DENDRO-CHEMICAL ANALYSIS OF SELECTED TREE SPECIES IN MIZORAM, NORTH EAST INDIA

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CERTIFICATE

This is to certify that the thesis entitled "**Dendro-chemical analysis of selected tree species in Mizoram, North East India**" submitted to the Mizoram University, Aizawl for the award of the degree of Doctor of Philosophy in Forestry is the original work carried out by **Mr. Wagmare Balraju** (MZU/ Ph.D./1198 of 06.08.2018) under my supervision. I further certify that the thesis is the result of his original investigation and neither the thesis as a whole nor any part of it was submitted earlier to any University or Institute for the award of any degree. The candidate has fulfilled all the requirements laid down in the Ph.D. regulations of Mizoram University.

His passion-oriented hard work for the completion of the research is to be duly appreciated.

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DECLARATION

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March, 2024

I **Wagmare Balraju**, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to do the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

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NOTATIONS AND ABBREVIATIONS

NOTATIONS

%	Percent
e.g.,	Exempli gratia
etc	Et cetera
p<0.01	Significant level at 1 percent
p<0.05	Significant level at 5 percent
^{O}C	Degree Celsius
mg	Milligram
kg	Kilogram
µg	microgram
m-^{3}	Cubic meter
cm	Centimeter

ABBREVIATIONS

AAS	Atomic absorption spectroscopy
ANOVA	Analysis of variance
AQI	Air quality index
BAF	Bio-accumulation index
Ca	Calcium
Cd	cadmium
CF	Contamination factor
CO	Carbon monoxide
Co	Cobalt
CO_2	Carbon dioxide
max	Maximum
min	Minute
Min	Minimum
Mn	manganese
Mg	Magnesium
MIW	Multi-isotopes iterative Westcott
Mn	Manganese
Cl	Chlorine
Cr	Chromium
Cu	Copper
CH_4	Methane
CPCB	Central Pollution Control Board
DBH	Diameter breast height
DS	Dumping site
ERI	Ecological risk index
EDXRF	Energy-dispersive X-ray fluorescence
ECM	Ectomycorrhiza
FS	Forest site
Fe	Iron
FGD	Flue gas desulphurization
Hg	Mercury
HNO_3	Nitric acid
H_2O_2	Hydrogen peroxide
HE	Heavy metals
Igeo	Geo-accumulation Index
ISFR	Indian state of forest report
IPCC	Intergovernmental Panel on Climate Change
K	Potassium
LA-ICP-MS	High-resolution laser ablation inductively coupled plasma mass spectrometry
TRW	Tree ring width
W	Tungsten
WHO	World health organization
Zn	Zinc

MSW	Municipal solid waste
NAA	Neutron activation analysis
NAAQS	of National Ambient Air Quality Standards
NEI	Northeast India
NH	National Highway
Ni	Nickle
NO_2	Nitrogen dioxide
OAs	Organic acids
P	Phosphorous
Pb	Lead
PTFE	polytetrafluoroethylene
RS	Road site
RSPM	Respirable suspended
SE	Standard error
SO_2	Sulfuric dioxide
SPM	Suspended particulate matter
SWM	Solid waste management
TE	Toxic elements
TD	Transportation Department

Chapter - 1
Introduction

Dendrochronology is a breach of science that deals with the study of the paleoclimatic, ecological, hydrological, glaciological, and archeological history of a region through analyzing patterns recorded in the cores of ice, wood, speleothems, etc. However, dendrochemistry is a sub-field of dendrochronology, in which the scientists use dendrochemical analysis of various elements and interpret the accumulation of toxic elements in dated tree ring cores in relation to the external environment. Researchers intended to discover temporal markers of environmental changes (Guyette and Cutter, 1993; McClenahen and Vimmerstedt, 1993) or to detect evidence of phytotoxicity turned to dendrochemistry (Kaminski, 1997). The concept of dendrochemistry was initially introduced by Lepp in 1975. He successfully reconstructed historical trends of toxic elements within an environment using tree ring cores. Substantial advancements have been made in utilizing tree ring core records for reconstructing pollution histories. In essence, this process involves the accumulation of toxic trace elements or heavy metals (HMs) from various parts of the ring-forming trees including the wood, roots, bark, leaves, and other plant tissues from the surrounding environments. The concentrations of toxic elements in the tree ring core can be accurately measured (Cui et al., 2013; Liu et al., 2018; Wang et al., 2022; Xu et al., 2017). In recent times, this method has been accepted worldwide for the reconstruction of past pollution history of contaminated sites by tracking the accumulation of HMs in annual tree ring growth data. Such studies have not been carried out in India previously, however, recently Balraju et al. (2023) have studied accumulation trends of different toxic elements in *Magnolia champaca (M. Champaca)* tree rings through a dendrochemical analysis at Tuirial dumping site in Mizoram, Northeast India. Authors recommended this species as a potential tree for the remediation of HMs from contaminated sites. This study has been conducted to assess the bioremediation potential of HMs in two common ring-forming tree species of Mizoram.

1.1. Environmental pollution

Since the beginning of the Industrial Revolution, human impact on Earth's system has accelerated and has noticeable changes in the Earth's atmosphere. In the early 2000s, a Dutch meteorologist and atmospheric chemist, Crutzen coined the term Anthropocene, a geological era marked by significant human impact on the earth's system, leading to various environmental consequences, including heavy metals or toxic trace elements pollution (Crutzen, 2016; Nachana'a Timothy, 2019). Although HMs are naturally found throughout the earth's crust. However, the exposure results of these metals mostly occurred due to increased circulation of these elements in the ecosystems through anthropogenic activities such as urbanization, industrialization, mining, and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds (Shallari et al 1998; Sarkar, 2002).

Pollution of HMs involves both essential and non-essential elements, some of which pose high ecotoxicological risks (Desideri et al., 2010; Kabata-pendias and Szteke, 2015). The nature of these HMs such as their occurrence, transport, and toxicity are mostly determined by the characteristics of the element, whereas soil factors such as texture, temperature, moisture, pH, redox conditions, and salinity may also play a significant role in the properties of these elements (Alloway, 2012). Increased greenhouse gas emissions are expected to disrupt hydrological patterns, boost temperatures, and increase the frequency of extreme occurrences of HMs (IPCC, 2014) and their ecotoxic consequences (Alloway, 2012; Biswas et al., 2018). In India, environmental issues related to HMs contamination caused by industrial development and the extreme extraction of natural resources are increasing. Greater amounts of toxic waste have been scattered and affecting thousands of places across the nation. Thus, even in the most remote locations, a significantly large number of populations are exposed to pollution from past and modern industrial practices as well as emissions into the environmental components (air, water, and soil).

In urban areas, municipal solid wastes (MSW) are primarily originating from human settlements, small industries, and commercial activities (Singh et al., 2011). The combined effects of industrialization and urbanization have contributed to a concerning rise in HMs concentrations across various environmental components, especially in dumping sites which lead to high levels of some potential HMs such as Cu, Pb, Zn, Fe, and Ni (Paradelo et al., 2011; Brahmasrene and Lee, 2017; Chen et al., 2021). Globally, urban areas generate an astounding amount (1.3 billion tonnes) of solid garbage each year, and this staggering figure is projected to reach 2.2 billion tonnes by 2025 (Scarlat et al., 2015). Inadequate solid waste management (SWM) and E-waste pose severe issues such as challenges to soil pollution and health risks, especially for the urban poor worldwide (Dutta et al., 2023).

In densely populated urban regions, proper poor SWM becomes a crucial concern (Singh et al., 2021) leading to environmental and health hazards, and an environmental injustice situation for those residing or working nearby solid waste processing and disposal facilities (Kubanza and Simatele, 2016; Njoku et al., 2019). Municipal waste dumping in cities of developing countries is a widespread issue primarily driven by the confluence of several factors. These factors include high population density, limited access to advanced waste disposal facilities, and a shortage of trained personnel (Minh et al., 2006; Ali et al., 2014). These dumping grounds unquestionably introduce an enormous quantity of HM pollutants into the soil ecosystem and the removal of these elements is difficult as they cannot be broken down even in low concentrations. Further, these metals are entering into the food web and having more severe consequences due to biomagnification. Therefore, the health and survival of all life forms are adversely affected by these hazards (Chen et al., 2021). The unavailability of historical site-specific data on exposure to pollutants is greatly hampered in analyzing the impacts of pollutants on forest ecosystems.

Continuous environmental monitoring is crucial for understanding the long-term impact of polluted sites and the influences of changing climate (Biswas et al.,2018 Nachana’a Timothy, 2019 Owen et al., 2020). Unfortunately, routine HM monitoring is often limited in time due to high industrial and anthropogenic activities. As a result, there are only restricted pollution records available for the past, especially in the soil (Zubair et al., 2021; Rasool et al., 2022), leaves (Petrova et al., 2014), tree bark (Barnes et al., 1976), mosses, and bryophytes (Evans and Hutchison, 1996), earthworms (Pizl and Josens, 1995), and mammals such as birds (Getz et al., 1977). These sources have been extensively used to assess the quantities of harmful elements, yet they only offer information about the contemporary concentration levels.

Trees serve as sensitive bioindicators capable of indicating and mitigating local and global environmental changes posed by various chemical pollutants (Padilla and Anderson, 2002). Due to constant exposure to the contaminated soil and air, trees absorb contaminants through various components (i.e., roots, leaves, and bark) and accumulate these pollutants in woods (Lepp, 1975; Sawidis et al., 2011; Cocozza et al., 2021; Balraju et al., 2022). Distinguishing between the number of hazardous elements taken up from the soil versus those deposited on leaves can be a challenging task as the trees are long-lived organisms, which reflects the cumulative effect of environmental pollution from both the soil and the atmosphere (Sawidis et al., 2011).

However, long-term data is necessary for the effective regulation of these harmful element pollutants and for understanding the trajectory of a given element in environmental settings. Long-term proxy data are required to assess the historical trend of contamination. Tree ring widths are used as a natural proxy record and a widely accepted method for understanding paleo-climatic environmental phenomena which provide an evaluation of chemical components across both space and time (Brienen et al., 2016; Danek et al., 2015; Binda et al., 2021; Dhyani et al., 2023; Bhattacharyya et al., 2023). Tree rings may be seen as a sensor of environmental changes since they record the occurrence of environmental events (Sheppard et al., 2007). Biomonitoring of environmental pollutants (Austruy et al., 2019; Nabais et al., 1999), reconstruction of long-term changes in the environment (Kuang et al., 2009; Ballikayaet al., 2022), and detection and dating of volcanic eruptions are some of the examples of applications for this technique (Pearson et al., 2009; Bollschweiler et al., 2010).

1.2. Heavy metals (HMs) uptake through plant-soil interaction

Plants have long been known to efficiently remove HMs from different contaminated sites. Some plants have been reported to remarkably survive and grow well in soil contaminated with raised levels of HMs, even though excessive HMs can adversely affect their physiology and overall survival. These survival mechanisms can be broadly categorized into three main strategies: exclusion, accumulation, and translocation. Exclusion primarily takes place in the root zone (rhizosphere), while accumulation and translocation processes occur within the plant itself (Antoniadis et al., 2017).

1.2.1. Exclusion: Plant strategies in the rhizosphere

The rhizosphere is characterized by complex interactions of root systems, soil substrate, and microorganisms, which is the major site for the uptake of HMs. Plants can influence the properties rhizosphere via root exudates and microbial interactions, which impact TM bioavailability, uptake, and tolerance. Plants exposed to HM have evolved TM-tolerant ecotypes with mechanisms to avoid and exclude HMs (Guerra et al., 2011). One such mechanism involves moving root biomass to "search" for locations with lower HM content (Kahle, 1993). Plants can also influence soil mechanical and hydrological qualities by secreting root exudates, which operate as a defence mechanism by excluding HMs (Vannoppen et al., 2015).

1.2.2. Root exudates, microorganisms, and Heavy metal bioavailability

Root exudates are low molecular weight organic compounds like organic acids, amino acids, polypeptides and proteins, aliphatic and fatty acids, sterols, and phenolics, etc. have the capacity to modify the chemical environment of the soil, consequently influencing the bioavailability of HMs (Antoniadis et al., 2017). Additionally, symbiotic relationships between plants and microorganisms play a pivotal role in plant adaptation to contaminated soils. For instance, the mutualistic symbiosis between plants and ectomycorrhiza fungi observed in European Aspen thriving in the soil heavily contaminated with HMs (Krpata et al., 2008), significantly impacts plant responses to heavy metals. These fungi store HMs within fungal hyphal vesicles in plant roots, thereby restricting HMs uptake by the tree (Bano & Ashfaq, 2013).

Non-mycorrhizal fungi, like endophytes found in shrubs and herbs growing on mine wastelands, have been demonstrated to influence adaptation to divalent ions such as Zn and Pb (Li et al., 2012). Furthermore, rhizobacteria can promote root growth and enhance TE bioavailability, ultimately affecting the uptake of HMs by plants (Antoniadis et al., 2017).

1.2.3. Accumulation and translocation of heavy metals

The translocation and accumulation are key processes for transporting HMs and ensuring the survival of trees. HMs are absorbed through soil water and transported toward the foliage, where elements such as copper (Cu), zinc (Zn), magnesium (Mg), iron (Fe), chlorine (Cl), and phosphorous (P) play essential roles in photosynthesis (Taiz et al., 2015). However, translocation can introduce challenges in dendrochemistry, as the transportation and storage of HMs in trees are highly variable and species-dependent (Liu et al., 2013; Stoltz and Greger, 2002). Suppose example, populus clone variations have shown varying ratios of translocation between the plant parts, often with 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 classify sequestration/compartmentalization and binding/chelation as fundamental mechanisms governing the translocation and accumulation of HMs. Sequestration of HMs takes place within the cell, encompassing structures like the cell wall and vacuole, which regulate the influx of HMs and prevent metabolic disruption. The prevalence of polysaccharides containing carboxyl groups in the cell wall serves as a crucial site for accumulation. The latter mechanism involves the utilization of various ligands to mitigate HM toxicity in the cytoplasm. Chelation with diverse ligands guides the transport and storage of HMs in plants for specific processes or their sequestration in different plant parts. These mechanisms determine the destinations within the plant where HMs are transported and stored (Guerra et al., 2011).

1.3. Interpreting dendrochemical analysis

Despite these adaptations, the substantial variability in the accumulation and concentration of HMs within tree rings and among individual trees poses significant challenges in dendrochemical analyses. This variability can complicate data interpretation, potentially influencing the outcomes of these analyses (Binda et al., 2021). Nevertheless, comprehending the interactions between plants and soil, as well as the mechanisms plants use for, HMs uptake, defense, and translocation in contaminated soils, remains essential for advancing scientific knowledge and refining dendrochemical methodologies.

1.4. Dendroecology

Dendroecology discusses various dendrochronological techniques and applications applied to study ecological problems (Fritts and Swentaam, 1989). The use of tree rings to monitor environmental changes was established by the American Astronomer A.E Douglass in the early 1900s who is credited as the founder of dendrochronology. Since then, dendrochronology has become a useful tool for studying climate variations (Fritts, 2012), extreme events (Hevia et al., 2018), and dating archaeological and historical structures (Bernasbei et al., 2019). The annual growth cycle of trees makes it possible to use tree rings as an indicator of temporal environmental changes.

Trees that grow in temperate climates have annual growth rings that are distinguished by light-colored early wood created during rapid growth season as in spring and dark-colored late wood created during slow growth period as either in summer or fall. Both biotic and abiotic factors have an impact on the variation in tree-ring width (TRW). Biotic influences include genetic differences between species and between individual trees, as well as aging. Temperature, precipitation, soil moisture, wind, nutrient availability, and light are all examples of abiotic variables. These characteristics are typically shared by all trees at a given location. They were making it possible to establish a link between variance in TRW and abiotic variables. Since the mid-1970s, the area of dedrochemistry has grown from dendrochronology as a method to reconstruct changes in the chemical environment (Lepp, 1975).

1.5. Dendrochemistry

Since the early 1970s, dendro-chemical techniques have been used to monitor historic changes in the chemical composition of soil and the atmosphere by analyzing the concentration of various elements in tree rings. The concept of dendrochemistry was proposed by Lepp (1975) for the first time. The author has successfully reconstructed the history of HMs using tree rings in the area of Great Britain. A fundamental principle of dendrochemistry is based on the analysis of the chemical composition of tree rings and to track the chemical composition of the environment at the time of their accumulation in the tree rings (Watmough, 1999). Dendrochemistry examines and interprets the inter-annual variations in element concentrations within the wood of tree rings. Initial studies have served as a catalyst to advance dendrochemistry in environmental monitoring (Watmough, 1999; Cocozza et al., 2016; Ballikaya et al., 2022). Dendrochemical investigations therefore have the potential to provide insight into how environmental changes, such as pollution, affect ecosystems over time.

A fundamental aspect of dendrochemistry involves understanding how trees absorb and accumulate HMs. Lepp (1975) identified foliage, bark, and roots as the primary pathways for HMs uptake with root uptake being the predominant route. Research into the absorption and translocation of HMs from bark to xylem has revealed minimal movement, as observed when radioisotopes of Mn and Zn were applied to the bark (Lin et al., 1995). This finding aligns with the fundamental role of bark (Binda et al., 2021).

Studies on the uptake of atmospheric HMs have demonstrated rapid accumulation of chemicals in the most recent tree rings, in contrast to root uptake, which can exhibit a time lag between deposition, uptake of HMs, and their appearance in tree rings (Peckham et al., 2019). This emphasizes the complex interplay between root systems, soil characteristics, and the uptake and storage of HMs in tree rings (Antoniadis et al., 2017; Balouet et al., 2012).

Many studies have consistently shown fluctuations in element concentrations within tree rings indicating their potential as environmental bio-indicators for hazardous elements in industrial and urban areas, dumping sites, and rural regions (Base and McLaughlin, 1984; Watmough, 1997; Nabais et al., 1999; McLaughlin et al., 2002; Siwik et al., 2010; Locosselli et al., 2020; Cocozza et al., 2021). Worldwide, different tree species have been used to reveal pollution histories in various countries. For instance, *Pinus massoniana* has been studied for 168 years to understand the pollution history of Fuzhou city (Chen et al., 2021). Oak (*Quercus pubescens* Willd) was used to assess HMs like Zn, Mn, Cs, and S reflecting the emission history of a cement plant in Central Italy (Cocozza et al., 2021). Ponderosa pine (*Pinus ponderosa*) provided insights into the absence of anthropogenic acid rain in Canada (Padilla and Anderson, 2002). Other studies have been conducted over the world to study the pollution history of the region using different potential species, for example, *Tipuana tipu* (Geraldo et al., 2014), *Pinus halepensis,* and *Populus nigra* (Austruy et al., 2019), *Populus bonatii,* and *Ailanthus altissima* (Liu et al., 2018), *Poicianella pluviosa* (Locosselli et al., 2020), and *Quercus pubescens* (Cocozza et al., 2021). Despite these advancements, further progress is still possible in extracting environmental contamination information stored in tree rings, which necessitates knowledge of the spatial variation of chemical constituents.

In India, particularly in Northeast India (NEI), several conifer and broadleaf tree species, including *Abies densa* (Bhattacharyya & Chaudhary, 2003), *Larix griffithiana* (Shah et al., 2014), *Pinus merkusii* (Shah & Bhattacharyya, 2012), *Pinus Kesiya* (Upadhyay, 2019; Thomte et al., 2022), *Pinus wallichiana* (Shah & Bhattacharyya, 2012), *Quercus serrata* (Upadhyay et al., 2019), *Toona ciliata* (Monsang et al., 2023), and *Tectona grandis* (Upadhyay et al., 2019), have been used for diverse dendroclimatological studies. However, dendrochemical studies have not been carried out earlier. This is the first record of dendrochemical studies in northeast India.

1.6. Scope of study

In the Anthropocene era, HM contamination posed a serious environmental problem (Briffa et al., 2020). Ever-increasing economic growth and a considerable increase in the human population with the advancement of human civilization are releasing a number of anthropogenic pollutants into the environment (Biswas et al., 2018). The mining sector alone releases billions of tones of toxic waste every year (Owen et al., 2020). Mining and related waste generation are expected to rise in the near future if energy production depends on non-renewable raw materials (Herrington, 2021).

Despite the advancement of environmental regulations over recent decades (Michanek & Zetterberg, 2012), the enduring consequences of historical contamination still loom over ecosystems and human health (Alloway, 2012; Nachana'a Timothy, 2019). It is imperative to grasp the historical pollution context to formulate effective strategies for addressing past pollution issues and implementing future mitigation measures (Chen et al., 2021). In this context, dendrochemistry emerges as a promising tool for unveiling detailed temporal and spatial pollution histories. This method offers insights into pollution dynamics, enabling us to assess the effectiveness of environmental regulations and mitigation programs (Binda et al., 2021). As a relatively young field of research, dendrochemistry has seen studies in the northeast part of such studies are very scanty. Particularly, in Mizoram state no studies have been conducted related to dendrochemistry except a few studies conducted on dendroclimatology, tree-ring growth, and climate relationship using different species; namely, *Tectona grandis*, *Pinus kesiya*, and *Quercus Serrata* (Upadhyay et al., 2019 & 2021). Further investigation is required in the dendrochemistry field 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 three different study sites, such as the Forest site (FS), Road site (RS), and Dumping site (DS) in the Aizawl, Mizoram. This study evaluated variations in patterns and trends of seven HMs, namely Zn, Pb, Fe, Mn, Cu, Ca, and Ni, and reconstructed past pollution history by using *Tectona grandis (T. grandis)* and *Magnolia champaca (M. champaca)* tree ring cores, in this study was used the atomic absorption spectroscopy (AAS). By revealing the dendrochemical signal's response to the accumulation capability of the tree species at three different study sites, this study aims to contribute relevant Knowledge to drive further the development of dendrochemical approaches for better understanding and management of historical and future HM pollution.

1.7. Objectives

The present work proposes the following major objectives

1. To analyze inter-annual elemental concentrations in tree rings of selected species.

2. To find out the most prominent element persisting in the tree rings in the area and to track possible physical sources of elements in the tree rings.

3. To identify species with strong efficiency of accumulating heavy metals from the ecosystems and to suggest indicator species for phytoremediation of heavy metals.

Chapter 2
Review of literature

Across the world, several researchers have performed many dendrochemical studies to track the pollution history of the contaminated site using dendrochronology (Binda et al., 202; Canning et al., 2023; Gačnik and Gustin, 2023; Liu et al., 2023). Such studies have very wide implications for environmental monitoring by obtaining long-term contamination records in urban areas which is a challenging task because of the unavailability of long-term authentic data on these parameters (Shekhar et al., 2022; Scharnweber et al., 2023; Liu et al., 2023; Li et al., 2023; Cobanoglu et al., 2023; Balraju and Tripathi, 2023; Balraju et al., 2022; Liu et al., 2024) In this case, tree ring records are one the most important natural proxies in paleo climatic studies as they have been found to feature a high resolution, accurate dating, high sensitivity to climate, long duration, and wide distributions (Yadava and Singh 2002; Frank et al., 2007; Dhyani et al., 2022; Dhyani et al., 2022; Shekhar et al., 2023; Chinthala et al., 2023; Bhattacharyya et al., 2023). Therefore, such studies have wide implications at different environmental scales that vary from a particular region to the globe. Different tree ring species have been used to develop an understanding of the pollution history of that region in a number of tree species found in that location (Bhattacharyya et al., 2012; Sheppard and Witten, 2022; Balraju and Tripathi, 2023). These studies provide a basic idea about contamination status and indicator species for the phytoremediation of HMs found in that region (Bhattacharyya et al., 2012). In this chapter, important dendrochemical studies carried out in India and other parts of the world have been reviewed.

2.1. Dendrochemical studies at the global level

Smith and Shortle (1996) have reported basic and induced features of tree biology which is required to understand the element's records in tree rings. Further, they studied tree preferential transport systems, the exclusion of some chemical elements in the process, and the impact of injury and infection on the chemistry that helps in making valid interpretations. Further, dendrochronological studies have been found to evolve new dimensions to address both the extent and causes of impacts of regional-scale environmental pollution and the function of forest ecosystems and their relationship with soil and biogeochemical cycles (Samuel et al., 2002). According to Samuel et al., (2002), dendrochemical studies are useful in studying the effects of acid rain and nutrient deposition in a particular region. Poussart et al., (2006) developed synchrotron x-ray microanalysis records of Ca for ringless *Miliusa velutina* and used them to estimate the age and growth history of trees. Further, they found a significant correlation of Ca in annual rings of trees and annual Ca maxima with the amount of rainfall during the dry season.

Nuhoglu (2006) investigated air pollution through tree rings of red pine (*Pinus brutia*) and energy dispersive spectrometer and found elements such as Al, Si, Mg, K, Fe, Ca, S, Zn, Ti. Smith et al., (2014) suggested that Energy-dispersive X-ray fluorescence (EDXRF) can be used for forensic applications of dendrochemistry. Kirchner et al., (2008) studied the trace metal accumulation in tree rings of Jeffrey pines (*Pinus jeffreyi*) using high-resolution inductively coupled plasma mass spectrometry to develop baseline values for trace elements (Al, Cr, Mn, Fe, cobalt Co, Ni, Cu, Zn, Sr, Cd, Ba, and Pb), to examine the intra-tree and inter-tree variability of these trace metals, and to assess differences in metal concentrations related to automobile traffic.

Laurent et al., (2009) use dendrochronology and dendrochemistry to date the tree rings and identify the metal concentration in tree rings of red ash (*Fraxinus pennsylvanica* Marsh.) respectively. The study reported the presence of lead and other metal trace elements (As, Cd, Cu, Ni, and Zn) in the xylem of the trees and identified the contamination events on a time scale. Hristovski and Melovski (2010) reported that the pith contains higher trace elements than the middle and outermost rings of the European beech (*Fagus sylvatica* L). Shepard et al., (2012) demonstrated the shapes of distribution, and inter-tree variability of trees within subsites and time periods using the Mann-Whitney test. The study revealed that for the inter-tree variation Tungsten (W) and Cobalt (Co) were higher within versus outside of Fallon. Baltrenas and Vaitkute, (2011) analyzed the manganese trends in tree rings of *Pinus sylvestris* L. and revealed that Mn concentration negatively correlated with soil ph and organic carbon, and also the Mn concentration decreased from heartwood to sapwood.

Leonelli et al., (2011) In this study they reported the tree recorded at the yearly scale variations in chemical elements and changes in heavy metals concentration over time, for this purpose, the tree rings are taken from European larch (*Larix decidua* mill) and they found the significant variation between the heartwood and sapwood with generally higher concentrations in the sapwood. Balouet et al., (2012) Demonstrated that dendrochemistry can be used to generate historical scenarios of past contamination of nearby former industrial groundwater by chlorinated solvents, by analyzing with EDXRF line scanning; revealing that EDXRF profiles showed tree rings had high concentrations of Cl. The patterns of Ca, Zn, and Potassium (K) were detected using the EDXRF technique and found helpful in identifying the physiological and anatomical processes within the tree. The arrangement of elemental profiles of EDXRF and radiographs permitted to visualization of the dendrochemical trends and distinguished the effects of internal physiological, anatomical, and pathological changes in tree-ring chemistry from external environmental events such as pollution impacts (Smith et al., 2014).

Şahin et al., (2013) Elemental constituents of tree ring samples from *Pinus nigra* trees grown in the Mediterranean region were analyzed using k and multi- isotope iterative Westcott (MIW) method of Neutron activation analysis (NAA). A total of 27 elements were identified from the analyzed tree ring samples and showed that elemental concentrations in tree rings are related to inter-tree ring variability, such as the local soil properties, insect or animal attacks, and internal physiological conditions that affect each specific tree. These changes can also be correlated with significant chemical changes in the soil due to contamination from the fallout of volcanic ash, acid rain, and the agriculture industry.

Xu et al., (2017) Concentrations of Cu, Zn, Pb, and Cd in soil and tree rings of urban forests around highways in Shanghai, China analyzed using the Geo-accumulation Index and Potential Ecological risk indexes (ERI) were used for assessing the contamination level of heavy metals. A significant increase in the concentrations of Cu, Zn, and Cd was found in soil compared to corresponding background values of Shanghai and tree rings showed a gradual increase in concentrations of Cu, Zn, and Pb in the past 10 years of study. They also concluded that Cd should be controlled on a priority basis.

Perone et al., (2018) The chemical composition of tree-ring wood was used to monitor the spatial-temporal variability of pollutants in Terni, Central Italy. High-resolution laser ablation inductively coupled plasma mass spectrometry (LA-ICP- MS) was used to determine trace element (Cr, Co, Cu, Pb, Hg, Mo, Ni, Tl, W, U, V, and Zn) index in tree-rings of downy oak. The presence of contaminants detected in tree rings reflected industrial activities over time and varied with the distance of the tree to the industrial plant. Schijf and Garvin (2018) presented microwave-digestion/Inductive Coupled Plasma-Mass Spectrometry as a new method for the analysis of eight trace metals (As, Cd, Co, Cr, Cu, Ni, Pb, V) in tree wood increment cores cut into sections representing 1–5 years of growth was presented.

Rocha et al., (2019) Dendrochemistry was used as a tool to trace anthropogenic contamination at a glassworks site in southern Sweden. The study combined the high-resolution tree ring series data with the sediment core's elemental profiles. ED-XRF and CS-ERF techniques were used to analyze the tree ring and sediment core samples respectively. The dendrochemical analysis detected the traces of Ba and changes in profiles of Cl, K, and Mn and confirmed the potential of the method to record environmental releases. Locosselli et al., (2020) Central Sao Paulo, Brazil, the air quality assessment has been using dendrochemistry tools, in this study various toxic elements concentrations of Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Mn, P, S, Sr, Zn in the bark of 62 trees, and its temporal trends industrial area. In this study (Al, Ba, Cu, Fe, Zn) toxic element concentrations are increasing due to industrial emissions.

Semeraro et al., (2020) Worldwide industrial and urban areas pollution increasing continuously, and it is a challenge for urban green management, pollution mitigation, and environmental monitoring, in this study they propose the analysis approach for the spatial and spatial-temporal distribution of pollution in the environment through dendrochemistry technique. Binda et al., (2020). The review highlights the growing interest in using chemical analysis of tree rings as a detailed environmental record over the past five decades. This method provides valuable information about the surrounding environment, including nutrient levels and pollutant presence. The study covers various determinable chemical species and their functions in trees, as well as the uptake mechanisms. It also delves into analytical techniques for tree ring analysis, emphasizing recent advancements that enhance the level of information accessible. Dendrochemical proxies have been applied to trace processes like environmental contamination, paleoclimate reconstructions, and tree physiology. The review offers case studies for each application, placing emphasis on the reliability of the tracing process

Cocozza et al., (2021). The study focused on 32 trace elements within the tree rings of downy oak trees situated near both a rural cement plant and an industrial area with multiple pollution sources. Tree cores were collected at a 1 km distance from each site, which was 8 km apart, spanning from 1990 to 2016. Using laser ablation inductively coupled plasma mass spectrometry, the researchers found that trace elements Cs, Mg, Mn, S, and Zn exhibited increasing levels since the early 2000s, coinciding with the cement plant's operations. However, there were no notable trends in tree rings from the industrial area, leading to questions about the translocation and volatility of certain elements. Other trace elements displayed minimal changes, indicating limited additional impact from industrial activity.

Bertin et al., (2021). This author demonstrates the potential of dendrochemical analysis for reconstructing past volcanic events in Northern Patagonia. The Calbuco volcano in Chile, ranked third in volcanic risk, experienced a significant sub-Plinian eruption in 2015, affecting Chile and Argentina. To better understand its eruptive frequency, researchers developed a continuous eruptive record from 1514 to 2016 using dendrochemical analysis of *Fitzroya cupressoides* tree rings. By comparing chemical records with historical eruptions, they identified chemical Tracers of past eruptions. Tree-ring width also decreased significantly during eruptions with a Volcanic explosivity index of 3 or higher. This revealed 11 previously unknown Calbuco eruptions, extending its history to the 16th century, with an average eruptive frequency of about 23 years.

Chen et al., (2021). In this study, the author addresses the pressing issue of heavy metal pollution in urban China. It presents a remarkable 168-year record of heavy metal concentrations (Fe, Mn, Cu, Zn, Ni, Cr, Cd, Pb, Co, and Sr) in *Pinus massoniana* tree rings from Fuzhou City, marking the longest such chronology in China. The metals exhibited varying distribution patterns, with notable migration trends observed in Mn and Sr, peaking at the innermost part of the tree rings. Co, Cd, and Pb displayed elevated concentrations near the heartwood-sapwood boundary. Ni, Cu, Cr, and Fe showed increasing levels, potentially due to migration towards the bark induced by physiological and environmental factors like tourism and traffic pollution.

Li et al., (2023). In this study, the authors address the issue of heavy metal pollution, not only in urban and industrial areas but also in remote regions lacking long-term monitoring data. Researchers focused on Chinese pine trees in the Jiuzhaigou World Natural Heritage site to analyze the concentrations of Pb, Zn, Cu, As, Cd, Co, Cr, and Ni, shedding light on pollution history. They also conducted source analysis and assessed the potential ecological risk of these heavy metal (loid)s. The findings revealed that Jiuzhaigou exhibited relatively high levels of heavy metal (loid) pollution, particularly in areas with intensive human activities like Nuorilang. The elevated concentrations hindered tree growth, with more pronounced effects at higher concentrations. The pollution was linked to human activities such as logging, infrastructure development, and tourism. Notably, even at low concentrations, Chinese pine trees proved valuable as bioindicators for heavy metal (loid) pollution and provided insights into long-term pollution trends and the biogeochemical cycle of these substances in forest ecosystems.

Fornasaro et al., (2023). The authors used a Chestnut tree trunk in the Monte Amiata mining district of Central Italy to track historical trends of atmospheric mercury (Hg) pollution. This district, known for world-class mining, also saw emissions from active geothermal power plants. The study observed a significant reduction in Hg levels in the tree rings, likely due to mine closures, dropping from over 200 µg kg^{-1} to below 100 µg kg^{-1}. However, recent levels, though lower, still surpass those in a reference area 150 km away. Chestnut bark consistently showed higher Hg concentrations than sapwood, indicating ongoing pollution. This research underscores the potential of tree rings as a cost-effective method for monitoring Hg changes in areas affected by mining and geothermal activity, offering valuable insights for impact mitigation and sustainable resource management.

Liu et al., (2023). In this study, the authors have heightened the progress and challenges in the dendrochemistry field. Tree rings serve as a natural archive, recording atmospheric elemental mercury (Hg) uptake through foliage and subsequent translocation via the phloem. This process enables the reconstruction of centennial trends in atmospheric Hg levels. Records from remote regions have effectively captured peaks in anthropogenic Hg emissions in Europe and North America during the 1960s-1970s, as well as the notable increase in Hg emissions in Asia since the 1980s. Combining Hg concentrations and isotopic signatures offers insights into historical atmospheric Hg trends and emission source shifts. However, the specific mechanisms of Hg translocation, including radial movement and the influence of environmental and tree physiological factors, remain incompletely understood. Further research should focus on elucidating these processes and their isotopic fractionation in tree rings, and on establishing correlations between tree-ring Hg profiles and atmospheric pollution levels in specific tree species. Additionally, developing robust statistical models is recommended to quantify the impacts of environmental and tree physiological factors on Hg accumulation and translocation in tree rings.

2.2. The dendrochemical studies from adjoining countries

Rahman et al., (2022). The authors reconstructed the past flood events using tree growth rings in Bangladesh, with 80% of its land as part of the Ganges-Brahmaputra-Meghna River system, which faces significant flood risk. Due to climate-induced factors, 16 major floods occurred between 1954 and 2017. Researchers conducted a tree-ring analysis in a moist tropical forest to understand the impact of extreme flood events on tree growth, anatomy, and oxygen isotope composition. They identified three severe flood years in 1974, 1988, and 1998. Flood conditions led to reduced tree-ring width (up to 53%) and vessel area (up to 28%), while vessel density increased by 23% as a protective response. Oxygen isotope composition decreased due to regional precipitation changes. Analyses showed that vessel density strongly correlated with water levels in the Manu River, suggesting it is a reliable indicator for river monitoring. This research sheds light on the effects of floods on tree physiology in flood-prone regions like Bangladesh and their implications in the face of climate change.

2.3. Dendrochemical Studies in India

The studies on dendrochronological research particularly on dendrochemistry are only a few from India which is taking a surge with time (Bhattacharyya et al., 2012; Borgaonkar, 2021; Balraju et al., 2022; Tripathi et al., 2022; Upadhyay et al., 2021; Balraju and Tripathi, 2023). These investigations were carried out both in temperate and tropical areas, although the majority of them were found in the western and eastern Himalayas (Upadhyay et al., 2022; Tshering et al., 2023). Tree ring pollution studies, however, have not yet been carried out (Bhattacharyya et al., 2012). However, some pollution-related studies were carried out in India as well as Northeastern (Rai 2009a; Rai, 2012a; Rai chutia, 2014).

2.4. Dendroclimatological Studies in Northeastern -India

Although few dendrochronological studies have been published from different parts of northeastern India except Nagaland and Tripura (Shah et al., 2014; Balraju and Tripathi, 2023). A number of dendrochronology-related articles were gathered and reviewed for their dendroclimatological potential. According to Borgaonkar et al., (2018) the *Abies densa* Griff chronology, which spans 490 years from 1504 to 1994, is the longest chronology that has been created for this area so far. Dendrochronological research in Northeast India pertaining to the species (e.g., *A. densa, L. griffithii, T. dumosa, P. wallichiana, Q. serrata, T. ciliata, T. grandis, P. kesiya,. P. merkusii*) have been carried out (Bhattacharyya and Chaudhary, 2003; Borgaonkar et al., 2018; Shah and Bhattacharyya, 2012; Shah et al., 2014; Singh et al., 2016; Shah et al., 2019; Keshav kumar Upadhyay, 2019; Monsang et al., 2023; Balraju and Tripathi, 2023). These nine tree species were used as the basis for tree- ring-based studies in northeast India that mainly concentrated on the reconstruction of climate history, the relationship between climate and tree growth, the reconstruction of river flow history, inter-annual density variation, and the development of climate proxies (Bhattacharyya et al., 2012; Bhattacharyya and Chaudhary, 2003; Balraju and Tripathi, 2023). *Pinus kesiya, L. griffithii, A. densa, and P. merkusii* are the species that are most frequently employed among these for dendrochronological studies (Bhattacharyya and Chaudhary, 2003; Borgaonkar et al., 2018; Shah and Bhattacharyya, 2012; Shah et al., 2019; Thomte et al., 2020; Bhardwaj et al., 2022; Gaire et al., 2023).

2.5. Northeastern pollution studies

Jain et al., (2019). The authors address the potentially harmful materials that were evaluated in a study of soil samples taken from the Kulsi River Basin in North East India. The study of 50 soil samples showed that the average concentrations of Co, Ni, Pb, and zinc Zn surpassed background values generally found in sedimentary rocks. The average concentrations of Co, Ni, Pb, and Zn were 2.30 mg/kg^{-1}, 9.41 mg/kg^{-1}, and 22.7 mg/kg^{-1}, respectively. This shows that anthropogenic influences have contributed to the introduction of certain metals into the environment.

Deka & Hassan, (2020). Crude oil, a crucial natural resource used on a global scale, drastically alters the physico-chemical characteristics of soil and water when it comes into contact with them. The injection of calcium-rich drilling fluids had an adverse influence on soil pH, according to this study's assessment of these effects. Between 18.3 mg/kg-1 and 94.0 mg/kg^{-1}, the Pb level of soil samples varied from control samples. Co levels in the soil were 10 times higher near drilling sites than in control areas as well. Cd levels rose, reaching a maximum of 49.6 mg/kg^{-1}. Concerning was the significant increase in Zn levels, which peaked at 404.5 mg/kg^{-1}. Between 72.5 mg/kg^{-1} and 510 mg/kg-1 of Mn were present. These results highlight the major effect of crude oil on soil quality, calling for attention and environmental protection in drilling operations.

Dutta et al., (2021). The authors examined soil samples from intensive vegetable cultivation areas in the Brahmaputra Valley, NEI, to assess the accumulation of Cd, Pb, Cr, and Ni, the research aimed to understand the impact of long-term agrochemical and organic manure use. In the study, researchers collected eighty soil samples from eight locations with over forty years of vegetable production. Notably, this research is the first of its kind in the region and assumes minimal industrial or urban pollution. Results showed varying metal concentrations, with Cd levels notably higher than reference values, indicating significant enrichment. Pollution indices categorized the soils as slightly to moderately polluted, while ecological risk indices indicated low overall risk but a moderately high risk for Cd. Malunguja et al., (2021). In a study conducted in two Assam Reserved Forests intersected by National Highway (NH-15), various ecological risk indices were employed to assess potential ecological risks.

The research also utilized regression analysis and the Pearson coefficient to predict the impact of metals on tree biomass stocks. The study highlights the elevated metal concentrations near roads in Reserved Forests, with Cd and Pb being the major contaminants, posing ecological risks. These findings emphasize the importance of addressing vehicular emissions and pollutants from traffic in these sensitive ecosystems.

2.6. Pollution-related studies in Mizoram

Particularly in Mizoram state where no such study has been carried out on dendochemistry except a few studies conducted on dendroclimatology, tree-ring growth, and climate relationship using different species; namely, *Tectona grandis*, *Pinus kesiya*, and *Quercus Serrata* (Upadhyay et al. 2019 & 2021). As a result of recent development activities in Mizoram, the state has witnessed an increase in air pollution; however, the real-time observations on heavy metal concentration are very limited to decode the effect of developmental activities on the environment. Considering this knowledge gap, this study evaluated variation in patterns of seven toxic trace elements, namely Zn, Pb, Fe, Mn, Cu, Ca, and Ni, and reconstructed past pollution history.

Balraju et al., (2023). The study utilized annual tree rings to investigate the historical climate and the impact of environmental changes on tree growth in NEI. Various tree species were used for dendrochronological studies in the region. However, prior research primarily focused on climate-tree growth relationships, leaving out the examination of tree ring connections with pollution history. To address this gap, the study focused on *M. champaca* tree rings to track the temporal distribution of seven elements (Zn, Pb, Fe, Cu, Ni, Ca, and Mn) at the Tuirial dumping site in Aizawl, Mizoram. The researchers collected core samples from 20 trees, spanning two decades from 1999 to 2019. An AAS was used to measure toxic element concentrations in the tree rings over the years. The findings revealed an increasing pattern of element concentrations with the age of the tree, with the highest concentrations observed in recent year ring growth. The range of element accumulations was as follows: Fe (20.46 to 30.10 mg kg^{-1}), Mn (16.19 to 28.24 mg kg^{-1}), Zn (13.86 to 27.4 mg kg^{-1}), Ni (9.02 to 17.08 mg kg^{-1}), Cu (6.08 to 14.69 mg kg^{-1}), Ca (7.33 to 14.35 mg kg^{-1}), and Pb (6.92 to 14.26 mg kg^{-1}).

NITI Ayog, (2018). The NITI Ayog report conducted a study in Aizawl, to evaluate air pollutants, Nitrogen dioxide (NO_2) the lowest (5.12 µg m^{-3}) was in the year 2020 and the highest (15 µg m^{-3}) was observed in the year 2022 and over a period from 2006 to 2022 (23.96 %) of concentration has been increased, were has Suspended particulate matter (SPM) the lowest (51 µg m-3) was observed in the year of 2020 and the highest (150 µg m^{-3}) recorded in the years of 2016 and over the year from 2007 to 2022 (12.25 %) of the concentration has been increased. Above all this are pollutants influencing the local air quality which is reflected in all the ambient air quality parameters that have been changing over the years. With this respect, the Air quality index (AQI) indicates that the study area experienced a decrease in air quality in the year 2018 (48 AQI) but in the year 2022 it changed to (80 AQI), which impacted the discomfort in breathing problems to sensitive peoples. However, at the road site location, the concentration of Sulfuric dioxide (SO_2) and Nitrogen oxides (NOx) were found to be below the permissible limit (80 µg m^{-3}) of National Ambient Air Quality Standards (NAAQS) Central Pollution Control Board (CPCB, 1994), but there are several reports that gaseous pollutants are related to respiratory diseases and reproductive and developmental effects even at low concentration (Curtis et al., 2006; Liu et al., 2003). The other study results from this region are (2.09 µg m^{-3}) commercial area (1.03 µg m^{-3}) Mizoram University for (SO_2) followed by 22.14 µg m^{-3}, 12.05 µg m^{-3} for (NO_2) and 250.07 µg m3, 130.12 µg m^{-3} for SPM and this data was during November 2011 to February 2012 (Rai, 2012a).

Moreover, heavy-duty vehicles coming from all parts of India through the National Highway of Sairang and Bawngkawn (NH-54) and public transportation and other private vehicle moments are usually high in this study area (Road site), and other than this stone quarrying activity is also in this area which leads to emission of dust or Particulate (Pand and Rai 2015), biomass burning through shifting cultivation is very common in this region (Panda and Rai, 2015; Rai, 2009a, 2012a; Rai and Chutia, 2014) and may also be a source of SPM and NO_2 pollution. Likewise, the sources of SO_2 are thermal power plants, petroleum refineries, steel manufacturing units, cement industries, and construction works are the sources of anthropogenic in India (Kuttippurath et al., 2022), but in study site construction (Aizawl airport construction started in December 1995 and national highway construction works) works and heavy-duty vehicles moments are the main sources.

Chapter 3
Material and Methods

3.1. Biogeographic characteristics of the Mizoram

The name of the ―Mizoram" generally originates from the combination of three components, "Mi" referring to the people, "Zo" denoting high-rise places like hills, and "Ram" signifying land (Joshi, 2005; Thirumal and Lalrozami, 2018). Therefore, the Mizoram can be translated as the "Land of the Hill people or Land of Highlanders." However, the Mizoram situated in the northeastern part of India, shares its borders with two international countries (i.e., Bangladesh to the west and southwest and Myanmar to the east and southeast) and three Indian states (Assam in the north, Tripura in the west and Manipur in northeast). Geographically, the state is located 21° 57′ to 24° 30′ N lat. and 92° 15′ E to 93° 29′ E long., encompassing a total land area of 21,081 square kilometers. Notably, around 5% of this land area is characterized by Quaternary sediments, primarily concentrated in river valleys (Pachuau, 2009). The Mizoram is characterized by its mountainous terrain, featuring rugged and geologically young landscapes. Geographically, this range is an extension of Manipur Naga Hills in the southern direction.

The hills of Mizoram are predominantly composed of Cenozoic rocks, with ages spanning from 2.6 to 65 million years. These rocks exhibit a diverse range of types including sandstone, limestone, and shale, contributing to the rich geological tapestry of the region (Lodrick, 2018). A distinctive feature of these hills is the presence of parallel ridges, succinctly aligned in a north-south direction. Interspersed among these ridges are small river gorges, adding further character to the landscape. The heights of these ranges are awe-inspiring, reaching nearly 7,000 feet (2,100 meters) at the pinnacle of Phawngpui (Kasambe et al., 2013).

Among the prominent rivers that grace Mizoram, the Kaladan (Chhimtuipui) River flows through the southernmost districts, traversing Mizoram Lawngtlai and Saiha before ultimately returning to Myanmar Rakhine state. Its source lies in the Chin State of Myanmar, marking the inception of this vital waterway. Additionally, the central region of Mizoram is blessed with the origins of the Dhaleswari (Tlawng), Tuirial (Sonai), and Tuivawl rivers. These watercourses gracefully wind their way northward, eventually converging with the Barak River in the Cachar District of Assam, playing a crucial role in the hydrology of the region (Kesari, 2011).

In the heart of Mizoram, the cancer tropic weaves its path, passing through significant locations such as the state capital, Aizawl. This vital pathway also touches upon Champhai, Chhawrtui, Darlung, and Phuldungsei, serving as a lifeline for transportation and connectivity within the state (Pachuau, 1994). This intricate network of geological features and waterways not only shapes the physical geography of Mizoram but also plays an integral role in the lives and livelihoods of its inhabitants.

3.2. Climatic characteristics of Mizoram

According to the Koppen-Geiger climate classification, Mizoram is characterized by a subtropical to tropical monsoon climate. (Champion and Seth, 1968). During summer, the higher hills have cooler temperatures, while the lower elevations are warmer and more humid. One distinctive aspect of Mizoram climate is the occurrence of north-westerly thunderstorms with intense rainfall in April and May.

The annual rainfall typically falls within the range of 2000-3500 mm and begins as early as April, lasting through to September. Mizoram likes a relatively even distribution of rainfall across the state, though the southwestern part receives slightly higher amounts. Temperature records with lows of around 11°C in winter and highs reaching up to 31°C during the summer or spring season (Rai, 2016; Upadhyay et al., 2021).

3.3. Soil characteristics of Mizoram

The predominant soil order in the state of Mizoram is Inceptisol, characterized by a composition of sandy loam and clay loamy soil with high levels of organic carbon content (Colney and Nautiyal, 2013). However, it's important to note that the soils in this region undergo important changes due to shifts in land use or land management, primarily resulting from the practice of shifting cultivation or jhum cultivation, which involves shorter fallow periods.

Cultivation on steep slopes without adequate soil conservation measures exacerbates the situation. This leads to issues such as surface runoff and soil erosion, particularly due to the unpredictable and erosive rainfall patterns in the area (Misra and Saithantuaanga, 2000).

3.4. Forest types in the Mizoram

According to the forest classification provided by Champion and Seth (1968), the predominant forest type in Mizoram is the tropical wet-evergreen forest. However, there are other forest types present in the state, which include semi- evergreen forests and tropical-moist deciduous forests. In certain areas, pockets of bamboo forests are also commonly found, showcasing a diverse range of forest ecosystems in the region. Growth of bamboo is prolific in the mid and lower layers of the evergreen forest. The prevailing bamboo species in the state is *Melocanna baccifera,* (MIRSAC, 2007). Within the tropical wet-evergreen forest, several crucial tree species growing luxuriantly that including *Amoora wallichii, Artocarpus chaplasha, Dipterocarpus turbinatus*, *Terminalia myriocarpa*, *Tectona grandis, Michelia champaca*, and *Mesua ferrea*.

The forest cover of the state spans approximately 18,006 square kilometers, equivalent to 85% of its total geographical area. Over time, there has been a decrease in forest cover, declining from 86% as reported in the Indian State of forest report (ISFR) of 2017 to 85% compared to the ISFR of 2019. This decrease signifies a loss of approximately 181 square kilometers when compared to the earlier ISFR 2017 report.

3.5. Tree ring cores sampling sites

Tree ring cores were sampled from the Aizawl Forest division, Mizoram. Under these forest divisions, three different study sites (i.e., Natural Forest Side (NFS), Municipal solid waste dumping ground (DS), and Trees growing at the roadside (RS) were chosen for this study (Tables 1).

Table 3.1. Sampling site details

Site Name	NFS	RS	DS
Sample species name	*Tectona grandis, Magnolia chamapca*		
Latitude	23.7741013° N	23.8234759° N	23.740021° N
Longitude	92.6750731° E	92.6635476° E	92.800347° E
Elevation (m)	2445.32	844.6	410.85
Slope of the site	Moderate	Moderate	Moderate
NT/NC	27/54	25/50	23/46

3.5.1. Natural forest site (NFS)

The Sairang forest area lies between 23° 48' 11.51" N lat. and 92° 37' 13.63" E long. The steep and rough topography of the Sairang area is home to a wide variety of flora and fauna (Rai, 2016). The area is covered with tropical and sub-tropical forests where the top story is mainly occupied by trees like *Albizzia chinensis, Bombax ceiba, Gmelina arborea, Tectona grandis, Magnolia champaca, Terminalia myriocarpa, Mesua ferrea, Toona ciliata, Schima wallichii,* and many more (Raman et al., 1988; Upadhyay et al., 2021).

3.5.2. Roadside (RS)

In the RS study area, the sample was collected from the Lengepui to the Silchar area road and this area lies between 23° 57' 26.16" N latitude, and 92° 37' 63.51" E longitude. This is road one of the national highways (NH 54) and this road has connectivity with the airport roadside this area falls under the Aizawl Forest division of Mizoram. Aizawl City is one of the fastest-growing cities and it is the best tourist destination place in the Northeastern states of India. This city connects Mizoram to neighbouring states like Assam, and Meghalaya, and the rapid moment of vehicles has been increasing on the roadways in recent years. The tourist population has been steadily increasing with numbers rising from 89,766 in 2018- 2019 to 1,32,616 in 2021-2022 (https://tourism.mizoram.gov.in/page/tourist-arrival- data). These numbers have also led to a corresponding increase in the number of tourist vehicles as well as other activities such as soil erosion, mining, stone quarrying, and shifting cultivation, which resulted from an increase in the concentration of heavy metals and particulate pollution in the atmosphere (Rai and Chutia, 2014). Aizawl city area is a very densely constructed commercial area with a major marketplace of Mizoram state and there are frequently heavy-duty vehicles coming from all parts of India through the National highway (NH-54). Due to the heavy moment of vehicles on these roads, they are mainly contributing to air pollution in urban areas, generating gaseous pollutants, such as NO_X, carbon monoxide (CO), methane (CH_4), and non-methane volatile organic compounds, and particulate matters (Bell et al., 2011; Dadea et al., 2017). The measurements of SPM (46–132 g m^{-3}), Respirable suspended particulate matter (RSPM) (38–58 g m^{-3}), NO_2 (3–13 g m^{-3}), and SO_2 (0.8–1.6 g m^{-3}) were recorded at these particular study locations. Vehicles and associated problems of traffic congestion are major contributors to the various sources of air pollution. Human activities, particularly tourism and heavy vehicle traffic, have a significant impact on the road route.

3.5.3. Municipal solid waste dumping ground or Dumping side (DS)

The DS is located at the latitude 23.73980 N and longitude 92.82290 E, about 25 kilometers from the city of Aizawl (Figure 1). The site falls under a humid subtropical climate, categorized according to the Koppen-Geiger climate classification (Saitluanga, 2017). The altitude in the sampling area varies between 800 to 1200 meters above mean sea level, with an average annual rainfall of 2350 mm. In summer, the usual temperature ranges between 20 and 30°C, while in winter, it falls within the range of 11 to 21°C. The Tuirial dump serves as a disposal site for various types of solid wastes, such as medical waste, domestic trash, demolition debris, chemical waste, electronic waste, and scrap metal. Over time, the amount of solid waste disposed of in the Tuirial municipal landfill has increased, posing a threat to the environment by accumulating them plants, soil, water bodies, and microorganisms. Large amounts of waste are transported to the landfill from the city of Aizawl. The stream and tree species that are close to a DS are being severely impacted by toxic materials as a result of a lack of adequate security measures. In the past, the site has been examined by researchers for its impact on nearby water supplies, and their findings revealed that the dump site contaminates spring water with hazardous substances (Laskar et al., 2022).

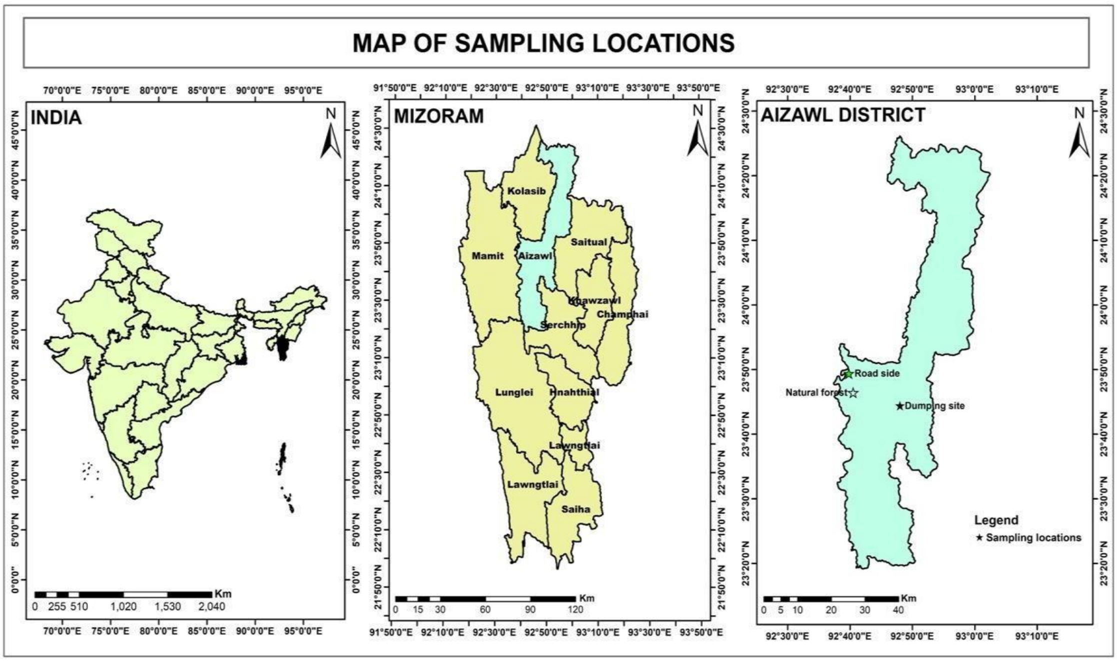


Figure 3.1. Map of the study area

3.6. Selection of tree study sites and the species

In this study, three different sites were selected; for example, a natural forest as a control site (NFS), a roadside (RS), and a municipal soil waste dumping ground (DS) tree species of the two species. The presence of selected tree species and their growth features like the formation of distinct tree rings were ensured within three sites selected for the study. The tree species selected for the subsequent dendrochemical studies were:

1. *Tectona grandis* (L. f.) commonly known as 'Teak' and Sagun belongs to the family *Verbenaceae* and it is a large deciduous tree native to India and Myanmar. These tree species of wood have excellent timber quality It is widely used for furniture making (Troup RS, 1921). *T. grandis* has ring- porous characteristics making it a distinct growth ring that is ideal for Dendrochronological and dendrochemical studies (Bhattacharyya et al., 2007; Borgaonkar et al., 2010)
2. *Magnolia champaca* (L.) Baill. Ex Pierre commonly known as 'Champaca' belongs to the family *Magnoliaceae* and is a large evergreen tree native to India. It is widely used for timber, aesthetic, and medicinal purposes (Nehru et al., 2014). The natural populations are found predominantly in the

evergreen and shola forests of peninsular India (AI-Sagheer, 2021). *M. Champaca* has distinct growth rings and anatomical characteristics, including demarcated ring boundaries and terminal parenchyma cells, and it is one of the promising tree species for dendrochronological and dendrochemical studies (Bhattacharyya et al., 1992).

However, these trees have the opportunity to be used in tree studies because of distinct tree ring features, and moreover, this species is abundantly available at selected sites. On this basis, these tree ring species were selected in this study.

3.6.1. Species description

***Tectona grandis*, Linn. f.**

Class	**:**	**Magnoliopsida**
Order	**:**	**Lamiales**
Family	**:**	**Lamiaceae**
Genus	**:**	**Tectona L. f.,**
Species	**:**	***Tectona grandis* L.f.,**

This tree is known by various vernacular names across different regions and countries. In Mizo, it is called "Tlawr," in Hindi "Sagun," in Malayalam "Thekku," in Marathi "Sagwan," in Kannada "Saguan," in Oriya "Singuru," in Tamil "Tekkumaram," and in Telugu "Adaviteeku." In various other countries, it goes by different names, such as "Kyun" and "Lyiu" in Myanmar, "Teck" in French, "Teca" in Spanish, "Mai Sak" in Thailand, "Djati" in Indonesia, and "Fati" in Malay.

T. grandis is a sizable deciduous tree characterized by its four-sided branchlets and a central pith. Its crown is rounded, and it boasts a clean, cylindrical trunk, often displaying buttresses or twists, and occasionally a fluted base. The leaves are sizeable, arranged oppositely, and have a broad elliptical or obovate shape, measuring roughly 30-70 cm in length and 25-40 cm in width. The bark exhibits shades of grey to light greyish brown, marked by shallow, lengthwise fissures. It ranges from 3.81 to 17.78 mm in thickness and tends to peel away in slender, elongated, corky flakes. (Troup RS, 1921).

T. grandis is a native species that originates in most of Myanmar, the Indian peninsula, Thailand, Jakarta, and other Indian Archipelago islands. Teak plantations on a small scale have been established in many areas of India outside of its natural boundaries, including Andhra Pradesh, Uttar Pradesh, Bengal, Bihar, Orissa, and the Andaman Islands, among others (Troup, 1921Additionally, it has been introduced to numerous tropical nations, such as Indonesia, Sri Lanka, Vietnam, Malaysia, various countries in the Caribbean, both East and West Africa, South America (Brazil), and Central America (Costa Rica) (Hedegart., 1976; Keogh., 1979).

T. grandis thrives in regions with a hot and relatively wet tropical climate, enduring high temperatures and occasional droughts during the summer season. In exceedingly damp areas, it gives way to evergreen forest species (Troup, 1921). While *T. grandis* can withstand light frost, such occurrences are infrequent within its natural habitat. The tree can flourish in areas with annual rainfall as low as 762 mm, including regions like Khandesh, Ahmednagar, Nimar, Buldana, and West Kurnool, as well as the west coast of India and the Tenasserim area in Myanmar. However, it exhibits its optimal growth in areas with consistent rainfall ranging from 1270 mm to 3810 mm.

In peninsular India, *T. grandis* exhibits an absolute maximum shade temperature of approximately 47.7°C and an absolute minimum shade temperature of around 2.2°C. These values, however, vary depending on the region. On the moisture-rich west coast, where teak thrives and reaches larger dimensions, the absolute maximum shade temperature ranges from 35°C to 37.7°C, while the absolute minimum shade temperature varies from 12.7°C to 16.6°C (Troup, 1921). In Myanmar famous *T. grandis* growing, the absolute maximum shade temperature ranges from 38.8°C to 43.3°C, and the absolute minimum shade temperature varies from 3.8°C to 12.7°C.

T. grandis trees undergo a distinctive seasonal pattern. They shed their leaves from November to January, remaining leafless for approximately three to four months. New leaves start to emerge between April and June, the timing dependent on the specific locality. However, trees in moist regions or along canal beds retain their foliage and experience a brief leafless period of about one month. This extended leaf presence and a steady supply of photosynthates likely contribute to the rapid growth of such trees (Palanisamy et al., 2009).

T. grandis typically produces panicles of small white flowers during the rainy season, which typically falls from June to July or September, although in exceptionally wet conditions, these flowers can appear as early as April. The fruit ripens between November and January, slowly falling from the tree (Troup RS, 1921).

T. grandis requires effective subsoil drainage and is not well-suited for dense, waterlogged soil conditions. It flourishes when planted in extensive, well-drained alluvial soil with a deep profile. These *T. grandis* trees attain impressive sizes and can create exceptionally uniform forests. The ideal soil for teak cultivation typically maintains a pH level within the range of 6.5 to 7.5 (Kulkarni, 1951; Tewari, 1992).

This species is renowned for possessing exceptional timber qualities. *T. grandis* wood is characterized as medium-weight, displaying hardness, strength, and robustness. It exhibits a specific gravity ranging from 0.55 to 0.70 and is known for its straight grain, coarse texture, and ring-porous structure. The sapwood of *T. grandis* is well-defined, presenting a color spectrum from white to pale yellow. In contrast, the heartwood boasts a rich, dark golden-yellow hue with discernible dark streaks. As it matures, the heartwood deepens in color and develops a distinctive, oily aroma. When appropriately seasoned, *T. grandis* wood is remarkably resilient, resistant to warping, and unlikely to split. It stands as one of the most enduring timbers globally, nearly impervious to fungus and white ant attacks, and highly resilient to decay. Although it may show minimal tendencies to crack or split during the seasoning process, with prudent caution against rapid drying conditions, it can be seasoned free from defects (Troup RS, 1921).

T. grandis possesses a ring-porous wood structure, rendering it well-suited for dendrochronological investigations. It stands out as the most extensively studied tropical species in tree-ring research, with comprehensive coverage of its various origins in Southeast Asia (Bhattacharyya et al., 2007; Borgaonkar et al., 2010).

***Magnolia champaca* (L.) Baill. ex Pierre**

Class	:	Magnoliids
Order	:	Magnoliales
Family	:	Magnoliaceae
Genus	:	Magnolia
Species	:	*Magnolia champaca* (L.) Baill. ex Pierre

Vernacular names – Ngiau (Mizo), Champa (Bengali), Chempaka (Hindi), Rae-champo (Gujarati), Chambugam (Tamil). In other countries is called an ilang-ilang (French), and, Cempaka (Indonesian).

The *M. champaca* is an evergreen or semi-deciduous small to medium-sized tree up to 50 m tall; bole straight, cylindrical, up to 200 cm in diameter, without buttresses; bark surface smooth, grey to greyish-white, inner bark fibrous, yellow to brown, crown conical to cylindrical. Stipules are adnate to or free from the petiole; leaves are simple, entire, and spirally arranged, the tree produces flowers and fruits all year. Beetles pollinate the protogynous flowers by feeding on the stigmas, pollen, nectar, and secretion from the petals. And its natural populations are predominantly found in the evergreen and shola forest of peninsular India (AI-Sagheer, 2021).

The *M. champaca* is a fast-growing species and it is found from the primary lowlands to the montane rainforest at elevations of up to 2100 m. The absolute maximum temperature is 35-40°C, and the absolute minimum temperature is 3-10°C. The *M. champaca* species is native and distributed in northeastern central, and northern India and Myanmar, Nepal, Indonesia, and Sri Lanka. Generally, these species are associated with *T. grandis*, *Schima wallichii*, *Castanopsis*, Alnus *nepalensis*, etc (Nehru et al., 2014).

The anatomy of the wood quality character is heartwood, which is olive- brown to dark brown with a greenish tinge when exposed and can be distinguished from sapwood, which is pale brown and up to 8 cm wide. Straight grain or slightly interlocked grain, fine to moderately fine, and even texture, and *M. champaca* wood has high quality and is commonly used for furniture, cabinetry, carvings, turnery, and pattern making; it has also been used to make cement-bonded wood-wool board.

The growth rings of *M. champaca* are distinct, and they possess unique anatomical characteristics, including well-defined ring boundaries due to terminal parenchyma cells. Due to these features, it has become a promising tree species for dendrochronological studies and dendro-chemical analysis (Bhattacharyya et al., 2012). The choice of the tree species was reliant on its capacity to form annual growth rings. The selected tree species *M. champaca* produces distinct annual growth rings and is abundantly available in the study area.

3.7. Methods

3.7.1. Sample collection

The standard dendrochronological sampling method was used to collect tree cores (Schweingruber, 2012; Speer, 2010) using a 5 mm increment borer (Haglöf Sweden). Cores were collected from the bole of each tree at diameter breast height (i.e., DBH, 1.37 m). The tree ring cores were obtained from the standing or live tree by extracting cores at 90° and 270° angles relative to the tree stem. During the coring process, care was taken to avoid the rotten or decayed portions of the tree. These areas are often recognized by a sudden change in coring resistance, making it challenging to extract the core barrel due to the lack of solid wood support for the threaded bit, which is needed to maintain and push against the reverse coring motion of the borer.

After coring, the tree ring cores were removed with the help of an extractor spoon. The extracted cores were then transferred to the paper straw to prevent damage and labelled with ID codes such as site name, species, core serial number, and collection date. Isopropyl alcohol was used during sample collection to reduce cross-contamination and the core samples were transported to the laboratory for further preparation and analysis. They were then stored at -20°C to maintain their integrity until the next steps of the study. A total of 40 tree ring core samples were collected from 20 trees at each site (i.e., NFS, RS, and DS). The sample details are given in the (Table 1).

3.7.2. Sample processing

The collected tree ring cores were finally allowed to air dry at room temperature to prevent any potential issues with shrinkage. After drying, the tree ring cores were affixed onto grooved wooden strips. These strips were filled with an ample amount of water-soluble glue, and the cores were positioned accurately within the grooves, ensuring that the cross-sectional area remained on the updated side. The sample details labelling IDs were then transferred to the side of the tree ring core mount, starting from the pith and extending toward the bark (Speer, 2010). Subsequently, the mounted tree ring core samples underwent surface polishing using sandpaper with varying grit sizes (100, 120, 200, 300, 400, 600, and 1000), beginning with 100 and concluding with 600, until their boundaries became discernible under the WinDendro scanner. (Fritts 1976; Schweingruber, 1988; Schweingruber et al., 1990).

3.7.3. Cross-dating of tree cores and measurements of tree ring characteristics

The tree ring was counted using a winDendro scanner from pith to bark end. The resolution was adjusted to visualize every single ring Clearly. After finishing of tree ring counting further analysis was tree ring width measurements for each dated tree ring core was done by using a winDendro scanner which is a computer-attached instrument system. This instrument measures the tree ring widths with a precision of 0.001 mm. The measurement of the tree ring was done from pith to bark end attempts were made to take measurements perpendicularly to the current ring boundary. A zero value was assigned to the previously identified missing rings (Holmes, 1983).

After careful observation of the tree ring characteristics under the stereo- zoom microscope, the processed tree rings were scanned and analyzed through winDendro to measure the tree ring width of the selected tree species (*T. grandis* and *M. champaca*).

3.7.4. Validation of tree cross-dating

After sample measurement, the COFECHA computer programme was used to check and confirm the cross-dating results for each tree ring core (Holmes, 1983; Grissino-Mayer 2001). Based on the COFECHA analysis best correlated with the master chronology series samples. These selected samples were used for chemical analysis to investigate 7 HMs (Zn, Pb, Fe, Mn, Ca, Cu, and Ni).

3.8. Sample preparation and laboratory procedure

The dated tree cores were ultrasonically cleaned with double-deionized water (Milli-Q Millipore) for 1 hour to get rid of any surface contaminants that got there during the coring or handling of cores. Tree cores were marked and divided into three-year segments under a stereo zoom microscope, each segment having three years of annual ring growth beginning at the cambium. Afterward, the samples were ground into a fine homogeneous powder using a ball mill.

Each wood sample weighing 50 mg from each segment was placed in a polytetrafluoroethylene (PTFE) tube containing 7 ml of Nitric acid (HNO_3) and 3 ml of Hydrogen peroxide (H_2O_2) for digestion. The digestion process was carried out using a microwave digester for 25 minutes at 150 °C. Once the digestion was completed, the solution was diluted with 5% HNO_3 to achieve a final volume of 30 ml. This dilution was done at a 1:5 ratio, meaning 5 ml of the digested sample solution was mixed with 25 ml of double-deionized water. Subsequently, the solution was filtered through a 0.45 mm syringe filter to remove any particulate matter. After filtering the samples, AAS was employed to investigate 7 elements Zinc (Zn), Lead (Pb), Iron (Fe), Manganese (Mn), Calcium (Ca), Copper (Cu), and Nickle (Ni). AAS has been a widely used technique in early dendro-chemical studies to determine the elemental composition of wood increment cores (Robitaille, 1981; Saarela et al., 2005; Fisher et al., 2002). The specific AAS model used in this study was the AA- 7000F, version 1.04, equipped with an air Acetylene (C_2H_2) flame a support gas flow rate of 15.0 (l/min), and a fuel gas flow of 2.2 (l/min). The analysis of the sample preparation and digestion was performed following the methods described by Padilla and Anderson (2002), Binda et al. (2021), Austruy et al. (2019), and Fisher et al. (2002).

3.9. Soil collection

The soil samples were collected from the three different study sites i.e., forest, road, and dumping sites. These soil samples were collected randomly from the tree ring samples site using a 10 cm scaled soil corer with an inner diameter of 5.2 cm, samples were gathered at three distinct depths: 0-10 cm, 10-20 cm, and 20-30 cm. Within each site replicate, two composite soil samples were obtained for each depth. Each composite sample was created by combining three randomly selected soil cores. This resulted in a total of 32 samples (2 composite samples x 3 depths x 3 site replicates) being collected. The samples were carefully packed into zip lock bags, labelled with their respective IDs, and transported to the laboratory for further processing. Subsequently, the soil samples were sieved through a 2 mm mesh. Finally, the soil samples were subjected to chemical analysis to investigate the presence of seven specific HMs (Zn, Pb, Fe, Mn, Ca, Cu, and Ni).

3.9.1. Analysis of elements from a soil sample

The soil samples homogenized by coning and quartering were dried at 75°C for 48 hours after they were ground to a fine powder. The concentrated HNO_3 and HCl were used in a 3:1 ratio to digest the dried and sieved soil samples (Narayanan et al., 2021). The solution was filtered, cooled, and diluted with 25 ml of distilled water. The digested liquid was filtered using Whatman No. 0.5 filter paper, and the total elements content of the filtrate was assessed using AAS, or atomic absorption spectrometry (McLaughlin et al., 2000; Gupta et al., 2010; Tang et al., 2015).

3.10. Statistical analysis

The collected data were summarized using Mean Standard error Maximum and Minimum values. To assess significant differences among the concentrations of HMs in tree rings, a one-way analysis of variance (ANOVA) was conducted, with significance determined at $p \leq 0.05$. To analyze the trends in element concentration within the tree rings, a line regression method was employed. All statistical analyses and graphical representations were carried out using Microsoft Excel 2010 and SPSS Statistics 25.

Chapter 4

Result and Discussion

4.1. Analysis of tree ring characteristics

The microscopic study of tree rings in *T. grandis* revealed a circular vessel arrangement that were ring-porous. While the earlywood vessels were large and few in numbers, the latewood vessels were tiny and numerous. Such trends are because of the lignification of the initial cells during the process of wood development and the formation of heartwood in the cells. On one hand, the sapwood rings were yellowish in colour and more difficult to distinguish. On the other hand, heartwood rings were dark brown in colour and easy to distinguish (Fig 4.1 A and B). This is because of diffused boundaries of the initial cells in sapwood as a result of overlapping borders with each other. False rings were also seen in a few samples; these were recognized by their anatomical differences, and in some cases, the cross-dating technique was used to find the same where annual anatomical differences were not obvious (Wimmer, 2002; Ahmed & Chun, 2011; Schweingruber, 2012; Upadhyay et al., 2019).

In the case of *M. champaca*, a clear zonation was observed between earlywood and latewood with a gradual change in wood colour (Fig 4.1 A and B). The heartwood is olive-brown turning to dark brown with a greenish ting upon exposure, clearly differentiated from the pale brown sapwood, and fibres are very thin-walled with distinctly bordered pits (Krishnamurthy and Sivaraj, 1990; Kannangara et al., 2020).

Figure: 4.1. Tree ring features of (A) *T. grandis* and (B) *M. champaca*

4.2 Tree ring chronology

4.2.1. COFECHA analysis

The master series of each species/site and the tree ring series were correlated, and the mean series intercorrelation was recorded (Table 4.1) In the final dataset, tree ring series having strong correlations with master series chronology were included. During the processes of analysis, the tree ring series with a weak correlation to the master series chronology and poor dating were excluded.

Table 4.1. Statistical details of tree ring chronology developed from Study sites

Species	Site	TS (YRS)	MSL	NT/NC	SIC	MS	SD	AC-1
T. grandis	NFS	1994-2020	27	20/40	0.415	0.221	0.636	0.328
	RS	1995-2020	26	20/40	0.405	0.284	0.588	0.074
	DS	1994-2020	27	20/40	0.404	0.258	0.647	0.050
M. champaca	NFS	1996-2019	24	21/43	0.471	0.201	0.627	0.356
	RS	1993-2019	26	21/43	0.409	0.278	0.502	0.067
	DS	1999-2019	21	21/43	0.412	0.289	0.532	0.073

MSL = Mean segment length in years; TS (YRS) = Time span of the chronology (years); NT/NC = Number of trees / Number of tree cores; MS = Mean sensitivity; SD = Standard deviation; AC 1 = First order autocorrelation.

The series inter-correlation for *T. grandis* at three different sites NFS, RS, and DS was recorded as 0.415, 0.404, and 0.405, respectively. For *M. champaca* the inter-correlation at three different sites was recorded as 0.471, 0.412, and 0.409, respectively (Table 4.1). These recorded values of series inter-correlation indicate that the samples from all sites share a degree of commonality in the discrete series contributing to the site chronology.

However, after successfully cross-dating the tree ring chronologies were established for two species. The length of the tree ring chronology of *T. grandis*, a broad-leaved species, at three different sites were: 27 years extending from 1994 to 2020 C.E. at NFS and DS, whereas at RS it was extended for 26 years extended from 1995 to 2020 C.E at the RS. Likewise, in *M. champaca* the length of ring chronology extended for 26, 24 years from 1993-1994 to 2019-2020 C.E. at NFS and RS, and it was extended for 21 years from 1999 to 2019 C.E. at DS (Table 4.1).

The mean sensitivity, a measure that reflects the variability in the width of successive tree rings (Fritts, 1976), is considered high and acceptable when it approaches a mean sensitivity of 0.2 (Speer, 2010). The mean sensitivity values in the present study for *T. grandis* were recorded as 0.221, 0.258, and 0.284 at the NFS, RS, and DS sites, respectively. However, mean sensitivity values were 0.201, 0.289, and 0.278, respectively for *M. champaca* at NFS, RS, and DS sites (Table 4.1) all falling within the acceptable limit at each of the sites. In dendro-climatological studies, the tree ring chronology of a species characterized by high mean sensitivity, a high standard deviation, and low autocorrelation is regarded as the most suitable for climate analysis (Fritts, 1976; Chaudhary et al., 1999; Bhattacharyya and Singh, 2000; Shah et al., 2007; Upadhyay et al., 2021).

Another significant statistical parameter for tree ring chronology is the standard deviation (Fritts, 1976). The standard deviation quantifies variations in both lower and higher frequency variances and indicates departures from mean values, both positive and negative. The current recorded standard values were: 0.636, 0.647, and 0.588, respectively at the NFS, RS, and DS sites for *T. grandis*. In the case of *M. champaca*, the corresponding values of standard deviations were: 0.627, 0.532, and 0.502, respectively for these sites (Table 4.1). The tree chronologies for two species at three different sites displayed high mean sensitivity and moderate to high standard deviation values indicating the presence of significant high-frequency variability and suggesting potential for dendrochronological studies (Fritts, 1976; Chaudhary et al., 1999; Bhattacharyya and Singh, 2000; Shah et al., 2007; Upadhyay et al., 2021).

Autocorrelation in tree ring chronology serves as an additional statistical measure to assess the extent of correlation between a given year's growth and the growth of earlier years. A high autocorrelation value suggests that a significant portion of the observed ring width was influenced by growth in previous years rather than external factors. In the current study, first-order autocorrelation values for *T. grandis* at the NFS, RS, and DS sites were recorded as 0.328, 0.050, and 0.074, respectively. In the case of *M. champaca* the values were recorded as 0.356, 0.073, and 0.067, respectively, at the FS, RS, and DS sites (Table 4.1). These values provide insights into the degree of dependence on the growth of the previous year in the tree ring chronologies (Fritts, 1976; Chaudhary et al., 1999; Bhattacharyya and Singh, 2000; Shah et al., 2007; Upadhyay et al., 2021).

Dendrochronological analysis suggests that the tree ring samples of two species are well-suited for dendrochronological studies. After considering the results of mean sensitivity, standard deviation, and first-order autocorrelation, the species were selected for further analysis of dendrochemistry. For this analysis, among all the tree ring samples, the seven best series samples demonstrated a strong correlation with the master chronology from each site and were selected for dendrochemical analysis.

4.3. Analysis of best Seven best series samples of *T. grandis* at three study sites

4.3.1. Natural forest site (NFS)

At the NFS, selected tree ring samples were chosen for dendro-chemical analysis. The samples from this tree ring exhibited high correlation values (i.e., 0.524 to 0.646) with the master series chronology (Table 4.2). This indicated that the chosen tree samples had a strong alignment with the overall master series making them ideal for further dendro-chemical investigation.

Table 4.2. Best series samples of *T. grandis* tree ring from the NFS

Sl.NO	Sample ID	TS (YRS)	Chronology length	Correlation with Master Chronology
1	TEGRNFS07A	1994-2020	27	0.646
2	TEGRNFS08B	1994-2020	27	0.654
3	TEGRNFS28A	1994-2020	27	0.555
4	TEGRNFS22B	1994-2020	27	0.571
5	TEGRNFS46A	1994-2020	27	0.551
6	TEGRNFS26B	1994-2020	27	0.539
7	TEGRNFS48A	1994-2020	27	0.524

Note: Sl.NO = Serial number; TEGRNFS = Tectona grandis forest site; TS (YRS) = Time span of the chronology.

4.3.2. Roadside (RS)

At the RS, tree ring samples were chosen for dendro-chemical analysis. The samples from this tree ring exhibited high correlation values (i.e., 0.448 to 0.683) with the master series chronology (Table 4.3). This indicated that the chosen tree samples had a strong alignment with the overall master series making them ideal for further dendro-chemical investigation.

Table 4.3. Best series samples of *T. grandis* tree ring from the RS

Sl.NO	Sample ID	TS (YRS)	Chronology length	Correlation with Master Chronology
1	TEGRRS09B	1995-2020	26	0.683
2	TEGRRS38A	1995-2020	26	0.617
3	TEGRRS08A	1995-2020	26	0.598
4	TEGRRS37A	1995-2020	26	0.501
5	TEGRRS29A	1995-2020	26	0.471
6	TEGRRS05B	1995-2020	26	0.449
7	TEGRRS19A	1995-2020	26	0.448

Note: Sl.NO = Serial number; TEGRRS = Tectona grandis road site; TS (YRS) = Time span of the chronology.

4.3.3. Municipal solid waste dumping ground or dumping site (DS)

At the DS, selected tree ring samples were chosen for dendro-chemical analysis. The samples from this tree ring exhibited high correlation values (i.e., 0.501 to 0.603) with the master series (Table 4.4). This indicated that the chosen tree samples had a strong alignment with the overall master series making them ideal for further dendro-chemical investigation.

Table 4.4. Best series samples of *T. grandis* tree ring from the DS

Sl. NO.	Sample ID	TS (YRS)	Chronology length	Correlation with Master Chronology
1	TEGRDS12A	1994-2020	27	0.603
2	TEGRDS50A	1994-2020	27	0.598
3	TEGRDS11B	1994-2020	27	0.578

4	TEGRDS42A	1994-2020	27	0.550
5	TEGRDS27B	1994-2020	27	0.523
6	TEGRDS51A	1994-2020	27	0.506
7	TEGRDS10B	1994-2020	27	0.501

Note: Sl.NO = Serial number; TEGRDS = Tectona grandis dumping site; TS (YRS) = Time span of the chronology.

4.4. Analysis of best Seven best series samples of *M. champaca* at three study sites

4.4.1 Natural Forest site (NFS)

At the NFS, selected tree ring samples were chosen for dendro-chemical analysis. The samples from this tree ring exhibited high correlation values (i.e., 0.577 to 0.825) with the master series chronology (Table 4.5). This indicated that the chosen tree samples had a strong alignment with the overall master series making them ideal for further dendro-chemical investigation.

Table 4.5. Best series sample of *M. champaca* tree ring from the NFS

Sl.NO	Sample ID	TS (YRS)	Chronology length	Correlation with Master Chronology
1	MACHNFS21A	1996-2019	24	0.825
2	MACHNFS27A	1996-2019	24	0.761
3	MACHNFS22B	1996-2019	24	0.643
4	MACHNFS19A	1996-2019	24	0.635
5	MACHNFS28A	1996-2019	24	0.607
6	MACHNFS24A	1996-2019	24	0.579
7	MACHNFS20A	1996-2019	24	0.577

Note: Sl.NO = Serial number; MACHNFS = Magnolia champaca at forest site; TS (YRS) = Time span of the chronology.

4.4.2. Roadside (RS)

At the RS, selected tree ring samples were chosen for dendro-chemical analysis. The samples from this tree ring exhibited high correlation values (i.e., 0.437 to 0.634) with the master series chronology (Table 4.6). This indicated that the chosen tree samples had a strong alignment with the overall master series making them ideal for further dendro-chemical investigation.

Table 4.6. Best series sample of *M. champaca* tree ring from the RS

Sl.NO	Sample ID	TS (YRS)	Chronology length	Correlation with Master Chronology
1	MACHRS18A	1993-2019	26	0.634
2	MACHRS33A	1993-2019	26	0.629
3	MACHRS32B	1993-2019	26	0.629
4	MACHRS14B	1993-2019	26	0.623
5	MACHRS21B	1993-2019	26	0.622
6	MACHRS02A	1993-2019	26	0.579
7	MACHRS11A	1993-2019	26	0.437

Note: Sl.NO = Serial number; MACHRS = Magnolia champaca at road site; TS (YRS) = Time span of the chronology.

4.4.3. Municipal solid waste dumping ground or Dumping side (DS)

At the DS, selected tree ring samples were chosen for dendro-chemical analysis. The samples from this tree ring exhibited high correlation values (i.e., 0.482 to 0.776) with the master series chronology (Table 4.7). This indicated that the chosen tree samples had a strong alignment with the overall master series making them ideal for further dendro-chemical investigation.

Table 4.7. Best series sample of *M. champaca* tree ring from the DS

Sl.NO	Sample ID	TS (YRS)	Chronology length	Correlation with Master Chronology
1	MACHDS24B	1999-2019	21	0.776
2	MACHDS31B	1999-2019	21	0.625
3	MACHDS25B	1999-2019	21	0.600
4	MACHDS22B	1999-2019	21	0.597
5	MACHDS08A	1999-2019	21	0.568
6	MACHDS20A	1999-2019	21	0.555
7	MACHDS21A	1999-2019	21	0.482

4.5. The inter-annual heavy metals concentrations of the *T. grandis* tree rings at three study sites

4.5.1. Zinc (Zn)

The Zn is a transition metal that occurs naturally in soil with an atomic number of 30, an atomic mass of 65.4, and a density of 7.14 g cm^{-3} (Davies and Jones, 1998). The Zn concentration ranged from 0.016 to 0.184 mg kg^{-1}, 0.824 to 5.052 mg kg^{-1}, and 2.93 to 8.81 mg kg^{-1} in FS, RS, and DS, respectively. In NFS, the highest mean concentration 0.184 mg kg^{-1} of Zn was recorded in recent years (2018-2020) in sapwood and the lowest Zn concentration 0.016 mg kg^{-1} was recorded in the beginning years (1997- 1999) in heartwood. The rate of change of Zn concentrations during the course of wood development in *T. grandis* was 430 % from 1994 to 2020 **(**Fig 4). In RS, the highest mean concentration of Zn was 0.052 mg kg^{-1} in the year 2018 to 2020 while, the lowest of 0.824 mg kg^{-1} was recorded in the year 1995 to 1997. The corresponding value of the rate of change of Zn concentration in RS was 5.127 % over the time (i.e., 1995 to 2020) (Fig. 4.2). In DS, the highest of 8.81 mg kg^{-1} of Zn mean concentration was recorded in the year 2018 to 2020 while the lowest mean concentration of 2.93 mg kg^{-1} was recorded in the year 1995 to 1997. The corresponding value of the rate of change of Zn concentration in RS was 200 % over the period (i.e., 1994 to 2020) (Fig. 4.2). The highest HM concentrations were reported in DS and RS samples compared with FS (Fig 4.2). Sapwood cells and the recently formed rings accumulated majority of the harmful heavy metal concentrations. The pith side had the lowest element concentrations, whereas the main bark side had the highest element concentrations.

However, Zn is an essential micronutrient that functions as a catalytic element for more than 300 enzymes and serves a structural role in the stabilization of several proteins (Fox and Guerinot. 1998). The usual Zn concentration necessary for the optimal growth of plants varies between 15 and 20 mg kg^{-1} dry weight (Cakmak et al., 1996). Zn has been reported to be harmful to flora, animals, and people over these concentrations (Cambier et al., 2014).

The main sources of Zn HM are fuel combustion, Solid waste, and industrial activities, such as mining, coal, waste combustion, and steel processing (Odabasi et al, 2016; Zamani et al., 2015) but in the study site solid waste, heavy-duty vehicles moments, waste combustion are common practices observed at the study site. The results showed that the concentration of Zn in the dumping sites surpassed the permissible levels advised by the WHO. This tree ring's HM concentration reflects the status of the pollution trend and the world's Zn production is still on the rise which means that more and more Zn ends up in the environment. Lastly, Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter.

4.5.2. Lead (Pb)

Lead is a metal with an atomic number of 82, an atomic mass of 207.2, and a density of 11.4 g cm^{-3} (Wuana and Okieimen, 2011). It is a naturally occurring bluish-gray metal that is usually found as a mineral combined with other elements such as sulphur (i.e., PbS, $PbSO_4$) or oxygen ($PbCO_3$), and its concentration in the earth's crust ranges from 10 to 30 mg kg^{-1}. Pb is the fifth most produced industrial metal, after Fe, Cu, Al, and Zn. The Pb concentration ranged from 0.013 to 0.141 mg kg^{-1}, 0.224 to 3.764 mg kg^{-1}, and 2.786 to 8.288 mg kg^{-1} in NFS, RS, and DS respectively. In NFS, the highest mean concentration of 0.141 mg kg^{-1} of Pb was recorded from the recent year 2018 -2020 in sapwood and the lowest Zn concentration of 0.013 mg kg^{-1} was recorded in the beginning years from 1997-1999 in heartwood. From 1994 to 2020, 92.60% of the rate changed Pb concentration during course of the *T. grandis* wood development year (Fig 4.2). Whereas in RS, the highest mean concentration of Pb was 3.764 mg kg^{-1} was recorded in 2018 to 2020 while the lowest of 0.224 mg kg^{-1} was recorded in 1995-1997. From 1995 to 2020, 1575 % of the rate changed during the year (Fig 4.2). In DS, the highest of 8.288 mg kg^{-1} of Pb mean concentration was recorded from 2018 to 2020 while the lowest of 2.786 mg kg^{-1} was recorded in 1995-1997. From 1994 to 2020, 197 % of the rate changed during the year (Fig 4.2). Here also highest HM concentration exists in the currently formed tree rings i.e., bark or sapwood cells. The results showed that the concentration of Pb in the RS and DS exceeded permissible levels advised by the

World Health Organization (WHO). It is clearly evident that the majority of the RS and DS samples were impacted by municipal solid waste and car emissions. This could be a response to rising Pb concentration in the tree ring. The permissible level of Pb has been exceeded, increasing the risk of lead poisoning through the food chain.

Lead is a non-essential toxic element that increases oxidative stress and causes lead poisoning by upsetting the antioxidant balance of mammalian cells. The WHO has set a maximum permissible level of Pb in plants at 2 mg kg^{-1} (Zaigham et al., 2012, Nazir et al., 2015). The results indicate an excess level of Pb at the study site.

4.5.3. Iron (Fe)

Iron is a transition element with an atomic number of 26 and a density of 7.8748 of 7.14 g cm^{-3} (Wuana and Okieimen, 2011). The Fe concentration ranged from 0.638 to 3.672 mg kg^{-1}, 2.952 to 6.354 mg kg^{-1}, and 3.860-9.970 mg kg^{-1}, NFS, RS, and DS respectively. In NFS, the highest mean concentration of 3.672 mg kg^{-1} of Fe mean concentration was recorded in recent years 2018-2020 in sapwood and the lowest Fe concentration of 0.638 mg kg^{-1} was recorded in the beginning years (1994 - 1996) in heartwood. The rate change of Fe Concentrations during wood development in *T. grandis* was 475.1 % From 1994 to 2020 (Fig 4.2). Whereas in RS, the highest mean concentration of Fe was 6.354 mg kg^{-1} in years from 2018 to 2020 while, the lowest of 2.952 mg kg^{-1} was recorded in 1995-1997. From 1995 to 2020, 115.1% of the rate changed during the year (Fig 4.2). Similarly in DS, the highest of 9.970 mg kg^{-1} of Fe mean concentration was recorded from 2018 to 2020 while the lowest of 3.860 mg kg^{-1} was recorded in 1995-1997. From 1994 to 2020, 158 % of the rate changed during the year (Fig 4.2).

Iron is necessary for plant growth, but iron poisoning symptoms show up in leaf tissues when flooding conditions permit microbial conversion of insoluble Fe^{+3} to soluble Fe^{+2} (Becker and Asch. 2005). This causes a reduction in plant yield and photosynthesis and an increase in oxidative stress and ascorbate peroxidase activity (Sinha et al., 1997; Arora et al., 2002).

4.5.4. Copper (Cu)

Copper is a transition metal with an atomic number of 29, an atomic weight of 63.5, and a density of 8.96 g cm^{-3} (Wuana and Okieimen, 2011). The Cu concentration ranged from 0.513-2.002 mg kg^{-1}, 2.042-7.36 mg kg^{-1}, and 2.678-6.727 mg kg^{-1}, in FS, RS, and DS respectively. In NFS, the highest mean concentration of 2.002 mg kg^{-1} of Cu was recorded in recent years (2012-2014) in sapwood and the lowest Cu Concentration of 0.513 mg kg^{-1} was recorded in the beginning years 1994-1996 in heartwood. The rate change of Cu concentration during wood development in *T. grandis* was 282.45 % from 1994 to 2020, (Fig 4.2). whereas in RS, the highest mean concentration of Cu was 7.36 mg kg^{-1} in the years 1995-1997 while the lowest of 2.043 mg kg^{-1} was recorded in 2018 to 2020. From 1995-2020, 260.2 % of the rate changed during the year wood development (Fig 4.2). Whereas in DS concentration ranged from 2.678-6.727 mg kg^{-1} and the rate of change was 149 % over time (Fig 4.2). A height of 6.7 mg kg^{-1} concentration was observed from 2018 to 2020. The highest Cu concentrations were observed in the RS and DS whereas the forest site had the lowest. The reason could be that the DS and RS samples are clearly displaying the pollution generated by vehicle emissions and municipal waste. Though the HM concentrations are currently below the WHO recommended limit, they are steadily increasing, so it is possible that they will increase in the future.

Cu is a crucial micronutrient for plant growth and development and takes part in various metabolic activities, including hormone signaling, mitochondrial respiration, photosynthetic electron transport, superoxide scavenging, and cell wall metabolism (Vatansever et al., 2017). However, an excess amount of Cu has inhibitory effects on a large number of enzymes, affecting several aspects of plant biochemistry, including photosynthesis, pigment synthesis, membrane integrity, metabolism of fatty acids and proteins, respiration, nitrogen fixation, and most importantly, blocking of photosynthetic electron transport, resulting in radical production that initiates peroxidative chain reactions involving membrane lipids (Fernandes and Henriques, 1991).

4.5.5. Nickel (Ni)

Nickel is a transition element with an atomic number of 28 and an atomic weight of 58.69 g cm^{-3} (Wuana and Okieimen, 2011). The Ni concentration ranged from 1.40-4.66 mg kg^{-1} 2.261 to 7.486 mg kg^{-1}, and 3.471-7.250 mg kg^{-1}, in NFS, RS, and DS, respectively. In NFS, the highest mean concentration (4.66 mg kg^{-1}) of Ni was recorded in recent years (2018-2020) in sapwood and the lowest Ni concentration (1.40 mg kg^{-1}) was recorded in the beginning years (1994-1996) in heartwood. The rate of change of Ni concentration during wood development in T. *grandis* was, 230.97 % from 1994 to 2020 (Fig 4.2). whereas in RS, the highest mean concentration of Ni was 7.486 mg kg^{-1} in the year 2018-2020 while, the lowest (2.261 mg kg^{-1}) was recorded in the year 1995-1997. From 1995-2020, 231.1 % of the rate changed during the year (Fig 4.2). Similarly in DS, a higher (7.42 mg kg^{-1}) concentration was observed in 2018-2020 while the lowest (3.471 mg kg^{-1}) was recorded in 1994-2020. From 1994-2020, 108.5 % of the rate changed during the year (Fig 4.2).

Ni, another critical plant micronutrient, is involved in numerous enzyme structures (Fabiano et al., 2015) and is crucial for different physiological processes such as ureolysis, methane biogenesis, acetogenesis, hydrogen metabolism, cellular redox status, stress tolerance/deficiency, and nitrogen utilization efficiency (Polacco et al., 2013, Maier et al., 1993, Ragsdale. 1998).

4.5.6. Manganese (Mn)

Manganese is a transition metal with an atomic number of 25 and a density of 7.21 g cm^{-3} (Wuana and Okieimen, 2011). The Mn concentrations ranged from ranged from 2.57-6.38 mg kg^{-1}, 2.73-7.65 mg kg^{-1}, and 3.227-7.863 mg kg^{-1}, in NFS, RS, and DS, respectively. In NFS, the highest mean concentration (6.38 mg kg^{-1}) of Mn was recorded in recent years (2018-2020) in sapwood, and the lowest Mn concentration (2.3 mg kg^{-1}) was recorded in the beginning years (1997- 1999) in heartwood. In RS, the highest mean concentration (7.86 mg kg^{-1}) of Mn was recorded in recent years (2018-2020) in sapwood, and the lowest Mn concentration (2.73 mg kg^{-1}) was recorded in the beginning years (1997- 1999) in heartwood. In RS, the highest mean concentration (7.9 mg kg^{-1}) of Mn was recorded in recent years

(2018-2020) in sapwood, and the lowest Mn concentration (3.22 mg kg^{-1}) was recorded in the beginning years (1997- 1999) in heartwood. The rate of change between heartwood and sapwood was also altered significantly, with 149.7% for FS, 180.4% for RS, and 143% for DS (Fig 4.2) The maximum concentrations of Mn in all three sites were observed in the year 2018 to 2020 while the lower values were recorded in the initial years (Fig 4.2). The results showed that the concentration of Mn in the RS and DS were lower than the permissible levels advised by the WHO. The samples of DS and RS tree ring cores were more variable, changing from year to year, and the trace element concentrations were steadily increasing. Sapwood cells and the recently formed rings accumulated the majority of the harmful trace element concentrations. The pith side had the lowest element concentrations, whereas the main bark side had the highest. The maximum permissible limit of Mn in plants is 200 mg kg^{-1}, (WHO, 1996). The recorded levels of Mn were within the prescribed limits.

4.5.7. Calcium (Ca)

Calcium is a transition metal with an atomic number of 20 and a density of 1.55 g cm^{-3} (Wuana and Okieimen, 2011). The Ca concentration ranges from 2.36-5.225 mg kg^{-1}, 2.837-6.619 mg kg^{-1}, and 3.914-7.432 mg kg^{-1}, NFS, RS, and DS, respectively. In NFS, the highest mean concentration (5.225 mg kg^{-1}) of Ca concentration was recorded in recent years (2018-2020) in sapwood and the lowest Ca concentration (2.36 mg kg^{-1}) was recorded in the beginning year (1994-1996) in heartwood. The rate of change of Ca concentration during wood development in *T. grandis* was 116.9 % from 1994 to 2020 (Fig 4.2). Whereas in RS, the highest mean concentration of Ca was (6.619 mg kg^{-1}) in the year 2018 to 2020 while, the lowest of 2.837 mg kg^{-1} was recorded in the year 1995 to 1997. From 1995 to 2020, 133.2 % % of the rate changed during the year (Fig. 4.2). In DS, higher mean concentration of Ca (7.432 mg kg^{-1}) was recorded in the year 2018-2020 while the lowest mean concentration (3.914 mg kg^{-1}) in 1994-1996. From 1994-2020**,** 88.52% of the rate changed during the year. Even while all three locations displayed a similar pattern, DS had the greatest Ca concentration.

Ca is the fifth most common element on the surface of the earth (Krebs, 2006). In plants, Ca is needed to activate enzymes, induce water flow and salt balance in cells, and activate K to govern the opening and closing of stomata (Hepler, 2005). It is involved in Cell growth, division, elongation, and various other biological activities (Berridge et al., 2000, Hirschi, 2004).

The HMs concentration in different sites in descending order was: Mn>Ca>Ni>Fe>Cu>Zn>Pb in FS, Mn>Ni>Cu>Fe>Ca>Zn>Pb in RS, and Fe>Zn>Pb>Mn>Ca>Ni>Cu in DS. In contrast to NFS, the HMs concentrations in DS and RS were monotonically increasing in the sample tree ring cores. The change in HM concentrations over time was affected by different factors such as environment, site/locality factors, growing conditions, uptake, and many others (Ferretti et al., 2002).

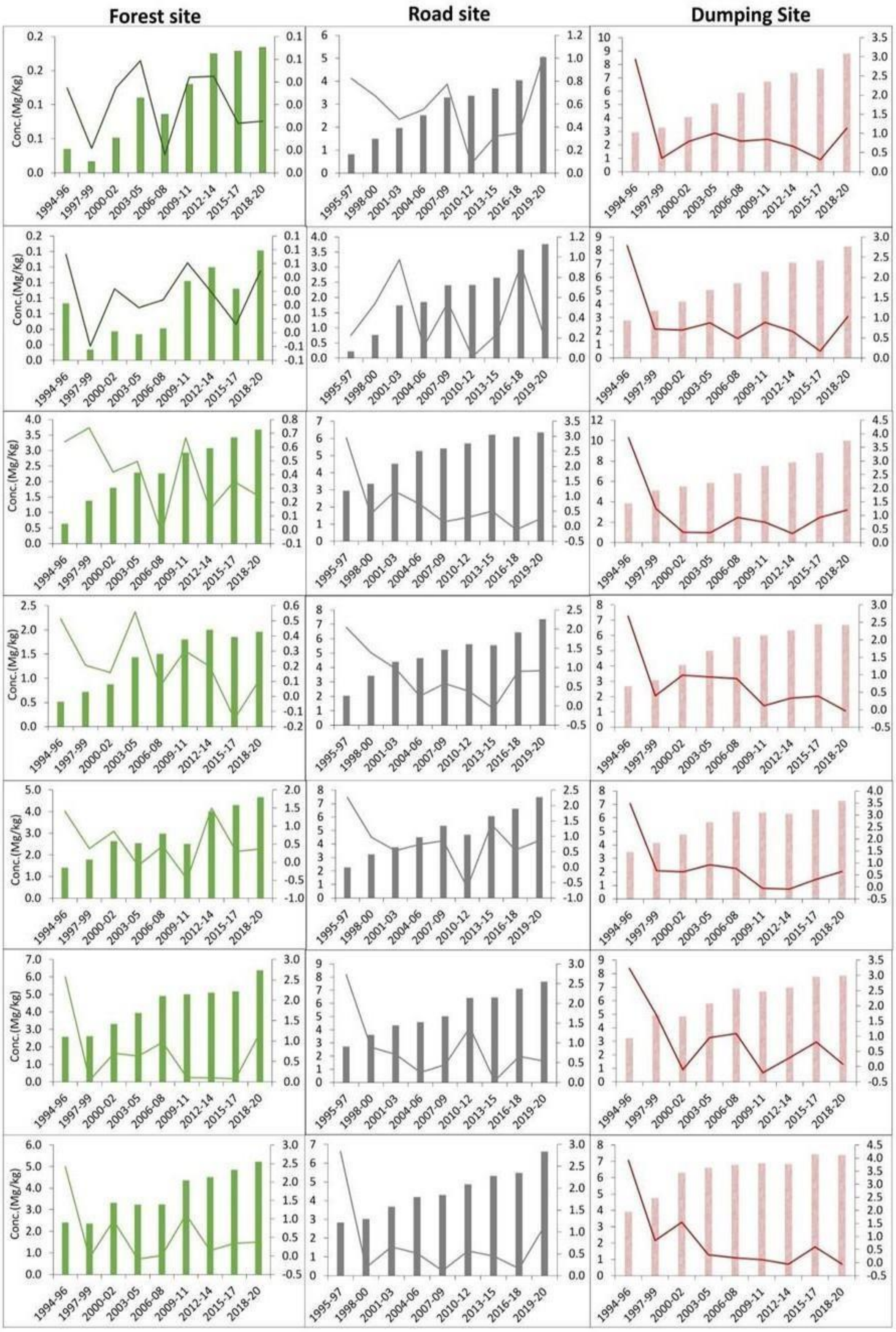


Figure 4.2. The inter-annual HMs concentration of *T. grandis* tree ring samples from study sites

4.6. Analysis of mean inter-annual HM concentrations

To assess the level of significance in periodical (every 3 years) variations in HMs concentration within tree ring cores, the analysis of variance (ANOVA) was performed in two trees and three different sites. The ANOVA result for this study is presented in Table 4.8.

The ANOVA result showed a significant (*p<0.05*) difference among the mean concentrations of Zn, Pb, Fe, Cu, Ni, Mn, and Ca in NFS, RS, and DS (Table 4.8). Results further indicated highly significant mean differences from three different sites. Sapwood cells and the recently formed tree rings accumulated the majority of the HMs on three sites. Similar findings were reported for *Pinus echinate, Pinus silvestris,* and *Tipuana tipu* (Baes and Mclaughlin 1984; McClenahen et al., 1989; Symeonides 1979; Locosselli et al., 2020).

Table 4.8. ANOVA results for different heavy metal (Zn, Pb, Fe, Cu, Ni, Mn) concentrations of tree ring of *T. grandis* at different study sites (NFS, RS, and DS). The mean values are ± 1SE. All values are significant at the *P* < 0.05 level of significance.

NFS	**1994-96**	**1997-99**	**2000-02**	**2003-05**	**2006-08**	**2009-11**	**2012-14**	**2015-17**	**2018-20**
Zn	0.03±0.0	0.01±0.00	0.05±0.01	0.17±0.02	0.08±0.02	0.13±0.01	0.17±0.01	0.17±0.00	0.18±0.17
Pb	0.07±0.04	0.01±0.00	0.03±0.01	0.03±0.01	0.04±0.01	0.10±0.01	0.12±0.01	0.09±0.02	0.14±0.00
Fe	0.63±0.09	1.37±0.16	1.79±0.27	2.29±0.29	2.26±0.22	2.93±0.20	3.07±0.28	3.42±0.22	3.67±0.22
Cu	0.51±0.08	0.71±0.21	0.87±0.19	1.43±0.17	1.50±0.19	1.80±0.23	2.00±0.29	1.85±0.33	1.96±0.24
Ni	1.41±0.07	1.78±0.19	2.63±0.27	2.53±0.17	2.98±0.27	2.51±0.45	4.00±0.43	4.30±0.38	4.66±0.40
Mn	2.57±0.05	2.61±0.19	3.30±0.33	3.94±0.56	4.90±0.44	5.01±0.38	5.10±0.65	5.17±0.48	6.38±0.39
Ca	2.40±0.14	2.36±0.06	3.32±0.60	3.23±0.18	3.24±0.25	4.36±0.35	4.51±0.31	4.85±0.34	5.22±0.37
RS	**1995-97**	**1998-00**	**2001-03**	**2004-06**	**2007-09**	**2010-12**	**2013-15**	**2016-18**	**2019-20**
Zn	0.82±0.	1.49±0	1.96±0.	2.51±0.	3.29±0.	3.37±0.	3.69±0.34	4.04±0.	5.05±0.30

	24	.43	47	39	41	37		35	
Pb	0.22±0.16	0.76±0.31	1.74±0.41	1.85±0.24	2.40±0.40	2.42±0.34	2.65±0.27	3.58±0.36	3.76±0.46
Fe	2.95±0.21	3.35±0.30	4.52±0.36	5.26±0.31	5.41±0.14	5.71±0.23	6.21±0.46	6.10±0.21	6.35±0.38
Cu	2.04±0.22	3.42±0.61	4.40±0.63	4.65±0.54	5.24±0.48	5.62±0.36	5.54±0.22	6.44±0.20	7.36±0.43
Ni	2.26±0.21	3.23±0.41	3.76±0.50	5.4±0.38	5.35±0.35	4.68±0.49	6.07±0.68	6.62±0.36	7.48±0.35
Mn	2.73±0.18	3.61±0.55	4.33±0.38	4.85±0.44	5.03±0.14	6.42±0.57	6.45±0.21	7.11±0.40	7.65±0.45
Ca	2.83±0.17	3.02±0.13	3.68±0.30	4.19±0.38	4.30±0.33	4.87±0.43	5.32±0.44	5.48±0.42	6.61±0.21
DS	**1994-96**	**1997-99**	**2000-02**	**2003-05**	**2006-08**	**2009-11**	**2012-14**	**2015-17**	**2018-20**
Zn	2.93±0.23	3.28±0.14	4.06±0.31	5.07±0.24	5.87±0.34	6.71±0.43	7.36±0.38	7.68±0.48	8.81±0.44
Pb	2.78±0.06	3.50±0.02	4.19±0.32	5.06±0.40	5.55±0.39	6.43±0.32	7.09±0.41	7.26±0.32	8.28±0.38
Fe	3.86±0.26	5.11±0.21	5.49±0.30	5.86±0.41	6.78±0.51	7.53±0.79	7.86±0.87	8.78±0.82	9.97±0.58
Cu	2.67±0.09	3.07±0.19	4.06±0.42	5.0±0.56	5.89±0.55	6.00±0.67	6.33±0.55	6.72±0.72	6.69±0.52
Ni	3.47±0.07	4.14±0.33	4.77±0.43	5.68±0.59	6.45±0.42	6.39±0.26	6.30±0.23	6.61±0.38	7.25±0.39
Mn	3.22±0.19	4.94±0.56	4.84±0.44	5.79±0.26	6.88±0.49	6.68±0.32	6.97±0.28	7.78±0.20	7.86±0.37
Ca	3.91±0.21	4.75±0.40	6.30±0.14	6.59±0.14	6.78±0.17	6.89±0.34	6.83±0.38	7.43±0.38	7.37±0.37

4.7. Trend analysis of HMs concentration of *T. grandis* tree ring at three study sites

The linear regression was used to determine the concentration trend over a time scale. The linear regression plots of all the HMs examined showed an increasing trend across the time scale (Fig 4.3). Element concentration changed as a function of time in different sites. In the NFS, the change in concentration of different elements over time was significantly (p<0.05) positively correlated (R^2 ranged from 0.59 for Pb to 0.97 for Fe) with time. In the RS, the change in concentration of different elements over time was significantly (p<0.05) positively correlated (R^2 ranged from

0.89 for Fe to 0.98 for Ni) with time. In the DS, the change in concentration of different elements over time was significantly (p<0.05) positively correlated (R^2 ranged from 0.78 for Cu to 0.99 for Pb) with time.

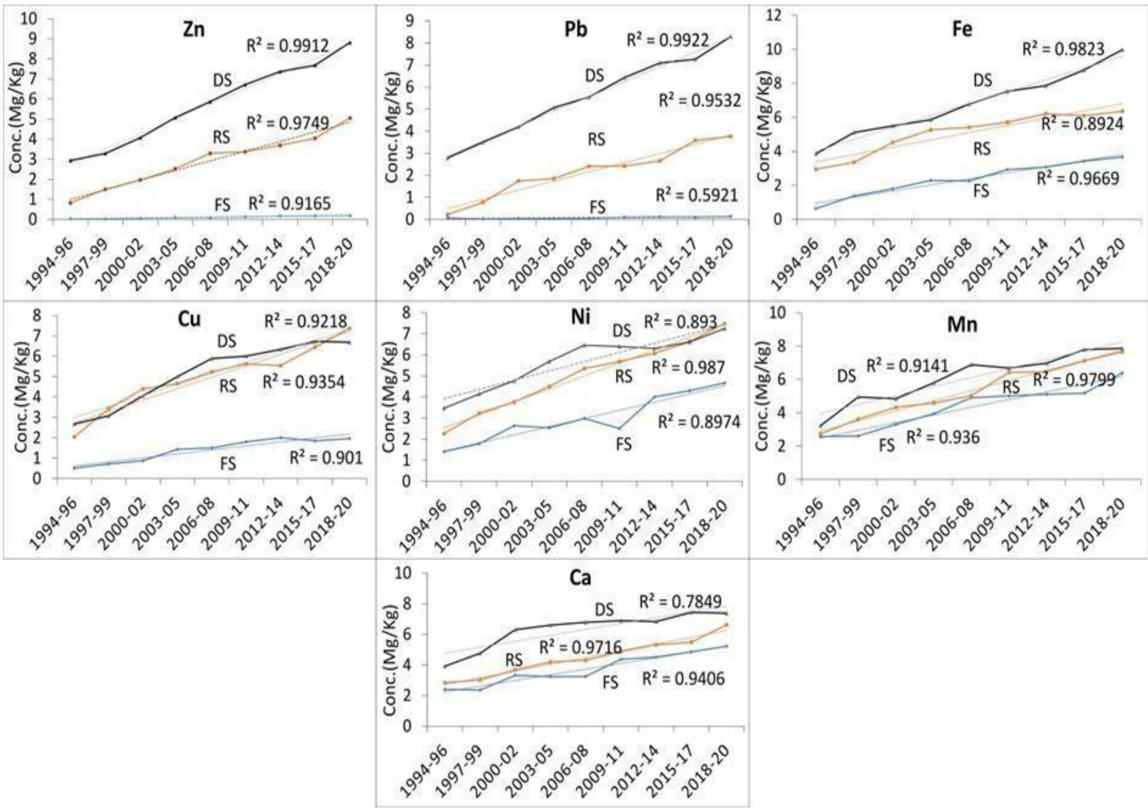


Figure: 4.3. Linear regression plot over the period FS (1994-2020), RS (1995-2020), and DS (1994-2020)

4.8. The inter-annual HM concentrations of the *M. champaca* tree ring at three study sites

4.8.1. Zinc (Zn)

The Zn concentration ranged from 0.105 to 0.682 mg kg^{-1}, 1.10 to 11.90 mg kg^{-1}, and 13.86 to 27.46 mg kg^{-1}, in FS, RS, and DS respectively. In NFS, the highest mean concentration (0.682 mg kg^{-1}) of Zn was recorded in the initial years (1996-1998) in heartwood and the lowest Zn concentration (0.105 mg kg^{-1}) was recorded in the beginning years (2017-2019) in Sapwood. The rate of change of Zn concentrations during the course of wood development in *M. champaca* was 549.52% from 1994 to 2020 **(**Fig 4.4). In the RS, the highest mean concentration of Zn was 11.9 mg kg^{-1} in the year 2017-2019 while, the lowest mean concentration of Zn 1.10 mg kg^{-1} was recorded in the year 1993-1995. From 1993 to 2019, 1033 % of the rate changed during the year (Fig. 4.4). In DS, an initial concentration of Zn (1999-2001) of 13.9 mg kg^{-1}, grew steadily over the years with the exception of 2008-2010. In 2017-19, the maximum concentration of zinc was reported at 27.5 mg kg^{-1} in DS, and over the time period from 1999 to 2019, (49.5 %) the rate changed in concentrations. In the *M. champaca* tree ring the greater Zn concentrations reported at the dump and road sites could be attributed to municipal garbage depositions and vehicle emissions that were accumulated in tree rings during the course of time.

4.8.2. Lead (Pb)

The Pb concentration ranged from 0.116 to 0.670 to 0.141 mg kg^{-1}, 0.597 to 6.205 mg kg^{-1}, and 6.92 to 14.26 mg kg^{-1} in FS, RS, and DS respectively. In FS, the highest mean concentration 0.670 mg kg^{-1} of Pb was recorded in the initial year 1996-1998 in heartwood, and the lowest Pb concentration 0.116 mg kg^{-1} was recorded in the recent years (2017-2019) in sapwood. From 1996 to 2019, 477.58 % of the rate changed Pb concentration during the course of the *M. champaca* wood development year (Fig 4.4). In RS, the highest mean concentration of Pb was 3.28 mg kg^{-1} was recorded in 2017 to 2019 while the lowest of 0.60 mg kg^{-1} was recorded in 1993-1995. From 1993 to 2019, 939.3 % of the rate changed during the year of wood development (Fig 4.4). In DS, the highest mean concentration of Pb during the year (1999-2001) was 6.29 mg kg^{-1} whereas the lowest (2.786 mg kg^{-1}) was recorded in years 2005-2007. The corresponding values of the rate of change of Pb concentration in DS was 197% over the period (i.e., 1993-2019), (Fig 4.4). The highest concentration of 14.26 mg kg^{-1} was recorded during 2017-2019, over the time from 1999 to 2019, the 51.49 % rate of change of concentration level indicates the increasing trend over time (Fig 4.4).

Here also highest HM concentration exists in the currently formed tree rings i.e., bark or sapwood cells. The results showed that the concentration of Pb in the RS and DS exceeded permissible levels advised by the World Health Organization

(WHO, 1996). It is clearly evident that the majority of the RS and DS samples were impacted by municipal solid waste and car emissions. This could be a response to rising Pb concentration in the tree ring. The permissible level of Pb has been exceeded, increasing the risk of lead poisoning through the food chain.

Lead is a non-essential toxic element that increases oxidative stress and causes lead poisoning by upsetting the antioxidant balance of mammalian cells. The (WHO, 1996) has set a maximum permissible level of Pb in plants at 2 mg kg^{-1} (Zaigham et al., 2012, Nazir et al., 2015). The results indicate an excess level of Pb at the study site.

Iron (Fe)

The Fe concentration ranged from 12.2-23 mg kg^{-1}, 11.9 to 28.78 mg kg^{-1}, and 20.4-31 mg kg^{-1}, NFS, RS, and DS respectively. In NFS, the highest mean concentration 22.7 mg kg^{-1} of Fe mean concentration was recorded in recent years (2017-2019) in sapwood and the lowest Fe concentration 12.2 mg kg^{-1} was recorded in the beginning years 1996 - 1998 in heartwood. The rate change of Fe Concentrations during wood development in *M. champaca* was 475.1 % From 1996 to 2019 (Fig 4.4). Whereas in RS, the highest mean concentration of Fe was 28.7mg kg^{-1} in years from 2017 to 2019 while, the lowest mean concentration of 11.9 mg kg^{-1} was recorded in 1993-1995 during the growth of heartwood. From 1993 to 2019, 115.1% of the rate changed during the year (Fig 4.4). whereas in DS, the highest of 30.1 mg kg^{-1} of Fe mean concentration was recorded from 2017 to 2019 while the lowest of 20.4 mg kg^{-1} was recorded from 1999 to 2001. From 1999 to 2019, 158 % of the rate changed during the year (Fig 4.4).

Iron is necessary for plant growth, but iron poisoning symptoms show up in leaf tissues when flooding conditions permit microbial conversion of insoluble Fe^{+3} to soluble Fe^{+2} (Becker and Asch. 2005). This causes a reduction in plant yield and photosynthesis and an increase in oxidative stress and ascorbate peroxidase activity (Sinha et al., 1997; Arora et al., 2002).

4.8.4. Copper (Cu)

The Cu concentration ranged from 1.96 to 5.58 mg kg^{-1}, 3.604 to 13.84 mg kg^{-1}, and 6.08 to 14.69 mg kg^{-1}, Cu in NFS, RS, and DS, respectively. In NFS, the highest mean concentration (5.58 mg kg^{-1}) Cu was recorded in recent years (2017- 2019), in sapwood and the lowest Cu concentration (1.852 mg kg^{-1}), was recorded in the beginning years (1996-1998). The rate change of Cu concentration during the course of wood development in *M. champaca* was 230.17% from 1994 to 2020 (Fig 4.4). whereas in RS, the highest mean concentration of Cu was 13.8 mg kg^{-1} in the years 2017-2019 while the lowest of 3.60 mg kg^{-1} was recorded in 1993-1995 to 2020. From 1993-2019, 284.01 % of the rate changed during the year wood development. In DS, the highest of 14.96 mg kg^{-1} of Cu mean concentration was recorded in the year 2017-2019 while the lowest of 6.08 mg kg^{-1} was recorded in the year 1999-2001. From 1999 to 2019, 200 % of the rate changed during the year (Fig. 4.4). Over the time period from 1996 to 2019, there was a 58.58% rate of change in HM concentration. According to the WHO, 10 mg kg^{-1} is the maximum allowable quantity of copper in plants, whereas daily human intake is restricted to 0.97–3.0 mg/day (Yan et al., 2006; Khan et al., 2022). Increasing Cu concentrations in tree rings indicate severe soil contamination at the road and dumping site, as well as the propensity of the tree species to absorb HM.

4.8.5. Nickel (Ni)

The Ni concentration ranged from 6.11 to 8.05 mg kg^{-1}, 4.464 to 15.80 mg kg^{-1}, and 9.02 to 17.08 mg kg^{-1}, in NFS, RS, and DS respectively. In NFS, the highest mean concentration of 8.05 mg kg^{-1} was recorded in recent years (2011-2013) sapwood and the lowest Ni concentration 6.122 mg kg^{-1}, was observed in current years formed rings (2017-2013). The rate of change of Ni concentrations during the course of wood development in *M. champaca* was 31.70 % from 1996-2019 **(**Fig 4.4). Whereas in RS, the highest mean concentration of Ni was 15.81 mg kg^{-1} in the year 2017-2019 while, the lowest of 4.46 mg kg^{-1} was recorded in the year 1993- 1996. From 1993 -2019, 251.89 % of the rate changed during the year. whereas in DS, the highest of 17.08 mg kg^{-1} of Zn mean concentration was recorded in the year 2017-2019 while the lowest of 9.02 mg kg^{-1} was recorded in the year 1999-2001.

From 1996-2019,47.18 % of the rate changed during the year. It's worth noting that the WHO has set a permissible limit of 10 mg kg^{-1} for Ni in plants (WHO, 1996). The increasing concentrations of Ni above the WHO permissible limit in trees are thought to be linked to an increase in the amount of waste disposed of at the tuirial landfill and vehicle emissions at the road site, potentially leading to its uptake by the trees over time.

4.8.6. Manganese (Mn)

The Mn concentration ranged from 10.0-13.46 mg kg^{-1}, 14.53 to 49.15 mg/kg, and 16.19 to 28.24 mg kg^{-1} in NFS, RS, and DS, respectively. In NFS, the highest mean concentration (13.46 mg kg^{-1}) of Mn was recorded in recent years (2017-2019) in sapwood and the lowest Mn concentration (10.0 mg kg^{-1}) was recorded in the beginning years (1996- 2019) in heartwood. The rate of change of Mn concentrations during the course of wood development in *M. champaca* was 221.26% from 1996-2019 (Fig 4.4), Whereas in RS, the highest mean concentration of Mn was 49.15 mg kg^{-1} in the year 2014 to 2016 while, the lowest of 14.53 mg $kg^{-1}$was recorded in the year 1993 to 1996. From 1993 to 2019, 251.89% of the rate changed during the year (Fig 4.4). whereas in DS, the highest of 28.24 mg kg^{-1} of Mn mean concentration was recorded in the year 2017 to 2019 while the lowest of 16.19 mg kg^{-1} was recorded in the year 1999-2001. From 1999 to 2001, 42.67 % of the rate changed during the year of growth *M. champaca* (Fig. 4.4). This suggests that Mn concentrations in RS experienced notable fluctuations over time. This data reflects the variability in Mn concentrations in DS as well. It's important to note that while the analyzed HM concentrations were continuously increasing, the recorded levels of Mn remained well within the maximum permissible limit of 200 mg kg^{-1} for Mn in plants, as stipulated by the WHO in 1998. This suggests that, despite the increasing trend, Mn levels in the examined sites remained within safe limits for plant health.

4.8.7. Calcium (Ca)

The Ca concentration ranged from 6.61 to 7.92 mg kg^{-1}, 3.694 to 16.64 mg kg^{-1}, and 7.33 to 14.35 mg kg^{-1} in NFS, RS, and DS, respectively. In NFS, the highest mean concentration of 7.92 mg kg^{-1} of Ca was recorded in recent years 2017-2019 in sapwood and the lowest Ca concentration 6.615 mg kg^{-1} was recorded in the beginning years 1996-1998 in heartwood. The rate of change of Mn concentrations during the course of wood development in *M. champaca* was 19.75% from 1996-2017(Fig 4.4), This indicates a relatively stable trend in Ca concentrations in FS over the specified time period. Whereas in RS, the highest mean concentration of Ca was 16.6 mg kg^{-1} in the year 2017 to 2019 while, the lowest of 3.7 mg kg^{-1} was recorded in the year 1993 to 1995. From 1993 to 2019, 133% of the rate changed during the year (Fig 4.4). This data suggests a considerable fluctuation in Ca concentrations within RS over the given period. In the case of DS, the results displayed a consistent upward trend. In DS, the highest of 14.35 mg kg^{-1} of Ca mean concentration was recorded in the year 2017 to 2019 while the lowest of 7.33 mg kg^{-1} was recorded in the year 1999-2001. From 1999 to 2001, 42.67 % of the rate changed during the year (Fig 4.4). Over the time span from 1999 to 2019, there was a 48.94% rate of change in concentration (Fig 4.4). This indicates a clear progression in Ca concentration within DS over the specified period. The increasing trend of Ca concentrations in tree rings across all sites suggests potential influences, such as changes in environmental factors or anthropogenic activities, which may contribute to these observed variations. Further investigation into the specific causes of these trends could provide valuable insights for environmental management and mitigation strategies.

The HMs concentration in different sites in descending order was: Mn > Ca > Ni > Fe > Cu > Zn > Pb, in NFS, Mn > Ni > Cu > Fe > Ca > Zn > Pb in RS, and Fe > Zn > Pb > Mn > Ca > Ni > Cu in DS. In contrast to NFS, the heavy metal concentrations in DS and RS were monotonically increasing in the sample tree ring cores. The change in HMs concentrations over time was affected by different factors such as environment, site/locality factors, growing conditions, uptake, and many others (Ferretti et al., 2002; Nikfar et al., 2023; Blavier et al., 2023).

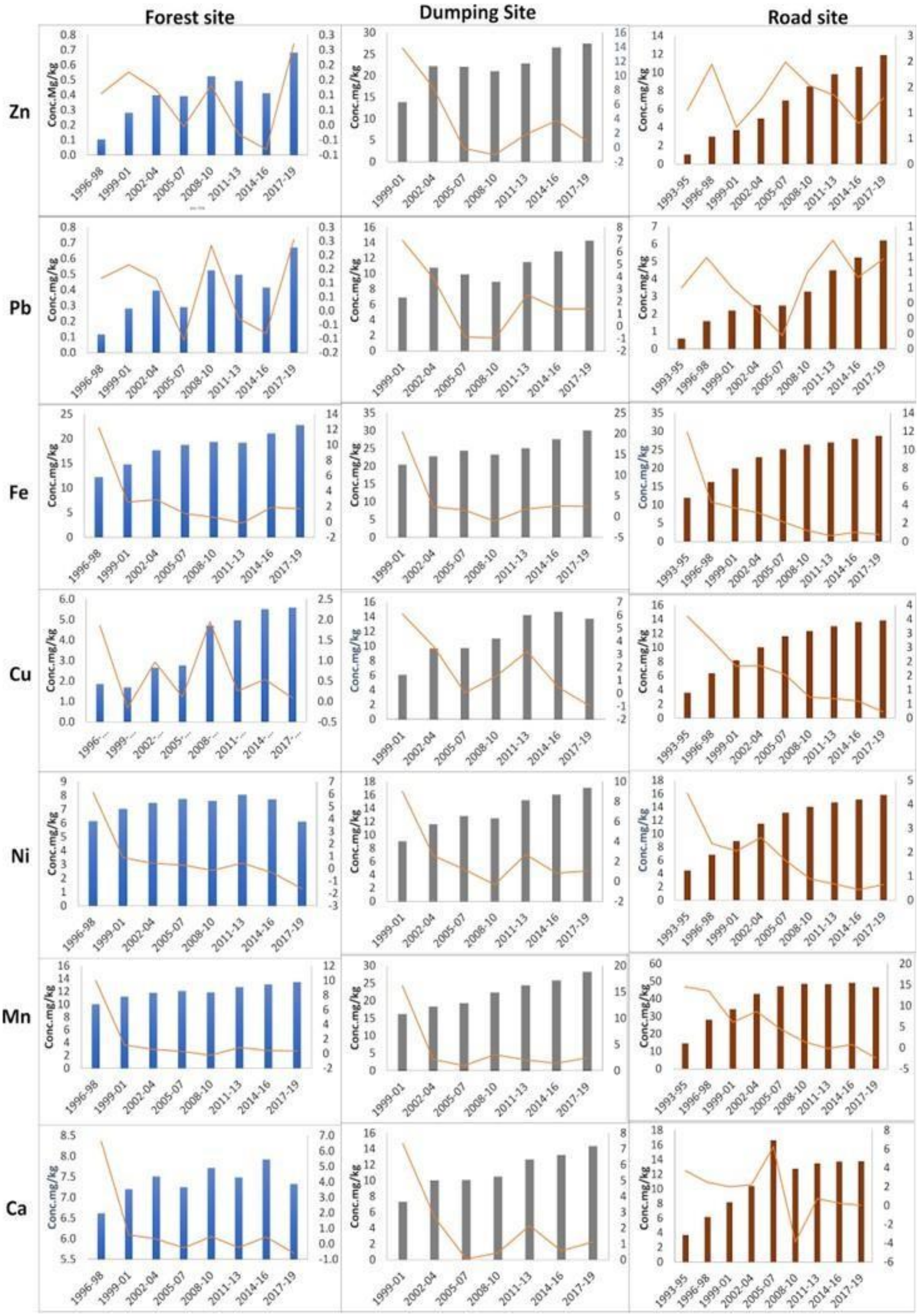


Figure: 4.4. The inter-annual HM concentration of *M. Champaca* tree ring samples from study sites

4.9. Analysis of mean inter-annual HM concentrations

To assess the level of significance in periodical (every 3 years) variations in heavy metals concentration within tree ring cores, the analysis of variance (ANOVA) was performed in two trees and three different sites. The ANOVA result for this study is presented in Table 4.9.

The ANOVA result showed a significant (*p<0.05*) difference among the mean concentrations of Zn, Pb, Fe, Cu, Ni, Mn, and Ca in NFS, RS, and DS, in DS, Ni was not significant (Table 4.9). Results further indicated highly significant mean differences from three different sites. Sapwood cells and the recently formed tree rings accumulated the majority of the HMs on three sites. Similar findings were reported for *Pinus echinate, Pinus silvestris,* and *Tipuana tipu* (Baes and Mclaughlin 1984; McClenahen et al., 1989; Symeonides 1979; Locosselli et al., 2020).

Table 4.9. ANOVA results for different HMs (Zn, Pb, Fe, Cu, Ni, Mn) concentrations of tree ring of *M. champaca* at different study sites (NFS, RS, and DS). The mean values are ± 1SE. All values are significant at the *p* <0.05 level of significance.

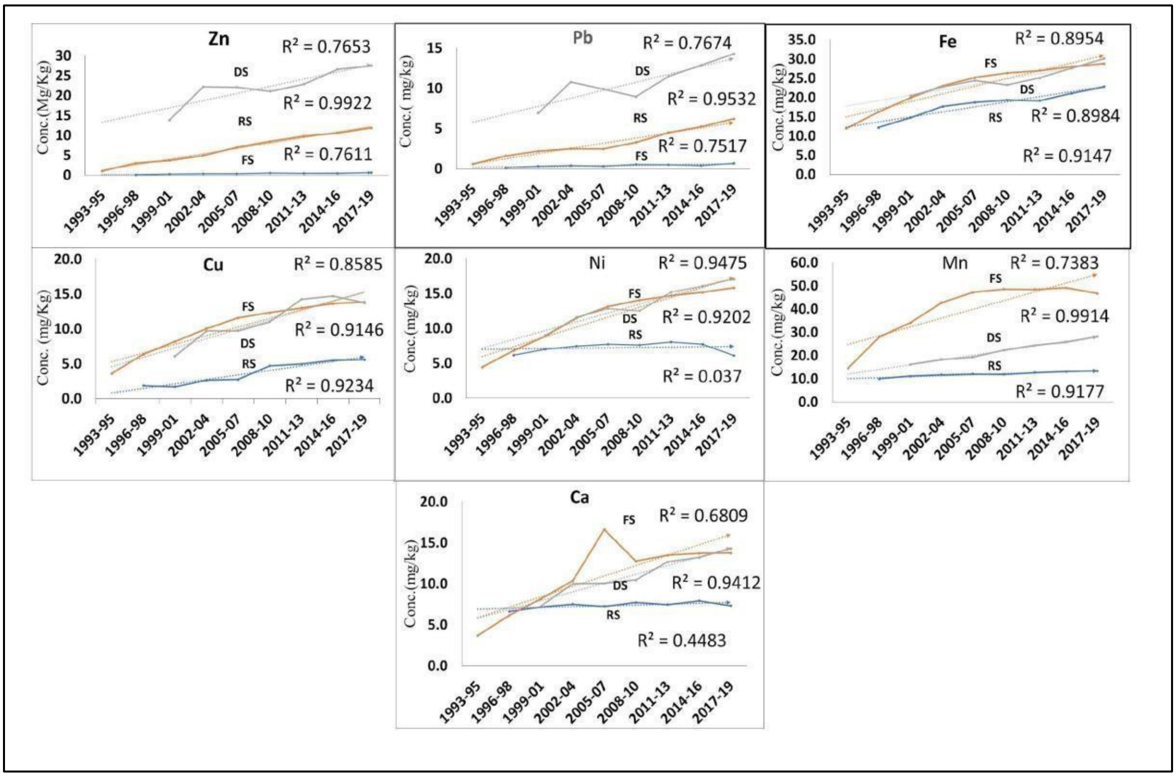
NFS	**1996-98**	**1999-01**	**2002-04**	**2005-07**	**2008-10**	**2011-13**	**2014-16**	**2017-19**	
Zn	0.10±00	0.28±0.11	0.3±0.23	0.39±0.27	0.52±0.39	0.49±0.34	0.41±0.25	0.68±0.27	
Pb	0.11±0.00	0.28±0.11	0.3±0.23	0.29±0.16	0.52±0.39	0.49±0.34	0.41±0.25	0.67±0.28	
Fe	12.2±0.72	14.7±1.49	17.6±1.5	18.7±1.24	19.3±1.45	19.1±1.32	21.0±2.13	22.7±2.53	
Cu	1.85±0.31	1.69±0.20	2.6±0.57	2.76±0.63	4.71±1.06	4.96±1.03	5.50±1.19	5.58±1.32	
Ni	6.1 ±0.14	7.03±0.36	7.4±0.40	7.74±0.56	7.61±0.75	8.05±0.57	7.72±0.83	6.11±0.34	
Mn	10.0±0.83	11.1±1.34	11.7±1.2	12.0±1.21	11.8±1.64	12.6±2.28	13.1±2.46	13.4±3.13	
Ca	6.61±0.50	7.19±0.41	7.5±0.57	7.24±0.23	7.71±0.47	7.48±0.50	7.92±0.52	7.32±0.43	
RS	**1993-95**	**1996-98**	**1999-01**	**2002-04**	**2005-07**	**2008-10**	**2011-13**	**2014-16**	**2017-19**
Zn	1.05±0.0	3.00±0.3	3.7±0.39	4.97±0.6	6.96±0.8	8.48±1.0	9.82±0.6	10.61±0.5	11.90±0.4

	9	7		3	4	1	6	7	2
Pb	0.60±0.17	1.59±0.26	2.1±0.31	2.50±0.31	2.47±0.31	3.28±0.16	4.50±0.66	5.23±0.58	6.21±0.79
Fe	11.9±1.6	16.2±1.83	19.9±1.7	23.0±1.61	25.1±1.23	26.3±1.47	27.0±1.41	28.01±1.54	28.78±1.98
Cu	3.60±0.30	6.35±0.44	8.19±0.5	10.0±0.67	11.5±0.40	12.3±0.26	13.0±0.36	13.62±0.26	13.84±0.42
Ni	4.46±0.66	6.83±0.72	8.88±0.81	11.5±0.67	13.1±0.38	14.0±0.29	14.7±0.52	15.16±0.45	15.81±0.44
Mn	14.5±0.8	28.0±2.97	34.0±3.0	42.7±2.41	47.1±2.08	48.5±1.74	48.3±1.53	49.15±1.47	46.68±3.08
Ca	3.7±0.6	6.17±0.57	8.1±0.53	10.3±0.64	16.6±4.73	12.7±0.32	13.4±0.29	13.74±0.18	13.77±0.44
DS	**1999-01**	**2002-04**	**2005-07**	**2008-10**	**2011-13**	**2014-16**	**2017-19**		
Zn	13.8±1.05	22.2±4.93	22.1±4.1	21.0±1.37	22.8±1.60	26.5±2.06	27.4±2.54		
Pb	6.92±0.82	10.7±2.48	9.9±2.14	8.94±1.65	11.4±1.29	12.8±0.83	14.2±0.74		
Fe	20.4±0.00	22.8±0.35	24.4±1.7	23.2±1.83	25.0±1.46	27.6±2.00	30.1±1.31		
Cu	6.09±0.21	9.69±1.90	9.7±1.52	11.0±0.88	14.2±0.65	14.6±0.97	13.7±1.07		
Ni	9.03±0.29	11.6±0.55	12.8±0.5	12.5±0.95	15.2±1.02	16.0±1.11	17.0±1.62		
Mn	16.9±2.85	18.3±2.56	19.2±1.3	22.3±1.45	24.4±1.52	25.7±1.40	28.2±1.77		
Ca	7.33±0.44	10.02±1.2	10.0±0.9	10.5±0.73	12.6±0.85	13.2±0.40	14.3±0.43		

NS no significance.

4.10. Trend analysis of HM concentration of *M. Champaca* tree ring in three study sites

The linear regression was used to determine the concentration trend over a time scale. The linear regression plots of all the HMs examined showed an increasing trend across the time scale (Fig 4.5). Element concentration changed as a function of time in different sites. In the NFS, the change in concentration of different elements over time was significantly (P<0.05) positively correlated (R^2 ranged from 0.037 for Ni -0.92 for Cu) with time. In the RS, the change in concentration of different elements over time was significantly (P<0.05) positively correlated (R^2 ranged from 0.73 for Mn -0.92 for Zn) with time. In the DS, the change in concentration of different elements over time was significantly (P<0.05) positively correlated (R^2 ranged from 0.76 for Zn -0.99 for Mn) with time. The variations in HM concentration over time can be attributed to a multitude of factors, including environmental influences, growing conditions, and uptake mechanisms within the trees (Ferretti et al., 2002; Augustin et al., 2005; Ballikaya et al., 2022).



4.11. Accumulation of HMs in *T. grandis* and *M. champaca* trees across sites

The comparative analysis was conducted to assess the accumulation of different elements by two tree species in different sites (Fig 4.6). In general, *M. champaca* has where we assess the concentration of various heavy metals (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) in both tree species using T-Test. The outcomes indicated that across all sites, the *M. champaca* tree displayed the highest concentration of toxic elements in its tree rings, whereas, in comparison, the *T. grandis* tree showed a relatively lower concentration.

4.11.1. Natural Forest site

A comparative analysis of the accumulation of different HMs in tree rings during the development of the tree was made within two species (*M. champaca,* and *T. grandis*) in NFS. The results were summarized in Fig 4.6. Orange colour bars represent *M. champaca* and blue colour bars represent *T. grandis*.

To find out the significance of the differences in mean concentrations was used. The statistical (T-Test) results of HMs accumulations in two species revealed a significant difference in concentrations of different elements (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) at a ($p < 0.001$) level of significance.

Overall, *M. champaca* observed a higher accumulation of HMs compared to *T. grandis* in the forest site. The results suggested that *M. champaca* tree rings were most suitable for phytoremediation in the region.

4.11.2. Roadside

A comparative analysis of the accumulation of different HMs in tree rings during the development of the tree was made within two species (*M. champaca,* and *T. grandis*) in RS. The results were summarized in Fig 4.6. Orange colour bars represent *M. champaca* and blue colour bars represent *T. grandis*.

To find out the significance of the differences in mean concentrations was used. The statistical (T-Test) results of HMs accumulations in two species revealed a significant difference in concentrations of different elements (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) at a ($p < 0.001$) level of significance.

Overall, *M. champaca* observed a higher accumulation of HMs compared to *T. grandis* in the forest site. The results suggested that *M. champaca* tree rings were most suitable for phytoremediation in the region.

4.11.3. Municipal solid waste dumping ground or Dumping site

A comparative analysis of the accumulation of different HMs in tree rings during the development of the tree was made within two species (*M. champaca,* and *T. grandis*) in DS. The results were summarized in Fig 4.6. Orange colour bars represent *M. champaca* and blue colour bars represent *T. grandis*.

To find out the significance of the differences in mean concentrations was used. The statistical (T-Test) results of HMs accumulations in two species revealed a significant difference in concentrations of different elements (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) at a ($p < 0.001$) level of significance.

Overall, *M. champaca* observed a higher accumulation of HMs compared to *T. grandis* in the forest site. The results suggested that *M. champaca* tree rings were most suitable for phytoremediation in the region.

In summary, the *M. champaca* tree demonstrated a remarkable ability to effectively accumulate HMs across the various sites, NFS, RS, and DS respectively. This finding underscores the suitability of the *M. champaca* tree for phytoremediation purposes, offering a promising solution for mitigating the presence of HMs in contaminated sites at the regional level (Aizawl). Further research and implementation of this approach could lead to significant improvements in environmental quality and the overall well-being of both ecosystems and human populations.

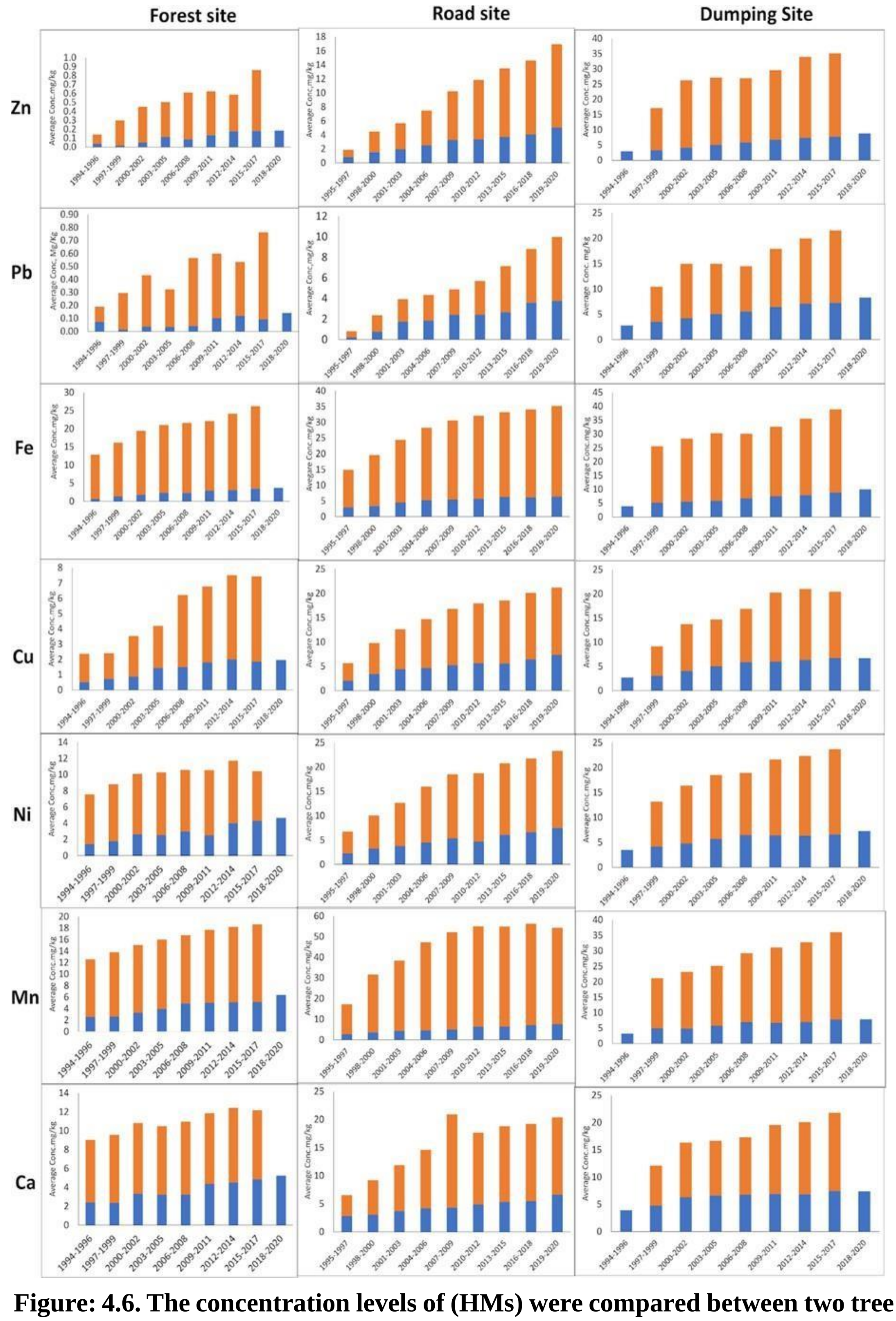


Figure: 4.6. The concentration levels of (HMs) were compared between two tree species across the study sites. (The Saffron colour represents *M. champaca*, while blue indicates *T. grandis*)

4.12. HM concentrations in soils of different sites

Analyzing soil samples in proximity to tree rings is an important step in considering the sources of HMs present in tree rings (Isinkaralar, 2022). Soil analysis can offer a valuable understanding of the HM status of the environment and help identify potential sources of contamination (Sanaei et al.,2022; Maharajan et al., 2023).

4.12.1. Mechanism of HMs uptake by trees

Trees absorb nutrients, water, and even HMs very often from the soil through roots, however, leaves and barks also absorb through the deposition of aerosols and hydrological inputs (Hagemeyer, 2000; Kalaivanan and Ganeshamurthy, 2016; Shahid et al., 2020). HMs taken up by trees were finally incorporated into annual growth rings. Analysis of soil sample help us to determine if the HM found in tree rings are originated from the soil (Binda et al., 2021). However, the whole mechanism of HM mobilization is uptake by the root system, xylem loading, translocation, and cellular compartmentation (Balouet et al., 2009; Cobanoglu et al., 2023; Kharazian et al., 2023).

4.12.2. Natural and Anthropogenic sources

There are two major sources of HMs found in the nature; one is natural sources from geological deposits and the other is from the anthropogenic sources such as human activities (like industrial processes, heavy-duty-vehicular emission, urbanization, and municipal solid waste) (Evangelou et al., 2007; Protasowicki, 2004; Ahmad et al., 2023). The analysis of soil samples for the concentration of different elements indicated the source of HM accumulation in tree rings from different areas of Mizoram.

4.13. Soils of the Natural Forest site

The soil analysis results of seven HMs (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) at the NFS from three depths (0–10, 10–20, and 20–30 cm) are summarised in Table 4.10. Depth-wise concentrations of HMs are shown in Fig. 4.7. In the NFS, the Mn concentration (50.6 - 53.4 mg kg^{-1}). Fe concentration (20.4–28.2 mg kg^{-1}, Table 4.10) was second in order after Mn in three soil depths at the NFS. Zn concentration (10.7–10.9 mg kg^{-1}) was minimum to a depth of 30 cm in the NFS. The concentration of other elements (Cu, Ni, and Pb) up to 30 cm soil depth in NFS were within the range obtained for Fe and Zn (Table 4.10).

Among the soil depth, all the HMs were significantly higher in the upper 20 cm soil depth compared to lower depths (Fig. 4.7). The HMs concentrations in descending order were: Mn > Fe > Ca > Zn > Cu > Ni > Pb. The HMs having higher concentrations in the soil showed higher accumulation in tree rings in NFS. This indicates that the bioremediation potential of the species depends on the availability of elements in the soil.

Table 4.10. Mean HM concentrations in soils up to 30 cm depth in NFS. Values are mean ± 1SE.

Soil Depth (cm)	DS	Zn	Pb	Fe	Cu	Ni	Mn	Ca
0-10	Min	10.7	2.06	20.4	6.48	7.05	50.6	10.4
	Max	10.9	2.62	28.2	9.78	7.07	53.4	15.4
	Mean	10.80	2.249	23.929	8.242	7.067	52.203	12.506
	±1 SE	0.09	0.32	3.95	1.66	0.01	1.41	2.63
10-20	Min	7.32	1.37	20.48	3.64	2.83	50.48	10.79
	Max	11.6	2.25	22.76	8.49	7.23	53.48	13.57
	Mean	10.116	1.673	21.573	6.206	5.719	52.143	11.94
	±1 SE	2.42	0.50	1.14	2.43	2.49	1.52	1.44
20-30	Min	8.47	2.68	20.48	4.87	7.34	20.48	5.48
	Max	9.87	2.75	23.49	6.48	7.35	24.07	6.81
	Mean	9.043	2.726	22.146	5.614	7.35	22.666	6.057
	±1 SE	0.73	0.03	1.53	0.81	0.00	1.91	0.68

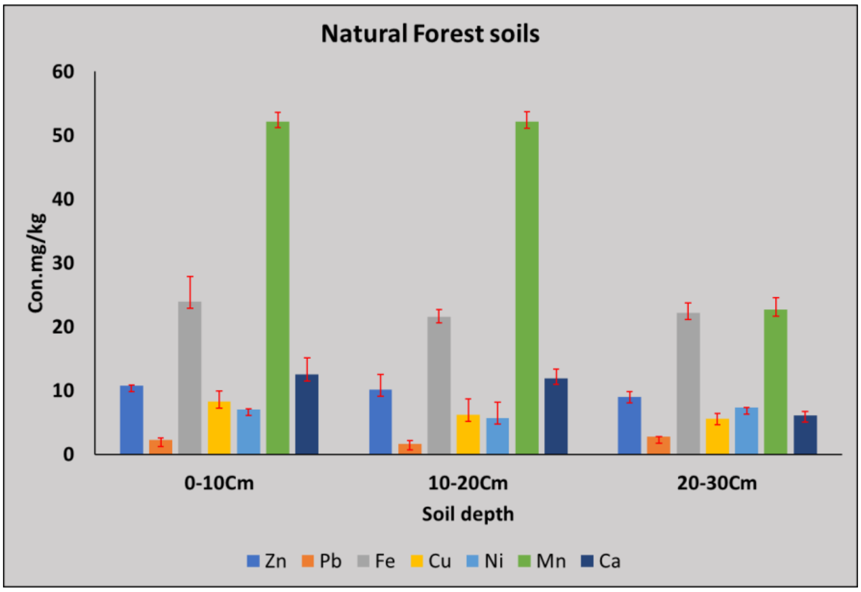


Figure: 4.7. Heavy metal concentration levels from the NFS soil samples (Mean ± 1 SE, N=3)

4.14. Soils of the Roadside

The soil analysis results of seven HMs (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) at the NFS from three depths (0–10, 10–20, and 20–30 cm) are summarized in Table 4.11. Depth-wise concentrations of HMs are shown in Fig. 4.8. In the RS, concentration (19.7–26.5 mg kg-^{1}, Table 4.10) was second in order after Mn in three soil depths at the NFS. Ni concentration (18.36-25.67 mg kg-^{1}) was minimum to a depth of 30 cm in the NFS The concentration of other elements (Zn, Cu, Ca, and Pb) up to 30 cm soil depth in NFS were within the range obtained for Fe and Zn (Table 4.10).

Among the soil depth, all the HMs were significantly higher in the upper 20 cm soil depth compared to lower depths (Fig. 4.8). The HMs concentrations in descending order were: Mn > Fe > Ca > Ni > Cu > Zn > Pb. The HMs having higher concentrations in the soil showed higher accumulation in tree rings in RS. This indicates that the bioremediation potential of the species depends on the availability of elements in the soil.

Table 4.11. Mean HMs concentrations in soils up to 30 cm depth in RS. Values are mean ± 1SE.

Soil Depth (cm)	DS	Zn	Pb	Fe	Cu	Ni	Mn	Ca
0-10	Min	8.47	5.69	19.7	12.58	18.47	49.78	18.97
	Max	10.5	5.84	23.57	16.49	20.46	51.45	20.45
	Mean	9.5	5.791	21.3	14.20	19.24	50.53	19.72
	±1 SE	1.0	0.08	2.00	2.03	1.06	0.84	0.74
10-20	Min	10.5	7.22	21.47	16.87	19.75	48.72	16.57
	Max	15.48	7.44	26.49	19.75	25.67	56.79	19.87
	Mean	12.862	7.302	24.48	18.43	21.971	51.793	18.37
	±1 SE	2.47	0.12	2.65	1.45	3.22	4.36	1.67
20-30	Min	8.97	7.90	20.68	10.58	18.36	36.28	11.34
	Max	11.56	7.97	26.87	15.48	19.55	39.87	15.48
	Mean	10.060	7.951	23.075	13.44	19.154	38.20	13.135
	±1 SE	1.34	0.03	3.32	2.50	0.67	1.80	2.12

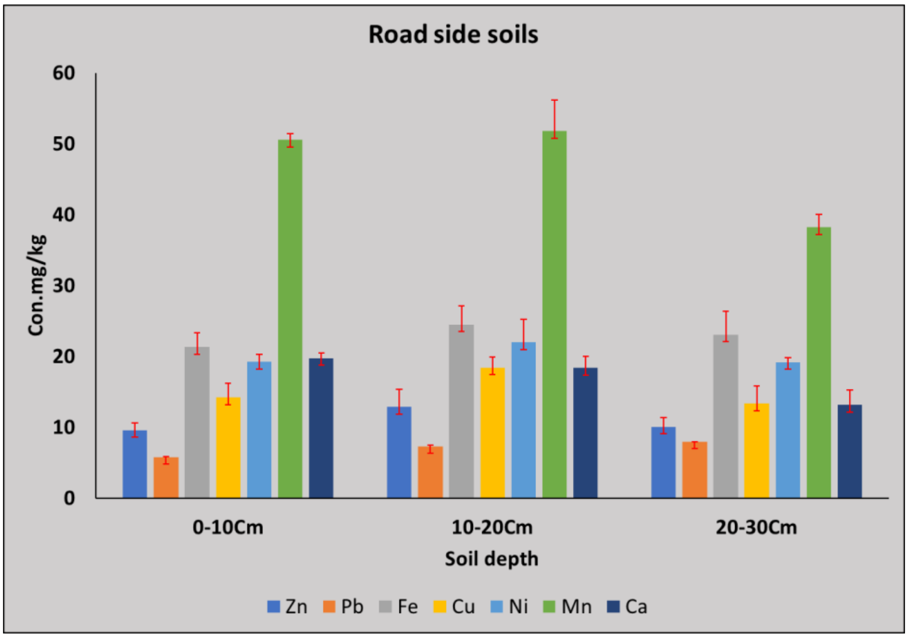


Figure: 4.8. HM concentration levels from the RS soil samples (Mean ± 1 SE, N=3)

4.15. Soils of the municipal solid waste dumping site

The soil analysis results of seven HMs (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) at the DS from three depths (0–10, 10–20, and 20–30 cm) are summarized in Table 4.12. Depth-wise concentrations of HMs are shown in Fig. 4.9. In the DS, the Fe concentration (29.6 – 39.5 mg kg^{-1}). Zn concentration (20.0-27.7 mg kg^{-1}, Table 4.12) was second in order after Fe in three soil depths at the DS. Ni concentration (4.59–7.8 mg kg^{-1}) was minimum to a depth of 30 cm in the DS. The concentration of other HMs (Pb, Cu, Mn, and Ca) up to 30 cm soil depth in DS were within the range obtained for Fe and Zn (Table 4.12).

Among the soil depth, all the HMs were significantly higher in the upper 20 cm soil depth compared to lower depths (Fig. 4.9). The HMs concentrations in descending order were: Fe > Zn > Pb > Cu > Mn > Ca > Ni. The HMs having higher concentrations in the soil showed higher accumulation in tree rings in DS. This indicates that the bioremediation potential of the species depends on the availability of HMs in the soil.

Table 4.12. Mean HMs concentrations in soils up to 30 cm depth in DS. Values are mean ± 1SE.

Soil Depth (cm)	DS	Zn	Pb	Fe	Cu	Ni	Mn	Ca
0-10	Min	20.87	11.69	35.79	10.23	4.58	8.97	6.48
	Max	23.67	11.78	38.47	10.61	7.48	10.84	7.48
	Mean	22.973	11.749	37.246	10.482	6.013	9.820	6.823
	±1 SE	1.56	0.05	1.35	0.21	1.44	0.94	0.57
10-20	Min	26.97	12.72	38.49	10.52	6.48	10.67	6.49
	Max	28.64	13.05	40.58	10.62	8.47	15.48	8.47
	Mean	27.767	12.917	39.582	10.563	7.805	12.285	7.372
	±1 SE	0.84	0.17	1.05	0.05	1.14	2.76	1.00
20-30	Min	19.64	12.38	28.64	11.83	3.48	8.69	6.49
	Max	20.67	13.05	30.48	12.63	6.47	9.68	8.47
	Mean	20.034	12.791	29.622	12.371	5.145	9.283	7.812
	±1 SE	0.55	0.36	0.92	0.46	1.51	0.51	1.13

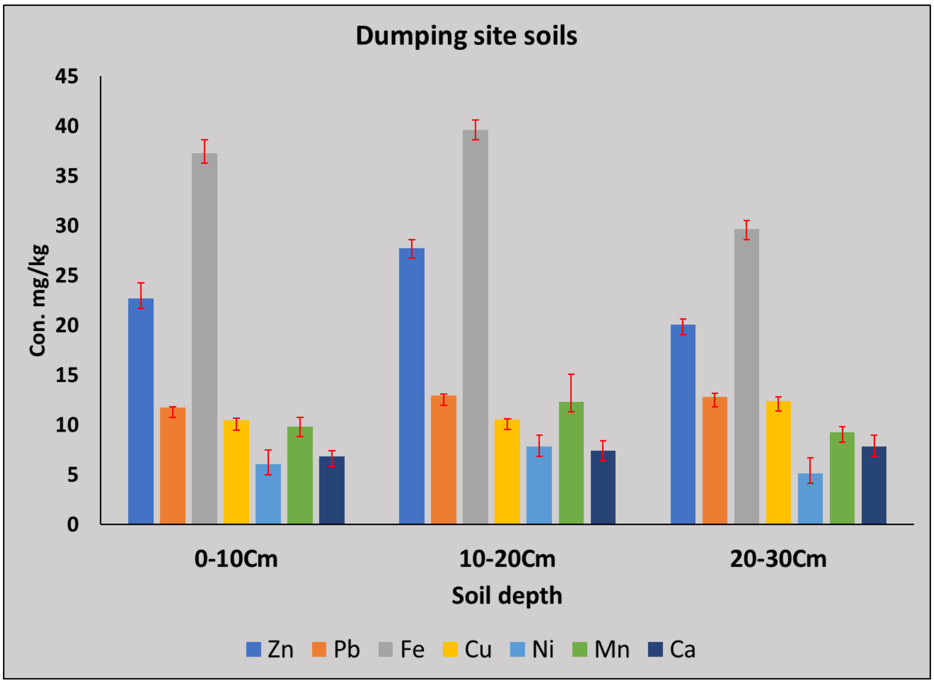


Figure: 4.9. HM concentration levels from the DS soil samples (Mean ± 1 SE, N=3)

4.16. Pollution assessment

To determine the efficiency of HM accumulation within an ecosystem, several pollution assessment indices are used, such as the Geo-accumulation Index (Igeo), Contamination Factor (CF), and Bioaccumulation Index or Bio-accumulation Factor (BAF). These indices help to measure the amount and impact of HM contamination in the ecosystem.

4.16.1. Geo- accumulation index (Igeo)

The Geo-accumulation Index (Igeo) is used to determine the estimate of the contamination or enrichment of HM, in sediments, and soils (Muller, 1981). It aids in determining the amount to which human activities have affected HM concentrations in the environment in comparison to natural or background levels.

Geo-Accumulation index (Igeo) = log2 (Cn/1.5*Bn)----------- (Formula 4.1)

Where Cn is the concentration of the assessed n^{th} metal

Bn is the background value of the n^{th} metal

Table 4.13 Geo-accumulation index (Igeo) and contamination level

I geo Class	Igeo Value	Contaminated level
0	Igeo < 0	Uncontaminated
1	0< Igeo <1	Uncontaminated/moderately Contaminated
2	1< Igeo <2	Moderately contaminated
3	2< Igeo <3	Moderately/strongly contaminated
4	3< Igeo <4	Strongly contaminated
5	4< Igeo <5	Strongly/extremely contaminated
6	5< Igeo	Extremely contaminated

*Adapted from Muller (1981)

4.16.2. Geo-accumulation assessment for NFS, RS, and DS

The Igeo values of different HMs in soil, including metals like Fe, Zn, Pb, Cu, Ni, Mn, and Ca were analyzed in three different studies NFS, RS, and DS, and Geo-accumulation Index (Igeo) of these metals were negative in the study area (Table 4.14). The negative Igeo values in soil indicated a significantly low contamination of HM in the soil (Olubunmi & Olorunsola, 2010).

Table 4.14 Geo-accumulation index (Igeo) and contamination level analyzed for NFS, RS, and DS

HMs	Igeo values			Igeo class	Contaminated level
	NFS	RS	DS		
Zn	-2.9	-2.8	-10.3	0	Uncontaminated
Pb	-3.5	-1.8	-1.0	0	Uncontaminated
Fe	-11.0	-10.9	-10.3	0	Uncontaminated
Cu	-1.6	-0.48	-0.9	0	Uncontaminated
Ni	-0.5	0.9	-0.6	0	Uncontaminated
Mn	-0.5	-0.43	-2.6	0	Uncontaminated
Ca	-0.5	0.16	-1.0	0	Uncontaminated

4.17. Contamination Factor (CF)

The CF is another important concept used to assess the contamination levels in an area due to HMs. It provides a numerical value that helps us understand how much the concentration of a specific metal in the environment deviates from its natural or background levels (Table 4.15).

The formula for calculating the CF is

$$CF = \frac{C_{metal}}{C_{background}} \quad \text{----------------(Formula 4.2)}$$

Were

CF = Contamination Factor for a specific metal.

C_{metal} = The concentration of the metal in the environment (soil, sediments, etc.)

$C_{Background}$ = The background concentration of the same elements in a relatively uncontaminated or natural environment

Table 4.15. Assessment of contamination Factor level

Contamination factor	Category level
<1	low contamination
<1 CF <3	moderate contamination
3< Cf <6	implies considerable contamination
CF >6	extremely high contamination

* Adapted from Muller (1969)

4.17.1. CF assessment for the NFS

The CF values at NFS were summarized in Fig 4.10. The analysis of various HMs, including Fe, Zn, Pb, Cu, Ni, Mn, and Ca, all showed CF values less than 1 or ≈ 1. These results indicate that the concentrations of these HMs in the NFS soil are lower than their background or natural levels. Hence, based on this CF assessment, it can be concluded that the area is not significantly polluted with these HMs. This positive outcome recommends that the NFS is relatively free from substantial contamination by these specific HMs.

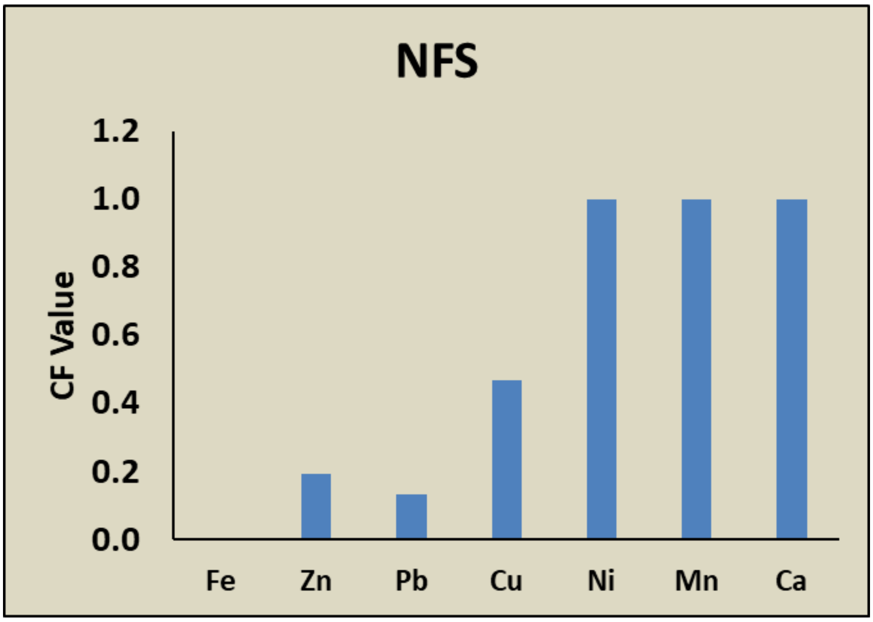


Figure: 4.10. Contamination Factor level at the NFS

4.17.2. CF assessment from the RS

The CF values at RS were summarized in Fig 4.11. The analysis of various HMs, including Fe, Zn, Pb, Cu, Mn, and Ca, all showed CF values less than 1 or ≈ 1. These results indicate that the concentrations of these HMs in the RS soil are lower than their background or natural levels. However, the Ni element stands out with a CF value of 3, indicating a moderate level of Ni contamination in the RS. These findings may be attributed to weathering processes affecting rocks and soil, as well as forest fire activities occurring on roads or in proximity to the study site. Hence, based on this CF assessment, it can be concluded that the area is not significantly polluted with these HMs.

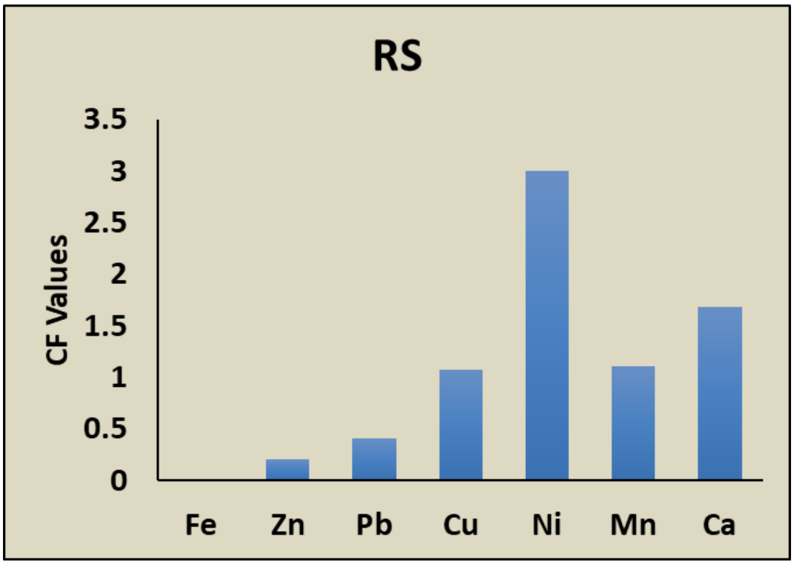


Figure: 4.11. Contamination Factor level at the RS

4.17.3. CF assessment for the DS

The CF values at DS were summarized in Fig 4.12. The analysis of various HMs, including Fe, Zn, Pb, Cu, Ni, Mn, and Ca, all showed CF values less than 1 or ≈ 1. These results indicate that the concentrations of these HMs in the RS soil are lower than their background or natural levels. Hence, based on this CF assessment, it can be concluded that the area is not significantly polluted with these HMs. This positive outcome recommends that the DS is relatively free from substantial contamination by these specific HMs.

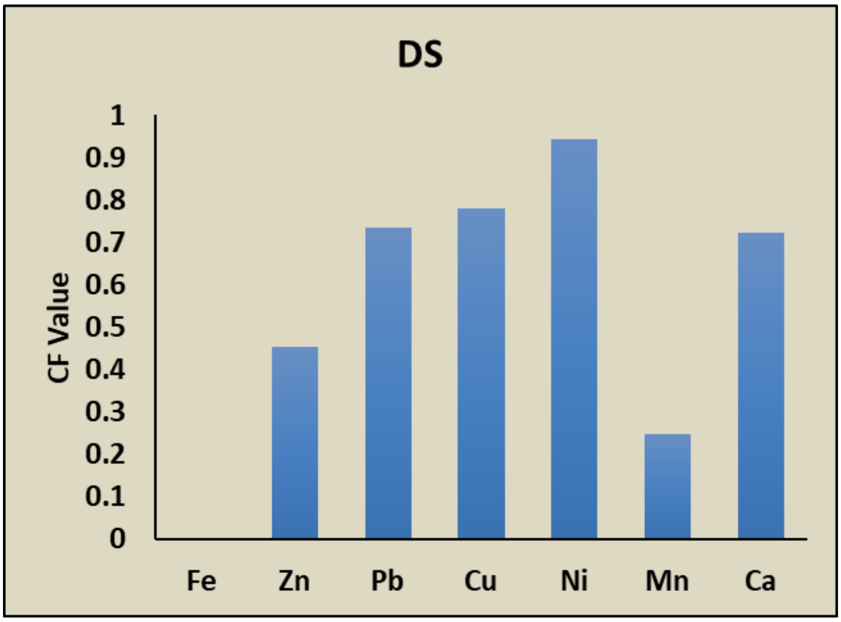


Figure: 4.12. Contamination Factor level at the DS

4.18. Bioaccumulation factor (BAF)

The BAF also known as the bioaccumulation index, is a measure used to determine the ability of a plant species to accumulate certain substances, typically contaminants or pollutants, from the environment (Streit, 1992; Coelho et al., 2018). In the context of phytoremediation studies, the BAF helps determine the potential of certain tree species to uptake and accumulate pollutants from the soil or water. Phyto-remediation is a technique that uses plants to remove, degrade, or stabilize contaminants from the environment (McIntyre, 2003; Pulford and Watson, 2003; Muthusaravanan et al., 2018; Shen et al., 2022).

Table 4.16. Bio-accumulation index analyzed for NFS, RS, and DS

Tree species	HMs	NFS (%)	RS (%)	DS (%)
T. grandis	Zn	0.35	8.97	8.16
	Pb	1.09	10.2	14.8
	Fe	3.52	7.40	6.39
	Cu	7.01	10.8	15.4
	Ni	14.8	8.09	29.9
	Mn	3.41	3.79	19.4
	Ca	12.2	8.74	28.7
M. champaca	Zn	1.54	20.6	40.7
	Pb	6.74	15.0	36.8
	Fe	30.3	33.3	29.9
	Cu	20.8	22.3	43.5
	Ni	40.4	19.2	91.3
	Mn	10.6	28.4	90.4
	Ca	27.2	21.43	65.2

Different plant species have varying capacities to absorb and accumulate HMs (Kabata-Pendias, 2004; Khan, 2005; Hołtra and Wojdyla, 2020) and the BAF provides a quantitative measure of this accumulation potential. The BAF is calculated as the ratio of the concentration of a particular contaminant in the plant tissue (usually the aerial parts like leaves or stems) to the concentration of the same contaminant in the surrounding soil or water. A higher BAF indicates a greater capacity of the plant species to accumulate specific pollutants (Oti, 2015; Chandra and Kumar, 2017; Chen et al., 2021; Mehta and Vyas, 2023).

The BAF index results are shown in Table 4.16 which indicated higher accumulation efficiency of *M. champaca* for HMs as compared to *T. grandis*, even at relatively low levels of concentrations in the soil. This may be attributed due to the fast-growing nature of the former than the latter. Similar reports are available in other studies over the globe for the same species or different species (Påhlsson, 1989; He et al., 2005; Pilon et al., 2005; Chibuike and Obiora, 2014). Fast-growing trees often have a greater capacity to absorb and accumulate substances from their environment. However, the growth rate and physiology of different tree species can influence their ability to accumulate HMs (Salt et al., 1995; Ferretti et al., 2002).

4.19. Comparative analysis of HM concentrations in study sites and WHO permissible limit

HM concentrations from the three distinct study sites were compared with WHO's acceptable limits shown in Table 4.17. Interestingly, the presence of elevated levels of several HMs such as Zn, Pb, Fe, Cu, and Ni in *M, champaca* tree species were within the range reported. These results indicated that *M. champaca* trees had a remarkable tolerance for these excessive concentrations. Based on these outcomes, *M. champaca* can be considered a more suitable species for the removal of HMs from the ecosystem. Additionally, it could serve as an indicator tree species for HM accumulation in these specific study areas. These tree species exhibit long lifespans, allowing them to accumulate HMs over longer time periods.

4.17. Comparison between WHO permissible limits and present study results (WHO, 1996)

HMs	WHO limit (mg kg^{-1})	*T. grandis*			*M. champaca*		
		NFS (mg kg^{-1})	RS (mg kg^{-1})	DS (mg kg^{-1})	NFS (mg kg^{-1})	RS (mg kg^{-1})	DS (mg kg^{-1})
Zn	20	0.18	5.0	8.81	0.682	11.90	**27.46**
Pb	2	0.14	**3.71**	**8.28**	0.67	**6.20**	**14.26**
Fe	20	3.67	6.35	9.97	**22.7**	**28.7**	**30.10**
Cu	10	2.0	7.36	6.72	5.58	**13.8**	**14.69**
Ni	10	4.6	7.48	7.25	8.05	**15.8**	**17.0**
Mn	200	6.38	7.65	7.86	13.46	49.15	28.24
Ca	-----	5.2	6.61	7.43	7.92	16.64	14.35

4.20. Transportation of the HMs from soil to tree ring

HMs enter plant systems via the following three routes: (1) absorption by roots from the soil solution; (2) absorption by leaves from the air; and (3) direct deposition onto leaf and stem segments (Lepp, 1975; Balraju et al., 2022). However, previous research has shown that the majority of HMs are absorbed by roots (Watmough and Hutchinson, 2003). The quantity of HMs absorbed by trees varies according to tree species, soil type, and pH (Vimmerstedt, 1995, Schaumloffel et al., 1998, Kirchner et al., 2008; Chen et al., 2021). The present research assumes that the majority of HMs enter the tree ring via the roots. In this study, Fe was the highest accumulated HMs in the tree rings, followed by Zn, Pb, Fe, Cu, and Ni.

4.21. Impact of socio-historical development of Mizoram on HM concentrations

Dendrochemistry represents historical changes of elements in the environment samples, e.g., in trees, it records historical changes of chemical elements in tree rings considering that the contaminants recorded in tree rings are immobile (Watmough, 1999; Maillard et al., 2016; Odabasi et al., 2016; Dobrzanska et al., 2021). However, once taken up, elements can bind to the xylem, phloem, or ray cells, or can continue to be mobile, being radially or vertically translocated in the stem (Hagemeyer, 2000). Their distribution within the stem may also be impacted by how the components are divided between the heartwood and sapwood. The micro- environment of trees can vary seasonally and spatially, which can affect how elements are distributed within the stem (Kirchner et al., 2008; Scanlon et al., 2020, Edusei et al., 2021). In order to reflect historical variations in environmental contents, it is necessary to pick the most appropriate HMs. Several HMs, including Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Sr, Pb, V, and Zn, have been studied in the past; however, As, Cd, Cu, Hg, Pb, and Zn are the most frequently studied ones (Kirchner et al., 2008; Saint Laurent et al., 2011; MacDonald et al., 2011; Smith et al., 2014; Wright et al., 2014; Mihaljevič et al., 2015; Maillard et al., 2016; Odabasi et al., 2016). Al, Ca, Fe, K, Mg, Mn, P, As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, and Zn were among the 19 HMs examined in the tree rings in this study and were considered suitable for dendrochemical studies as they were frequently encountered (Odabasi et al., 2016). Additionally, vehicular emissions exhaust them as the primary metallic pollutants from the industrial zone and from roadside pollution (Balraju and Skylab, 2022; Semeraro et al., 2020; Alterio et al., 2020; Bardule et al., 2019).

Previously, no studies have been conducted on HM contaminations in Mizoram, and there is a lack of data recording vehicular emissions. In order to show the relevance of the proxy data historical variation is measured, provided the contents of HMs measured over a time scale in the *T. grandis* and *M. champaca* tree rings sampled from the different study site variation is observed. The Zn, Pb, Fe, Cu, Ni, Mn, and Ca concentrations were significantly higher in RS and DS samples compared to the NFS. In addition, low variation was observed in the NFS samples. The HM concentration has increased in trend over the last decades. However, over the last five decades, Aizawl, Mizoram state has started to urbanize rapidly due to population growth, and industrialization. In this respect, people require more goods and services with respect to the rapidly increasing vehicular movements (Devi, 2021) on the roads and this could be the main reason for the increase in HM concentration in the soil samples from roadsides.

In DS, the major cause of increasing pollution may be due to the rapid growth of population and urbanization, as well as the unorganized management of solid waste materials, and various hazardous materials generated by hospitals, automobiles, small-scale industries, and household waste materials. The estimated growth of MSW generation at the Turial dumping site is shown in Table 4.18 (Aizawl).

Table 4.18. Projected solid waste material in the Turial dumping solid waste area

Year	Population	Waste generation (kg/capita/Day)	Solid waste Qty (T/Year)
2011	3,13,185	0.400	45,723.55
2016	3,58,203	0.420	54,965.35
2021	4,08,098	0.442	65,816.8
2026	4,62,873	0.464	78,456.75
2031	5,22,526	0.488	93,085.95

Source: Draft EIA Report —Development of Landfill Site for Aizawl City —[F. No.10-73/2010- IA-III].

4.22. Air pollution status in the roadside study area

The ambient air quality data was taken from the State Pollution Control Board, Govt. of Mizoram to check the roadside air pollution status. This data of annual mean concentrations of SO_2, NO_2, and Suspended Particulate Matter (SPM) was analyzed (mean, standard error, standard deviation, minimum, and maximum) and are summarized in Table 4.19**.** The observation from data during the period from 2006 to 2022 is demonstrated in Fig 4.13. During this period, SO_2 was the lowest (0.8 µg m^{-3}) observed for the year 2017, and the highest (2.8 µg m^{-3}) was noticed in the year 2006. From 2006 to 2022 a 44 % decrease has been observed for the study region. Likewise, in the case of NO_2 the lowest (5.12 µg m^{-3}) was observed for the year 2020 and the highest (15 µg m^{-3}) was observed for the year 2022 and overall, from 2006 to 2022, a 23.96 % increase was observed. The lowest (51 µg m^{-3}) SPM was observed in the year 2020 and the highest (150 µg m^{-3}) was in the year 2016 and concentration has been increased by 12.25 % over the years from 2007 to 2022. Above all these pollutants are influencing the local air quality which is shown in Table 4.20. The AQI indicated a decrease in air quality in the year 2018 (AQI = 48) but in the year 2022, it changed to (AQI = 80). However, at the roadside location, the concentration of SO_2 and NOx were found to be below the permissible limit (80 µg m^{-3}) of NAAQS (CPCB, 2009), but there are several reports that gaseous pollutants are related to respiratory diseases and reproductive and developmental effects even at low concentration (Curtis et al., 2006; Liu et al., 2003). Other studies from this region reported 2.09 μg m^{-3} for commercial areas, 1.03 μg m^{-3} for Mizoram University for SO_2 followed by 22.14 μg m^{-3}, 12.05 μg $m^{-3}$for NO_2, and 250.07 μg m^{-3}, 130.12 μg $m^{-3}$for SPM respectively which were reported from November 2011 to February 2012.

Table 4.19: The concentrations of Ambient air quality parameters (SO_2, NO_2, and SPM) recorded during 2006-2022. The mean values are ± 1 SE.

Parameters	SO_2	NO_2	SPM
Mean ± SE	1.98 ± 0.09	8.78 ± 0.58	99.4 ± 7.46
Minimum	0.8	5.12	51
Maximum	2.88	15	150

In the study area RS Aizawl, as per the record from the Transport Department, Aizawl, the number of vehicles in the city has considerably increased from 1,76,248 in 2019 to 5,74,908 in 2023. This is recorded as a significant growth of 69.34 % in the number of vehicles registered in the city (Fig 4.14). Moreover, heavy-duty vehicles coming from all parts of India through the NH of Sairang and Bawngkawn (NH-54) and public transportation and other private vehicle movements are usually high in this study area RS, and other than this stone quarrying activity is also reported in this area which leads to the emission of dust or SPMs (Panda and Rai, 2015), biomass burning for shifting cultivation is also common in this region (Panda and Rai, 2015; Rai, 2009a, 2012a; Rai and Chutia, 2014) and may be a significant source of SPM and NO_2 pollution in the air. In India, usually, the anthropogenic sources of SO_2 are thermal power plants, petroleum refineries, steel manufacturing units, cement industries, and construction works (Kuttippurath et al., 2022), but in the study site, construction works at Aizawl airport started in December 1995 and NH construction works and heavy-duty vehicles movements are considered as the main sources.

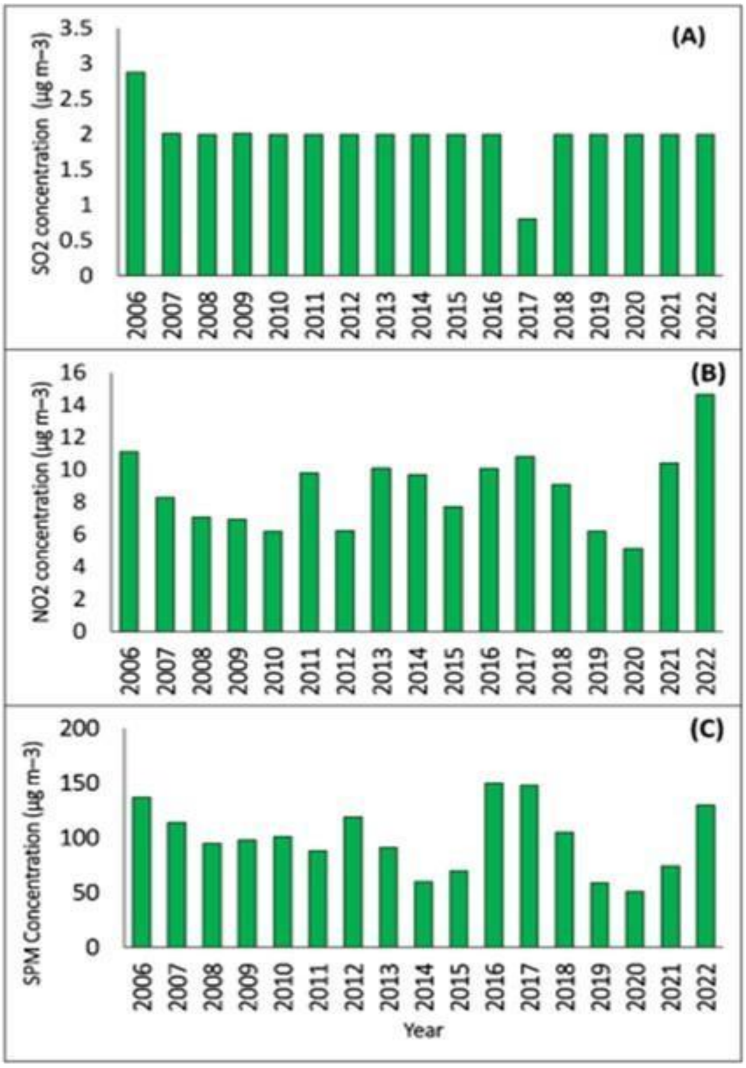


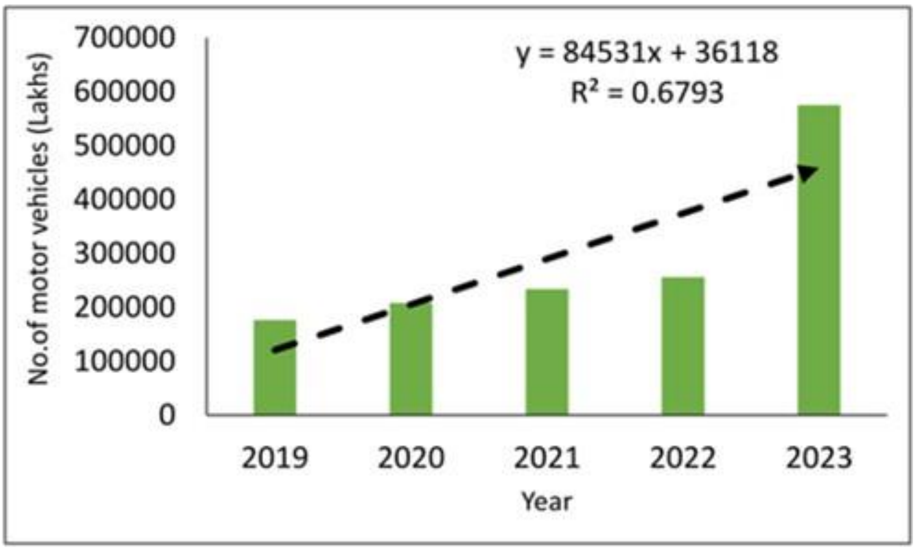
Figure: 4.13. Air pollutants trend along the year wise, (A) Sulphur dioxide (SO2), (B) Nitrogen dioxide (NO2), and (C) Suspended particulate matter (SPM)

Fig 4.13, A shows a decrease in SO_2 concentration over the years or a constant trend in recent decades (2007-2022). This could be because of innovative environmental regulation and the implementation of effective control technologies such as Flue Gas Desulphurization (FGD) and scrubbers which is also reported by Kuttippurath et al., (2022).

Table 4.20 Air quality index in the study site

AIR quality index		AQI Range Associated Health Impacts
Year	**AQI**	0 - 50 Minimal Impact
2018	48	51 - 100 Minor breathing discomfort to sensitive people
2019	45	101 - 200 Breathing discomfort to people with lung, and heart disease, children, and older adults
2020	48	201 - 300 Breathing discomfort to people on prolonged exposure
2021	60	301 - 400 Respiratory illness to the people on prolonged exposure
2022	80	> 401 Respiratory effects even on healthy people

(Sources: Pollution Control Board Mizoram, Government of Mizoram)



(Sources: Pollution Control Board Mizoram, Government of Mizoram)

Figure: 4.14. The trend of motor vehicles registered in the transportation department over the years from 2019 to 2023

4.23. Tourist visiting scenario in Aizawl, Mizoram

Tourism is considered as an 'engine of economic growth' (De Vita et al.2015 p. 16.652). However, there are numerous economic, social, and environmental negative effects associated with this industry. Hence, this industry is a substantial contributor to environmental degradation (Bella, 2018; Dogru et al., 2020). Especially in terms of air pollution from vehicles engaged with the tourism industry has negative impacts on local and global levels, for emission of Carbon dioxide (CO_2) in the environment. (Ciarlantini et al., 2023). Aizawl, Mizoram secured 12th rank among all northeast states in terms of tourist arrivals (NITI Ayog, 2018). In this respect, most of the vehicles running in this study route has main connectivity to the capital city of Mizoram (Aizawl).

Table 4.21. Tourist arrival trends in Aizawl, Mizoram (2009-2022)

Years	Domestic Tourists	Foreign Tourists	Total Tourists
2009-2010	57,639	6,75	58,314
2010-2011	57,623	6,19	58,242
2011-2012	63,512	7,44	64,256
2012-2013	64,631	7,12	65,343
2013-2014	64,583	9,06	65,489
2014-2015	67,554	8,62	68,416
2015-2016	66,583	8,30	67,413
2016-2017	67,223	9,87	68,210
2017-2018	68,679	11,55	69,834
2018-2019	88,122	16,44	89,766
2019-2020	1,59,534	21,43	1,61,677
2020-2021	20,474	90	20,564
2021-2022	1,32,099	5,17	1,32,616
Total	**9,78,256**	**11884**	**9,90,140**

(Sources: Tourism department, Government of Mizoram)

The tourist census is recorded by the Tourism Department of Mizoram from time to time. Domestic tourist arrivals in the state have increased from 57,639 in 2009-2010, to 1,32,099 in 2021-2022 (Table 4.21) registering an average growth of over 56.63 % during the said period. Similarly, international tourist arrivals have also increased from 675 in 2009-2010 to 2,143 in 2018-2020 (Table 4.21) with a significant growth of 68.50 % during the period. However, the maximum number of tourists (1,61,677; including 1,59,534 domestic and 2,143 international visited Mizoram in the year 2019-2020 (Fig 4.15 A & B).

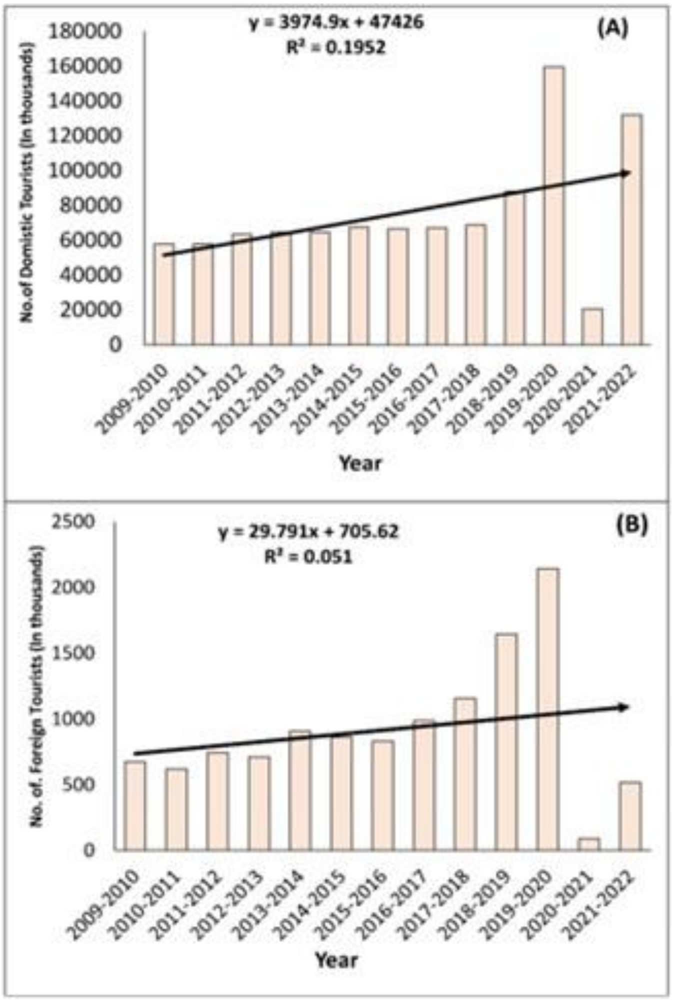


Figure: 4.15. Trends of Tourist (A) domestic and (B) Foreign flow in Aizawl, Mizoram. During the period from 2009 to 2022

However, the studied area (RS) also has some level of pressure on the air quality which is visible in the air quality index (Table 4.20). Based on the AQI, each year, the air quality is degrading. Some studies have already suggested that tourism has an impact on air pollutants such as NOx, PM_{10}, and $PM_{2.5}$ (e.g., Zeng et al., 2021; Russo et al., 2020; Robaina et al., 2020; Zhou 2019; Lee et al., 2015; Saenz-de-Miera and Rossello, 2014), which have negative effects on human health. This could be a reason for increasing HM concentrations in the tree rings in the study area. In the future, there is scope to track the exact sources of the heavy metals by studying the soil and leaf HM concentrations and their correlations with tree rings that might give a complete idea about the sources. However, some studies suggest that higher plants act as bio-monitors of aerial HM pollution because of their bio-accumulative characteristics (Rai, 2008, 2009b, 2012b; Verma and Singh, 2006). Higher plants not only intercept metals from atmospheric deposition but also accumulate them in the soil (Verma and Singh, 2006). Airborne HMs, when deposited in the soil, are taken up by the plants through their root systems and are translocated to other parts of the plant through an active uptake mechanism (Panda and Rai, 2015; Rai, 2008, 2012b; Shparyk and Parpan, 1990; Verma and Singh, 2006; Balraju et al., 2022). The present study found out that the *M. champaca* and *T. grandis* species' HMs concentration was reflected in the tree ring. This signifies them as bio-indicator tree species for monitoring HMs in the environment.

2.25. Implications for pollution

Tree rings serve as historical records of pollution, accessible through dendrochemistry, primarily for environmental monitoring and urban planning support. However, according to the findings of the study, *M.champaca* had the highest concentrations of Zn, Pb, Fe, Cu, and Ni (27.46 mg kg^{-1}, 14.26 mg kg^{-1}, 30.10 mg kg^{-1}, and 17.0 mg kg^{-1}) which were higher above the permissible limit in the plant suggested by the WHO, *M. champaca* tree has a potential for soil and air pollutant accumulation that can be used for Zn, Fe, Pb, Cu, and Ni phytoremediation. As a bioindicator, *M. champaca* has the capacity to reconstruct past levels of air and soil pollution, as well as changes in Pb, Zn, Mn, Cu, Ca, Fe, and Ni concentrations.

2.26. How this research tackles regional, national, and global priorities:

Dendrochemistry research aligns with several Sustainable Development Goals (SDGs) due to its interdisciplinary nature and its potential to address various environmental and societal challenges. Here's how it connects with specific SDGs:

Goal 13: (Climate Action): Dendrochemistry provides valuable insights into past climate variations through the analysis of tree rings. By studying isotopic compositions, elemental concentrations, and growth patterns in tree rings, researchers can reconstruct historical climate conditions with high precision. This data helps to understand climate change trends, identify climate-sensitive regions, and assess the impacts of climate change on ecosystems and communities. Additionally, dendrochemistry contributes to climate mitigation efforts by informing strategies for forest management, carbon sequestration, and climate-resilient land use practices.

Goal 15: (Life on Land): Dendrochemistry plays a crucial role in monitoring the health and dynamics of terrestrial ecosystems. By analyzing tree rings for indicators of environmental stress, such as nutrient levels, pollution, and drought, researchers can assess ecosystem health and resilience. This information is essential for biodiversity conservation, sustainable forest management, and land restoration initiatives. Dendrochemistry also helps to understand the impacts of human activities, such as deforestation, urbanization, and land degradation, on terrestrial ecosystems, thus supporting efforts to protect and restore land resources.

Goal 6: (Clean Water and Sanitation): Dendrochemistry contributes to water resource management by providing insights into water quality and contamination. By analyzing tree rings for pollutants, such as heavy metals, pesticides, and organic compounds, researchers can identify sources of water pollution and assess the effectiveness of remediation measures. This information is valuable for ensuring clean and safe drinking water, protecting aquatic ecosystems, and promoting sustainable water use practices. Additionally, dendrochemistry helps to understand the interactions between terrestrial and aquatic ecosystems, including nutrient cycling, sediment transport, and hydrological processes, thus supporting integrated water resource management approaches.

Chapter 5
Summary and Conclusion

Trees provide proxy records of environmental changes caused by different anthropogenic activities over time. These changes are captured by trees in the form of variations in tree-ring widths and elemental composition in the wood. Tree rings have temporally resolved environmental archives which can be widely used to reconstruct both natural and human-induced changes that occurred over the past hundreds of years. Therefore, the analysis of tree rings provides a crucial advantage in understanding environmental changes due to the extensive historical records. These records serve as a baseline for analyzing changes in both natural and human-induced factors, such as climate, land-use patterns, and chemical variations in the environment. The threat of accumulation of harmful elements in many ecosystems is increasing because of rapid industrialization, urbanization, construction of roads, vehicular emissions, increasing tourist influx, burning of fossil fuels, mining, and inadequate management of industrial effluents. In the Anthropocene era, pollution caused by rising levels of hazardous metal elements has become a major problem, especially in urban and roadside areas due to high traffic influx, diverse industrial activities, and improper dumping of garbage. Therefore, the health and survival of all life forms are adversely affected by these hazardous elements which are too difficult to break down or perish even in low concentrations. The unavailability of historical site-specific data on exposure to pollutants greatly hampers analyzing the impacts of pollutants on different ecosystems. These issues can be addressed using local emission data, distance, directional wind frequency, measurements of HM accumulation in the environment, and/ or in combination with these methods.

Since the early 1970s, dendro-chemical techniques have been used to monitor historic changes in the chemical composition of soil and the atmosphere. Indeed, dendrochemistry has already demonstrated its immense potential in conducting environmental studies, as evidenced by a wealth of published research in different regions across the globe. This field of study harnesses the chemical information stored within tree rings to provide valuable insights into historical environmental conditions and human-induced changes. The application of dendrochemistry has yielded a plethora of findings that contribute significantly to our understanding of past events and their implications for the present and future.

The strength of dendrochemistry lies in its ability to serve as a time machine, allowing us to peek into the past and discern trends, anomalies, and the effects of human activities on our environment. This methodology has proven invaluable in reconstructing historical records of pollution levels, pinpointing the sources of contamination, and evaluating the success or failure of environmental management strategies.

In this study, tree ring samples of *T. grandis* and *M. champaca* were collected from the Aizawl Forest division. It underscores the immense potential of *T. grandis* and *M. champaca* trees in reconstructing contamination history, observing HMs, and exploring their suitability for phytoremediation purposes. The analysis of the contamination history of seven elements (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) over different time periods for *T. grandis* and *M. champaca* tree rings showed their wide annual variability in various elements.

The enduring repercussions of anthropogenic activities come to light through the notably elevated concentrations of HMs found in trees located near dumping sites and roads. In the present study, areas with high pollution levels in the soil as well as air (e.g., dumping sites and roadsides) showed high accumulation of these elements in the tree rings as compared to natural forests. Notably, when comparing the two tree species, *M. champaca* exhibited the highest accumulation of HMs in tree rings because of its fast-growing ability. Most elements started accumulating in the initial year, followed by a continuous increase, with the highest concentration found in the most recently formed (sapwood) tree rings.

In this study, *M. champaca* had the highest concentrations of different HMs (27.46 mg kg^{-1} for Zn, 14.26 mg kg^{-1} for Pb, 30.10 mg kg^{-1} for Fe, 14.69 mg kga^{-1} for Cu and 17.0 mg kg^{-1} for Ni respectively) were above the permissible limit in the plants as suggested by WHO (1996). *M. champaca* tree is a potential pollutant accumulator from both soil and air. This tree species can be used for phytoremediation of Zn, Fe, Pb, Cu, and Ni. The findings of this study demonstrate that *M. champaca* tree species can be effectively used as a bio-accumulator to absorb these HMs and retain them for an extended period of time. Hence, this species can be recommended for plantation in polluted areas to aid in the bioremediation of HMs for prolonged durations as better mitigation measures for remediation of soil pollution load. The reported concentration values exceeded the background values of these elements reported from unpolluted soils in Mizoram, indicating an increasing pollution level in the surrounding areas of the study sites.

The present study is the first-ever tree ring study from Aizawl, Mizoram. The study shows that dendrochemistry can help in understanding the impact of pollution levels on the ecosystem at the regional level. Further, this study can help in developing strategies for better management plans for pollution control sustainable environmental management in the region. It has the potential to illuminate the future of contaminated sites amidst a changing climate. Additionally, it plays a pivotal role in influencing forthcoming endeavors focused on mitigating and rejuvenating ecosystems affected by human activities. At this point, further research, raising awareness, and policy support are essential for environmental protection.

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Photo-plates


Natural forest site

Roadside


Municipal solid waste dumping site

Tree ring core sample collection from different study sites

Soil samples from different fields site

Mounting and polishing process of tree ring samples

Counting and dating of tree ring core samples

3-year annual tree ring core segment, making powder using a ball mill

Powder of tree ring sample

Tree ring sample digestion process using microwave digester

Soil sample digestion process using hot plate

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- Forest Products: Value addition, marketing, and entrepreneurship development

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ABSTRACT

DENDRO-CHEMICAL ANALYSIS OF SELECTED TREE SPECIES IN MIZORAM, NORTH EAST INDIA

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DEPARTMENT OF FORESTRY

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MARCH, 2024

DENDRO-CHEMICAL ANALYSIS OF SELECTED TREE SPECIES IN MIZORAM, NORTH EAST INDIA

BY

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Submitted

In partial fulfillment of the requirement of the Degree of Doctor of Philosophy in Forestry of Mizoram University, Tanhril, Aizawl

Thesis Title: Dendro-chemical analysis of selected tree species in Mizoram, North East India

Background

Trees serve as valuable proxies for documenting environmental changes resulting from various human activities over time. These changes manifest in the form of variations in tree-ring widths and the elemental composition of wood. Tree rings are precise chronological records widely utilized to reconstruct natural and human-induced changes occurring over the past few centuries to millennia. They offer a crucial advantage in analyzing environmental shifts due to their extensive historical records. These records serve as a foundation for assessing alterations in both natural and human-induced factors, such as climate, land-use patterns, and chemical fluctuations in the environment.

The threat of harmful element accumulation in numerous ecosystems is on the rise due to rapid industrialization, urban expansion, road construction, vehicular emissions, increased tourism, fossil fuel combustion, mining activities, and insufficient management of industrial effluents. In the Anthropocene era, pollution resulting from elevated levels of hazardous metal elements has become a significant concern, particularly in urban and roadside areas with high traffic volumes, diverse industrial operations, and improper waste disposal. Consequently, these hazardous elements adversely impact the health and survival of all life forms, and their removal, even at low concentrations, proves to be a formidable challenge.

However, the lack of historical, site-specific data on pollutant exposure significantly impedes the analysis of the effects of pollutants on various ecosystems. These challenges can be mitigated by using local emission data, distance measurements, directional wind frequency, toxic element accumulation measurements in the environment, or a combination of these approaches.

Since the early 1970s, dendro-chemical techniques have been employed to track historical shifts in soil and atmospheric chemical compositions. Lepp (1975) pioneered the concept of dendrochemistry, successfully reconstructing the history of toxic elements using tree rings. These initial studies acted as a catalyst, propelling dendrochemistry forward as a vital tool in environmental monitoring.

To effectively combat pollution, it is crucial to comprehend the spatio-temporal variations and evolution of heavy metal elements, as well as their interactions. The tree ring stands out as a frequently tapped source of proxy data, offering reliable dating and wide distribution, making it a key resource in illustrating changes in chemical compositions across space and time. The chemical composition of tree rings mirrors the annual ambient chemistry at the time of ring formation.

Research gap

In Northeast India, dendrochemical studies are very scanty, particularly in the state of Mizoram where no such study has been carried out yet, except a few studies conducted on dendroclimatology, tree-ring growth, and climate relationship using different species: namely, *Quercus serrata*, *Pinus kesiya* and *Tectona grandis*. As a result of recent developmental activities in Mizoram, the state has witnessed a tremendous increase in air pollution; however, the real-time observations on heavy metal concentration are very limited to decode the effect of developmental activities on the environment. Considering this knowledge gap, this study evaluated variation in patterns of seven heavy metals, namely Zn, Pb, Fe, Mn, Cu, Ca, and Ni, and reconstructed past pollution history by using *Tectona grandis* and *Magnolia champaca* tree ring cores from three different locations, i.e., undisturbed forest site, roadside, and dumping site in Aizawl, Mizoram.

Objectives

1. To analyze inter-annual elemental concentrations in tree rings of selected species.
2. To find out the most prominent element persisting in the tree rings in the area and to track possible physical sources of elements in the tree rings.
3. To identify species with strong efficiency of accumulating heavy metals from the ecosystems and to suggest indicator species for phytoremediation of heavy metals.

Methods

Sample collection

Samples were systematically collected using standard dendrochronological techniques from three distinct study sites, which were referred to as forest sites, road sites, and dumping sites. To collect these samples, an increment borer was employed, and a specific method was followed. From each tree, two core samples were collected, and from each study site, a total of 40 such cores were collected. The first core was taken at an angle of 90°, while the second core was extracted at a 270°angle. The tree ring core sample was collected at the breast height (DBH i.e., 1.37m).

To ensure proper identification and organization of the collected core samples, they were transferred into paper straws. Each core was then carefully labelled with a unique ID, which included information such as the site name (FS, RS, or DS), the species name, the core's serial number, and the date on which it was collected. This meticulous labelling process helps maintain a clear record of the origin and characteristics of each core sample, making it easier to analyze and interpret the data during subsequent studies and research, and were then transported to the laboratory, and stored at -20°C until further preparation and analysis.

Sample processing

The collected tree ring core samples were first allowed to air-dry, after which they were affixed to wooden mounts using water-based adhesive and secured with masking tape. Relevant labelling information was transcribed onto the side of each core mount. To enhance the visibility of the cores' ring boundaries under a stereo-zoom microscope, they were meticulously polished using a range of sandpapers with different grit sizes, including 100, 120, 200, 300, 400, and 600 grits. The dated series was measured to a precision of 0.001 mm. Cross-dating was performed to calculate the calendar years of heavy metal components using the COFECHA program which ensured cross-accuracy dating.

Laboratory procedure

To remove any surface contaminants introduced during the coring or handling of samples, the dated tree-ring cores were ultrasonically cleaned with double-deionized water (Milli-Q Millipore) for an hour. The annual rings of the dried cores were then cut into segments from bark to pith direction under binocular microscopes; each segment included three annual rings and the final 7 best series tree ring cores from each study site were used for the dendro-chemical analysis of seven heavy metals (Zn, Pb, Fe, Mn, Ca, Cu and Ni). A wood sample of 0.05 g from each segment was placed in a PTFE tube with 7 ml of HNO_3 and 3 ml of H_2O_2 to digest for 25 minutes at 150°C, and then the sample was digested using a microwave digestor. After diluting the solution with 5% HNO_3 to a final volume of 30 ml (1:5 ratio i.e., 5 ml digested sample solution diluted with 25 ml double-deionized water), it was filtered through a syringe filter (0.45-micron filter).

Soil sample collection

Soil samples were collected from three distinct study sites: forest, roadside, and dumping areas. Using a 10 cm scaled soil corer with an inner diameter of 5.2 cm, samples were extracted from depths of 0-10 cm, 10-20 cm, and 20-30 cm. Within each site, two composite soil samples were formed for each depth from replicates, with each composite created by combining three randomly chosen soil cores. This process yielded a total of 32 samples (2 composites x 3 depths x 3 site replicates). The samples were meticulously labeled, placed in zip-lock bags, and transported to the laboratory for subsequent procedures. At the lab, the soil samples were sieved through a 2 mm mesh, followed by a comprehensive chemical analysis targeting seven specific elements (Zn, Pb, Fe, Mn, Ca, Cu, and Ni).

Laboratory procedure for soil sample analysis

The soil samples were homogenized via coning and quartering, then dried at 75°C for 48 hours before being finely ground. A mixture of concentrated HNO_3 and HCl in a 3:1 ratio was used to digest the dried and sieved soil samples. After digestion, the solution was filtered, cooled, and diluted with 25 ml of distilled water. The resulting liquid was then filtered using Whatman No. 0.5 filter paper, and the total elemental content was determined using Atomic Absorption Spectrometry (AAS).

Results

A comparative analysis was carried out between two selected tree species with the goal of identifying which of these species exhibited a greater accumulation efficiency of heavy metals. The study focused on assessing the concentrations of various heavy metals, specifically Zn, Pb, Fe, Cu, Ni, Mn, and Ca within the tree rings of both species. To perform this comparison, a T-test was employed as the statistical method.

The results of this analysis revealed that, regardless of the study sites considered, the *M. champaca* tree consistently exhibited a higher concentration of these heavy metals within its tree rings. In contrast, the *T. grandis* tree displayed a comparatively lower concentration of these heavy metals in its tree rings. This indicates a notable disparity in the heavy metal accumulation between the two tree species, with the *M. champaca* tree showing a higher propensity for accumulating these elements compared to the *T. grandis* tree.

In the soil samples at the study sites, at the forest and roadside, manganese (Mn) exhibited the highest concentration, with lead (Pb) registering the lowest. The depths of 10-20 cm and, in some instances, 20-30 cm, displayed the highest concentrations of HMs. These elements followed the order of Mn > Fe > Ca > Ni > Cu > Zn > Pb. Meanwhile, at the dumping site, nickel (Ni) displayed the lowest concentrations, whereas iron (Fe) showcased the highest. Notably, the maximum concentration was typically observed at a depth of 10 to 20 cm. The arrangement of HM concentration at this site was: Fe > Zn > Pb > Cu > Mn > Ca > Ni.

Conclusion

The study conducted in the Aizawl Forest division focused on the potential of *T. grandis* and *M. champaca* trees in reconstructing contamination history, monitoring heavy metals, and their suitability for phytoremediation. The research analyzed tree ring samples from both tree species, assessing the concentrations of seven metals (Zn, Pb, Fe, Cu, Ni, Mn, and Ca) over various time periods. The findings revealed a consistent increase in heavy metal concentrations year by year, with notable variations.

Surprisingly, trees near pollution source areas such as dumping site and roadside exhibited higher heavy metal concentrations compared to unpolluted areas, highlighting the enduring impact of human activities. Among the two tree species, *M. champaca* had the highest concentration of elements. The annual accumulation of these metals in the tree rings varied, with the highest levels occurring in the most recently formed tree rings.

The study identified *M. champaca* as accumulating higher concentrations of Zinc, Lead, Iron, Copper, and Nickel even exceeding WHO permissible limits, making it a potential candidate tree for phytoremediation of these elements. The research suggests that *M. champaca* can effectively absorb and retain toxic elements, making it suitable for plantation in polluted areas to mitigate soil pollution over extended periods. The reported concentration values surpassed background levels in the region, indicating an increasing pollution level in the study area.