solid solution, HFO - hydrous ferric oxide, Qz – quartz [SiO_2], Mag – magnetite [$Fe^{2+}Fe^{3+}_2O_4$], Tnr – tenorite [CuO].
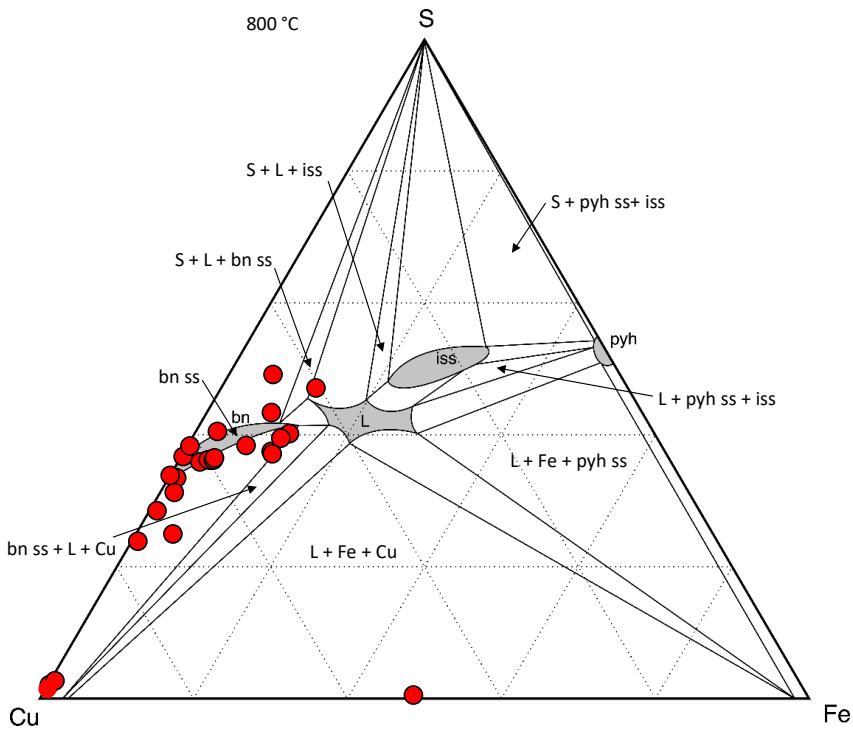
Figure 11 Chemical composition in at. % of the sulfidic spherical particles found in the Luanshya topsoils were plotted in an isothermal phase relations plot for the ternary Cu-Fe-S system at 800°C (Tsujimura and Kitakaze, 2004). Ternary plot adapted from Wohlgemuth-Ueberwasser et al. (2013). The stable phases at 800°C are bornite, pyrrhotite, and a sulfide melt. Legend: bn bornite [Cu_5FeS_4]; iss intermediate solid solution; po pyrrhotite [$Fe_{1-x}S$ (x = 0 to 0.17)]; py pyrite [FeS_2].

The main Cu-bearing minerals belonged to the sulfide and oxide groups. Often the proper classification was unachievable as compositions were not stoichiometric. Most anthropogenic particles formed intermediate solid solutions of bornite, chalcanthite, cuprospinel, native Cu, covellite, delafossite, diginite, and HFOs, among others. These were typically spherical in shape. These particles often appeared weathered. Such findings, in conjunction with

the labile nature and exchangeability of the majority of topsoil Cu shown by SEP results, implied vertical leaching of contaminants.

Kabwe samples were also subject to speciation studied but are only briefly mentioned in the next Chapter.

3.2.   Contamination source tracing using Pb isotopes

This chapter explores successful and unsuccessful attempts at using the tracing signature capabilities of Pb isotopic ratios. These were used in all Annexes, but only the case of soil contamination was reported here. Other uses (tree rings and fires) were described in their particular chapters. In a way, this chapter serves as an introduction to succeeding ones.

Why is Pb exceptionally useful as a tracer? What makes Pb isotopic ratios superior to other elements? Besides being a fairly common element with well-established and easy-to-reproduce measurement methods, Pb isotopes are notoriously unchanging during the whole mining and smelting processes that ore typically undergoes (Shiel et al., 2010). Hence, by knowing the Pb signature of the ore, one might determine if the Pb present in the soils originates from these processes. Slags, flue gas, and wind-blown particles should all exhibit the same ratios.

3.2.1. Defining the contamination signature

Collected slags always had high levels of metals, especially the ones relevant to that site.

In Kabwe slags, Pb concentrations ranged from 6700 to 17100 mg kg^{-1}, while their $^{206}Pb/^{207}Pb$ isotopic composition was 1.142 to 1.157, averaging at 1.148. The 95 % prediction interval for individual values of $^{206}Pb/^{207}Pb$ was [1.135, 1.161]. This interval became our *slag ratio* or *contamination signature*, meaning that if studied materials had this Pb ratio and natural phenomena could not justify it, we would know that Pb, at least partially, originated in the anthropogenic processes. In the case of Luanshya, this interval was defined at $^{206}Pb/^{207}Pb$ = [1.219, 1.309].

3.2.2. Lead ratios in the soils

The behavior of the Pb ratios in the soil profiles was generally the same for all profiles, sites, and cities (Figure 7). The ratios at the top of the profiles (topsoils) contrasted with deeper layers since deeper Pb was believed to be primarily geogenic while topsoil Pb originated in mixing. When these ratios did not vary in depth, it was in profiles located in mining sites. Hence geogenic Pb was interchangeable with contaminating Pb. Examples of this would be the polluted soils in Kabwe (Figure 7).

Most remote sites, and even the case of uncontaminated soils (discussed in Chapter 3.1.), also exhibited higher concentrations of Pb compared to deeper layers. That Pb build-up likely happened due to some other reason.

Looking at the example of Kabwe first, we observed that the four collected topsoils had the following signatures: P1, $^{206}Pb/^{207}Pb$ = **1.142**; P2, $^{206}Pb/^{207}Pb$ = **1.149**, R1, $^{206}Pb/^{207}Pb$ = **1.145**; R2, $^{206}Pb/^{207}Pb$ = **1.157**. These values were within the local contamination signature, confirming that the anthropogenic contamination penetrated the soil layers to a maximum depth of 25 cm (Figure 7). Even Pb present in distant sites seemed mostly originate from these processes, revealing the reach of the wind-blown particles from the slag dump. A SEP can determine if labile contaminants are of anthropogenic origin since Pb is not known to fractionate during leeching. Such was explored in the next chapter.

In Luanshya, we could not use this method to show that Pb present in topsoils originated in human activities. There was a slight increase in Pb concentrations in topsoils compared to mineral layers close to the smelter (Figure 7), and the heat map of Pb seemed to suggest that the smelter was an epicenter (Figure 8). However, the Pb isotopic measurements did not corroborate this hypothesis. There was a difference in organic Pb ratios and mineral Pb ratios (Figure 7), but the ratios in the topsoils ($^{206}Pb/^{207}Pb$ = **1.168** and **1.159**) did not match the local contamination signature. However, since these values were

lower than the ones of underlying layers, there must be another source of contamination. Perhaps there was a mixing of different types of contaminating Pb.

3.2.3. Other sources of contamination

Other authors have described cases where Pb isotopic ratios in topsoils differ from those in mineral layers without any obvious sources of contamination (Mihaljevič et al., 2011; Tyszka et al., 2012). While accepting the probable impact of local industry, we proposed that most of this Pb originated from the legacy use of leaded gasoline. The literature supported this idea (Dunlap et al., 2008; Forest et al., 2020; Odigie and Flegal, 2014). In Luanshya, leaded gasoline would have had the following ratio: $^{206}Pb/^{207}Pb= 1.15 \pm 0.003$ (Mihaljevič et al., 2015). Another source could have been the deposition of atmospheric Pb. Bolhöfer and Rosman, in a series of works, compiled Pb atmospheric data for the whole world (Bollhöfer and Rosman, 1997, 2001, 2002), which we used in all of our studies. The closest data available to Luanshya was for the Namibian desert ($^{206}Pb/^{207}Pb$ = 1.076 to 1.141). Both sources probably played a part in lowering the Pb ratios in the Luanshyan topsoils and were more significant than the local smelter activities. Thus, the differences in isotopic ratios in our soils are most likely derived from capturing atmospheric Pb and mixing with the geogenic counterpart and were not related to the mining and smelting activities specific to Luanshya.

3.3. Tree rings as an environmental archive

This chapter summarizes the findings in Annex III, where pine tree rings were suggested to be usable as an environmental archive for historical smelter production. The proposed hypothesis stated that the analysis of individual tree rings, or 3-year segments in our case, can be used to reconstruct past atmospheric/soil composition, similar to how ice cores are used. However, this property of pine trees is reasonably studied and accepted in the dendrochronology community. The novelty was achieved when we could not only suggest and present possible environmental events but also match the temporal variations with the known smelter yearly production amounts.

As previously mentioned, tree ring samples were collected at two sites in Kabwe (Figure 5). One tree was located nearby the local smelter and slag dumps, and the second was in a remote location close to the main road leading out of the city. The quality of Kabwe soils, as discussed in the previous chapter, reflects the uncontrolled mining and smelting activities that happened there and the presence of a large open-air slag dump. A contamination $^{206}Pb/^{207}Pb$ isotopic signature for Kabwe was calculated from a 95% prediction interval (mean ± 2 standard deviation) and defined as $^{206}Pb/^{207}Pb$ = [1.135, 1.161]. Hereafter referred to as contamination signature.

The oldest tree rings were determined to have formed in 1963 in the tree that grew close to the smelter. The remote tree, however, dated only from 1987.

The mine was active from 1906 to 1994 producing 0.8 Mt of Pb and 1.8Mt of Zn (Kamona and Friedrich, 2007).

3.3.1. Metals in tree rings

All trees exhibited the presence of some metals within their biomass (Figure 12a). Zinc and Cu have some biological significance for a tree; Pb does not. As opposed to expected, the tree selected to function as a control, situated in a remote site, possessed more metals in its biomass than the tree that grew closer to the source of the pollutants (polluted: 6.35 mg kg^{-1} Cu, 7.76 mg kg^{-1} Zn and remote: 10.2 mg kg^{-1} Cu, 10.6 mg kg^{-1} Zn). Such was especially true in the case of Pb (6.48 mg kg^{-1} on the remote site compared to the closer to the dump: up to 1.55 mg kg^{-1}).

The remote tree was located near one of the major highways of Zambia (Figure 5), which could explain the more elevated levels of Pb due to the heavy traffic movement. Unfortunately, we could not collect samples from more trees since there were none in the area. Other studies have also found more Pb in remote trees compared to trees near the contamination sources (Mihaljevič et al., 2015). One other reason was that perhaps at this distance, contaminants might be more easily absorbed (by the leaves and bark) could be the reduced size of wind-blown particles. Smelter-derived particles at <1 µm contain more Pb than larger particles (Csavina et al., 2014).

44
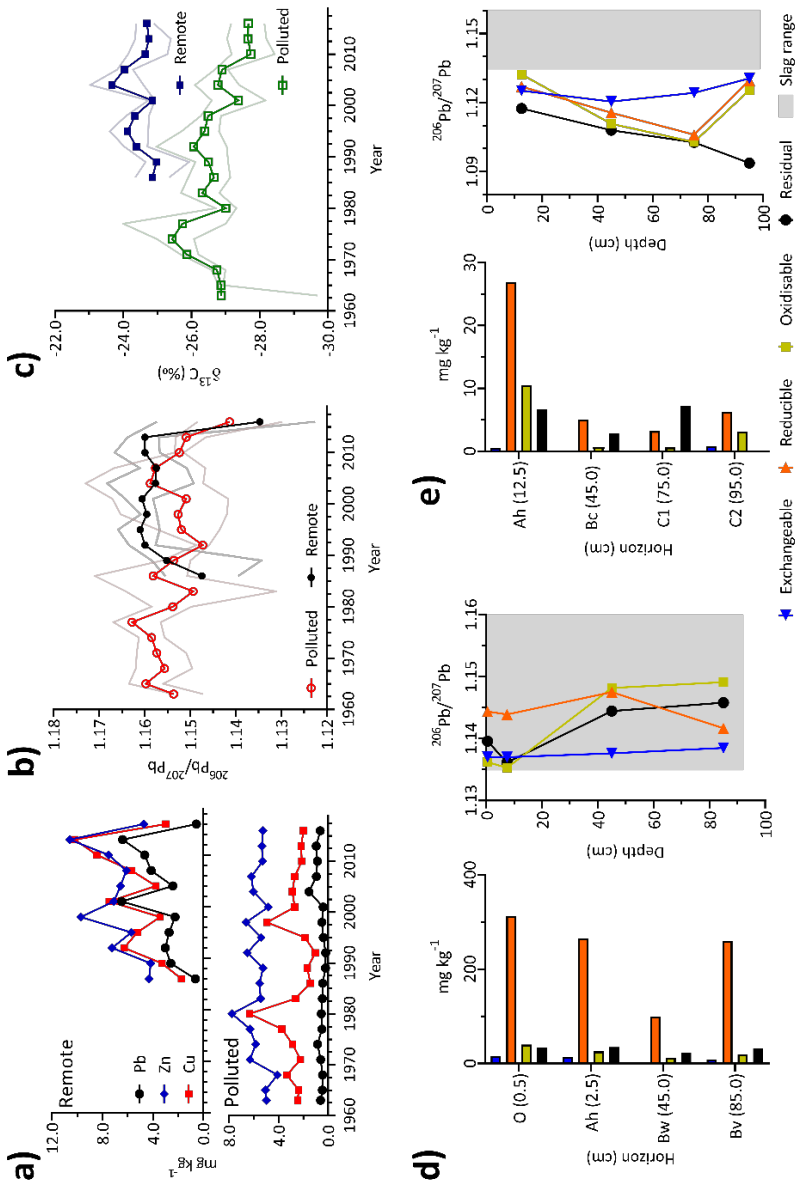
Figure 12 a) Elemental concentrations of Cu, Zn, and Pb, b) $^{206}Pb/^{207}Pb$ ratios, and c) $\delta^{13}C$ in both trees' biomass. The lighter and darker lines represent the range and average of the observed values. d) Concentrations of Pb and $^{206}Pb/^{207}Pb$ ratios in the polluted and e) remote soils in the individual SEP steps. Plots adapted from Baieta et al. (2021).

The same authors showed that even in smaller particles, concentrations decrease rapidly with the distance from the smelter (Csavina et al., 2012), leaving us to conclude that this phenomenon requires further investigation.

3.3.2.   Pb and C isotopic ratios in tree rings

The Pb isotopic composition was similar in both trees (average: polluted $^{206}Pb/^{207}Pb$ = 1.536 and remote $^{206}Pb/^{207}Pb$ = 1.558, Figure 12b). These values fell within the contamination signature, suggesting that the Pb in the trees' biomass originated in mining and smelting production.

The SEP results showed that nearly no Pb was bound in the soil's exchangeable fraction, implying that the Pb speciation was inadequate to be easily accessible for root uptake (Figure 12d, e). Therefore, the Pb must have entered the tree through above-ground uptake processes (aerosol deposition on bark or leaves). The Pb isotopic ratios of the fraction of available Pb in the soils ($^{206}Pb/^{207}Pb$ = 1.144, 1.120; in the polluted and remote soils, respectively) did not match the signature of the Pb present in the tree biomass, confirming the above statement.

Therefore, the wind-blown particles originating in the slag dump or expelled into the atmosphere by the smelter activity must have been the origin of this Pb. These particles shared the Pb isotopic ratios of the smelting processes and ore which, once fallen on a tree, were absorbed into its biomass. Other authors have studied and confirmed that above-ground processes sometimes are

46

the main entry-point of Pb into wood (Lepp and Dollard, 1974; Watmough, 1999).

One established way to study and describe the changing conditions throughout the lifetime of a tree is to look at the varying carbon isotopes present in the tree biomass. A review on the matter was composed by van der Sleen et al. (2017). For the work executed in this thesis, $\delta^{13}C$ was used as a stress indicator for tree growth (Figure 12c). Varying amounts of SO_2 in the atmosphere due to increased smelter production should result in variable $\delta^{13}C$ values. The acidification of the atmosphere reduces the quality of the air, causing plants to stress. This stress leads to a partial or total closure of their stomata, suppressing the tree assimilation process and decreasing the discrimination of ^{13}C (Time et al., 2018). The tree ring $\delta^{13}C$ values were consistently higher in the remote site than in the contaminated one, although they seem to mimic each other (Figure 12d). A Person's correlation showed that both trees' signals, even with significantly different values, were strongly correlated (r = 0.77, p <0.001), suggesting that both trees were part of the same system or affected by the same changes.

3.3.3. Tree ring archive vs. yearly smelter production

Finally, these records were plotted alongside the actual smelter yearly production amounts to test the accuracy of local pine tree rings' potential as an environmental archive for local anthropogenic activities (Figure 13). The smelter production amounts were compiled from the USGS annual reports

(U.S. Geological Survey, Bureau of Mines, 1964-1993). The availability of smelter

records only went as far back as 1959, but the smelter had already been active

for 53 years.
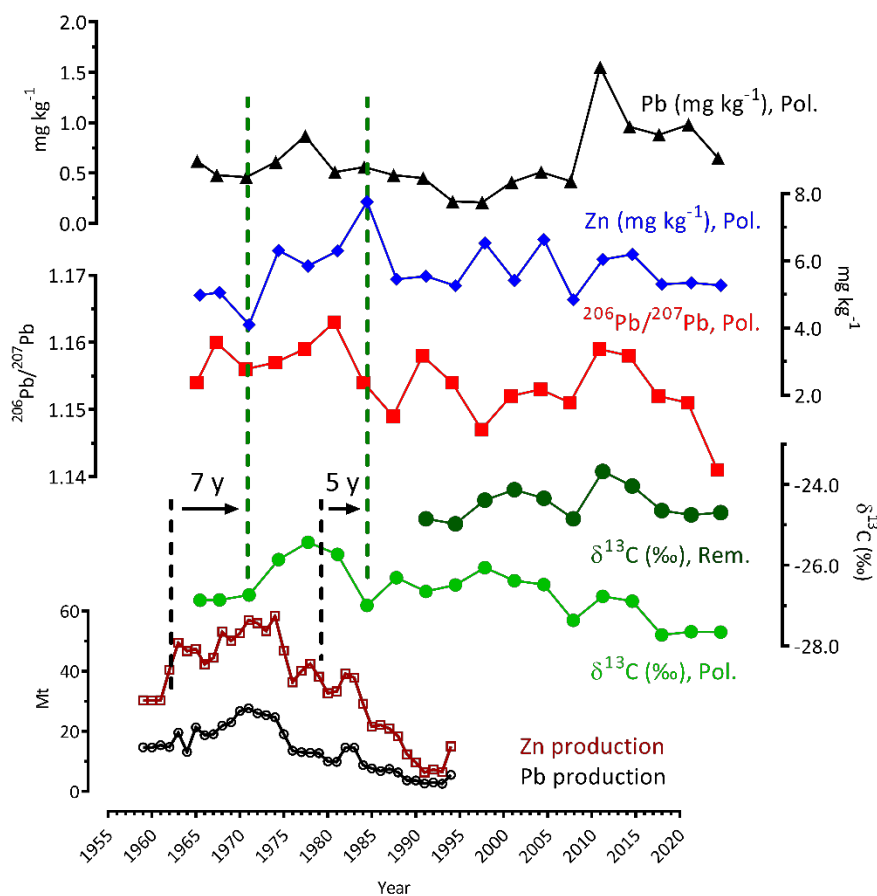
Figure 13 Tree ring isotopes and metal concentrations compared to the Kabwe smelter's historical production records. Plots adapted from Baieta et al. (2021).

When compared, we verified that the production trends of Zn and Pb correlate

with the tri-yearly variations in metal concentrations and isotopic shifts in

the tree ring record. This apparent dependency, however, was not immediate.

A delay of the tree record compared to the smelter records of 5 to 7 years was observed. Other authors have observed that apparent correlations between the tree ring record and the smelter production records can be blurred or smoothed out and may suffer a delay of up to 10 years (Lageard et al., 2008; Watmough and Hutchinson, 2002). We verified that small changes in production were not visible in the tree ring record, but more extensive changes were. It should be kept in mind that in the presented data, each point is a 3-year, 3-core average, which may further the visible shift or inaccuracy of results. An in-depth description of the statistical analysis of the data is available in Annex III.

The statistical analyses supported the following statements:

- Lead in the contaminated tree significantly reflects the cumulative effect of several previous years of production. The most statistically significant linear dependence was on three earlier years of production delayed by one year in the record.

- The Pb isotopic changes were also linearly dependent on Pb production. Periods of higher smelter production increased the $^{206}Pb/^{207}Pb$ ratio, while periods of lower production decreased it. Occasionally, the background aerosol signature could also significantly reduce this ratio ($^{206}Pb/^{207}Pb$ = 1.067 to 1.090, Bollhofer and Rosman, 1997).

- The concentrations of Zn in the tree biomass depended on the smelter's yearly production. However, the statistical analysis showed that the causation is not as evident as in the case of Pb.

- The δ^{13}C in the contaminated tree correlated with the Zn and Pb production values. Statistical verification yielded that only up to 1986 did the δ^{13}C values correlate better with a 5-year shift. Post-1987, both tree ring records behaved similarly.

There was a spike in all variables noticeable from 2000-2010. Since the smelter was inactive by then, the trees must have been influenced by some other natural or anthropogenic event. We also assumed that it might be possible that the trees reacted slower to the 1994 increase; however, doubtful. There might be some increase in traffic or other pollution sources or even freak weather events like a dry year or extremely wet. However, we were not able to find any to support their existence.

3.4. Lead isotopes in soils affected by fires

This chapter features the findings discussed in Annex IV, where we strove to provide an answer to the question: 'How does forest fire affect the Pb isotopic composition of soil?' For this purpose, soil samples were collected in a site that had suffered a recent forest fire and in an analogous unburned area. The SBS was assessed in situ and varied from level 1 to level 3. Level 5 was found exclusively at the base of the local pine trees.

3.4.1. Fire effects on the soil

Wildfires are known to affect several properties of the soil depending on the burning temperature. For example, pH is expected to increase in fires that burn at temperatures >450-500 °C (Arocena and Opio, 2003; Santana et al., 2018). We did not make such observations. The temperature was high enough to reduce an average of 23 % of TC in the O-horizons of healthy soils to a mere 8 %, or total consumption. Organic matter is not typically affected during very low-intensity fires (Varela et al., 2015). Substantial consumption is expected at temperatures >200-250 °C, while total consumption requires temperatures >460 °C (Giovannini et al., 2001). Our fire only affected the top 5 cm of soil, and the different sampling sites were exposed to different temperatures.

We used samples of bedrock and soils from lower depths to determine whether the soils had suffered some form of prior contamination. We concluded that the topsoils had more Pb than underlying layers, attributed to the legacy of leaded gasoline usage and industrial activities (Figure 14a).

Careful analysis revealed that the concentrations of Pb increased in the soil affected by fires of lower temperatures, which was also noticeable in the higher amount of this metal in the ashes collected in the same area. The same was not observed in the area that suffered the higher temperature fire. The literature supports the increase of metal concentrations in the topsoil (Bartkowiak and Lemanowicz, 2017; Santorufo et al., 2021).
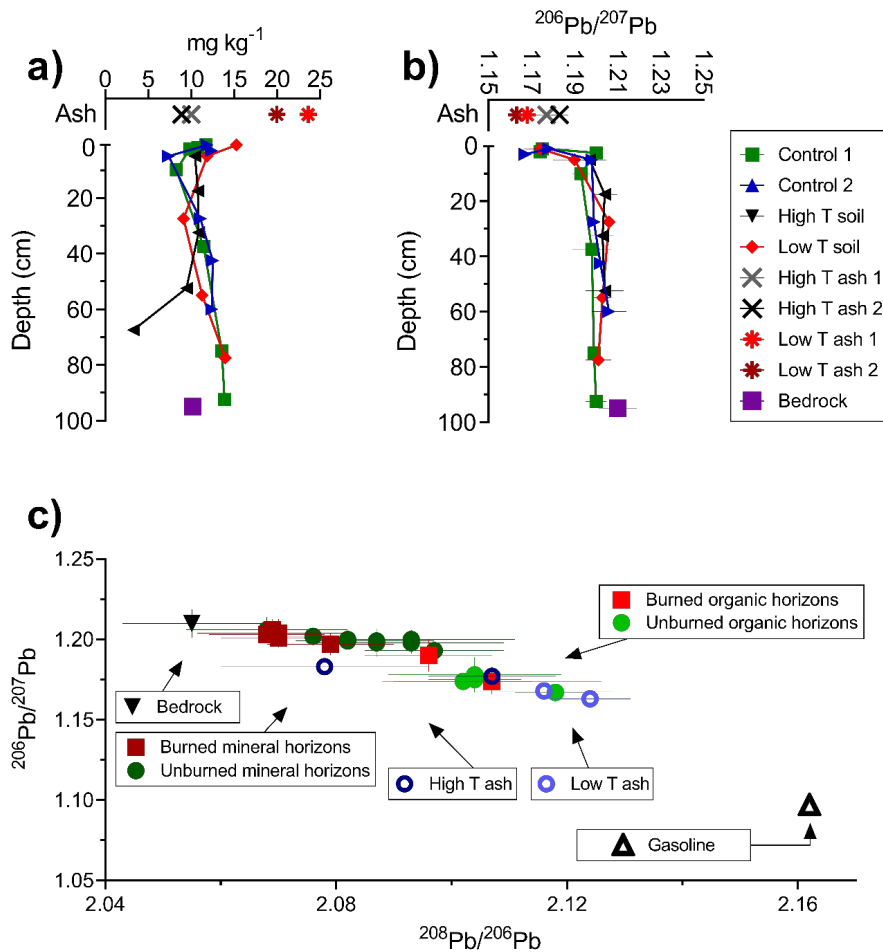
Figure 14 a) Lead concentrations and b) isotopic ^{206}Pb/^{207}Pb ratios of all soil profiles, ashes, and bedrock, c) A three-isotope plot (^{206}Pb/^{207}Pb vs. ^{208}Pb/^{206}Pb) where Pb isotopic compositions of soils and ash are displayed. The gasoline values were taken from (Bollhöfer and Rosman, 2002). Plots adapted from Baieta et al. (2022).

3.4.2. Fires affecting the soil ^{206}Pb/^{207}Pb ratio

The description of post-fire soils allowed for a better interpretation of the Pb isotopic ratios and their variance (Figure 14b). The local bedrock had a ^{206}Pb/^{207}Pb

ratio of 1.210, similar to the mineral layers of all soils. As previous data revealed, the fire reach was limited to the top 5 cm of soil.

Our observations revealed that the top layer of the soil burned at higher temperatures had a ratio of $^{206}Pb/^{207}Pb$ = 1.197, and adjacent ash, $^{206}Pb/^{207}Pb$ = 1.180. The topsoil that burned at a lower temperature, and retained some organic matter, shared a similar isotopic ratio with the unburned ones ($^{206}Pb/^{207}Pb$ = 1.174). Nearby ash had an average ratio of 1.166, a significant decrease. We proposed and justified that the temperature dependence was due to the different natures of the Pb that volatilizes.

Most of the anthropogenic Pb that accumulated in topsoils originated probably in leaded gasoline usage, which in Portugal had the following signatures: $^{206}Pb/^{207}Pb$ = 1.097 ± 0.001; $^{208}Pb/^{206}Pb$ = 2.162 (for more details, please refer to Annex IV). This ratio was much lower than the geogenic Pb ratios of soils. Hence, natural topsoil signatures are lower than in mineral layers since that Pb results from mixing. Lead in the form of halogenides from leaded gasoline is more volatile than from mineral origin. Lead in mineral forms has been shown to volatilize significantly only at temperatures higher than 600-650 °C (Tuhý et al., 2021).

A fire that burned at a temperature high enough to volatilize anthropogenic Pb, lower in $^{206}Pb/^{207}Pb$, but not mineral Pb, would increase the signature of the soils ($^{206}Pb/^{207}Pb$ = 1.197). A fire that burned at lower temperatures, not volatilizing

any Pb, would only serve to accumulate this metal in topsoil and ash, explaining the results. The isotopic ratios of ash were used to confirm these findings (Figure 14c). Ash collected at the higher temperature site had an isotopic signature much closer to the geogenic one (ash: ^{206}Pb/^{207}Pb = 1.177, 1.183 to bedrock ^{206}Pb/^{207}Pb = 1.210) when compared to ash collected in the low-temperature site (^{206}Pb/^{207}Pb = 1.168, 1.163), which was similar to, even if slightly lower than, the signature of the organic layers (^{206}Pb/^{207}Pb = 1.167 to 1.178).

Assuming all soils had the same ^{206}Pb/^{207}Pb ratios before the wildfire event, much more anthropogenic Pb must have been released from the soil burned at a higher temperature. These findings imply that the Pb isotopic ratios in burned soils depend on the burning temperature. Future works may use this property to determine forest fire temperatures (assuming the natural soil ratios are known).

4. General conclusions

1. Soil contamination

Soil contamination in mining and smelting towns was extensively studied. We concluded that unregulated smelting activities are indeed a source of contamination, especially shown by the spatial distribution of contaminants. Soils surrounding these facilities exhibited extremely high concentrations of locally processed metals. These concentrations greatly exceeded the values suggested by regulating agencies. Only the top 10 – 25 cm of soil was contaminated by those activities for all studied elements.

The sources of contamination were not only the mining and smelting activities but also wind-blown particles that originated in the open-air slag dumps.

In Kabwe, the primary contaminant, Pb, was not mobile in the soils. However, in Luanshya, smelter-originated Cu was bound in sulfides and oxides and highly labile, as shown by the SEP procedure and apparent weathering under SEM analysis. Contaminant-bearing smelter-originated (probably wind-blown) particles were spherical, which indicated its genesis as rapidly solidifying melt in flue gas chambers.

At the date of this thesis submission, smelter surrounding soils in Kabwe, Luanhsya, and Selebi Phikwe were in desperate need of remediation and immediate attention.

2. Contamination source tracing

Lead isotopes proved to be a good contamination source tracing when Pb was one of the contaminants. Such was verified in soils and tree biomass. In deeper soil layers, Pb ratios reveal possible leeching due to mixing anthropogenic and geogenic ratios.

Isotopic determinations coupled with speciation analysis were shown to have the potential to demonstrate the entry point of metals in tree biomass. In our case, Pb entered the tree through above-ground processes (absorption by leaves and bark). The $^{206}Pb/^{207}Pb$ ratio of available Pb in the soil did not match the Pb present in the tree biomass leading to leaves and bark being the only possible solution.

Lead from leaded gasoline represents a considerable portion of today's Pb in topsoils in all studied sites. One might assume this is a global trend considering the varied surveyed locations, from Europe to Africa.

3. Dendrochronology

Pine trees were shown to function as a good archive for past environmental changes since the composition of individual tree rings was sensitive to a local smelter's historical activity. We observed this for nearly all variables. Major peaks or crashes in production were recorded with a 5 - 7 year delay.

Among the studied variables, Pb and C isotopes related the most accurately to the production amounts.

4. Post-burn Pb isotopes

Burning temperature determines if Pb undergoes volatilization or accumulation, affecting the Pb isotopic composition of remaining ash and soil. Gasoline-originated Pb in topsoils was readily volatilized since its bound in halogenides, while geogenic Pb proved more stable, as indicated by the isotopic measurements. Considering the different isotopic ratios of differently sourced Pb and the different volatilization temperatures, we suggested that it may be possible to determine the burning temperature after the fact. Such could be achieved only for a soil where the conditions and variables before burning were well documented.

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62

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Annexes

Annex I

Table SP1 – Selected metallic contents of the studied soils in Selebi Phikwe.

Site	Soil / Horizon		Depth cm	Ni mg kg^{-1}	Cu mg kg^{-1}	Pb mg kg^{-1}
P1	Ah		0-1	356	807	27.8
			0-5	205	468	21.1
			5-10	48.0	165	14.9
			10-20	70.2	197	14.6
			20-30	106	252	15.1
			30-40	146	316	14.8
	Bw	ferralic	40-50	315	565	15.3
			50-60	474	629	14.7
			60-70	696	165	14.3
	Bv	petrophlintic	70-80	563	87.9	12.6
P2	O	liter	0-1	306	185	7.92
	Ah		0-5	188	258	15.2
			5-10	77.9	51.7	16.4
			10-20	76.3	29.2	15.8
			20-30	77.9	28.5	16.2
	Bw	ferralic	30-40	60.5	29.7	16.2
			40-50	66.8	32.9	16.2
			50-60	62.7	31.9	15.7
	BCg	plinthic	60-70	66.9	33.3	16.1
			70-80	78.4	37.2	16.1
			80-90	77.7	35.7	16.6
P3	O	liter	0-5	33.7	47.5	30.5
			5-10	25.0	40.5	30.8
	Ah		10-15	22.9	39.5	31.1
			15-20	25.7	44.5	31.1
			20-30	25.3	42.9	30.3
			30-40	25.3	43.0	30.6
			40-50	26.7	43.7	30.1
	Bw	ferralic	50-60	30.7	49.0	32.2
			60-70	29.8	46.7	30.2
			70-80	30.4	48.9	30.2
	BC		80-90	31.2	49.5	29.7

[a]Cation exchange capacity; [b]Oxalate-extractable Mn. Fe. and Al; [c]Total carbon; [d]Total sulfur

Table SP2 - Description of the major properties of the studied soils in Selebi Phikwe.
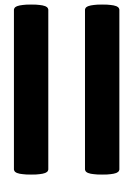
Site	Soil / Horizon	Depth	Granulometry (%)			pH H$_2$O	pH KCl	CEC	FeO$_x$	MnO$_x$	AlO$_x$	TC	TS
		cm	Clay	Silt	Sand	std units	std units	cmol+ kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	mg kg^{-1}
P1	Ah	0-1				3.18	2.74	8.50	296	0.58	8.98	13.2	4530
		0-5				3.19	2.85	9.50	502	1.04	22.8	6.88	2220
		5-10				3.72	3.51	10.5	38.7	0.43	42.7	2.57	215
		10-20	30.1	3.70	60.2	3.74	3.39	12.5	42.2	0.22	54.9	2.94	283
		20-30				3.70	3.30	17.5	38.1	4.92	55.1	2.98	329
		30-40	38.5	5.00	56.5	3.73	3.33	20.0	56.6	6.84	76.9	2.87	348
	Bw	40-50				4.11	3.52	17.0	38.7	29.6	41.5	3.17	255
	ferralic	50-60				4.49	3.81	24.5	34.7	40.6	34.0	2.68	212
		60-70	34.5	4.60	60.9	5.11	4.08	25.5	43.3	24.5	40.2	2.58	187
	Bv petrophlintic	70-80				5.90	4.65	19.0	28.0	17.0	23.7	2.20	127
P2	O liter	0-1				6.36	5.96	32.5	98.9	6.05	14.2	97.7	47400
		0-5				6.20	5.12	20.5	167	6.07	22.2	46.8	4860
	Ah	5-10	16.3	6.00	77.7	7.26	5.32	10.0	66.3	8.31	17.3	6.68	1290
		10-20				7.51	7.07	9.00	53.3	16.4	20.8	3.68	1930
		20-30	10.6	8.90	80.5	7.50	7.11	12.5	50.2	18.4	23.8	2.69	2230
	Bw	30-40				7.58	7.13	12.5	49.3	12.8	29.3	2.57	1570
	ferralic	40-50				7.61	7.21	15.0	53.2	12.4	26.4	2.49	1830
		50-60				6.77	6.96	10.0	47.9	9.7	28.2	2.71	3030
	BCg	60-70	20.5	5.60	73.9	6.97	7.82	16.0	57.0	11.0	37.5	2.31	2740
	plinthic	70-80				7.25	7.78	19.5	55.2	6.19	31.9	2.76	2750
		80-90				7.24	7.82	17.5	64.1	13.6	32.3	2.40	2970

			Depth											
	O		0-5				6.59	5.27	19.0	61.2	19.2	33.2	10.8	91.2
		liter	5-10				6.21	4.80	22.0	40.6	20.2	25.1	8.96	62.9
	Ah		10-15	28.9	10.3	60.8	6.04	4.64	21.5	53.9	24.6	34.0	7.91	64.5
			15-20				5.59	4.08	17.5	60.4	17.0	40.8	7.95	106
			20-30				5.33	4.00	18.0	45.5	7.37	33.9	5.73	102
P3			30-40				5.81	4.05	18.0	58.5	15.9	42.4	5.22	127
			40-50	42.1	5.90	52.0	5.69	4.12	21.0	57.2	7.50	39.7	4.25	84.0
	Bw		50-60				5.59	4.17	22.5	66.5	6.28	37.6	3.70	89.8
		ferralic	60-70				5.45	4.16	27.5	52.5	6.04	34.7	3.87	96.9
			70-80				5.62	4.12	21.0	71.5	8.22	35.9	3.42	92.2
	BC		80-90	43.2	8.00	48.8	5.91	4.27	24.0	77.2	7.04	39.9	3.39	83.8

Table SP2 - Selected metallic contents on the different SEP steps extracted from the Selebi Phikwe soils.

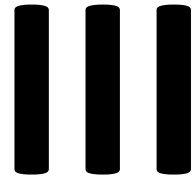| Profile	Depth	Horizon	Exchangeable			Reducible			Oxidisable			Residual		
			Ni	Cu $mg\ kg^{-1}$	Pb	Ni	Cu $mg\ kg^{-1}$	Pb	Ni	Cu $mg\ kg^{-1}$	Pb	Ni	Cu $mg\ kg^{-1}$	Pb
P1	10-20	Ah	28.4	77.3	0.08	6.28	58.5	1.74	9.73	36.6	0.81	23.5	25.0	2.40
	30-40	Bw	84.3	157	0.06	28.9	125	2.21	25.4	64.4	1.22	42.8	40.8	3.82
	70-80	BCr	324	46.4	0.00	355	81.1	2.62	69.8	23.5	0.86	71.3	35.5	3.90
P2	1-0	O	145	7.26	0.03	82.3	28.1	1.50	63.2	124	0.93	35.0	29.5	0.89
	5-10	Ah	21.0	5.25	0.00	16.1	16.3	1.86	12.1	14.1	0.94	24.6	13.7	1.68
	30-40	Bw	12.8	0.08	0.00	19.2	3.31	1.72	9.03	4.72	1.06	30.1	15.2	2.06
	60-70	BCg	3.44	0.10	0.05	5.55	4.24	1.91	5.42	4.02	0.97	38.1	19.2	2.79
	80-90	BCg	3.58	0.2	0.01	6.77	5.12	2.76	21.1	8.88	1.41	48.3	23.0	3.23
P3	10-15	Ah	1.38	0.11	0.06	2.83	6.82	5.94	2.60	6.81	1.38	16.4	19.2	3.44
	40-50	Bw	0.60	0.33	0.12	1.20	6.64	5.91	2.36	7.04	2.64	20.3	26.6	5.19
	90-100	BC	0.60	0.38	0.14	1.63	6.81	7.44	3.67	7.29	3.17	22.8	28.8	4.97

Annex

II

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Annex

III

Annex

IV

Baieta R., Vieira A. M. D., Vaňková, M., Mihaljevič M. (2022). Effects of forest fires on soil lead elemental contents and isotopic ratios. *Geoderma* 414, 115760. DOI: 10.1016/j.geoderma.2022.115760, IF = 7.42