Exploring Novel Strategies for Locating, Assessing, and Rehabilitating Australian Abandoned Coal Mines

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BSc

Thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

13th July 2023

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Certificate of Original Authorship

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Abstract

Mining has a long history in Australia, and while the mining industry has been highly profitable for the national economy, mining activities have left behind a complex legacy of degraded and contaminated lands. To achieve better outcomes for the environment and local communities, this thesis aims to enhance our understanding of the extent of mined lands, the ongoing risks of ecological and human harm, as well as develop new solutions for sites which no longer have custodians or financial means for expensive rehabilitation regimes.

Since the industrial era began, there have been no comprehensive databases of the locations of closed and abandoned mine sites maintained for many regions of the world, including Australia. As such, the locations of many mines have been lost from public knowledge, with no way for managers to assess the risks of land and water contamination. To address this knowledge need, I created an integrated framework for identifying abandoned mine sites using a combination of satellite imagery, historical records, geographic evidence, and local knowledge. I tested this framework within the Newcastle, Illawarra, and Lithgow regions of NSW, Australia and identified 61 abandoned coal mines which are currently unaccounted for, with 56% of all mines in the Newcastle region being unmarked (N = 32), 36% in the Illawarra region (N = 22), and 20% in the Lithgow region (N = 7).

Following on from this, I set out to quantify the continued environmental risks pose by heavy metal soil contamination at three legacy coal mines I identified in the Greater Sydney region. Focusing on heavy metal elements Co, Cu, Zn, Pb, Ni, As, Mn, and Cr concentrations in soils, I show that regardless of time since closure and vegetation status, these mines site are still highly contaminated, with most heavy metal concentrations recorded much higher than Australian National Environment Protection Measures (NEPM). Site comparisons showed interesting differences between heavy metal concentrations within the upper and lower soil profiles, particularly between the remediated and non-remediated sites. Using spatial analysis, I was able to identify hot spot patterns in heavy metal accumulation on site, which demonstrates spatial mapping of pollution is a useful tool for improving our understanding of the origins and movements of mine pollution.

Next, I build on the previous work by comparing two methods for measuring heavy metal contamination and predicted plant uptake, while also trialling five Australian native grasses as mine site remediators. I showed that a combined approach of both Diffusive Gradients in Thin films (DGT) and sequential metal analysis should be considered when conducting site assessments in to heavy metal pollution. My results also indicate that Australian native grass species *Chloris truncata* and *Imperata cylindrica* have potential for phytostabilisation of Cu and Zn on mine sites, while *Dichanthium sericeum* showed phytostabilisation potential for Cu and Cr. *Themeda triandra* also stood out as a capable phytoextractor of Zn pollution.

In summary, this research highlights the importance of improving current practices around legacy mine site assessment and management, while also offering simple but effective ways to do so. I show that while these sites are still a significant source of heavy metal pollution, several Australian native grasses are a viable option to mitigate future pollution risk.

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Acronym List

NEPM – National Environment Protection Measures

NSW – New South Wales

QLD – Queensland

DGT - Diffusive Gradients in Thin films

LMP – Legacy Mines Program

Heavy metals – Metals and metalloids

Pb – Lead

Zn – Zinc

As – Arsenic

Co – Cobalt

Mn – Manganese

Cu – Copper

Cd – Cadmium

Cr – Chromium

EIL – Ecological Investigation Levels

NOAMI – National Orphaned and Abandoned Mines Initiative

CRM-LO-D – Certified References Material Loam

CRM – PINE – Certified Reference Material Pine

EPA – Environmental Protection Agency

ICP – MS – Inductively Coupled Plasma – Mass Spectrometry

GIS - Geographic Information System

WGS84 - World Geodetic System 1984

PCA – Principle Components Analysis

ANZECC - Australian and New Zealand Environment and Conservation Council

DNA - Deoxyribonucleic Acid

PPM – Parts Per Million

PPB – Parts Per Billion

AMD – Acid Mine Drainage

C4 – 4-carbon organic acid (oxaloacetate)

BCF- Bioconcentration Factor

TF – Translocation Factor

EDTA - Ethylene Diamine Tetra acetic Acid

DTPA - Diethylene Triamine Pentacetate Acid

LMWOAs - Low Molecular Weight Organic Acids

NH_4OAc - Ammonium acetate

HNO_3 - Nitric Acid

H_20_2 - Hydrogen Peroxide

Declaration of Contribution to Each Chapter

The contribution of co-investigators and myself are detailed below.

Chapter 2: Lost but Not Forgotten: Identifying Unmapped and Unlisted Environmental Hazards including Abandoned Mines

I lead the conceptualisation, data curation and analysis, investigation, methodology, data visualisation, and writing of the paper, with contributions as follows. Conceptualization, Brad Murray and Megan Murray.; Formal analysis Brad Murray; Validation Megan Murray; Visualization Grace Chambers; Writing—original draft, Brad Murray, Leigh Martin and Megan Murray.; Writing—review and editing, Brad Murray, Leigh Martin and Megan Murray. Also, three anonymous reviewers provided constructive feedback on the original manuscript, which was published in *Sustainability.*

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Chapter 3:

I lead conceptualisation, investigation, methodology and analysis, data interpretation, and writing the chapter, with contributions from others as follows. Thomas and Gary Young investigation, Helen Price methodology analysis, Dan Krix linear model building and data analysis and results, Megan conceptualisation, data interpretation, and Writing – original draft, reviewing, and editing.

Chapter 4:

I designed and led the project, with conceptualisation, investigation, methodology, data interpretation and writing the chapter, with contributions from others as follows. Darren Koppel analytical contribution through making DGT binding gels, and DGT methods, Helen Price sample preparation and analysis; Dan Krix data analysis and visualisation; Megan Murray conceptualisation, data interpretation, and Writing – original draft, reviewing, and editing.

Chapters 1-5:

Final thesis manuscript reviewed and edited by Megan Murray, Kirsty Milner, and Gemma Gillette

Chapter 1: General Introduction

1.1 Australian Research Context

Australia built a large portion of its historical national wealth on the mining boom of the 20th century, with little longer-term understanding of the enduring environmental impacts of these activities (Lamb et al., 2015). As of 2022, Australia remains the largest global exporter of metallurgical coal, liquefied natural gas, iron ore, and bauxite, as well as the second largest global producer of thermal coal, and a leading producer of uranium, gold, and copper (Thurtell et al., 2022). Collectively, these resources are high-value contributors towards the modern national economy, with combined earnings from mining activities generating billions of dollars each year, accounting for 14% of Australia gross domestic product in 2021-22 (MCA, 2020; Thurtell et al., 2022). While mining has had, and continues to play, a significant role in the economic growth of Australia, coal production and exports, in particular thermal coal, will likely wane in the future, as local and global shifts towards renewable energies and resources are realised (Everingham et al., 2018). Renewable resources provide a comparatively cheaper, cleaner, and more accessible form of energy compared to fossil fuels, and are becoming an integral part of Australia's national transition to 'net zero' emissions (Burke et al., 2022; Victoria et al., 2021). As Australia moves away from coal-based energy, lands altered by the operations of coal mining will require rehabilitation, a land management strategy that, historically, has delivered suboptimal outcomes for many areas (Dahlgren, 2022; Unger et al., 2012; Unger et al., 2020). In this Doctoral thesis, I aim to explore and address some of the key problems associated with coal mining rehabilitation in Australia, focusing on the lingering impacts of legacy mines in Greater Sydney Region of New South Wales (NSW). Through a combination of abandoned mine site identification, mapping, site soil contamination profiling, and manipulative glasshouse studies, I aim to elucidate problems with current industry practices while also trialling new, cost-effective, and sustainable approaches to achieve soil decontamination and rehabilitation of Australian coal mines.

While this thesis specifically focuses on abandoned coal mines, much of the literature addressing contamination and rehabilitation of metal and mineral mines is also relevant. Further, I expect my research findings could be easily extrapolated out to mine sites in general. For this reason, throughout the thesis, other relevant types of mining will be discussed interchangeably at times, with coal mining.

1.2 The Legacies of Historic Mining Activities

Mining booms are a global phenomenon, driving widespread changes for the Earth's surface and subsurface environments. Beyond Australia, nations including USA, Canada, Brazil, China, India, and New Zealand also report a deep and extensive legacy of environmental damage in the wake of historical mineral extraction (Lukacs & Ortolano, 2015; Mack et al., 2010; Pope & Trumm, 2015). A mine's ownership and age, including whether the mine is currently operational, closed but maintained by a caretaker organisation, or closed, disowned, and abandoned long ago, often gives some indication of the extent and types of pollution to be expected for the site (Cooke & Lane, 2015; Wright et al., 2015). For example, operational mines across the world are legislated to limit the amount of pollution they generate, however, regulations are often not enough to prevent these operations form polluting, with the building large tailings dams, dumping of waste ores, and intentional releases of wastewater continue to cause ongoing and at times large-scale environmental problems for surrounding regions (Ali et al., 2017; Fernandes et al., 2016). In a notable example of this, the failing of the Bento Rodrigues tailings dam in the state of Minas Gerais, Brazil, in 2015 resulted in the release of 60 million cubic metres of highly contaminated mud which impacted more than 650 Km of downstream river systems and killed 19 people (Dias Carneiro, 2016; Fernandes et al., 2016). The environmental impacts on local biota and ecosystems from this single, catastrophic spill event may be irreversible (Fernandes et al., 2016; Segura et al., 2016). Smaller spills or intentional pollutant releases are more common, with many present-day mines operating with permitted pollution licenses which enables them to release small but regular volumes of contamination (Thomashausen et al., 2018). While intending to prevent environmental catastrophes, studies have shown that many aquatic species simply cannot survive downstream of contaminated flow releases (Perlatti et al., 2021; Price & Wright, 2016; Wright et al., 2017b).

Comparable to intentional ongoing pollution releases from modern mines, abandoned mines can also generate ongoing and significant pollution to surrounding environments. Here I will note that the term abandoned mines is often used interchangeably with legacy, orphan, and/or derelict mines. Throughout this thesis, I will use the term abandoned as an umbrella term to mean any mine or mined land that remediation requirements cannot be assign back to any individual, company, or organisation (Pepper et al., 2021).

As old underground workings destabilise and fill with water, they may consequently become significant sources of environmental pollutants, including wide-reaching contamination of groundwater aquifers and downstream surface waterways (Wang et al., 2021). This type of environmental damage is commonly associated with coal mines, and in particular areas which have a long history of mining. As technology and safety protocols evolved for mining companies, many operations have moved towards direct surface or open-cut mining (Mudd, 2007, 2010; Scott et al., 2010). While common now, this method is vastly different from the traditional approach to coal mining where coal was mechanically remove from horizontal underground workings with vertical shafts providing ventilation, and transport passages for workers and coal (Scott et al., 2010). Many of these operations will access multiple coal seams located at different depths in the strata, inevitably moving within and below the groundwater table. While operational, heavy investment in water pumping is required to keep mine sites from flooding, as groundwater fills the newly created cavities and voids. In most cases, pumping ceases immediately once an operation is closed or abandoned, resulting in the tunnels and shafts inevitably filling with water (Kim & Choi, 2018). There have been numerous studies showing that in flooded underground mine workings, the water is often acidic, while also being saturated with various heavy metals, oxides, and sediments (Mokhov, 2011; Skousen et al., 2019 and references therein; Wright et al., 2018). Over time, water from underground operations seeps to the surface, causing deposition of these contaminants in soils and sediments, leading to long lasting, complex and expensive environmental problems that are often present for decades to come (Cook et al., 2015; Delaney, 1998; Lukacs & Ortolano, 2015; Mack et al., 2010).

In New South Wales, current mines are legislated to rehabilitate under the Mining Act 1992, however, as abandoned mines have no clear owner, the management of these operations falls to the Legacy Mines Program (LMP) which is managed by the NSW government. The LMP states that they have a database of 645 mines, which are prioritised for rehabilitation through identifying risk to human health and the environment. In chapter 2 of this thesis, I will explore this and other similar programs more, applying a method for testing the effectiveness of the current system in identifying, mapping, and rehabilitating abandoned mines in NSW.

1.3 Heavy Metal Contamination from Mines

Metals and metalloids, from here on in this thesis referred to as heavy metals, are one of the most persistent contaminants documented in mine sites across the world (El Rasafi et al., 2021). Lead, zinc, copper, cadmium, arsenic, manganese, and chromium contamination commonly arise from mining process such as the storing of tailings, and waste stockpiles, and mining inducted contaminated ground water, surface run-off, and contaminated soils and dusts (Schneider et al., 2019; Schneider et al., 2022; Worlanyo & Jiangfeng, 2021). It is important to note that levels of soil heavy metal contamination is not always stable, making management difficult. For example, studies have shown that acute spikes in heavy metal concentrations are a significant problem, with increased heavy metal concentrations detected in waterways around mines often recorded after rainfall events (Gore et al., 2007; Harrison et al., 2003; Kavehei et al., 2021; Seen et al., 2004; Wadige et al., 2016). The common factor with these studies is the lack of vegetation on these sites, which results in contaminated overland flows of water causing unmanaged erosion and deposition of contaminated soil and sediments (Kavehei et al., 2021). Once deposited, unstable contaminated soils and sediments can quickly dry and are prone to spreading in the form of lightweight dust. Studies conducted on the soils and dust from mining sites have proven a direct correlation between contaminated soils and increased heavy metal concentrations in humans (Ettler et al., 2020; Tuhy et al., 2021) and animals (Carrasco-Rueda et al., 2020; Hernandez-Plata et al., 2020), with dermal contact or oral ingestion of contaminated dusts, foods, and water cited as common pathways of exposure (Carrasco-Rueda et al., 2020; Ettler et al., 2020; Fu & Xi, 2020; Wcislo et al., 2022). Heavy metals can cause a broad range of severe health effects for those impacted, including respiratory and renal disease, protein damage, metabolism disruption and a range of cancers (Fu & Xi, 2020; Kiran et al., 2021; Sall et al., 2020; Wcislo et al., 2022).

1.4 Environmental Factors Influencing Heavy Metal Bioavailability

To successfully rehabilitate legacy mine sites, a detailed understanding of not only the concentrations of contamination but also the bioavailability of the contaminant is needed. The term ‘bioavailability’ is ambiguous and can mean different things in different contexts, and while it is also an important factor in human health, for the purpose of this thesis I will only explore the effects heavy metal bioavailability has on plants.

Kim et al. (2015) states that the bioavailability of heavy metal in the environment is a 3-step process whereby: (1) environmental availability refers to metals in pores waters and the desorption processes involving a wide range of physiochemical properties; (2) environmental bioavailability which refers to the processes that control uptake by plants; and (3) toxicological bioavailability or accumulation potential of heavy metal inside an organism. In the context of this thesis, I am concerned with the biologically accessible or mobile fraction of heavy metals in both soils and plants, so from here on in this thesis I will combine the terms environmental availability and environmental bioavailability into the umbrella term bioavailability for consistency.

The bioavailability of heavy metal in soils is regulated by a complex mix of chemical reactions between metal species and the soil matrix which influence the solubility, or insolubility, of metals and therefore the ease of movement within the soil matrix and into plant tissues (Antoniadis, Levizou, et al., 2017; Kabala & Singh, 2001; Kim et al., 2015). In order for any metal to be bioavailable for plants, the metal must also be water soluble (Aydinalp & Marinova, 2003; Zeng et al., 2011). It is generally accepted that the sorption (i.e., chemical binding) and desorption of heavy metals in the pore waters of the soil matrix is a process which largely influences the bioavailability of metals for plants (Eid et al., 2020). Sorption-desorption reactions influence heavy metals on the surface of soil particles, regulating movement of metals between solid and solution phases, therefore, sorption capacity may be also a reliable indicator of metal mobility and bioavailability (Basta et al., 2005; Degryse et al., 2009). Several factors influence the sorption capacity of soil include cation exchange capacity (CEC), pH, redox potential, organic matter, soil structure, and presence Fe-Mn oxides (Antoniadis, Levizou, et al., 2017; Antoniadis et al., 2019; Eid et al., 2020; Kabala & Singh, 2001; Kim et al., 2015; Liu et al., 2017; Zeng et al., 2011). However, changes to soil pH and

CEC are the most important factors regulating sorption-desorption kinetics and bioavailability of heavy metals in soils.

1.4.1 pH and Bioavailability

Environmental pH influences the solubility and movement of minerals in both soils and waters (Zeng et al., 2011). pH is a major driving factor in regulating the sorption process in soils due to a mix of H^+ protons being strong competing sorbates and the impact of pH on the ionization of functional groups and metal speciation broadly. Generally, at low pH, protons in the soil matrix compete with free cations for binding sites, resulting in less heavy metal sorption, more free metal cations in the soil solution and, therefore, more bioavailable for plants (Tahervand & Jalali, 2017). With increasing pH, this reaction reverses and the binding of metal cations to soil particles tends to increase (Antoniadis et al., 2019; Shaheen et al., 2013; Zeng et al., 2011). In a study by Sungur (2016) it was shown decreasing pH led to increased mobilisation of Pb, Cd, and Cr, indicating these metals were weakly bound to the soil matrix. Similarly, Chuan et al. (1996), showed while redox potential played a role in metal mobilisation, the main effect came from decreasing the soil pH, with Pb, Cd, and Zn mobility increasing between 14% and 100% depending on the soil pH levels. In the context of abandoned coal mines, given the combination of sandy, water-saturated soils and highly acidic conditions may greatly increase the heavy metal bioavailability (Speir et al., 2003), this should be examined relative to native plants which may be included in rehabilitation plans, and whether the increased metal bioavailability will cause toxicity to plant species, or inversely, if this is able to facilitate metal accumulation in plants and phytoremediation success for a site.

1.5 Assessing Metal Bioavailability Using Diffusive Grade Technology

With complex, interplaying chemical factors influencing the bioavailability of heavy metals in soils, the ability to accurately measure the bioavailable fraction, as opposed to total metal which may be semi-bound to soil particles and not bioavailable, is important. When considering mine sites, the bioavailability of heavy metals can influence many aspects of a rehabilitation plan, including considerations on the safety of site workers. Diffusive gradients in thin films (DGT) is a technology developed by Zhang et al. (1998) for the purposes of measuring bioavailable trace elements in water, but has since been expanded to accurately measure bioavailable elements in soils and sediments, whilst also predicted to correlate with plant uptake (Agbenin & Welp, 2012; Davison & Zhang, 2012; Harper et al., 1998; Nolan et al., 2005; Santner et al., 2015; Zhang et al., 2001)

DGT works on the principle of Fick's first law of diffusion, where the flux of elements will move down a concentration gradient from high to low (Ernstberger et al., 2005; Harper et al., 1998; Zhang et al., 1998). DGT technology uses this principle to measure the flux of metals moving down a known concentration gradient over time. Stated briefly, DGT samplers consist of a simple composition of different membrane layers sandwiched into a plastic piston, with inner layers composed of ion exchange layer, resin layer, diffusive gel layer, and ion-permeable hydrogel filter membrane (Harper et al., 1998). Through contact with the soil, available ions in pore waters move through the membrane and diffusive gel layer before being irreversibly bound within the resin gel (Zhang et al., 1998). Measuring ions recovered from the resin gel over known deployment time will give an indication of the mass of bioavailable heavy metal in the soil solution (Santner et al., 2015; Zhang et al., 1998; Zhang et al., 2001). Resin binding also results in the alteration of the heavy metal concentration gradient in the soil matrix and causes the movement of trace elements from soil solids to soil solution (Ernstberger et al., 2005). This process replicates diffusion, desorption, and supply of heavy metal from soil matrices into plant roots (Agbenin & Welp, 2012; Ernstberger et al., 2005; Koppel et al., 2021; Yoon et al., 2006), making it an ideal technique for the comparison of total metals to bioavailable metals in soils, while also identifying correlations with plant health, growth, and metal accumulation.

1.6 Plant Response to Metal and Metalloid Contamination

It is generally accepted that there are nine essential metal micronutrients needed for plant nutrition and growth: copper (Cu), iron (Fe), zinc (Zn), nickel (Ni), molybdenum (Mo), chloride (Cl), selenium (Se), boron (B), and manganese (Mn) (Hansch & Mendel, 2009). Without these, plants cannot achieve the range of cellular processes necessary for homeostasis and tissue growth. While these essential elements are required in soils to support plant survival, excessive concentrations can cause cellular toxicity. Other heavy metals have no known use in plant nutrition or survival; the most geologically abundant of these include lead (Pb), arsenic (As), cadmium (Cd), and mercury (Hg) (Gaur & Adholeya, 2004). Although this second group of non-essential metals may seem more directly harmful for plant communities, any heavy metal occurring in high concentrations can cause severe environmental problems (Hall, 2002). Globally, a small number of plant species have adapted to survive in phytotoxic levels (i.e., generally agreed as harmful to plants) of certain heavy metals in soils, with each species shown to employ one or more of a range of different tolerance and survival mechanisms (Clemens, 2019). If a plant species is able to actively remove heavy metals from soils or water, it is considered to be a 'phytoremediator' species.

1.7 Phytoremediation: Definitions and Processes

Phytoremediation is a broad term which encompasses a range of different plant-pollutant uptake and adhesion mechanisms but, in general terms, these plants can decontaminate sites as well as stabilise contaminants *in situ* in an environmentally sustainable and cost-effective manner (Arthur et al., 2005). Depending on the plant species, and pollutant type, a range of different decontamination mechanisms have been defined in plants. Four of the most widely known processes are phytoextraction, (i.e., where heavy metals are removed from soil into the plants biomass), phytovolatilisation (i.e., modifying contaminant and releasing to the atmosphere), phytostabilisation (i.e., containing contaminant within the soil) and rhizofiltration (i.e., filtration of water using submerged plant roots) (Chaney et al., 1997; Salt et al., 1995; Salt et al., 1998). Other technologies include, phytohydraulics, where deep rooted plants draw contaminated water out of aquifers (Hong et al., 2001) and phytodegradation, or the breaking down of harmful organic compounds into safer products, have also become more commonplace terms within the literature (Rahman & Hasegawa, 2011).

As a general rule, plants well-adapted to survive in harsh environments (e.g., lower in key nutrients and higher in toxic contaminants) may be suitable candidates for phytoremediation. In an extensive review by Van der Ent et al. (2013), plants were classified into four different groups depending on their relationship with heavy metals in soil: (1) 'Normal' plants, which simply do not survive in the presence of toxic levels of heavy metals; (2) 'Bioindicator' species, which naturally grow on contaminated soils and often have traces of metals in their tissues; (3) 'Excluders' which are capable of surviving over a wide range of heavy metal concentrations, doing so by implementing specialised strategies which minimise metal uptake; and (4) 'Accumulators' which are a rare type of plant that can not only withstand relatively high concentrations of heavy metals compared to all other species, but also translocate these metals into their below and above ground biomass without experiencing phytotoxicity.

There are over 374,000 unique species of plants on Earth (Christenhusz & Byng, 2016). The number of species found to be heavy metal accumulators has been rising as phytoremediation research progresses, with over 450 heavy metal accumulating species identified spanning across 45 angiosperm families (Bhargava et al., 2012; Krzciuk & Gałuszka, 2015; Rascio & Navari-Izzo, 2011). About 25% of these heavy metal accumulators reside within the family *Brassicaceae*; other families rich in hyperaccumulators include *Asteraceae, Euphorbiaceae, Rubiaceae, Fabaceae, Scrophulariacea, Myrtaceae, Proteaceae, Caryophylaceae,* and *Tiliaceae* (Rascio & Navari-Izzo, 2011; Reeves, 2006; Reeves et al., 2018). By definition, a true 'hyperaccumulator' is a phytoremediator which transfers high concentrations of metals from soils into above-ground biomass (Reeves, 2003). This concept was further articulated by Van der Ent et al. (2013) who proposed the following concentration criteria for different metals and metalloids in dried above-ground foliage: 100 µg/g for Cd, Se and Tl; 300 µg/g for Co, Cu and Cr; 1,000 µg/g for Ni, Pb and As; 3,000 µg/g for Zn; and 10,000 µg/g for Mn, with plants growing in their natural habitats.

Focusing on key heavy metals examined within this thesis, globally, there are a total of 53 Cu, 8 Pb, and 20 Zn-hyperaccumulating species that are currently known (Reeves et al., 2018). While these specific hyperaccumulators are relatively rare compared to the whole global flora, focused research has been invested into identifying new plant species with the ability to remove higher amounts of metals from soils. Resulting from this, two types of metallophytes (i.e., metal tolerant plant) have been identified (Baker et al., 2010). Species endemic to soils possessing high levels of natural metal concentrations have been classified as 'obligate' metallophytes. These occur solely within this type of environment, and due to physical limitations, cannot survive in non-metalliferous environments (Van der Ent et al., 2013). The second type of metallophyte is known as 'facultative' species. These are species which are not completely restricted to metal rich soil environments and, in some cases, display divergent populations of species. For example, different populations of the herbaceous flowering species *Anisopappus chinensis* collected from metal rich and non-metalliferous areas in Africa expressed significantly different capacities for heavy metal uptake (Lange et al., 2017). It is important to define the obligate and facultative metallophytes, as when looking for species which will likely survive in mine site rehabilitation, facultative plants provide a more practical option.

1.8 Australian Phytoremediation: Hyperaccumulators and Phytostabilisers

Within Australia, only two plant species currently meet the strict criteria for heavy metal hyperaccumulation: *Stackhousia tryonii* and *Gossia bidwillii* (Abubakari et al., 2021; Bhatia et al., 2005; Bhatia et al., 2004; Fernando et al., 2007). *Stackhousia tryonii* is a small herbaceous species endemic to the serpentine soils of Queensland and has been shown to accumulate very high concentrations of Ni (3,640 to 41,260 mg / kg^{-1}) into above ground biomass (Bhatia et al., 2005; Bhatia et al., 2004). While a remarkable species, it is unfeasible to use as a phytoremediator for Ni-polluted soils as it is known to be an obligate metallophyte. The second native Australian hyperaccumulator species is more promising, and further research is warranted. *Gossia bidwillii* is a sub-tropical *Myrtaceae* shrub from Queensland and northern New South Wales and has been shown to accumulate significant amounts of Mn, Zn, and Co in both young and old leaves (Abubakari et al., 2021; Fernando et al., 2007). Two other native Australian species have showed promise as Ni accumulators, *Rostellullaria adscendens var. hispida* (1790 to 2190 mg / kg^{-1}) and *Commelina ensifolia* (1090 to 1490 mg / kg^{-1}) (Reeves, 2003). Yet, the ability of these species to accumulate high levels of Ni is highly variable, not only between different populations of the two species but even inside the tissues of individual plants (Reeves et al., 2015).

While globally hyperaccumulator species are rare (Rascio & Navari-Izzo, 2011), many species of Australian native plants have demonstrated use as heavy metal excluders, therefore able to be incorporated in phytostabilisation plantings. Recent research conducted on soil naturally occurring high levels of Zn, Cu, and Pb, showed species *Eriachne mucronata, Bulbostylis barbata, Polycarpaea spirostylis*, and *Tephrosia virens* all significantly restricted heavy metal uptake, keeping concentrations in above ground biomass well below soil concentrations (Tang et al., 2021; Tang et al., 2022). Several species of *Acacia* have also been identified as excluders of Zn, Cu, and Pb, with species found growing well on abandoned mine tailings and waste dumps (Kabas et al., 2017; Lamb et al., 2010; Nirola, Megharaj, Aryal, & Naidu, 2016; Nirola, Megharaj, Aryal, Thavamani, et al., 2016). The ability of these species to tolerate high soil contamination levels by restricting heavy metal outside of root tissues indicates Australian native plant species have value for rehabilitating contaminated mine sites within Australia and promoting the re-establishment of native biodiversity. This will be one of the key questions addressed in Chapter 4 of this thesis.

1.9 Native Grasses for Contaminated Australian Mines

Since European colonisation, the vast majority of the biodiverse grassy woodlands which once dominated much of NSW have been largely cleared for residential, agricultural, or industrial purposes, including mine site establishment (Ladouceur & Mayfield, 2017). This has resulted in the degradation of essential regions of temperate NSW and their associated ecosystem services, with reduced soil quality, dryland salinity, habitat fragmentation, increases in invasive weed density, and nutrient enrichment now commonplace issues (Dobson et al., 2006; Prober et al., 2002; Smith et al., 2018). Similar activities have impacted the grasslands of northern NSW and southern Queensland, with widespread clearing resulting in many of these areas now classified as endangered ecological communities (Morgan et al., 2017). While little can be done to erase the errors of past, returning highly degraded regions to pre-disturbance integrity is an area of global research which has received much attention in the last 40 years. Of note, mining companies operating in many nations of the globe must now agree to return the land to a similar condition to what was originally found on the site (Dragovich & Patterson, 1995). Due to the positioning of Australia's coal deposits, a focus on the regeneration of Australian native grasslands and increasing the abundance and cover of native grasses should be a priority. In order to succeed, the components of any successful rehabilitation plan must include the community composition, species richness, structure, and densities to be correctly tailored for a given site (Shackelford et al., 2018). Although several mining companies have publicly strived to achieve this goal, the results to date have shown mixed success, often accomplishing lower species diversity and less sustainable outcomes than originally envisioned (Shackelford et al., 2018).

While native grasses are touted as one of the most climate resilient and cost-effective options for Australian site rehabilitation, several factors have been shown to limit their successful implementation. For example, low seed germination and low seedling emergence have been cited in case studies of native grasses (Farley et al., 2013). The longer-term establishment requirements of native species in general has limited the success of mine rehabilitation programs, with one study suggesting that as many as 97% of mine sites post-rehabilitation could not be classified as similar to their pre-mined quality (Shackelford et al., 2018). In the eastern seaboard states of NSW and Queensland (QLD), much of the land used for traditional below-ground mining has already experienced other transformation due to agricultural practices on the surface, therefore, a return to native grasslands still suitable for animal grazing has been deemed a more acceptable target for land managers (Huxtable et al., 2005). In this vein, further information on the establishment, growth, and success of native grasses in degraded soils is an important step in progressing the field of grassland rehabilitation.

1.10 Chapter Outlines

The overarching aims of this thesis were to (1) determine the prevalence of abandoned mines in a landscape formerly occupied by a large number of active mines than in the present day; (2) assess the ongoing impacts of heavy metal soil contamination from abandoned mines on surrounding soils; (3) compare the accuracy of two extraction methods for measuring heavy metal concentrations in Australian native grasses grown ex-situ in mine soil; and (4) test the capacity of Australian native grasses to phytoremediate soils contaminated with heavy metals identified in the field soils found at abandoned mines. The research in this thesis was performed within the Greater Sydney region, in New South Wales on the east coast of Australia. This region provided a valuable opportunity to assess the surface impacts caused by abandoned coal mines due to the region's long history of underground mining, paired with a paucity of appropriate post-closure mine management.

The chapters in this thesis fall within the overarching subject of abandoned mine management. In **Chapter 2**, a desktop approach was selected as the most suitable method for accurately considering the broad geographical scope of the study. This consisted of compiling current databases, community knowledge, and satellite imagery to determine what number of abandoned coal mines where missing from current databases. Ground-truthing of sites identified by employing this desktop methodology resulted in the selection of three different mine sites for further investigation in **Chapters 3 and 4**. Previous research on two of the three selected sites has shown significant problems with heavy metal rich acidic waters leaching from underground workings. While this link has been strongly documented in previous studies, in **Chapter 3**, I set out to employ a methodology that would identify if heavy metal contamination was still present in the soil of these legacy sites, and further document if the movement of contaminated water, soils, sediments, and dusts can be identified through heat mapping the concentration of contaminants. The original plan for Chapter 3 of this thesis was to analyse both soil and plant samples found at the three selected abandoned mine sites, with the hope of identifying if plants growing on these contaminated sites were up taking the metals found within the soil. Unfortunately, the Canyon Colliery was situated in one of the worst hit areas of the 2019-2020 Black Summer Bushfires, with all vegetation at the site severely impacted. For this reason, I reassessed my research aims and focused solely on heavy metal soil analysis. A sequential metal analysis technique for measuring total heavy metals in soils was chosen as it is cited as the most commonly used within both scientific studies and professional site assessments. While the sequential soil sampling method is the mostly commonly used, as you will read throughout this thesis, total metal concentration is not always the most accurate measure of the level of threat posed by a contaminant. The methodology selected for **Chapter 4** addressed this issue by comparing the accuracy of different heavy metal sampling techniques in the soils and tissues of five Australian native grasses. Specially made rhizotrons were created to allow non-destructive access to the soil and rhizosphere of five Australian native grasses grown under glasshouse conditions. The soils, root tissues, and shoot tissues were analysed to determine which method was the most accurate predictor of metal uptake by plants. In this chapter, I compared the ability of the five selected Australian native grass species to accumulate heavy metals within the root and shoot tissues. Within the literature, bioconcentration and translocation factors of greater than one indicate a species may be considered a phytostabiliser or phytoextractor. The methodology chosen to address this aim sought to identify species useful for the rehabilitation of the metal affected soils found within **Chapter 3** of this thesis. These different but linked methodologies were chosen to addresses a range of questions that I believe builds on the current knowledge base centred on the broad but connected topic of mine management and rehabilitation. I will now briefly introduce specific chapter aims before each is readdressed in detail within each chapter and readdressed and synthesise in **Chapter 5**.

The aim of **Chapter 2** was to establish and test empirically a novel framework for identifying abandoned mines currently not listed on accessible databases. I first aimed to 1) create a new framework for identifying abandoned mines; 2) test this framework within the heavily mined Sydney basin; and 3) use the data collected to create examples of up-to-date geospatial maps. When I began researching the issues caused by abandoned mines in the Greater Sydney region, it quickly became apparent that mines were missing from the publically accessible databases. It is arguable the most important first step in the management of abandoned mines that an accurate and up to date database of sites is being kept. To address this knowledge need, I conducted a desktop study to identify the proportion of NSW underground coal mines that are not listed in current government databases. My research framework allowed the discovery of 61 unmapped coal mines which are not listed on current NSW databases or maps. The main outcome of this work was the creation of a new framework to find and identify lost mines by utilising a wide variety of publicly accessible evidence. This new framework was tested within regions of Newcastle, Lithgow, and Illawarra, with newly identified lost mines able to be added to currently incomplete Australian public inventories and results displayed with GIS maps.

Building on this research, **Chapter 3** set out to quantify the ongoing risks of soil contamination in abandoned mines by sampling three abandoned mine sites identified in **Chapter 2**. A wealth of high-quality research on the effects of legacy mines on water quality within NSW exists, but there is little information regarding the conditions of the soil on these sites. Hence, I aimed to discover if the soil of abandoned coal mines is contaminated with heavy metals. To do so, I selected two un-remediated sites and one semi-remediate site from the northern and western coalfield of the Greater Sydney Basin. At each site, top and bottom soil profiles were analysed for total concentrations of Cr, As, Pb, Mn, Ni, Co, Cu and Zn. These metals were chosen for analysis through a combination of pre-sampling and data collected from the Nation Pollutant Inventory and compared against Ecological Investigation Levels (EIL) for soil and groundwater provided by the National Environment Protection Measure (NEPM) in Australia and corresponding international guidelines. I then compared differences in heavy metal contamination across the three sites, which have seen varied levels of remediation effort. The two mines in the northern coalfield, Neath and Abermain No 2 Colliery, have seen no rehabilitation since closing decades ago, while the Canyon Colliery situated within the western coalfield was rehabilitated to a degree considered acceptable to be amalgamated back into the Blue Mountains National Park. This presented me with a unique opportunity to compare metal concentrations within the upper and lower profiles of the soil, where I predicted the vegetation present on the Canyon site would phytostabilise the site, resulting in higher levels of metal remaining within the upper layer of soil when compare to Neath and Abermain No. 2. Lastly, I focused on visualising the soil contamination found on the three mine sites and identifying if contamination patterns were associated with historical mining activities, erosive processes, or a mixture of both. Areas consistent with historical mining activities and naturally created gullies, channels, and seeps where identified and mapped before a geospatial layer containing heavy metal concentrations was overlayed. I then used spatial visualisation tools to plot the movement of heavy metals vertically and laterally across the three mine sites, and to characterise whether the contamination is uniform across the site or still displaying remnant hotspots from former activities. Results from these questions showed that the three abandoned mines sites are presently contaminated with levels well above Australian and international guidelines. Further, there was no clear indication that the vegetation cap on the Canyon Colliery site was containing heavy metals within the upper profile, although, the cap did appear to contain a significant amount of metals within the lower profile indicating that more research is warranted. Finally, that heavy metal concentrations did in fact hotspot around areas of historical storage, and increased concentrations across sites appeared to follow erosive processes. The results from Chapter 3 add information to the previously under researched area soil contamination within and around NSW numerous abandoned mines. The data collected in this chapter shows the importance of managing abandoned coal mines, while also offering information that could be used to for targeted soil sampling resulting in more simply and effective site soil analysis methodologies.

Chapter 3 showed that the soils at the sampled abandoned coal mines are still contaminated with a range of heavy metals and those metals are freely spreading through erosive processes. Previous research confirms that waterways downstream of abandoned mines within the study area are consistently contaminated with the same heavy metals identified in chapter 3.

In Chapter 2 of this thesis, I show that with the Greater Sydney area alone, there are a large number of mines which are currently classified as abandoned, meaning ownership and associated rehabilitation costs are almost impossible to assig. For this reason, expensive soil techniques for removal of heavy metal contamination are unlikely to be implemented.

In **Chapter 4** I provide evidence based solutions to the contamination problems highlighted in **Chapters 2 and 3** by comparing two different heavy metal sampling techniques, with the hope of identifying the most accurate test for quantifying soil contamination levels and associated plant metal uptake. For eight different heavy metals, sequential soil sampling (i.e., total metal) was combined with DGT film analysis to examine correlations between heavy metal soil bioavailability and the uptake of metals by five Australian native grasses grown in mine soils collected from Abermain Number 2 Colliery, NSW. I then examined the phytoremediation potential of the same five Australian native grasses by calculating the bioconcentration factors and translocation factors. These two measures are a relatively simple method of identifying plants species suitable for use in the technologies of phytostabilisation or phytoextraction. Results from this chapter showed that while DGT was a more accurate predictor for Ni and Zn uptake in T. triandra and C. truncata, both techniques proved as overall good predictors for plant heavy metal uptake. This chapter also identified three Australian native grass species with the potential for use as phytostabilisers and one species as a potential phytoextractor. Further, all five species tested survived well within simulated mine site conditions, indicating that all species warrant further research within this important field.

In **Chapter 5** I synthesise all my research findings and discusses patterns in the context of current research, as well as future directions for this important research field. In this chapter the general aims for each data chapter are readdressed and a common thread is provided for how each chapter links together, with suggestions for further research included.

Chapter 2: Lost but Not Forgotten: Identifying Unmapped and Unlisted Environmental Hazards including Abandoned Mines

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2.1. Abstract

Environmental databases play an essential role in the management of land and communities, including mapping and monitoring environmental hazards over time (i.e., abandoned mines). Over the last century, mines have closed for many reasons, but there has been no comprehensive database of the locations of closed and abandoned mine sites kept for many regions of the world. As such, the locations of many mines have been lost from public knowledge, with no way for managers to assess the risks of land and water contamination, as well as subsidence. To address this knowledge need, we present an integrated framework for identifying abandoned mine sites using a combination of satellite imagery, historical records, geographic evidence, and local knowledge. We tested this framework within the Newcastle, Illawarra, and Lithgow regions of NSW, Australia. We identified 61 abandoned coal mines which are currently unaccounted for in mine registries, with 56% of all mines in the Newcastle region being unmarked (N = 32), 36% in the Illawarra region (N = 22), and 20% in the Lithgow region (N = 7). These findings demonstrate that our framework has promising utility in identifying historic and unmarked environmental hazards in both national and international contexts.

2.2. Introduction

The first data chapter of my thesis was a desktop study focused on building a framework for identifying abandoned mines which are currently unmarked on publicly accessible databases. The initial plan for this thesis was to begin with soil and vegetation sampling of abandoned coal mines found within the greater Sydney region. When examining the databases, there appeared to be a significant gap in the number of mines displayed. This lead me to the first research aims of my thesis which were 1) create a new framework for identifying unmarked coal mines; 2) to test this framework within coal mining hot spots within the Sydney basin, and 3) to create examples of up-to-date maps which spatially compare missing sites to existing data on government databases. This chapter became the foundation of the thesis, with both preceding chapters linked specifically to the data collected by implementing this framework. For chapter 3, three mines discovered using the framework from chapter 2 were selected for heavy metal soil analysis to discover if these site do pose a risk. The results from this study identified a significant risk, leading the collection of soil from the most contaminated mine site is identified in chapters 2 and 3 for use in a glasshouse phytoremediation experiment in chapter 4. This chapter was published in the international journal of Sustainability, and therefore some it may be edited or presented with slight differences when compared to the preceding data chapters.

2.2.1 Unmarked and Unmapped Abandoned Mines

Environmental databases can provide a historical reference of species and conditions, often utilized to create and test models to predict future change and impacts (Goldewijk, 2001; Kattge et al., 2011; Walther, 2010; Walther et al., 2002). Such databases play an essential role in the management of land and communities, with models now capable of predicting many important risks, from epidemiological analyses of health issues (Jones et al., 2008), species range shifts over time (Chen et al., 2011; Thomas et al., 2004; Walther, 2010; Walther et al., 2002), assessment of bushfire severity (Dutta et al., 2016), to the localised impacts of climate change (Benard, 2015; Thomas et al., 2004). A common goal of public databases is to accurately collect and organise large volumes of data in ways that will allow continuous updating. Ideally, this is done using open-source web-based systems which can be accessed and edited by relevant responsible stakeholders. The use of databases is particularly important when examining issues over continuous timeframes. When databases are regularly updated with fresh and relevant information, large scale trends and patterns may become more apparent, leading to better decision-making capabilities. In this context, however, accurate information regarding particular environmental risks and degradation may be difficult to obtain. This is because records may be incomplete or absent, particularly where hazardous industrial activities may have been conducted prior to the introduction of modern approval and regulatory processes. Indeed, historic and hazardous land-use activities such as mining, gas works, smelters and the petroleum industry are a major source of land contamination and long- term ecological impairment (Lamb et al., 2015; Peterson et al., 2003; Z. H. Weng et al., 2012; Wright et al., 2017a; Wright et al., 2018). Identifying such 'lost' environmental and hazardous legacies is a vital step toward remediating damaged ecosystems and mitigating impacts on public health and safety.

In the context of mining activities, countries such as the United States of America, Canada, and England all continue to experience environmental legacies as a result of mining (Alpers et al., 2016; Armitage et al., 2007; Azcue & Nriagu, 1995; Cherry et al., 2001; Fields, 2003; Mayes et al., 2009; Thienpont et al., 2016). While it might not be possible to determine the complete number of abandoned mines, which can be described as land that has been mined but rehabilitation requirements cannot be assign back to any individual, company, or organisation, several attempts have been made to collate this data, and to varying degrees display the information in databases and maps (EPA, 2004; OSMRE, 2019; TCA, 2019; USGS, 2011). This is an important step in the identification and management of abandoned mines, however, the scale of the problem combined with a lack of funding has often meant producing accurate and up to date data, particularly on a national scale, is a significant problem. The importance of creating a national mining inventory within England and Wales was realised after privatization of the mining sector resulted in the closure of many underground mines. As the mines where no longer actively managed, they filled with water resulting in continued significant degradation of the nation's waterways (Johnston 2008). In one study conducted for the UK Government's Department of Environment, Food and Rural Affairs, it was shown that abandoned mines within England and Wales may be polluting as much as 10% of the water bodies across the UK (Jarvis et al., 2008). The UK coal authority provides an interactive map of mining activities across the UK (TCA, 2019) however, very little information can be extracted from this map. Similarly, the Abandoned Mine Land Inventory System (AMLIS) portal is an initiative that aims to identify and remediate abandoned mines across the USA by combining the knowledge and resources of multiple levels of government, local tribes, and organisations (OSMRE, 2019). The initiative estimates that there are up to 500,000 abandoned mines throughout the country, many of which have been classified as a threat to environment and health. The US geological society is one of the partners that aims to collate the data from all departments and produce a national map. While this is a step in the right direction, currently no such map exists.

One country that has made a large-scale effort to not only identify, but also map the sites of abandoned mines is Canada. The National Orphaned and Abandoned Mines Initiative (NOAMI) is a multijurisdictional co-operative initiative among government, industry, Aboriginal traditional owners, and other associated organisations. While the program has a large scope, one of the main goals at the creation of NOAMI was to build an interactive web based national inventory, which was launched in 2015. Using the inventory, it is easy to see the impact abandoned mines have and continue to have within the country. For example, 749 places classified as abandoned sites which have been classified as a potential threat to human health, and/or the environment. There are a further 6434 sites which are classified as unlikely or unable to impact human health or the environment (NOAMI, 2018).

Here, we present a novel approach to identify unmapped and unlisted hazardous environmental legacies. The success of overseas programs such as NOAMI has relied heavily on government support and funding. We believe the easy to apply nature of this method may minimize the amount of resources which are currently needed to direct programs so large. Our approach integrates information from a diverse range of sources including government databases, local industry and historical publications, community records, personal accounts, as well as satellite imagery to spatially map environmental legacies that have until now been unlisted. Importantly, this approach has general applicability and could be applied to any type of industry that has left a legacy of currently unidentified environmental hazards. In the present study, we demonstrate the utility of our approach by building a new database of hazardous environmental legacies resulting from a long history of coal mining in the Sydney Basin of eastern Australia. In previous times, collecting information of this nature concerning the spatial distribution of coal mines was not always of the highest priority.

Indeed, prior to the worldwide tightening of mining industry standards, information about not only conditions of mines, but also locations of mines were rarely collected or centralized for easy access. Our intention with building this framework is to provide a state-wide best practice approach for environmental hazard identification. Ideally, we would like to see the creation of an NSW abandoned mine database which in time could be amalgamated with the current databases from all states and territories across Australia, with the long-term aim of creating a national database.

2.3. Materials and Methods

2.3.1. Study region

Resource mining in Australia has been historically extensive and is currently estimated to have resulted in the creation of > 55,000 abandoned mine sites scattered around the country (Unger et al., 2012). In the state of New South Wales (NSW) alone, there are estimated to be as many as 600 abandoned mines, with 112 situated on protected crown land (Hehir, 2014). Furthermore, at least seven of these sites are currently considered to be high risk to both human health and the environment (Hehir, 2014). This problem is exacerbated by the lack of information regarding location and condition of many abandoned mines, with NSW lacking a sufficient database of relevant information (Unger et al., 2012). Many of these sites have seen very little or no rehabilitation, resulting in large scale degradation of the surrounding landscape, which will likely continue into the future.

The NSW Planning, Industry and Environment administers the Legacy Mines Program which does not have current mapping available for public use (NSW Government, 2023). All Australia states are independent of each other and only one website, administered by Geoscience Australia (GA), provides a national-scale hazard inventory with The Australian Mines Atlas. One of the key objectives of the mines atlas is to provide a up to date, detailed site-specific information for mining sites within Australia (GA, 2017). While this page is a good source of information for currently operational mines, it does not feature many older, historical mines that have been inactive for several decades.

Located on the east coast of Australia, the Sydney Basin is an area of Permian-Triassic sedimentary rock ranging from Batemans Bay in the South to Newcastle in the north. The

Sydney Basin covers an area of 64,000 km^2, and contains one the largest black coal reserves in the country. The Sydney Basin is divided into 4 smaller sub regional coalfields: The North under the city of Newcastle (NC); North-West centred around the Hunter Valley (NWC); the West Beginning at Lithgow (WC); the South covering the Illawarra (SC). Presently, the largest production of mined materials come from the North-Western coalfield, with a large number of active surface mining operations. As the aim of this research is to focus on ceased mining operations, the NWC will not be included in this study.

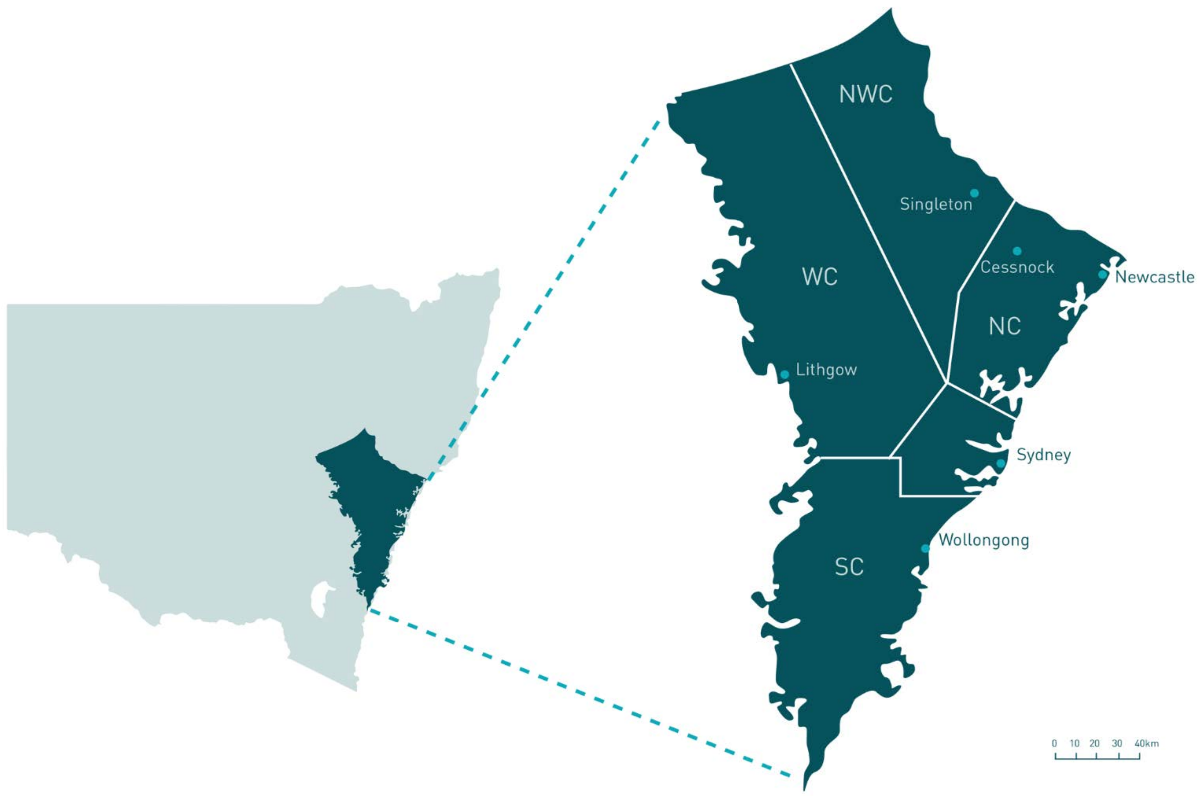

Figure 2.1. State map of NSW with insert highlighting the 4 regional coalfields examined in this study.

2.3.1.1. Sub-region 1: Northern Coalfield (NC)

Now consisting of primarily vineyards and other agricultural industry, the Northern Coalfields were once subjected to heavy underground coal extraction. Located 200 km from Sydney and close to the coastal town of Newcastle, the area relied on the shallow, sulfur-rich coal reserves common in the area (Ward et al., 2007). At the peak of production in 1925, the industry employed more than 10,000 workers and produced a large amount of exportable coal (Delaney, 1998). Currently, 2000 people from the area are employed within the mining industry, however no new mines are planned as the focus shifts towards the north-western and western coalfields (Rand, 2014).

2.3.1.2. Sub-region 2: Western Coalfield (WC)

The Western Coalfields begin approximately 100 km west of Sydney CBD and holds a high level or national and international importance. A large proportion of the coal reserve sits beneath The Greater Blue Mountains World Heritage Area (GBMWHA), which comprises the largest area of undisturbed, protected bushland in Australia. This area is also home to range or protected, threatened and endemic flora and fauna (OEH, 2018). Of similar importance are the water production values within the area, with the majority of the Sydney city catchment falling within the western coalfield. While mining has slowed within the coalfield, a mixture of underground and surface mining operations are still producing in the area.

2.3.1.3. Sub-region 3: Southern Coalfield (SC)

The Southern Coalfields are found within the Illawarra region 50 kms south of Sydney. The area is considered a biodiversity hotspot, with a large amount of unique local flora and fauna (OEH, 2018). The high biodiversity in the area is attributed to the steep rise from coastal plane to a plateau which creates a rainforest environment rarely found in the Sydney area (OEH, 2018). While the ecological importance is well known, the area is also a major coal mining region in NSW, with a large number of underground operations.

2.3.2. Framework for Identifying Unlisted and Unmarked Mines

The Southern, Western and Northern parts of the Sydney Basin were examined independently of each other in an attempt to quantify the numbers and locations of all coal mining operations, both historical and currently active. To do this, we created a three-step process to recover all possible information about previous mining operations within the designated areas (Figure 2.2).

Figure 2.2. The framework for discovering abandoned and unregistered mines for addition into current databases.

In order to fully assess the potential extent and impacts of hazardous industry contamination and land degradation, it is imperative to create a framework for locating and classifying unmarked and unmapped hazards. A framework such as this is a valuable land management tool, not only for Australian lands, but for all countries impacted by historical hazardous industries. The Sydney basin provides a unique opportunity to test this framework by examining the effects of coal mining in its various forms, as a variety of operational, recently closed, and abandoned underground mines are scattered across the basin.

This study aims to i) create a new framework for identifying environmental hazards; ii) to test this framework within coal mining hot spots within the Sydney basin, and iii) to create examples of up-to-date maps. Using a multi-disciplinary approach, data collected using the new framework will be spatially mapped and compared to existing data on government databases. We aim to report likely raw materials on sites, site condition, and the potential ecological risks posed by the previously unidentified mines. Essentially, the goal of this framework is to provide a best-practice approach for environmental hazard identification that can be readily adapted for other purposes.

2.3.2.1. Step 1. Assemble Evidence

Search of Government Databases and Existing Inventories

The first step was to consult all available government data relating to location of coal mines of all operational status. These data were collected primarily from local and state government reports and websites. For all areas, marked mines were identified using the government website "Australian Mines Atlas" and "Australian Geoscience Information Network (AUSGIN)". These digital tools provided a base of knowledge for each designated area. From here, all other government data sourced from areas such as the Subsidence Board, NSW Minerals Council, local area council, and Office of Environment and Heritage were examined.

Examination of Historical Publications from Local Industries

The next step of the process was then to look into the local industries operating within the area. Large companies such as Broken Hill Propriety Ltd. (BHP), Glencore, Peabody Energy, Wollongong Coal, and Coal and Allied were all used to collected information about the current mining operations of my sample areas. All of these operators provide reasonably detailed information regarding current operations, future planning, history, and rehabilitation records of previous projects.

Investigation of local knowledge: Historical community records and personal accounts

The third and often most fruitful step comes from collecting local knowledge. Here a range of different stake holders are engaged, including historians, environmental groups, libraries, newspapers and universities. All of these different groups and organisations provided access to a range of resources including websites, journals, grey literature, reports and books. For each of the three study sites, this step is where the majority of previously unknown sites were located. Two areas of local knowledge in particular stood out against the others: the environmental groups following mining pollution events; and the historians documenting the building of industry within communities. We found many environmental groups had significant local knowledge and were good at engaging media to get their message of mine pollution out into the community. Similarly, as coal mining and their associated rail once played a large part in building of these areas, the detail included in many of these books, websites, and reports was invaluable.

2.3.2.2. Step 2. Data Conformation

A mixture of satellite imaging and ground truthing was used to identify the exact location of the mines listed. Image analysis followed a similar method to (Mudd, 2010) where images from the most recent cloud free day were sourced from Google Earth Pro, version 9.142.0.1 CNES Airbus satellite. All images examined at a scale of 100 m with eye altitude of 1600 m. Much of the information came with coordinates or a general location, however these were often found to be inaccurate following satellite map analysis. The exact locations of many of the historical mine sites were found through examining maps and satellite images of the focal regions. A range of particular markers were identified, with common markers including the presence of equipment, capped mine entry points, unusual water bodies, and the visible presence of coal chitter piles (Figure 2.3). Other markers include nearby streets named after mining-related activities (e.g., Colliery St), and long, linear 'scars' in the landscape left behind by old railway lines (Figure 2.4) and cement covered portals all further helped to identify the exact location of many long-closed mining operations with a high degree of certainty

2.3.2.3. Step 3. Establish Accurate Information Systems

The final step of this project is to collate newly discovered site data into an accessible information system to provide more information for the public and a higher degree of certainty regarding the data. After the creation of up-to-date maps and information systems, merging of existing and discovered mine sites provides the most reliable estimation of the presence of underground coal mines within the regions examined. For the purposes of this project, three new maps of each region were generated, showing existing and discovered mines and GPS coordinates of the most likely portal locations for each mine were also provided based on visual evidence, along with the last known names for each mine and the dates each mine was closed (i.e., if known).

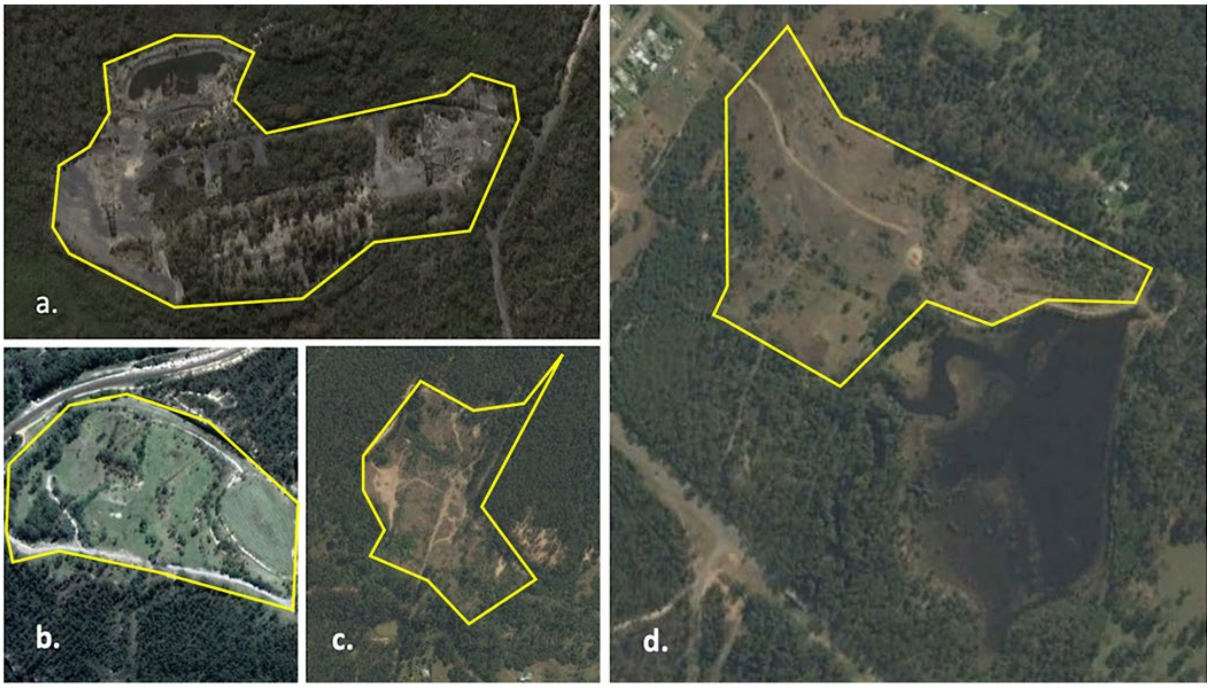

Figure 2.3. Satellite imagery taken from latest version of Google Earth Pro showing (a) North Cliff Colliery, (b) Canyon Colliery, (c) Neath Colliery, (d) Abermain No. 2 Colliery. Yellow line indicates each mines surface footprint. Photos captured April 30, 2020.

Figure 2.4. Satellite imagery of Neath Colliery with annotations displaying the locations of the original train line (- -) and nearby Colliery St. Photo captured April 30, 2020.

2.4. Results

A total of 90 marked mines were located and identified using the framework (Appendix A). After comprehensive enquiries investigating published information and local knowledge, a total of 61 unmarked mines were discovered (Figure 2.5).

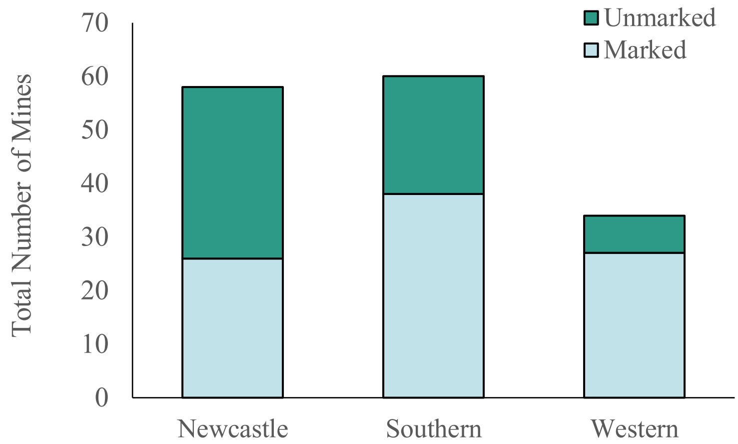

Figure 2.5. Number of mines marked on the government databases and the unmarked mines identified for each coalfield region in the Sydney basin.

Unmarked mines comprise a large proportion of total mines within each of the three examined regions. The NC holds the highest proportion of unmarked mines, with a total of 56% of all mines in the area being unmarked (n = 32) compared to marked (n = 25) (Figure 2.6). Following this is the SC, with 36% of all known mines in the area being unmarked (n = 22) compared to marked (n = 38) (Figure 2.7). Lastly, the WC contains 20% more unmarked mines (n = 7) than are listed on the public inventory (n = 27) (Figure 2.8). A large proportion on historic or abandoned mines are currently unmarked within the NC (Figure 2.6).

The region of Kurri has a particularly high density of unmarked mine sites, with many of these positioned within close proximity to major rivers, or tributaries. Similarly, the SC (Figure 2.7) sees a large number of unmarked mines in close proximity to marked ones. Due to the topography of the area, the majority of mine entries and pit top structures are situated in a line running along the Illawarra escarpment.

The vast majority of unmarked mines in the SC region are situated within 10 km of the coast. Due to the steep topography and high rainfall, mining run-off terminates directly into the Indian Ocean. Unmarked mines in the WC (Figure 2.8) are situated close to major rivers and tributaries feeding the World Heritage listed Blue Mountains National Park and one of Sydney's largest drinking water reservoirs. Through the comprehensive search of records and documents of mining in NSW, 44 instances of dates when the unmarked mines were permanently closed for operations were also found. Collating data on the closure of unmarked mines reveals an apparent pattern of increasing closure rates from the 1800s onwards (Figure 2.9). In both regions combined, only two mine closures went unmarked after the 1960–1989 period, with both mines located in the SC. No data were found relating to unmarked mine closures in the WC.

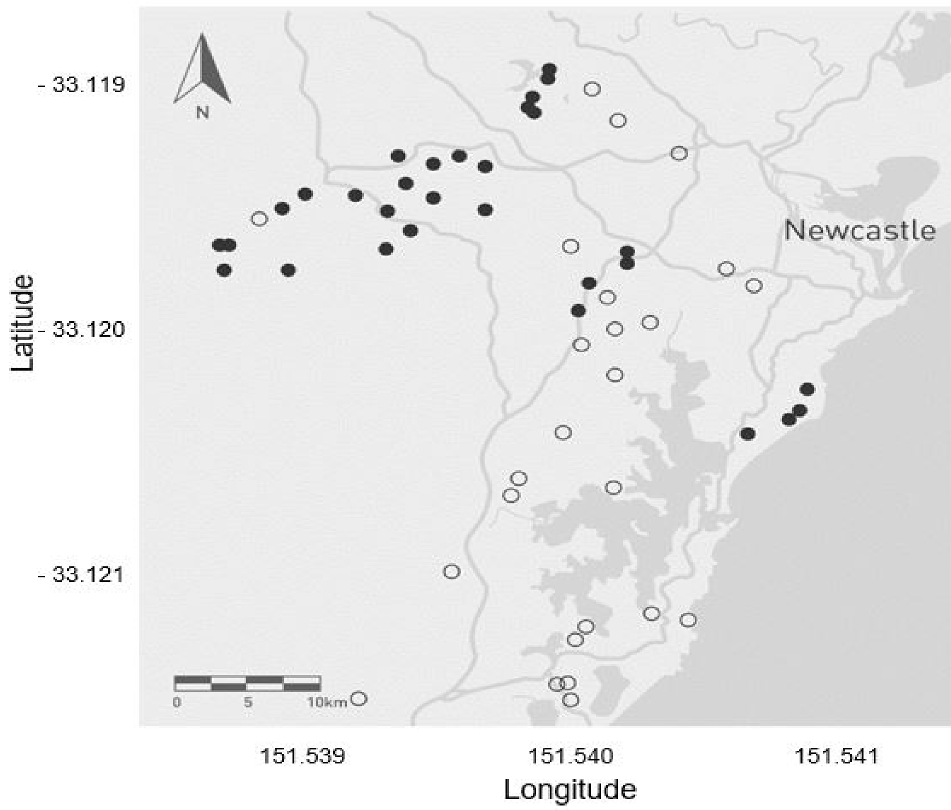

Figure 2.6. Marked mines (●) and unmarked mines (○) of the Newcastle Coalfields.

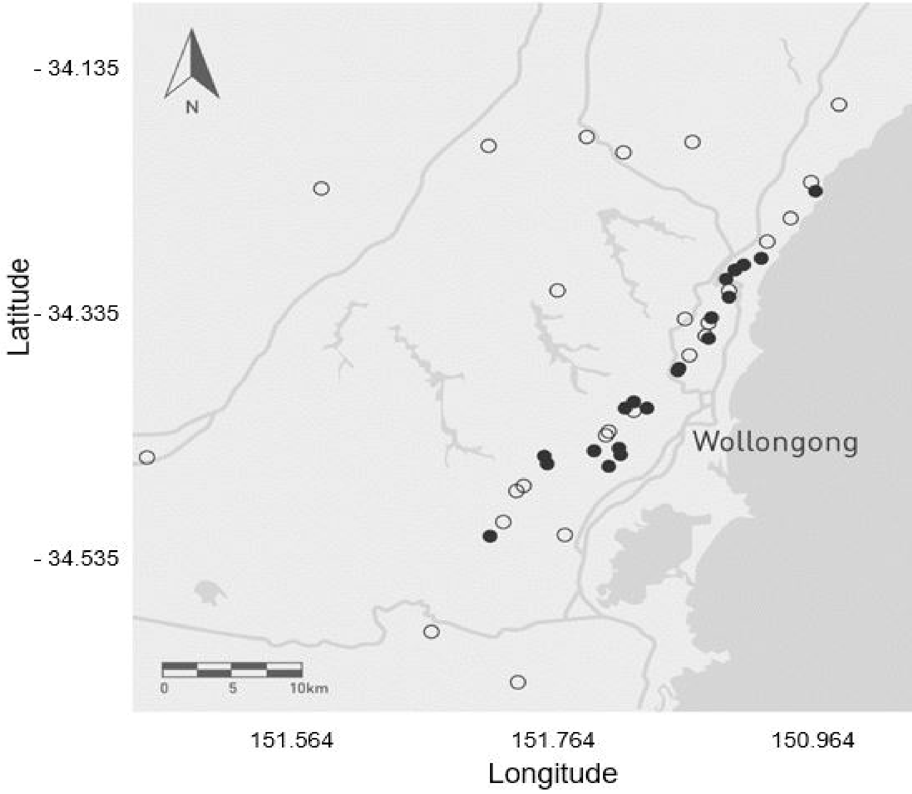

Figure 2.7. Marked mines (●) and unmarked mines (○) of the Southern Coalfields.

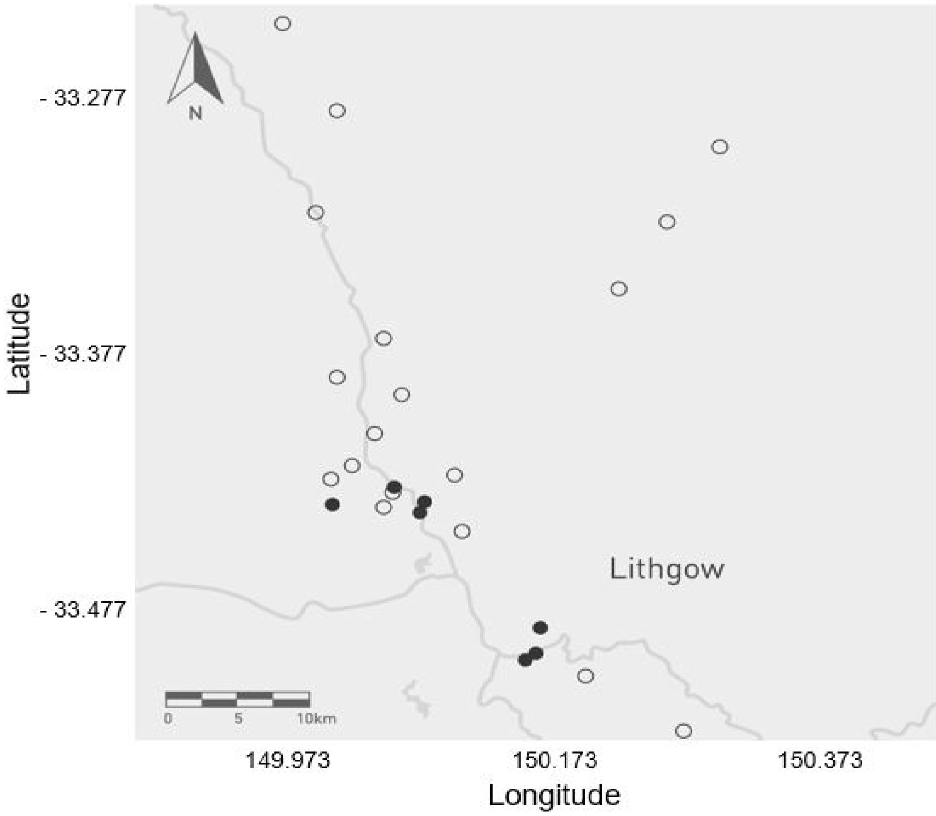

Figure 2.8. Marked mines (●) and unmarked mines (○) of the Western Coalfields.

The National Pollutant Inventory 2020–2021 (NPI, 2021) was used to further investigate the likelihood of contamination risk from abandoned mines (Figure 2.9). Based on this model for Australia, the vast quantity of contamination for each of the six heavy metals are still confined to the original mine sites. This indicates abandoned, un-remediated mines have the potential for heavy metal leaching under fluctuating environmental conditions (e.g., weathering, erosion, floods, and land subsidence)

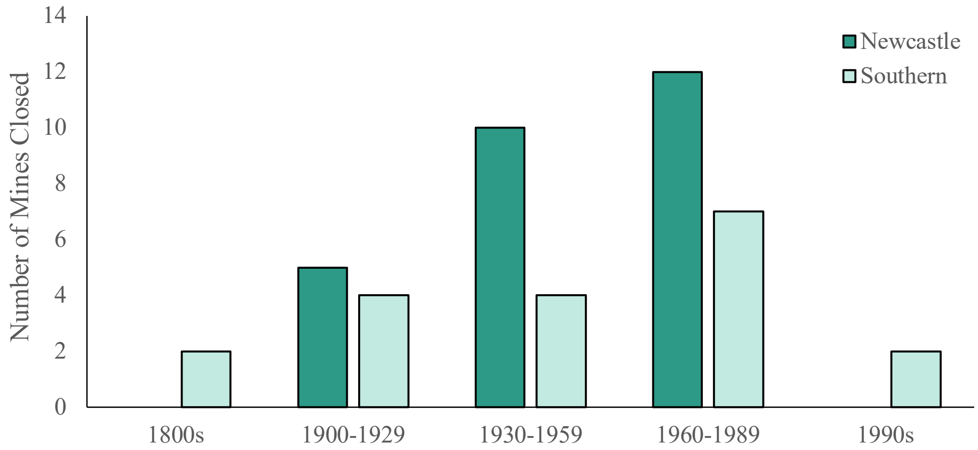

***Figure 2.9**. Closures of unmarked mines in Newcastle and Southern Coalfields across time.*

2.5. Discussion

2.5.1. The Most Impacting Abandoned Mines

Analysing the temporal patterns in mine closures within the region reveals peak closure patterns for the districts; Both the SC and NC had the highest closures of mines not found on government databases within the period between 1960 and 1990 (Figure 2.9). This time period aligns with the introduction of the Environment Planning and Assessment Act (1979) which required operators of mines and other hazardous industries to implement a range of different site remediation measures while operating and post-closure (NSW Government, 1979). This act, combined with mines becoming less profitable or exhausting coal reserves, may have pushed many operators to close before they were legislatively obliged to rehabilitate. Based on combined satellite and historical evidence, it appears that the main objective when closing a mine was to fill or cap the portals, remove any pit top structures, and cover the area with available fill. This resulted in a number of abandoned sites which have shown little evidence of recovery when compared to the surrounding unmined references sites. Early closure in the face of a tightening regulatory environment and subsequent inadequate remediation is likely to a feature common to many historic hazardous industries. While laws and regulations now require the responsible party to rehabilitate these sites, the companies which owned them in many cases no longer in exist, making the enforcement of remedial works next to impossible.

While more than 50 years have passed since the beginning of the peak closure period of underground mining operations in the Illawarra and Newcastle regions, many sites still display visible signs of degradation, with very little to no native vegetation established on many of sites (Figure 2.3). The lack of vegetation re-establishment is likely compounded by several factors, including over compacting of soil, lack of nutrients, low pH, erosion, run-off from contaminated mine workings, and heavy metal contamination (Zhi Dang et al., 2002; Hu et al., 2015; Lamb et al., 2015; Maddocks et al., 2009; Z. Weng et al., 2012). Data taken from the National Pollutant Inventory indicate that coal mining contributed thousands of kilograms of zinc, manganese, lead, nickel, and copper into the environment. Interestingly, the pollutant inventory classifies aggregated heavy metal contamination collected at coal mine sites into two different categories: Emissions or transfers. Emissions are the uncontrolled, unintentional release of heavy metals into the environment, where transfers are the moving and storing of contaminants into tailings dams or other storage areas (NPI, 2021). The latter is by far the greatest contributor of heavy metals into the environment, making up more than 98% of total contamination. While it is a positive that these are not being freely released into the environment, it does lead to the question of what happens to these post-mine closure.

2.5.2. The Ongoing Impacts of Unmarked Mines

Metals such as Mn, Fe, Zn, Ni, Cu, Cr, and Pb are common examples of what may remain on sites post-mining, left to move freely through natural cycles of wind and water erosion (Bhuiyan et al., 2010; Dudka & Adriano, 1997; Li et al., 2014; Schaider et al., 2007; Schneider et al., 2019; Wright et al., 2018). In the areas of NC and SC, rainfall induced erosion of the surface poses a major problem, with contaminated water free to move into local rivers and streams (Zhi Dang et al., 2002). The Neath Colliery site is one such example. The soil on the site has distinctive yellow colouring, which follows the water erosion marks. With very little vegetation present, the yellowing of the soil follows the erosion tracks made by rain and subsequent run-off. Furthermore, it appears that the underground workings are now full of water, and constant seep issues red and orange water onto the surface of the site (Bell et al., 2000; Mokhov, 2011). The yellowing of the soil and deep red and orange of the water are indicative of acid mine drainage (Ali et al., 2017). The pollution on this site is significant and post any rainfall event contamination likely move freely into the nearby Swamp Creek. While a problem, the Neath Colliery is just one of eleven unmarked sites situated close to Swamp Creek alone.

Contaminated runoff may also be a significant problem within the Illawarra region due to its broadly steep topography, excessive annual rainfall, and close proximity to high density housing, and environmentally sensitive areas. The surface operations of all current and historic mines in the area are situated alone the high plateau of the Illawarra escarpment, an area which spans altitudes from sea level to over 500 m (Ashcroft et al., 2008). This combined with an average annual rainfall of 1100 mm (BOM, 2018) results in high levels of storm water runoff travelling through a range of sensitive areas before terminating in the Pacific Ocean. With 22 mine sites unmarked, the questions of proper site remediation post closure are surely valid. Without knowledge of the previous site contamination above, heavy metals may be causing a range of environmental issues. Water sampling conducted within the SC and WC has identified significant impacts caused by intentional and unintentional water releases (Price & Wright, 2016). Studies measuring the impacts of coal mining on river health have commonly shown increases in Al, Zn, Fe, Cu, As, Mn, Pb, and Ni (Ali et al., 2017; Belmer et al., 2014; Wright & Ryan, 2016). The excessive levels of these contaminants lead to reductions in macroinvertebrate species richness and abundance (Belmer et al., 2014; Wright et al., 2017a). These studies also stated that this effect continued for as much as 22 km downstream of the initial sampling point. In the context of the Illawarra region, contamination from unmarked mine sites may be causing a range of problems to local communities, and sensitive terrestrial and aquatic environments.

2.5.3 Considerations to Improve Public Mine Inventories

The practice of marking all mine sites will result in a more successful and detailed form of mine site monitoring; however, the current practice of marking sites with singular points may not be detailed enough to constitute and best practice approach to displaying all necessary information. While sufficient for open cut operations, using a singular point to identify underground operations—which often span for kilometres in several directions— can lead to problems, in particular regarding post-closure remediation works. By moving away from the point-based locator, and towards a polygon style system, stakeholders may receive a more correct representation of all possible impacts cause by underground developments. All current mines show the extent of their underground operations as a polygon within their environmental assessment plans. The polygons in these maps give the viewer a more accurate idea of the possible impacts and extend of underground operations.

The tightening of mining regulations has resulted in easy public access to newer site maps; however, plans of older mines were found to be much harder to locate during this investigation. We found that the majority of the unmarked mines did not have any publicly available site maps. The Work Health and Safety (Mines) Act 2013, states that for the safety of all workers accurate plans of mines must be retained and the blueprint of all historic mining activities in the area must be sought out to prevent mining accidents. This indicates that these plans are on record but currently difficult for the public and the scientific community to access.

Although mining operators maintain detailed maps of underground workings, these maps are seldom released to the public. Due to the extent of underground mining activities, and the potential for environmental contamination and subsidence beyond the marked portal point, it is suggested that public inventories of mine sites be revised to include area polygons reflecting the mine's actual footprint below-ground, rather than single points at the portal entry point, to improve the accuracy of assessing risks. The Canyon Colliery in the Blue Mountains NP is marked as a single point on all relevant databases and has seen a level of site remediation since its closure in 1995. While this is a positive step for land management, the lack of information regarding the underground workings of the mine has been shown to be problematic for monitoring contamination originating from the old mine. Situated 3.5 km east of the mine, and well into the NP, two old drainage shafts constantly leak acidic water into Jinki and Dalpura Creeks, which are both tributaries of the Grose River (Wright, 2012). Zinc levels coming from the Dalpura drain site have increased by more than 3000% when compared to the upper reaches of the river, with a value of 388 ppb. This value is well in excess of the ANZECC trigger value of 8 ppb, and should be a main focus of the Canyon Collieries site remediation (ANZECC, 2000). This is just one example of how marking mine sites as a polygon, rather than a point, will increase mining land use transparency and also improve site monitoring, contaminant risk assessment, and the land management and remediation outcomes for mining companies in Australia.

By applying the site discovery method described to regions of interest, it is possible to comprise a more correct database of hazardous industry operations and areas of likely environmental impact, both past and present. This provides a critical resource for land managers who seek, to identify and rectify the impacts of environmental hazards. This should be a priority step for government on local, state, and national levels. Furthermore, it is suggested that current descriptive information on the location of mines and other hazards should be updated to map sites as polygons reflecting the entire operation's footprint. This will lead to more accurate impact representation, as well as better remediation outcomes in the land management sector.

2.6. Limitations

This study developed and tested a framework for discovering lost environmental hazards using the study area of NSW. The framework was tested in three different regions of NSW using one type of mine (i.e., below-ground coal) and does not include assessing and mapping the below-ground workings or on-ground measurements of contamination or subsidence risk. The 'confirmation' of the sites within this paper indicates presence rather than extent, and further on-ground analysis is required to accurately assess the extent of each mine.

2.7. Conclusions

Unmarked environmental hazards, such as abandoned mines, pose serious risks to the environment and communities. Identifying such hazards is particularly difficult where industries historically ceased operations prior to the introduction of regulatory standards. Difficulties in identifying abandoned hazardous activities may be overcome using a combination of satellite imagery, historical records, geographic evidence, and local knowledge. A framework applying this approach was successful in identifying 61 abandoned coal mines in three coalfields in NSW Australia. Identifying previously unmarked environmental hazards is critical for understanding current and future risks for landowners, traditional custodians, and governments alike.

Chapter 3: Investigating the Contamination Profiles of Three Large Abandoned Coal Mines in New South Wales

3.1. Abstract

The Greater Sydney Basin is one of the world's largest resources of bituminous black coal and since its discovery the area has been heavily mined, many of which have now been abandoned. In recent years, much research has shown that the abandoned mines in the area are contributing significant amounts of heavy metal contamination to surrounding waterways, but very little research has focused on the soil contamination present at these sites. I address this question by investigating the ongoing presence of heavy metal soil pollution across three large, legacy underground coal mines situated within the Greater Sydney Basin. Sequential heavy metal analysis using Induced Coupled Plasma Spectrometry was conducted on soil samples taken from the top and bottom profiles and results compared to Australian and international soil standards for ecological and human health. My results found that the three mines sampled all recorded maximum levels above Australian and international environmental investigation levels with some analytes recorded values up to 40 times higher than recommended maximum levels. While all mines were contaminated, there was distinct differences between the upper and lower profiles when comparing between analytes and mine sites, and spatial analysis of the data showed movement of heavy metals appear to be following patterns of erosive processes. This study shows that more investment into abandoned mine management is needed to prevent the potential spread of heavy metal contamination from soils to surrounding waterways.

3.2. Introduction

In chapter 3, the heavy metal contamination of three abandoned coal mines identified in chapter 2 was investigated. Much research has examined water contamination coming from both abandoned and operational coal mines in the Greater Sydney region, but through my research I identified a lack on scientific data about the condition of the soil on these sites. The aims of this chapter were to 1) discover if abandoned coal mines in Australia still contain environmentally harmful levels of heavy metals; 2) to compare the soil profiles of the three mine sites to identify whether there has been positive decontamination impacts resulting from rudimentary site rehabilitation activities; 3) to identify heterogeneity in the concentrations of heavy metals across the mine surfaces, with hotspots anticipated around train lines and likely historical stockpiles of coal. This chapter builds on the research presented in chapter 2, showing that due to a significant contamination risk contained within the soil, accurate and update databases of location and condition of abandoned mines is an essential factor in abandoned mine management. Further, the data collected in this chapter was used to identify the most contaminated soil of the three mines studied, which was collected and used in the phytoremediation experiment of chapter 4.

3.2.1. The Contamination Potential of Abandoned Mines

Despite scientific consensus on the central role fossil fuels play in accelerating global warming, coal combustion remains a common power source used throughout the globe. Although global demand for coal decreased in 2020, the economic rebound in the wake of the Coronavirus emergency has seen coal use increase in 2021. The annual IEA Global Energy Review indicated a recent 5% rebound in global coal use (IEA, 2021) compared to pre-covid 2019 levels. As mining operations expand to extract more resources, so too does the industry's environmental footprint. Coal mining has been identified as one of the largest sources of heavy metal contamination relative to all other anthropogenic processes (Weng et al., 2012).

A significant body of research has been conducted on the surface soil polluting potential of heavy metals in black coal. In terms of its geological composition, coal is a highly combustible sedimentary rock comprised of organic and inorganic materials (Ward, 2016). Primarily consisting of carbon, oxygen, nitrogen, and hydrogen, coal also contains non-combustible inorganics referred to as 'ash content' (O'Keefe et al., 2013). Ash content varies across deposits, and can include non-coal sedimentary rocks, volcanic tuffs and low-quality coal (Dai et al., 2017). Metals and metalloids, hereby known as heavy metals, can be found in trace quantities throughout coal and coal ash with varying quantities of Pb, Ni, Zn, Co, Mn often recorded (Dai et al., 2017; Querol et al., 1995; Ward, 2016). The substantial volumes of coal excavated to surface environments can cause a magnifying effect for local ecosystems, where heavy metal elements naturally found at relatively trace levels may become vastly elevated through mining and cause significant environmental problems (Mudd, 2010). Due to the inability of heavy metals to be broken down into safer compounds, unlike many organic pollutants, each individual stage of the mining process creates the opportunity for persisting heavy metal contamination (Cujic et al., 2016). This results in the formation of potential heavy metal pollution pathways which, once created, can be highly difficult to control (Cooke & Lane, 2015; Cujic et al., 2016).

3.2.2. Mine Site Activities and Heavy Metal Contamination

Despite the type of mining, or commodity extracted, one of the most common contributors of heavy metal into soils and sediments is through the on-site storage of stockpiles, waste rock, tailings, and ashes (Ali et al., 2018; Pandey et al., 2016; Shu et al., 2002; Z. Weng et al., 2012).

Several studies have identified the storing of wastes as significant contributors of environmental heavy metal contamination across all types of mining (Johnson & Hallberg, 2005; Rodriguez et al., 2009). In recent years, environmental impact plans combined with government legislation should result in more stringent prevention of this type of pollution (Belmer et al., 2014; Everingham et al., 2018) compared to traditional operations which did not sufficiently manage the spread of heavy metals from waste products well. In many instances, worker activities on these sites and beyond site boundaries exacerbated widespread regional contamination.

For example, creating and maintaining large stockpiles of mine tailings and waste rock on the surface of mine sites has been shown to cause elevated heavy metal concentrations across a much broader area (Zhi Dang et al., 2002; Fernandez-Caliani et al., 2009). Prior to current environmental protection practices, these heavy metal-rich materials were also used as surface site fill, post mine closure, effectively assisting the persistence and spread of heavy metal pollutants across the sites (Bell et al., 2001; El Khalil et al., 2008). Centuries of mining in Australia has provided a unique opportunity to study the problems of heavy metals in post-mined soils. For instance, movement of contaminants through normal weathering processes is a common problem. Regardless of a mine's age, research has shown that heavy metal concentrations increase in topographical depressions and move downhill towards rivers and creeks (Dang et al., 2002). This is further compounded by the almost universal nature of legacy mine sites supporting little-to-no vegetation establishment (Ashley et al., 2004). Studies have identified heavy metal concentrations in low lying soils and sediments of legacy mines will increase in years of high rainfall (Abraham et al., 2018; Harrison et al., 2003; Kavehei et al., 2021). For example, between the years of 2007 and 2008, the Sunny Corner lead-zinc-silver mine in Western NSW recorded large rises in heavy metal concentrations within the site sediments of Cu (299 to 750), Zn (369 to 1900), and Pb (580 to 7300 mg / kg) after two consecutive La Niña years. By 2010, following a vastly drier El Niño year, the concentrations had fallen to 440, 706, and 5,200 mg/ kg respectively (Kavehei et al., 2021). Similarly, Harrison et al. (2003) showed heavy metal fluctuations from abandoned mine sites in the Greater Blue Mountains World Heritage Area, NSW, were closely correlated with high and low rainfall events.

3.2.3. The New South Wales Context

The northern, southern, and western coalfields of the Greater Sydney Basin are one of the world's largest resources of bituminous black coal (Thurtell et al., 2022; Z. Weng et al., 2012). Since widespread mining operations commenced in 1790s, the coalfields of Greater Sydney have endured heavy volumes of underground coal mining operations (Hutton, 2009; Mudd, 2010). In more recent years, the environmental impacts of mining activities in this region have been well-researched, with particular focus given to mines within the southern and western coalfields. Previous research in these regions includes monitoring heavy metals found in waterways downstream of operational and closed mines. Elevated levels of Zn, Mn, Ni, and Co are often measured in the receiving streams of underground coal mines (Ali et al., 2017; Ali et al., 2018; Belmer et al., 2014; Birch et al., 2001; Wright & Ryan, 2016). Evidence from a

2017 environmental study in Australia, revealed that the water chemistry of the Wollangambe River was significantly altered for kilometres downstream of a mine discharge when compared to unimpacted ecological reference sites (Wright et al., 2017b). Notable shifts in macroinvertebrate communities were also recorded, with decreases in species richness and abundance correlated with water heavy metal concentrations coming from mining discharge points. Further, Price and Wright (2016) showed levels of heavy metal pollution in nearby waterways were similar when comparing both currently operational and long closed and abandoned mine sites in Australia. For water bodies, this infers that the environmental impacts of operational coal mines may be similar to the long-term water pollution still generated from flooded workings seeping from abandoned coal mine sites. In comparison, considerably less research has been conducted on the impacts of similar mines found in the Northern Coalfield (NC). Further, while large quantities of research regarding the water quality of these sites has been recorded, very little research has focused on the legacy impacts of heavy metal accumulation in the topsoil of closed coal mines in the NC (Herndon et al., 2019).

3.3. Research Aims

The overarching goal of this chapter was to investigate the ongoing presence of heavy metal soil pollution across three large, legacy underground coal mines situated within the Greater Sydney Basin. In this study, I examined two large, abandoned mine sites from the NC region while also sampling one large semi-remediated site from the Western Coalmine (WC) region.

I aimed to discover if abandoned coal mines in Australia still contain environmentally harmful levels of heavy metals, with a focus on Cu, As, Cr, Pb, Zn, Mn, Co, and Ni and their individual spatial patterns across the sites. I hypothesised that heavy metal contamination would still be present across the mine sites, despite decades of operational inactivity, in concentrations exceeding safe Australian EIL's and other international exposure guidelines. Secondly, I aimed to compare the soil profiles of the three mine sites to identify whether there has been positive decontamination impacts resulting from rudimentary site rehabilitation activities. I hypothesised that the rehabilitated mine site (Canyon colliery) would show higher levels of heavy metals in the upper soil layer than Neath and Abermain collieries due to phytostabilisation by the vegetation on the site.

Thirdly, due to the age of these study sites and previous sources of heavy metals (e.g., large waste stockpiles), I hypothesised that there would be significant heterogeneity in the concentrations of heavy metals across the mine surfaces, with hotspots anticipated around train lines and likely historical stockpiles of coal. I further hypothesise that the sites with little to no vegetation would see significant movement from hotspot areas as metals move due to natural erosive processes.

3.4. Materials and Methods

Soil samples were collected from three abandoned coal mines in the Permian-Triassic coal deposit of the Greater Sydney Basin on the East Coast of Australia (Hutton, 2009). The Greater Sydney Basin is situated within the Greater Sydney-Gunnedah-Bowen Basin, which spans over 1,500 km (GA, 2017). The area is split geographically into coalfield subregions, with the northern coalfield (NC) around the Newcastle and Hunter Valley region; the southern coalfield (SC) of Wollongong; and the western coalfields (WC) beginning near Lithgow (Fig 3.1). Originally, I planned to sample sites from each of the different coalfields in the Greater Sydney Basin, however, due to restricted access, only sites from the western and northern coalfields could be sampled. The Neath and Abermain sites in the northern coalfield were chosen because they possess visible signs of coal waste rock, erosion, and little vegetation. The Canyon site situated in the western coalfield was chosen as it has seen a decent amount of remediation while remaining visually similar to the northern sites in terms of coal waste

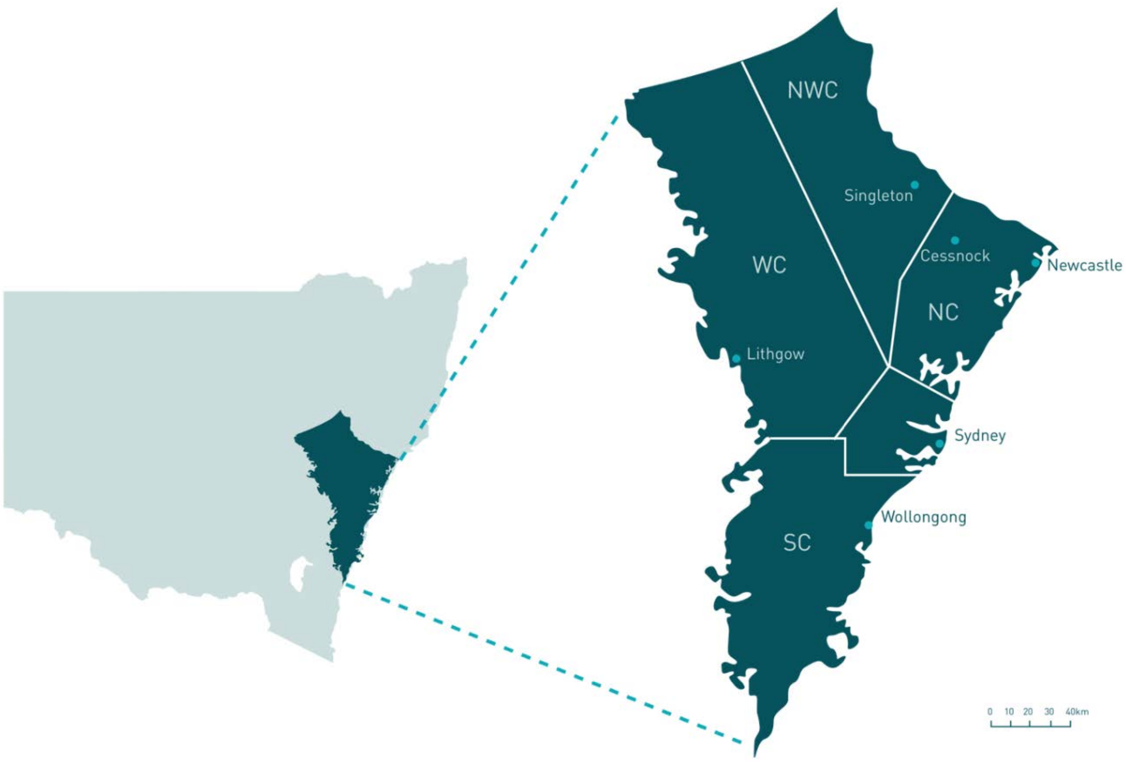

Figure 3.1. A regional map of New South Wales showing the four distinct coal fields that make up the Greater Sydney Basin

3.4.1. Abandoned Mine Sites in Study

i. Abermain No 2 Colliery, Kurri Kurri

The Abermain no 2. Colliery was an underground coal mine which operated in the northern coal fields in the Kurri Kurri region west of Newcastle (-32.85994, 151.40132). A large-scale operation for its time, the mine operated for 53 years between 1910 - 1963 (Delaney, 1998). Soil on the site is strongly varied in surface composition, however, it is predominantly comprised of up of loamy sand, and sand mixed with large remnant pieces of coal waste rock (Fig 3.2). Much of the sand classification is likely from the fine particles of coal dust common on the site.

Figure 3.2. Visible coal waste rock widespread across the grounds of abandoned Abermain No. 2 Colliery. Photo taken October 2019.

Topographically, the site falls from 60 m elevation at the most southern point to 55 m elevation at the northwest corner. While the lowest point is 55 m, most of the site only experiences a slight gradient of 2 metres both north to south, and east to west. Examining historical data collected in Chapter 2, the train line and two surface portals are all that remains of the above-ground operations. Bricks and other building materials scattered on parts of the site may infer the location of buildings, but further site investigation is required. Currently, a proportion of the site is zoned ‘SP2’ for infrastructure and is being used for storage of road gravels and other construction materials. The roads to the site were well maintained. No visible evidence of acid mine drainage, or yellow crusts in the coal suggests a lower Sulphur content on the surface relative to other mines in the region.

ii. Neath Colliery, Neath

The Neath Colliery is located within the Northern Coalfields, approximately 120 km north of Sydney CBD (151.4089, -32.8204). The mine ceased production in 1959, yet some coal washing operations continued until 1988 (Delaney, 1998). Remains of the colliery operations are no longer visible, however scars from the train line remain in the landscape.

Figure 3.3. Coal wastes and land surface cracks visible at Neath Colliery.
Photo taken October 2019.

The most topographically distinct of the three sites with a total elevation fall of 16 m over 400 m. The lowest point is found at 59 m elevation on the most eastern aspect of the site, where a gradual slope rises towards the west to 65 m, before steeply rising to a maximum elevation of 75 m at the south-west corner. While east to west sees gradation, the site is flat when measured from north to south with a slight fall of 2 metres. A seep from the now covered up cast shaft is seeping water onto the surface of the site, heading in an easterly direction towards Swamp Creek, which eventually feeds into the Hunter River. The water from the seep flows into two small man-made dams and ranges in colour from vibrant yellow, oranges, and deep red. Much of the surface of the water in the top dam is covered in a thick black material. Soil is a composite of sandy loam (Fig 3.3 - 3.4) mixed with coal waste rock. In areas where water has eroded into the surface of site, a yellow discoloration has accumulated. While the site is large, and little is known about the below-ground pit top structures, the position of the old railway offered a promising focal point for sampling.

The impacted land around what was once the Neath Colliery is approximately 15 Ha, and predominantly bare or covered with various grasses, native shrubs, and *Acacia spp*. (Fig 3.4).

Figure 3.4. Native shrubs growing in coal-heavy sandy waste rock.

Photo taken October 2019.

Canyon Colliery, Bell

Canyon Colliery is located within the Western Coalfields approximately 95 km NW of the Sydney CBD (-33.53188, 150.2704). Since its closure in 1997, the site has been remediated to some degree, with native grasses and a scattering of small native trees covering most of the site (Fig 3.5). While there is a range of native Australian species present, they appear to be stunted in growth, and in generally unhealthy condition. It is a flat site which slopes slightly west and towards the northeast corner. The highest point is found in the middle of the site at 1031 m above sea level. The site gradually falls 6 m towards NE corner to an elevation of 1025 m at the lowest point. The most westerly point of the site slopes to an elevation of 1027 m. At each of these lower site points, surface water collection occurs. Historical satellite imagery shows heavy tilling of the soil around the time of its closure, which corresponded with the homogenous soil condition across much of the site.

Figure 3.5. Canyon Colliery pit top area revegetated with Australian native grass species *Poa labillardierei*. Photo taken December 2019.

Canyon colliery is classified as loamy sand and has a visibly similar to soil composition to the other two study sites. It has a heavy presence of coal waste rock spread across the site grounds (Fig 3.5). The sampling area measures 8.5 Ha and is surrounded on the northern site by the remnants of the old train line.

3.4.2. Field Sampling Methods

The sampling procedure for Canyon, Neath, and Abermain No. 2 collieries is shown in Fig 3.6. Using GPS coordinates, a sampling grid was overlaid on the map and point samples taken at Neath colliery (N = 56), Canyon colliery (N = 47), and at Abermain no. 2 colliery (N = 58). Sampling points were evenly spread across each site, with some variability in distances between points arising due to GPS software accuracy. Canyon colliery was larger than the other two sites, so samples were further apart (approx. 50 m), while Neath and Abermain colliery samples were collected from similar distances apart (approx. 25 m). Examining the satellite images, Neath and Abermain collieries have cleared areas which were not sampled in this experiment (Neath top north area of the map and Abermain north-eastern area). These were excluded due to recent vehicular disturbance.

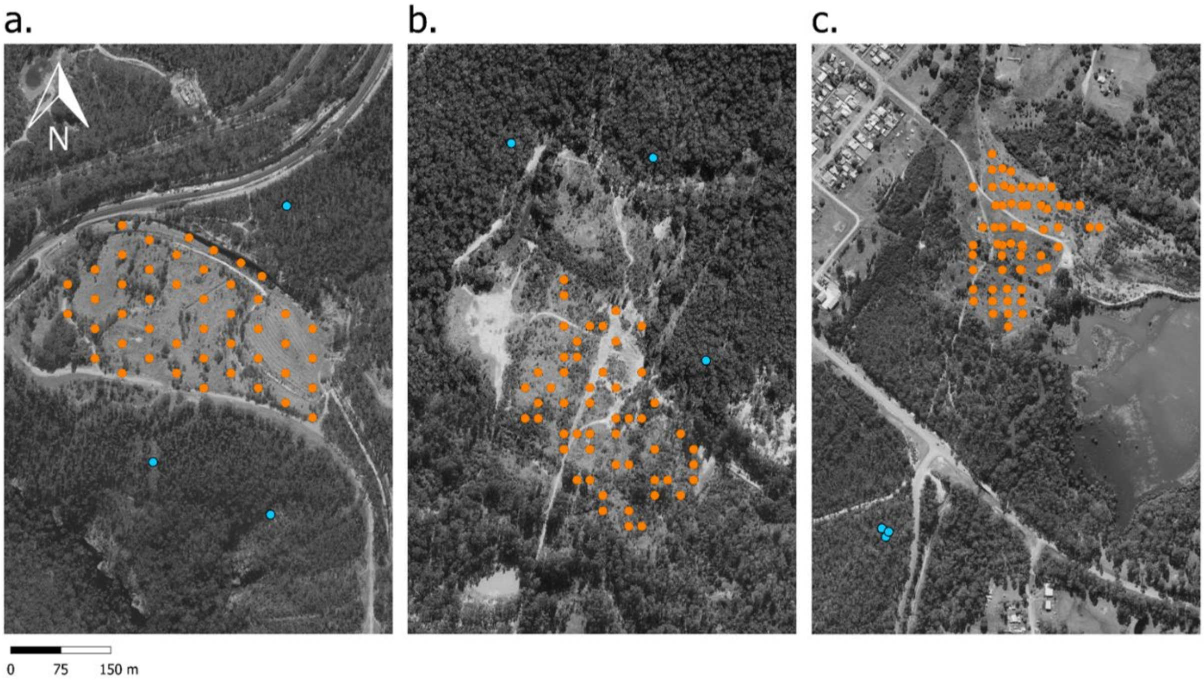

Figure 3.6. Sampling procedure for Canyon Colliery (a), Neath Colliery (b), and Abermain No. 2 Colliery (c). Paired soil samples (i.e., upper and lower) are shown in orange and ecological reference samples are shown in blue.

Three control samples were collected at each site (N = 9) from ecological reference areas at the nearest unimpacted bushland site. At each point for both mine and ecological reference sites, soil samples were collected from the top (0 - 50mm) and the bottom (250 - 300mm) of the soil profile using a 1-meter-long stainless-steel auger to allow for a consistent comparison of data. All soil samples were collected in sterile 25 ml polypropylene jars before transportation to UTS laboratories for analysis.

3.4.3. Soil Analyses

Physiochemical properties of the soil were analysed using a range of methods:

i. Soil pH

pH was measured using 1: 5 soil: water suspension method (Rayment & Higginson, 1992). Whereby, 10 g of soil was dried at 40 °C for 48 hours before being sieved to < 2 mm. The drying temperature was chosen to best replicate air drying and prevent acidification of the sample. Following sieving, 50 mL of Milli-Q water was added to the sample and stirred consistently over a 30-minute period. Triplicate samples of pH were taken for each soil matrix (Table 3.1) using an Oakton Benchtop pH 2700 meter.

ii. Particle Size Analysis

Particle size analysis of mine site samples were conducted using the Malvern Mastersizer 2000 with 1 g of soil from each mine site prepared in the same manor mentioned in 3.3.3.i before being suspended in 500 mL of Milli-Q water. Each sample was subjected to sonication for 5 minutes to ensure thorough mixing before entering the machine. For each mine site, five replicate samples were measured and particle size averages were taken (Table 3.1).

iii. Sequential Method for Total Inorganic Metal Analysis

To determine the total concentration of inorganic metal contamination on the mine sites, soil samples were oven dried at 80°C for 48 hours before being sieved to < 2mm. Sub-samples of soil (1 g) were hot acid digested at 95°C on The Environmental Express HotBlock using a combination of ultra-pure Seastar Nitric Acid ((HNO_3) 70%) and Analytical Reagent Hydrogen Peroxide ((H_2O_2) 30%) as per procedures outlined in method EPA 3050B.

Each digestion contained 1g of certified reference material (CRM-LO-D, Choice Analytical), procedural blanks, and spiked recovery samples to detect any in-process contamination during sample preparation and exclude the potential for inaccurate data due to complex soil matrices. Post-digestion, all liquefied samples were filtered using Minisart 0.45-micron syringe filters and subjected to 1:40 dilution with Milli-Q water (Arium Pro VF Ultrapure Water Purification System) before elemental analysis in inductively coupled plasma-mass spectrometry (Agilent ICP-MS 7700). Analytes of focus were Pb, Co, Cu, Zn, Ni, Cr, As, and Mn. Internal and external ICP-MS calibration standards were used for further confidence in elemental results. Multi-element ICP calibration standard EPA 200.7 in 5% nitric acid (ICP-200.7-10, High Purity Standards) and a six-element ICP internal standard (IV-ICPMS-71D, Inorganic Ventures) were used to maintain the calibration of the ICP-MS unit.

Complex matrices of the mine soils resulted in interferences at dilutions factors of 20 x and 40 x so a 150 x dilution factor was used. Spiked recoveries for all three mines were within acceptable limits 100 ± 10%. Recoveries of Certified Reference Material 'Loam Soil Level D' were within acceptable limits 100% ± 10% except for As and Ni which measured 120.13% and 85.50% respectively.

Table 3.1. General soil conditions including pH compared across the study sites.

Mine Site	Soil pH	Clay (%)	Silt (%)	Sand (%)	USDA classification
Neath	3.88 (±0.02)	5.24 (±0.02)	31.53 (±0.20)	63.23 (±0.22)	Sandy loam
Canyon	6.33 (±0.18)	1.43 (±0.03)	28.48 (±0.60)	70.09 (±0.63)	Loamy sand
Abermain No.2	6.69 (±0.08)	0.8 (±0.01)	13.53 (±0.14)	84.76 (±0.16)	Loamy sand

3.4.4. Statistical Analyses of Metal Contamination

To visualise the multivariate patterns of the metal concentrations across the soil samples, a principal components (PCA) analysis was conducted (i.e., metal concentrations in ppm, ln transformed, scaled, and centred prior to analysis).

To answer the first and second research questions of this study, metal concentrations among the mines and between soil profiles were analysed using linear mixed models of the ln transformed metal concentrations (i.e., eight models) were fitted using mine (i.e., three level fixed categorical factor), soil profile (two level fixed categorical factor; lower and upper), a mine x profile interaction term and a random term for sample (i.e., lower, and upper samples were collected as pairs, so these samples were not spatially independent).

To further quantify the relative size of the difference between the profiles and determine if the mines may be exhibiting signs of metal loss from the upper profile through erosive or water runoff processes, the ratio of the lower profile metal concentration to the upper profile metal concentration was calculated for each of the spatially paired samples, so that a value greater than one would indicate lower concentrations of metals in the upper profile, relative to the lower soil profile. To examine this, linear models for each metal were fitted with mine site as the sole explanatory factor. The model estimated ratios for each mine were then tested to determine if they differed from a value of one, and therefore showed a statistically significant difference across the sites.

Finally, to test the relationship between metal concentrations between profiles and if these were consistent among the mines, metals in the lower profile were modelled using a continuous term for the metal concentrations in the upper profile (i.e., both ln transformed), a fixed categorical factor for mine (i.e., a three-level categorical factor), and an upper profile x mine interaction term. All analyses were conducted with R Statistics version 4.1.2 (R Core Team, 2020) using the R packages *lme4* (Bates et al., 2015) for mixed models, *car* (Fox & Weisberg, 2019) for ANOVA significance testing, and *emmeans* (Lenth, 2022) for parameter estimation and significance testing.

3.4.5. Mine Site Spatial Mapping

Heat mapping and data visualisation was used to answer the third research question regarding the movement of heavy metals around the three coal mine sites. I used the "Magma" colour ramp to represent the concentration of metals in the soil, so that spatial patterns can be easily identified. In this study, yellow colours indicate high metal concentrations, while purple colours indicate low concentrations. Heatmaps are used in this study to investigate if the movement of contaminants was linked to erosive processes areas contaminated with acidic water. GIS maps were created using Free and Open Source QGIS, version 3.16.2 Hannover. World Geodetic System 1984 datum (WGS84) was projected onto both hybrid and terrain layers sourced from Google Maps. Heatmaps were created using QGIS Heatmap function of Inverse Distance Weighted (IDW) interpolation of individual points within vector layers. Maps were scaled to 1:3000, with each point assigned a radius of 0.0005 degrees (approx. 50m).

3.5. Results

3.5.1. Heavy Metals Compared Across Soil Profiles

From the PCA, two groups of metals showed a positive relationship: Co, Mn, Ni and Zn, and the other being As, Cr, Cu and Pb, with the former group being the most strongly interrelated (Fig 3.7). The PCA score for the mines showed large overlaps, with the strongest pattern being lower concentrations of As, Cr, Cu and Pb in some samples of the Abermain mine (Fig 3.7).

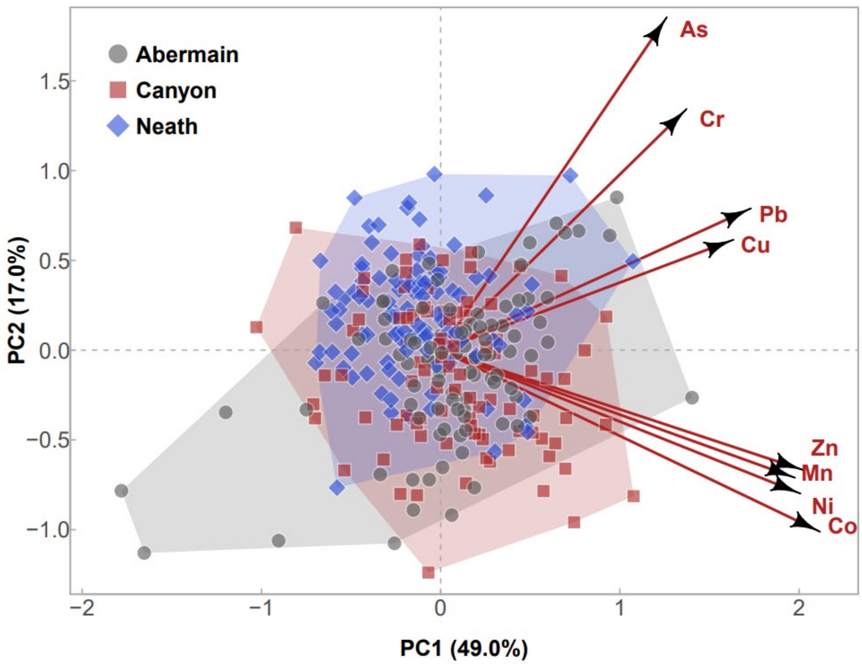

Figure 3.7. PCA analysis of heavy metal co-occurrences concentrations (including combined upper and lower profile samples) at three mine sites.

When comparing the concentration of each metal among mines and between soil profiles the following metal concentrations were significantly different among mines, with no significant profile or mine by profile differences. Levels of As differed significantly among the mines, with higher As found at Neath, relative to Abermain, and Canyon not significantly different to either (χ^2 = 7.851, DF = 2, p = 0.02; Table 3.2; Fig. 3.8a, b). Concentrations of Pb were significantly higher at Abermain mine relative to Neath, with Canyon mine showing an intermediate level not significantly different to either (χ^2 = 12.626, DF = 2, p = 0.002; Table 3.2; Fig 3.8e,f). Cu was the only metal that did not differ in concentrations among mines or between profiles and showed a non-significant mine x profile interaction (χ^2 = 1.69, DF = 2, p = 0.4; Table 3.2; Fig 3.8c, d).

Table 3.2: Results from the linear mixed models used to compare metals by mine, profile, and mine x profile interaction. Significant results are shown in bold.

Response	Terms	χ^2	DF	P-value
Arsenic	Mine	7.851	2	**0.02**
	Profile	0.02	1	0.9
	Mine x Profile	3.654	2	0.2
Cobalt	Mine	28.514	2	**< 0.0001**
	Profile	0.704	1	0.4
	Mine x Profile	33.505	2	**< 0.0001**
Chromium	Mine	4.672	2	0.1
	Profile	0.045	1	0.8
	Mine x Profile	7.588	2	**0.023**
Copper	Mine	1.69	2	0.4
	Profile	3.627	1	0.057
	Mine x Profile	0.282	2	0.9
Manganese	Mine	59.065	2	**< 0.0001**
	Profile	14.283	1	**0.0002**
	Mine x Profile	34.535	2	**< 0.0001**
Nickel	Mine	11.554	2	**0.003**
	Profile	7.201	1	**0.007**
	Mine x Profile	18.013	2	**0.0001**
Lead	Mine	12.626	2	**0.002**
	Profile	0.006	1	0.9
	Mine x Profile	0.542	2	0.8
Zinc	Mine	54.096	2	**< 0.0001**
	Profile	0.524	1	0.5
	Mine x Profile	18.785	2	**< 0.0001**

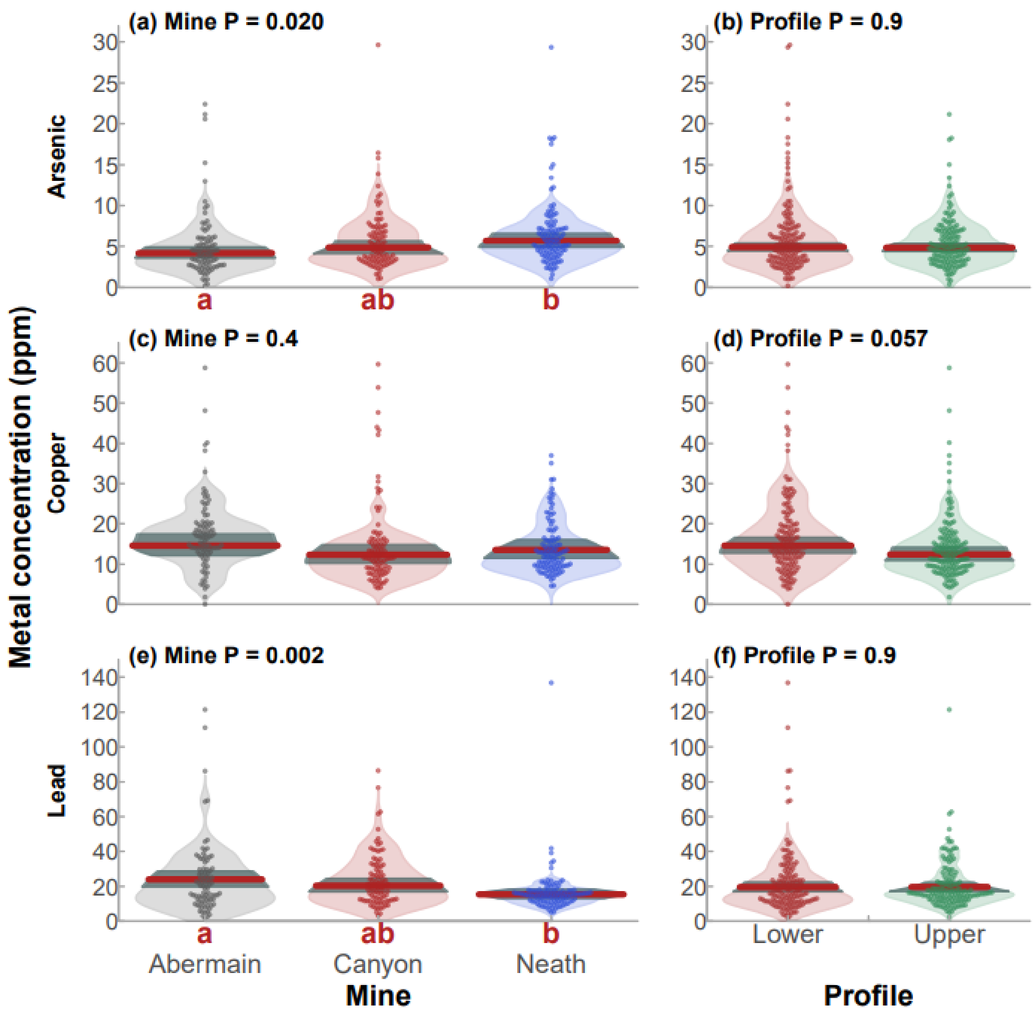

Figure 3.8: Violin plot showing metal concentrations by mine and profile. Where the P value is significant, red letters below the x-axis indicate significant differences and groupings among the mines. As no significant difference between profiles was found, left side graph shows total metal concentrations (combined top and bottom). Right graph shows combined the difference between top and bottom profiles for the three mines combined.

A significant mine x profile interaction emerged for concentrations of Co, Cr, Mn, Ni and Zn (Table 3.2). Co showed significantly higher concentrations in the lower profile relative to the upper profile at Canyon mine, (χ^2 =33.505, DF = 2, p < 0.001; Fig 3.9a) and the converse at Neath mine (χ^2 =33.505, DF = 2, p = 0.0002; Fig 3.9a), while no significant difference was found at Abermain ((χ^2 =33.505, DF = 2, p = 0.2; Fig 3.9a). Cr was significantly lower in the lower profile compared to the upper profile at Neath mine (χ^2 =4.672, DF = 2, p = 0.024; Fig 3.9a), with no significant difference between profiles at Canyon mine (χ^2 =4.672, DF = 2, p = 0.2; Fig

3.9b) and Abermain mine (χ^2 =33.505, DF = 2, p = 0.5; Fig 3.9b). For Mn, the lower profile showed smaller concentrations relative to the upper profile at Neath only (χ^2 =34.535, DF = 2, $p < 0.0001$; Fig 3.9c), with neither Canyon mine (χ^2 =34.535, DF = 2, p = 0.9; Fig 3.9c) or Abermain mine (χ^2 =34.535, DF = 2, p = 0.9; Fig 3.9c) showing a significant difference between profiles. Ni was significantly higher in the lower profile at Canyon mine (χ^2 =11.554, DF = 2, $p < 0.0001$; Fig. 3.9d), with no significant differences between profiles at Abermain mine (χ^2 =11.554, DF = 2, p = 0.9; Fig. 3.9d) or Neath mine (χ^2 =11.554, DF = 2, p = 0.2; Fig. 3.9d). The lower profile of Canyon mine showed significantly higher Zn concentrations (χ^2 =54.096, DF = 2, p = 0.007; Fig. 3.9e), while at Neath mine this pattern was reversed with significantly higher concentrations in the upper profile (χ^2 =54.096, DF = 2, p = 0.0008; Fig. 3.9e). No significant difference in Zn was found between profiles at Abermain (χ^2 =54.096, DF = 2, p = 0.7; Fig. 3.9e).

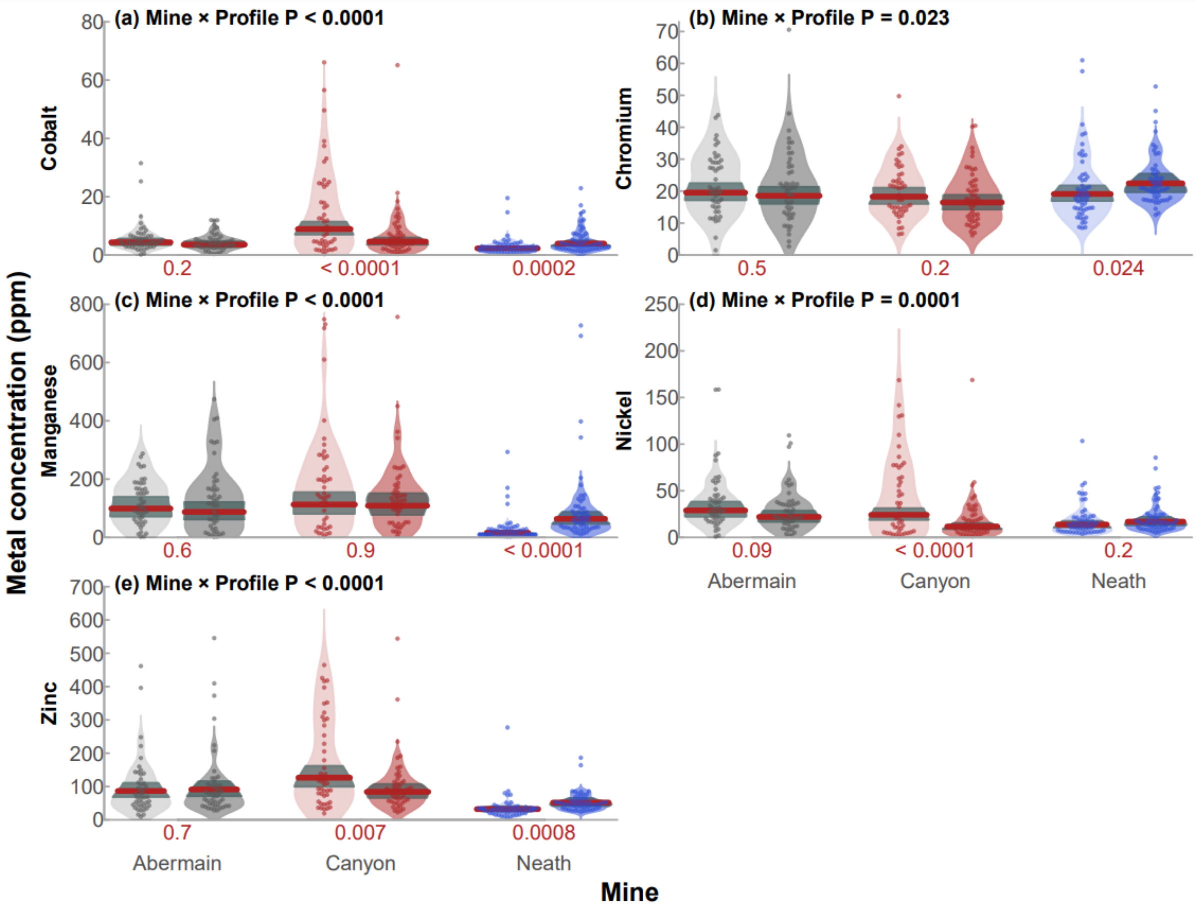

Figure 3.9. Metal concentrations grouped by mine. The lower profile is shown to the left and the upper profile to the right for each mine. The red numbers indicate the P value for the differences between upper and lower profiles at each mine.

3.5.2. Heavy Metal Pollution Compared Across the Three Mine Sites

The lower to upper profile ratios for at least one mine were found to differ significantly for Co, Cr, Mn, Ni and Zn (Table 3.3; Fig. AB3.9). Ratios for Co at Canyon mine indicated the mean concentration in the lower profile was close to twice that in the upper profile ($t = 4.227$, DF = 141, $p < 0.0001$), while Neath showed approximately half the concentration in the lower profile relative to the upper ($t = -3.825$, DF = 141, $p < 0.0002$;Table 3.3; Fig. AB 3b). Cr concentrations in the lower profile of Neath mine were approximately 85% of the concentrations in the upper profile ($t = -2.339$, DF = 141, $p = 0.021$; Table 3.3; Fig. AB 3c). Mn at Neath was more than twice as high in the upper profile ($t = -7.176$, DF = 141, $p < 0.0001$;

Table 3.3; Fig. AB 3e). At Canyon mine, the lower profile Ni concentration was around twice as high as the upper profile (t = 4.484, DF = 141, p < 0.0001; Table 3.3; Fig. AB 3f). Zn showed opposing patterns in Canyon and Neath mines, with the lower profile at Canyon mine showing a lower profile concentration 1.5 times that of the upper profile (t = 2.773, DF = 141, p = 0.006; Table 3.3; Fig. AB 3h), and Neath showing a half the concentration in the lower profile relative to the upper profile (t = -3.484, DF = 141, p < 0.0007; Table 3.3; Fig. AB 3h). The upper to lower profile ratios for As, Cu and Pb showed no significant difference any of the mines (Table 3.3; Fig. AB 3).

Table 3.3: Statistical summary showing tests of the equality of the lower to upper profile ratio by mine.

Response	Mine	Mean	SE	DF	t ratio	P
Arsenic	Abermain	-0.006	0.096	141	-0.063	1
	Canyon	0.157	0.095	141	1.652	0.1
	Neath	-0.119	0.089	141	-1.342	0.2
Cobalt	Abermain	0.219	0.158	141	1.388	0.2
	Canyon	0.661	0.156	141	4.227	**< 0.0001***
	Neath	-0.557	0.146	141	-3.825	**0.0002***
Chromium	Abermain	0.038	0.076	141	0.494	0.6
	Canyon	0.101	0.075	141	1.339	0.2
	Neath	-0.164	0.07	141	-2.339	**0.021***
Copper	Abermain	0.152	0.137	141	1.105	0.3
	Canyon	0.199	0.136	141	1.467	0.1
	Neath	0.164	0.127	141	1.297	0.2
Manganese	Abermain	0.161	0.216	141	0.746	0.5
	Canyon	0.044	0.213	141	0.205	0.8
	Neath	-1.426	0.199	141	-7.176	**< 0.0001***
Nickel	Abermain	0.301	0.163	141	1.844	0.07
	Canyon	0.723	0.161	141	4.484	**< 0.0001***
	Neath	-0.216	0.15	141	-1.438	0.2
Lead	Abermain	0.085	0.145	141	0.589	0.6
	Canyon	0.079	0.143	141	0.55	0.6
	Neath	-0.111	0.133	141	-0.834	0.4
Zinc	Abermain	-0.021	0.152	141	-0.14	0.9
	Canyon	0.417	0.15	141	2.773	**0.006***
	Neath	-0.488	0.14	141	-3.484	**0.0007***

3.5.3. Comparing contaminant concentrations in upper and lower soil profiles

Upper profile concentrations related significantly and consistently (i.e., without significant mine x upper profile interactions) to the lower profile metal concentrations, for all metals with the exception of Zn (Table 3.4), which showed no significant interaction between upper and lower profile ($F_{1, 136} = 0.513$, $P = 0.5$)

The upper and lower profile of each mine site was mapped to visualise hotspotting and movement of analytes horizontally and vertically across the sites. In a sample of maps from the Canyon colliery (Fig. 3.10) Co is seen in higher concentrations within the bottom profile close to the train line, while hotspotting appears in the top profile around the bottom left corner (Fig. 3.10a). Pb in the bottom profile is more widely spread across the site compared to the top profile (Fig. 3. 10b). The hotspot in this image aligns with the historical stockpile location for the colliery. Cu follows a similar pattern to Co in the bottom profile, while concentrations in the top profile are widely dispersed across the site (Fig. 3.10c).

In the Neath Colliery site, Co concentrations in the bottom profile display hotspotting on the likely position of the original coal stockpile, with concentrations in the top profile likely migrated with weathering processes downhill towards the bottom right site corner where acidic water pools for underground mine seeps (Fig. 3.11a). Mn concentrations are double in the top profile compared to the bottom profile, following similar spatial distributions as Co (Fig. 3.11a, b). Zn concentrations are higher in the bottom profile, but upper and lower profiles appear to follow a similar movement pattern towards the lower corner of the site (Fig. 3. 11c). Heatmaps of other metals at Canyon (Fig. AB 4-5) and Neath collieries (Fig. AB 6-7) and all metals for Abermain colliery (Fig. AB 8-9) are presented in Appendix AB.

Table 3.4. Results from linear mixed models which used the upper profile metal concentrations to model the lower profile metal concentrations, including statistical interactions. All significant results ($P \leq 0.05$) have been bolded.

Response	Terms	SS	F	DF	P
Arsenic	Upper profile arsenic	15.031	43.696	1	**< 0.0001**
	Mine	0.957	1.391	2	0.3
	Upper profile arsenic x Mine	0.174	0.253	2	0.8
	Residuals	47.47		138	
Cobalt	Upper profile cobalt	11.784	13.833	1	**0.0003**
	Mine	43.341	25.438	2	**< 0.0001**
	Upper profile cobalt x Mine	0.167	0.098	2	0.9
	Residuals	117.561		138	
Chromium	Upper profile zinc	6.677	34.098	1	**< 0.0001**
	Mine	0.349	0.891	2	0.4
	Upper profile chromium x Mine	0.563	1.438	2	0.2
	Residuals	27.025		138	
Copper	Upper profile copper	8.635	8.595	1	**0.004**
	Mine	0.006	0.003	2	1
	Upper profile copper x Mine	2.956	1.471	2	0.2
	Residuals	138.644		138	
Manganese	Upper profile manganese	6.867	5.398	1	**0.022**
	Mine	113.669	44.676	2	**< 0.0001**
	Upper profile manganese x Mine	0.508	0.2	2	0.8
	Residuals	175.557		138	
Nickel	Upper profile nickel	18.688	19.318	1	**< 0.0001**
	Mine	16.492	8.524	2	**0.0003**
	Upper profile nickel x Mine	0.081	0.042	2	1
	Residuals	133.5		138	
Lead	Upper profile lead	3.999	6.038	1	**0.015**
	Mine	4.762	3.595	2	**0.03**
	Upper profile lead x Mine	3.536	2.669	2	0.07
	Residuals	91.402		138	
Zinc	Upper profile zinc	0.327	0.513	1	0.5
	Mine	45.853	35.929	2	**< 0.0001**
	Upper profile zinc x Mine	2.115	1.658	2	0.2
	Residuals	86.782		136	

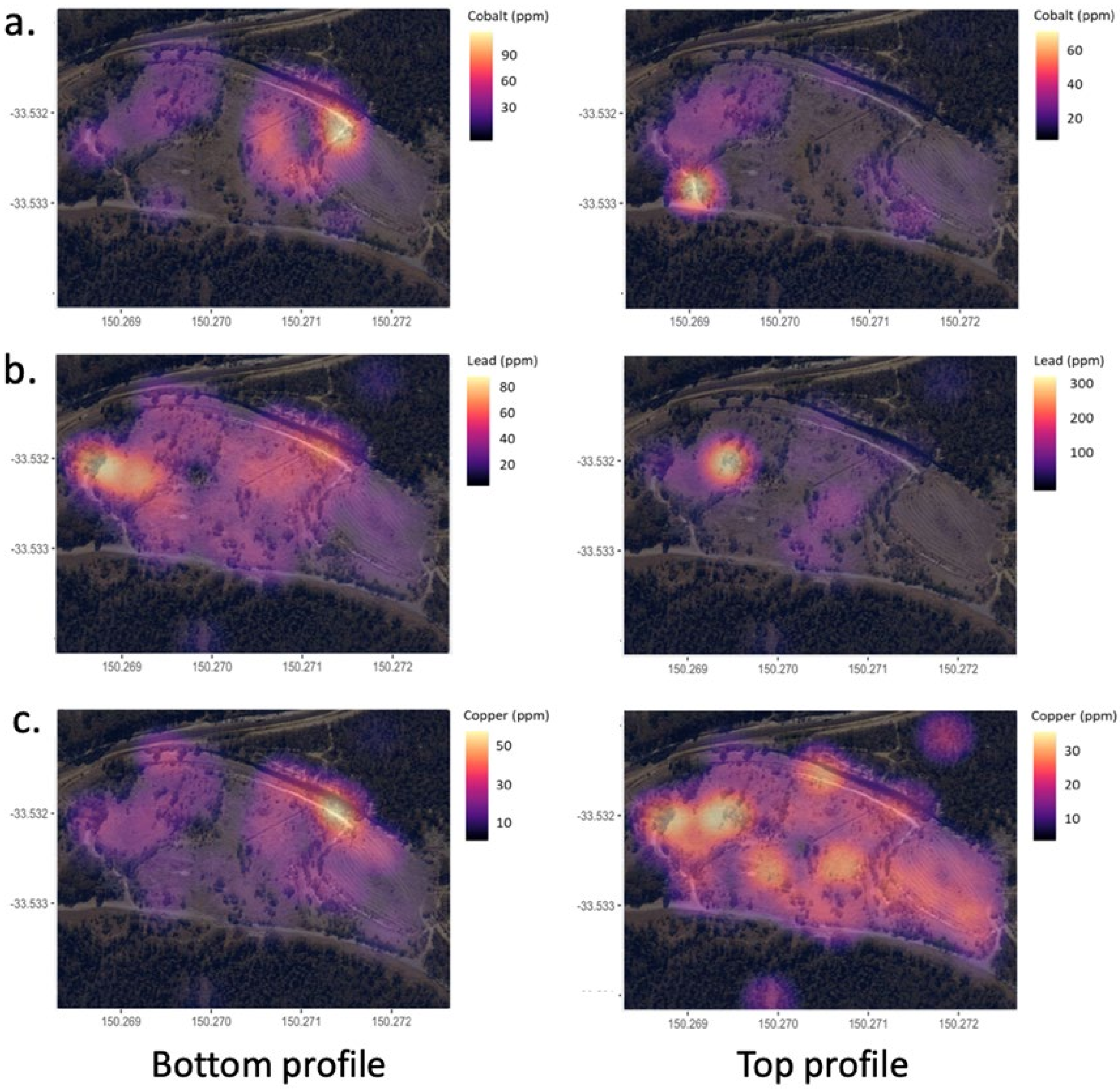

Figure 3.10. Heatmaps visualising hotspots and spatial distribution of contaminants within the top and bottom soil profiles at Canyon Colliery. Note the differences in scale between bottom and top profiles.

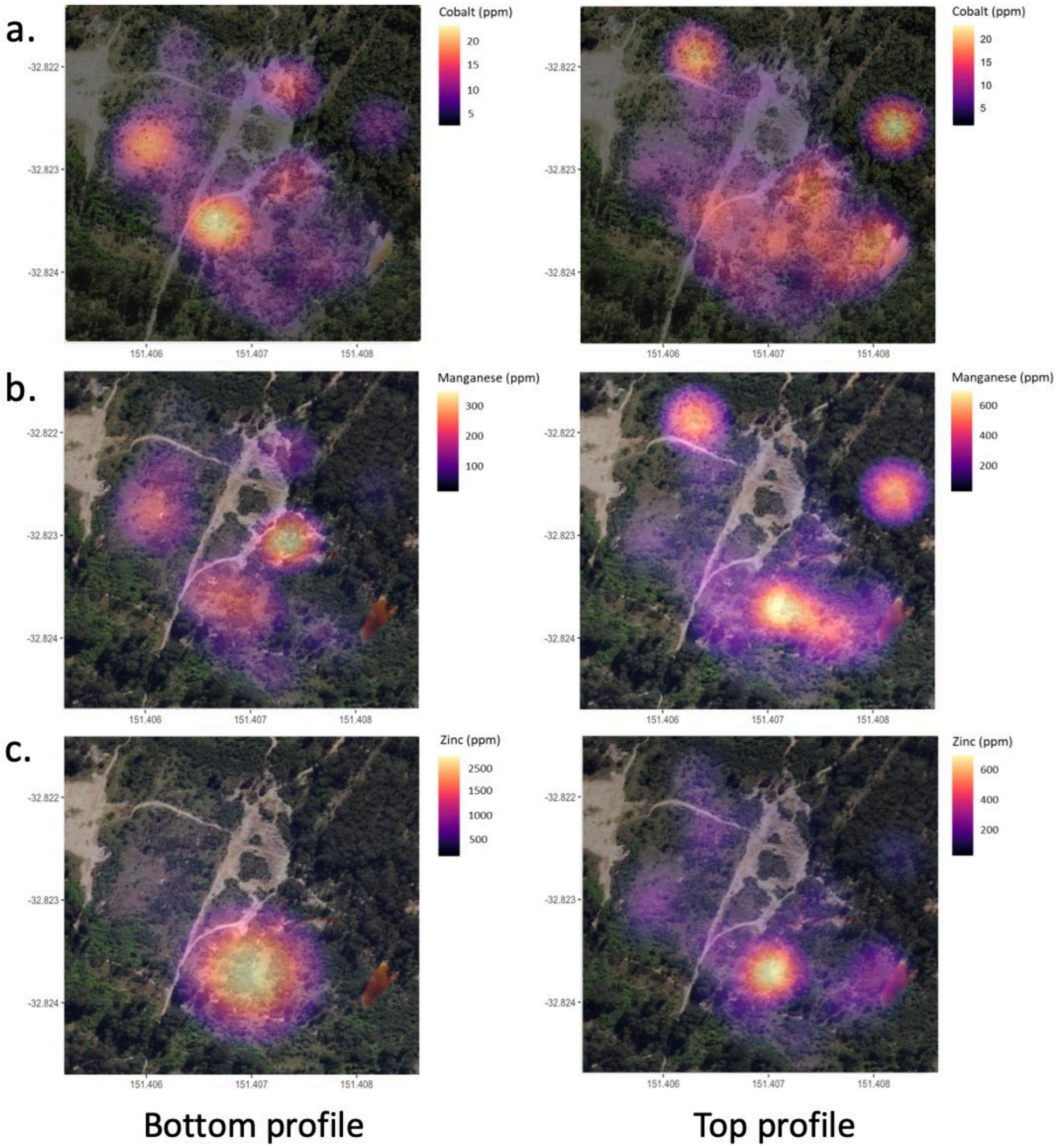

Figure 3.11. Heatmaps visualising hotspots and spatial distribution of contaminants within the top and bottom soil profiles of Neath Colliery. Note the differences in scale between bottom and top profiles.

3.6. Discussion

3.6.1. General Trends in Heavy Metal Pollution across the Mine Sites

My first aim was to discover if abandoned coal mines in Australia still contain environmentally harmful levels of heavy metals, with a focus on Cu, As, Cr, Pb, Zn, Mn, Co, and Ni and their individual spatial patterns across the sites. Mean, minimum, and maximum concentrations were measured for all heavy metal analytes across the three mine sites (Table AB1). When examining mean heavy metal concentrations, only Zn at the Abermain site consistently recorded concentrations above Australian EIL's, however, across all three mine sites, all heavy metal analytes except Cr recorded maximum values above Australian environmental investigation levels in at least one point sample (Table. AB 1). High range data rather than whole-site averages may be more useful when considering contamination levels on the sites, particularly in the instances of polluted sites likely to show hotspots. Several studies beyond Australia have examined the patterns of heavy metals on the surfaces of abandoned coal mines (Freitas et al., 2004; Li & Ji, 2017; Li et al., 2017; Moreno-Jimenez et al., 2009; Tordoff et al., 2000) and also show large upper-range readings in heavy metal concentrations are common due to the presence of contamination hotspots.

3.6.2. Comparing Australia's Heavy Metal Guidelines to International Limits

When examining the three large mine sites in this study, Ni, Zn, and Mn all stood out as highly elevated at all sites (Table. AB 1), despite decades of site inactivity. The presence of Ni, Zn, and Mn has been commonly associated with coal mining in the Sydney region (Ali et al., 2017; Price & Wright, 2016) with high concentrations recorded in water coming directly from mine discharge points, subsidence areas, and surface run-off in proximity to underground mines (Belmer et al., 2014; Belmer & Wright, 2020; Morrison et al., 2019). With maximum metal levels greatly exceeding Australian NEPM (2013) EIL, as well as other international safety thresholds (Tables AB.7, AB.8). While Pb did not consistently exceed Australian guidelines, it will also be discussed as it highlights important differences between Australian guidelines and the rest of the world. Discussion centres on the potential hazards of these metals to environment and human health as reported in the literature.

Mn exceeded NEPM (2013) guidelines at all three sites, with the highest concentration reaching close to 3000 ppm, six times higher than the EIL for this analyte (Table AB 1.).

Interestingly, Australia is one of the few countries with designated pollution investigation levels for Mn in soils (Table AB 7.). Within the literature, it is suggested that Mn soil contamination is often overlooked due to a combination of its natural abundance in the earth's crust and role of essential micronutrient for humans, animals and plants (Queiroz et al., 2021). While Mn is essential for plant growth in small amounts (He et al., 2005; Nagajyoti et al., 2010) in excess, it can cause phytotoxicity and impair the absorbance of other essential nutrients (El-Jaoual & Cox, 1998). While it appears many countries are currently not identifying Mn as a soil contaminant of concern, an ever growing body of research is likely to change this (Petitjean et al., 2021; Pinsino et al., 2012). In combination to the elevated levels of Mn identified in this study, PCA analysis of the mine soils showed high levels of Mn were also a reasonably strong predictor of high Zn across all three locations. This aligns well with previous studies outside of Australia that show both Mn and Zn are often occur together in highly elevated concentrations in coal mines (Adhikari & Mal, 2021; Herndon et al., 2019; Pan et al., 2021; D. Wang et al., 2022).

EIL's for Zn are relatively low when compared to other nations at 200 ppm, and all mine sites showed maximum soil levels well above Australian limits (Table. AB 7. Table. AB 8.). Zn was the only heavy metal in this study to record both average and maximum concentrations higher than safe guideline levels, with Abermain recording levels more than 40 times higher than the recommended maximum Zn limits. The high levels of Zn across these sites is of significant environmental concern for species in nearby terrestrial and aquatic ecosystems. Zn toxicity has been demonstrated to reduce plant photosynthesis and respiration rates thereby causing stunted growth and eventual phytotoxicity (Kaur & Garg, 2021). While this study specifically focused on soil samples and soil limits, it should be considered that the ANZECC trigger values for the protection of 95% of freshwater species is set at only 8 ppb, and 2.4 ppb for 99% protection (ANZECC, 2000) (Table. AB 8.). With soil concentrations as high as they are on all three mine sites, this suggests any movement of Zn from soils to waters would be seriously harmful for aquatic invertebrates, plants, and other species through direct pollution contact, or possibly trophic interaction (Wright & Burgin, 2009; Wright et al., 2018).

Ni was also found in elevated levels at all sites and all soil profiles. Ni is a common heavy metal associated with coal and coal mining. Kozar et al. (2020) showed that while coal deposits vary, the concentration of nickel in coal seams can be high. High levels of Ni have been found in abandoned coal mine waste water (Das et al., 2020) which can cause ecological disruption for several decades after the mine site has become inactive (Belmer & Wright, 2020). Regarding risks to the community, Ni is a primary cause of dermatitis in humans and has been shown to increase the risk of cancer and DNA disruption (Genchi et al., 2020; Stohs & Bagchi, 1995).

Comparing Pb concentrations with NEPM Pb EIL and international standards, the vast difference between Australian and international guidelines is highlighted (Table AB 7.). In Australia, the NEPM Pb EIL is 600 ppm, whereas international investigation levels are often much lower, ranging between 35 ppm in China and 300 ppm in Canada (Table AB 7.). In this study, Pb was found in concentrations above Australian NEPM guidelines only in the bottom profile of Abermain (636 ppm), however, if comparing to safe limits from outside of Australia and Canada, all but one location would be considered polluted to levels of environmental concern. Analysis from all three study areas showed Pb levels were also significantly higher than ecological reference values taken in areas adjacent to the mines. This aligns to previous research that showed that one of the most common sources of Pb in the environment comes from coal incineration (Das et al., 2020; Nagajyoti et al., 2010). This is a worrying trend in the context of human health, as high exposure to bioavailable forms of lead can cause reproductive impairment, haematological, gastrointestinal, cardiovascular, and neurological problems, with Pb exposure considered a leading cause of developmental problems in affected children (Daniali et al.; Kim et al., 2012; Stohs & Bagchi, 1995; Wani et al., 2021).

3.6.3. Differences between Soil Profiles across Mine Sites

Comparing the three legacy mine sites, I hypothesised that due to phytostabilisation, Canyon (i.e., the moderately rehabilitated site) would retain higher concentrations of metal in the top soil profile. While the PCA analysis indicated the three mines to be overall similar in metal concentrations when combining top and bottom profiles. When comparing top and bottom profiles within a site Canyon recorded significantly higher levels of Co, Zn, and Ni in the bottom rather than top profile. In contrast to Neath recorded Co, Mn, Cr, and Zn levels significantly higher in the top than bottom profiles. Abermain recorded no differences between metal concentrations in top and bottom profiles. This was the reverse of my hypothesis that Canyon would record higher levels in the top profile due to phytostabilisation binding heavy metals within the rhizosphere. Firstly, I discuss the high levels of heavy metals found in the top profile at Neath. Second, I address the low metal concentrations in top profiles at Canyon.

I suggest the high concentrations of heavy metals found in the top profile at Neath are due to a combination of contamination of water and the presence of contaminated site fill. Legacy mines contribute heavy metals to the environment through several pathways, one of the most well-known being acid mine drainage (AMD). While not specifically measured in this thesis, the presence of AMD at the Neath site, indicated by the deep red colour of drainage water on the site (AB 10.), is a likely contributor to elevated metal concentrations in the top profile. A continuous seep issues from the mine portal indicating the underground workings are flooded and likely being recharged by groundwater (Wright et al., 2018). Several studies within Australia have shown AMD to significantly contribute to water contamination (Wright & Burgin, 2009; Lei et al., 2010; Wright et al., 2018; Wright et al., 2011), but less research has highlighted the impact on soils as seen here. The AMD problem at Neath is significant and should be a focal point of any future remediation plan, however, it does not explain all of the contamination on the site. Neither Canyon nor Abermain have visible signs of AMD, and Neath shows areas of elevated heavy metals in areas not impacted by AMD. In a study conducted at a legacy mine in NSW, Kavehei et al. (2021) quantifies that while 64% of site contamination can be traced back to leachate coming from underground workings, the remaining 36% comes from contaminated waste piles on the site. This is supported by Gore et al. (2007) who showed elevated levels of Co, Cu, Fe, Mn, Ni, Pb, and Zn in surface soils and sediments are directly related to contaminated fill used in the mine site's original remediation process. All three mine sites sampled show visible coal waste within the soils, indicating contaminated fill is a likely cause of continued surface soil contamination.

Analysis of the remediated Canyon colliery showed significantly higher levels of Co, Zn, and Ni in the bottom profile compared to top, in contradiction to my hypothesis that heavy metals would be bound in higher concentrations within the top profile of the rhizosphere. While this hypothesis did not stand, the pattern does suggest certain heavy metals were being bound in lower profiles of the rhizosphere. The dominant species on the Canyon site was *Poa* *labillardierei* a dense tussock forming grass growing up to 1.2m in height. While known as shallow root species (Jones & French, 2021) the lower profile sampling depth of 250-300mm was still sampling within the rhizosphere, suggesting the species was phytostabilising some contaminants on the site. Interestingly, Hayes et al. (2003) showed *P. labillardierei* to be a possible extractor of Cu, Zn, and Pb in contaminated mine soils offering a further possibility that the variation between the top and bottom profiles at Canyon was due to plant up take. Unfortunately, this hypothesis could not be tested due to the Black Summer Bushfire, a point I cover in more detail within Chapter 5 of this thesis.

3.6.4. Heterogeneity and Hotspots across the Mines

For Aim 3, I set out to identify hotspots of heavy metal concentrations and identify if contaminants were spreading from the mines through erosive processes.

Spatial analysis heatmaps showed hotspotting of note around two particular areas for different reasons. First the ecological references samples at Neath recorded levels much higher than expected from an undisturbed sample. I suggest this may indicate movement of contaminated dust due to the limited vegetative cap on this site. Weathering of mine soils creates small, fine particles that move more easily into the environment (Masto et al., 2011) and have been shown to travel significant distance from legacy mine sites causing long lasting contamination (Bian et al., 2009; Schneider et al., 2015; Schneider et al., 2019; Schneider et al., 2022). The second hotspot area of interest appeared to be related to the position of the train line scars and therefore the historical stockpiles of coal. Coal and associated waste have been shown to contain high levels of heavy metals (Das et al., 2020; Kusin et al., 2018) and due to heavy metals elemental nature and inherent inability to break down into safer constituents, these historical coal dumps may be an ongoing source of contamination (Bian et al., 2009). This is an important consideration for the management of abandoned mines. Quick and focused sampling around the trainlines and historical waste dumps of abandoned mines, if known, could give an overview of the contamination levels of the sites without the need for exhaustive procedures. It also highlights the importance finding an ecological reference sample at a distance outside of the likely impacts of dust contamination.

3.7 Conclusion

This research showed that legacy mines in NSW are still contaminated with heavy metals in levels considered to be environmental harmful. Ni, Zn, and Mn recorded concentrations well over Australian EIL guidelines consistently across the three sites, regardless of rehabilitation status. Comparing the revegetated Canyon site to the Neath site indicated that significant differences between soil profile and heavy metal concentration may suggest species on the site were acting as phytostabiliser for Zn, Co, and Ni. Spatial analysis of heatmaps appears to show that heavy metals are moving around the mine site in response to erosive processes. This information can be used to strengthen the management of abandoned mines and has the potential for helping to develop targeted and cost effective site sampling methods for future site assessments

Chapter 4: Using DGT and Sequential Metal Extraction to Explore the Phytoremediation Potential of Five Australian Grass Species

4.1. Abstract

Phytoremediation technology offers a promising solution for rehabilitating numerous abandoned mines in Australia. Abandoned mines often contribute to heavy metal contamination in soils, but existing measurements typically consider total metal concentrations without accounting for metal availability. This study compares sequential heavy metal analysis with DGT film analysis to determine the more accurate sampling method for predicting heavy metal uptake in five Australian native grass species. The phytoremediation potential of these grasses is then assessed by measuring the movement of heavy metals from soil to root tissue and root tissue to shoot tissue. The grasses are grown in rhizotron pots that provide access to the plants' rhizospheres. Mature plants are cultivated in contaminated mine soil obtained from an abandoned coal mine in NSW, and the concentrations of total and bioavailable heavy metals in the soil are compared. Both techniques prove accurate in predicting heavy metal availability overall, with DGT being particularly effective for Ni and Zn uptake in *T. triandra* and *C. truncata* compared to controls. Furthermore, comparing DGT Pb concentrations to total Pb across all species reveals that although the total concentration in the soil is high, very little Pb is bioavailable for plant uptake. These findings emphasize the need for employing a range of techniques to accurately assess degraded sites, as no single technique suits all species and metals. Furthermore, all five native grass species survived well in contaminated mine soils, with *C. truncata* and *I. cylindrica* demonstrating potential for phytostabilisation of Cu and Zn, while *D. sericeum* shows potential for Cu and Cr phytostabilisation. *T. triandra* stands out as the sole species displaying phytoextraction potential, particularly for Zn translocation. Given the abundance of unmanaged abandoned mine sites in Australia, these grass species offer a viable option for ongoing rehabilitation efforts.

4.2. Introduction

The final data chapter of this thesis further builds on the work presented in chapters 2 and 3, by identifying real world solutions to the problems identified throughout this thesis. In chapter 3, I used the sequential metal extraction methods to identifying heavy metal contamination of soils from three mines discovered in chapter 2. This method is commonly used to quickly prove total metal contamination of sites in both scientific studies and professional site assessments. While commonly used, this method does not take into account the impact of metal speciation and associated bioavailability. Within the literature, the technology of Diffusive Gradient Thin films (DGT) has be shown to overcome this problem, giving accurate predictions of available metal content in soils, sediments, and water. The aims of chapter 4 were to 1) compared DGT and sequential extraction techniques as predictors for the heavy metal uptake of five Australian native grasses grown is soil collected from one of the abandoned mines identified in chapter 2, and sampled in chapter 3; and 2) To identify the phytostabilisation or phytoextraction potential of the same five native grass species by examining the heavy metal bioconcentration and translocation factors. The overall hope for this chapter was to find species with the potential for the phytoremediation of mine sites in NSW.

4.2.1 Remediation, Rehabilitation, and Restoration

Extractive processes cause widespread changes on the Earth's surface and subsurface environments requiring actions to improve conditions on site once the activities have ceased. Within scientific literature and public policy, the terms land 'rehabilitation' and 'restoration' are used interchangeably (Hernandez-Santin et al., 2020; Mukhopadhyay et al., 2013). The overlapping nature of these processes may account for this confusion, but key differences exist between the two. While sharing many common site management methods (e.g., planting new trees, applying soil amendments), these processes are initiated on notably distinct levels of site degradation and are often designed for different, site-specific end goals. Rehabilitation aims to restore sites from some existing level of ecosystem functionality and integrity, whereas ecological restoration refers specifically to the recovery of an ecosystem that has been highly degraded, damaged, or destroyed by natural or anthropogenic activities, (Gann et al., 2019). Restoration goes a step further than rehabilitation, instead of repairing existing ecological services and processes, the goal is to return a site to its pre-existing, historical condition by reintroducing and rebuilding biotic and abiotic features that are absent, or if the damage is too great, a hybrid system which represents something close to the original habitat (Doley & Audet, 2013). Both of these processes require researching and reconstructing missing attributes of the original ecosystem, including the community structure of flora and fauna, ensuring representation across all functional groups with the overall goal of creating self-sustaining, integrated ecosystems that are resilient to anticipated external stresses (e.g., droughts, fires, seasonal rainfall events, etc.) (Gann et al., 2019; McDonald et al., 2016).

In this context, mines are often rehabilitated, rather than restored, as the anthropogenic changes to the abiotic and biotic features of these sites are often significant and irreversible without major intervention. Restoration of mined lands is a challenging task and, in many instances, may be unfeasible from ecological and economic perspectives. For example, if the creation of an open-cut coal mine destroyed an old growth rainforest, the impact on the site will likely cause irreversible physical and biological changes and restoring the site with the same levels of ecosystem function and complexity is considered extremely difficult (McDonald et al., 2016). Further complicating the ecological restoration of sites is the limited access to reference bushland areas in regions where widespread land clearing has occurred beyond the site boundaries. Lamb et al. (2015) stated that for any restoration project to be successful, the disturbed mine site should not only have experienced minimal degradation but also be located close to a parcel of undisturbed, representative reference bushland that can serve as template for the restoration project. In addition, the structural and functional complexity of these reference sites need to be studied and understood sufficiently to be accurately replicated on target sites (Hernandez-Santin et al., 2020). The combination of these factors makes full restoration unachievable in the context of many open-cut mining projects, relegating management of most sites towards rehabilitation. While this is a major issue that should be more accurately addressed in the approval stage of a mines life, for existing projects, the targets for rehabilitation are less about returning land to a pre-existing ecosystem and rather recovering some utility from the land. Irreversible changes to soil composition, hydrology, and chemistry are common on mine sites, regardless of this, a level of objective success can be achieved with clearly defined goals and strategies.

In terms of mine rehabilitation, it is important to identify realistic goals, for example, resorting some level of ecosystem function and services, or creating self-sustaining pastoral land (Gann et al., 2019). Rehabilitation goals will differ depending on the type of mining and level of disturbance, initially focusing on restoring basic ecosystem process, before expanding to more complex processes such as revegetation and the creation of self-sustaining habitats (Suding et al., 2004). It should be noted that the process of remediation often comes before rehabilitation, which focuses on controlling and addressing site contamination. Preventing the spread of contamination to surrounding environments, while also providing action to address the original degradation. This process is often the necessary first step of rehabilitation of mine sites, so from here on in this thesis the two terms will be amalgamated into remediation.

4.2.2. Mine Remediation

In open-cut coal mines, the overburden of soil is removed to the depth of the coal seam before the coal is removed. Most mines consist of multiple seams so the process can be repeated many times, resulting in mines with footprints as large as 250 square kilometres (Goldenberg, 2014). Open-cut coal mining dramatically changes the soil structure and integrity, meaning the remediation of these mines is significantly different to that of an underground mine. In Australia, 80% of current coal mining operations are open cut (GA, 2022), resulting in most research focusing on the restoring soil function in terms of structure, hydrology, biological and chemical composition (Doley & Audet, 2013; Lechner et al., 2016). Regardless of the vast majority of operations being open-cut, there is utility in studying the remediation of the surface of underground mine sites for several reasons. If the void of an open cut mine is filled, either progressively throughout the life of the mine, or backfilled post closure (Lechner et al., 2016), the problems and goals of remediating underground and open cut mines become remarkably similar. Soil compaction, altered site hydrology, chemical changes to the soil composition, invasive species, habitat fragmentation, loss of the native seedbank, and low species richness are all common factors impacting post-mined lands (Lamb et al., 2015; Suding et al., 2004; Z. Y. Wang et al., 2022; Worlanyo & Jiangfeng, 2021).

With the right resourcing, the remediation strategies used on large open-cut coal mines could be successfully applied to legacy mines in NSW, with particular focus on minimising the impact on water bodies downstream of mines. Legacy mines have been abandoned and left with surface coverings of mine spoils and wastes, which result in acid mine drainage, soil compaction, and unmanaged surface erosion (Cheng et al., 2009; Weyer et al., 2019; Worlanyo & Jiangfeng, 2021). This thesis has covered in detail the current effects of this wide scale problem, however, there is positive research indicating that when defined goals are set, mine sites can achieve a satisfactory level of remediation (Cao, 2007; Worlanyo & Jiangfeng, 2021). Many legacy sites within NSW may benefit from the remediation technique of ripping the current topsoil and adding a layer of more productive topsoil to make the site more suitable for revegetation. In a study by Bennett et al. (2021) it was shown that while soil depth on rehabilitated open cut sites did not reach that of control sites, grasses used in the studies were able to take water and nutrients from the spoil layer. With many mines soils displaying significantly reduced water holding capacity (Ngugi et al., 2015), the ability of grasses to inhabit these conditions could vastly improve rehabilitation of many sites. It should also be noted that while the water holding capacity is reduced compared to reference sites, Ngugi et al. (2015) showed that as the rehabilitated sites aged, the water retention of the soils improved dramatically, with oldest site studied only marginally different from the unmined soil. This can have a major effect on vegetation management of a site, highlighting the importance of continuous management post-rehabilitation. With continued inputs and well-defined goals and strategies, mined lands may become high functioning and productive agricultural landscapes, often more productive than the land before mining (Bennett et al., 2021; Melland et al., 2021).

It should be stated that the abandonment of legacy coal mines in NSW, and legacy mines in general, is not without reason. Mines may be abandoned for various reasons, but commonly these reasons are high production costs, lower commodity price returns, geotechnical problems, and a lower demand for coal on overseas markets (Laurence, 2011). This paired with often long periods of time since closure, does make it difficult to assign remediation responsibility. Regardless, the legacy of contamination continues in many sites unabated, and without action will realistically continue for decades to come. The issue of legacy mines is a large and complex problem with no simple solution, however, this should not prevent those who are responsible from addressing the problem. While the studies so far covered in this chapter relate to open cut mines, I believe that with the right management and regulatory input, it is possible to apply the same standard of rehabilitation to legacy underground mines in NSW.

4.2.3. Predicting Metal Uptake by Plants

Plants can be used to minimise erosion or weathering of soils, while also minimising the infiltration of contaminated water into soil (Herndon et al., 2019). Further, plants may even be used to store metals or metalloids, hereby known as heavy metals, within plant tissues such as roots and shoots through the process of phytoremediation. All plants possess a level of metal tolerance, however only a small percentage can survive in heavily contaminated soils (Ali et al., 2013; Ashraf et al., 2019). While this is an important factor, arguable more important is a knowledge of the bioavailable fraction of contaminant in the soil. While several mechanisms for measuring bioavailability of heavy metals have been suggested, the complex nature of plant heavy metal uptake means no single method may be used in all situations. Nolan et al. (2005) address in detail three common methods, and the conditions that must be met for successful measurement of plant available heavy metals. Looking at free ion activity and total heavy metal concentration in soil, they state that the speed of uptake by plants, and the resupply of heavy metals from the solid phase must be carefully regulated for these measurements to be considered predictive of heavy metal availability. Sequential extraction aims to overcome this problem by using different strength extractants to measure heavy metal in line with supply speeds; however, this still does not accurately account for all mechanisms or mixing of metals between distinctive pools (Ernstberger et al., 2005; Zhang & Davison, 2005).

In contrast, diffusive gradient thin film (DGT) overcomes these problems by imitating the mechanism in which the plants uptake heavy metals. As metals move from the pore water into the DGT binding layer the concentration gradient surrounding the piston will lower. This will result in resupply from complexes of metals in the solid phase, meaning all labile species, or metals which can freely dissociate from surrounding soil matrix will be measured (Zhang & Davison, 2005). This process is similar to metal uptake by plants, as the rhizosphere interface becomes depleted, resulting in a concentration gradient which causes heavy metal resupply from the surrounding soil through dissociation of complexes and soil particles (Lehto et al., 2006).

4.3. Research Aims

Within the literature there is disagreement as to what heavy metal extraction technique best predicts the uptake of heavy metal in plants. Previous research has been conducted on the heavy metal phytoremediation potential of Australian native grasses *Astrebla lappacea, Themeda triandra, Imperata cylindrical* (Fu et al., 2016; Ng et al., 2016)*, Chloris truncata, and Dichanthium sericeum* (Lamb et al., 2010; Lamb et al., 2012) with a focus on germination or toxicity using single or multi element nutrient solutions experiments. To build on this body of work, I aimed to test 'real world' contaminated soils taken from Abermain number 2 colliery, conducting a glasshouse study using rhizotrons allowing for non-destructive access to the rhizosphere. To my knowledge, DGT has never been used to measure the uptake of bioavailable metals in these five species, and previously no research has looked at how these species preform under conditions found at legacy coal mines in NSW.

Aim 1: I compared DGT and sequential extraction techniques as predictors for the heavy metal uptake of five Australian native grasses grown is soil collected from a NSW legacy coal mine. The soil and plants tissues was examined for heavy metals As, Co, Cr, Cu, Mg Ni, Pb, and Zn with the aim of identifying an accurate predictor of plant heavy metal uptake.

Aim 2: Using statistical modelling and the measurement of bioconcentration and translocation factors (see 4.3.6 for definitions), I compared concentration differences between soil, root, and shoot tissue of the same five native grass species. I aimed to identify the phytostabilisation or phytoextraction potential (see sections 1.7, 1.8, and 4.3.6 for definitions) of these species hoping to find species suitable for the remediation of mine sites in NSW.

4.4. Materials and Methods

4.4.1. Physiochemical Properties of the Soil

Soil pH was measured as detailed in section 3.3.3i. Cation exchange capacity was measure at the Eurofins laboratory in Sydney using the LTM-MET-3060 Cation Exchange Capacity by bases & Exchangeable Sodium Percentage. Total soil nitrogen and carbon were measured using LECO TN/TC (Rayment & Higginson, 1992).

4.4.2. Rhizotron Experiment

The growth experiment was conducted from 9 August to 18 December 2020 in a roof top glasshouse at University of Technology Sydney coinciding with the spring/summer growth period of C4 (4-carbon organic acid (oxaloacetate)) plant species. Daytime air temperature ranges for the months of the study were: September (13- 39.36 °C); October (15.5- 38.93 °C); November (15.3- 56.28 °C); December (18.8- 50.86 °C).Average light intensity between 12:00 and 17:00 was 588.8 W/m^2, with a range of 10.61- 1191.88 W/m^2. Relative humidity of the glasshouse over the study period ranged from 25-94%.

Grasses were grown in special designed pots called rhizotrons with inner dimension of 288 x 200 x 25 mm (height x length x width) with a total volume of approximately 1.4 L (Fig. 4.1). All rhizotrons had a clear removable face plate to allow for easy access to the root zone. Rhizotrons were grown at 45-degree angle with removable plate facing down to encourage roots to grow along the plate. At all times throughout the experiment the rhizotrons were covered with reflective foil to minimise effect of light and heat within the rhizosphere.

Soil for the experiment was collected from Abermain No. 2 Colliery (see Chapter 3). To replicate a real-world revegetation experiment, soil was mixed with (potting mix) 80:20 ratio by volume of dried soil. Three rhizotrons were set up without the addition of plants as controls.

For each of the five species (Section 4.3.3.) three plants per rhizotron were grown from seed, with germination completed on average between 5 to 14 days. Rhizotrons with no germination after 14 days were reseeded, with all then germinating within the next 4 days. Excessive seed was used to ensure germination, with any extra plants thinned after 30 days. Initially rhizotrons were watered to total water holding capacity daily, until plants became well established. After this water until holding capacity occurred every three days. Roots of the grasses reached the bottom of the rhizotrons 40 days post sowing. After 80 days growth, for each rhizotron (including controls) three DGT gels (Section 4.3.4) were deployed in soil wetted to 100% water holding capacity for a total of 24 hours.

Following deployment of DGT gels plants were destructively harvested. Above ground biomass was separated at soil surface and roots were washed before all biomass was oven-dried at 40 °C for three days.

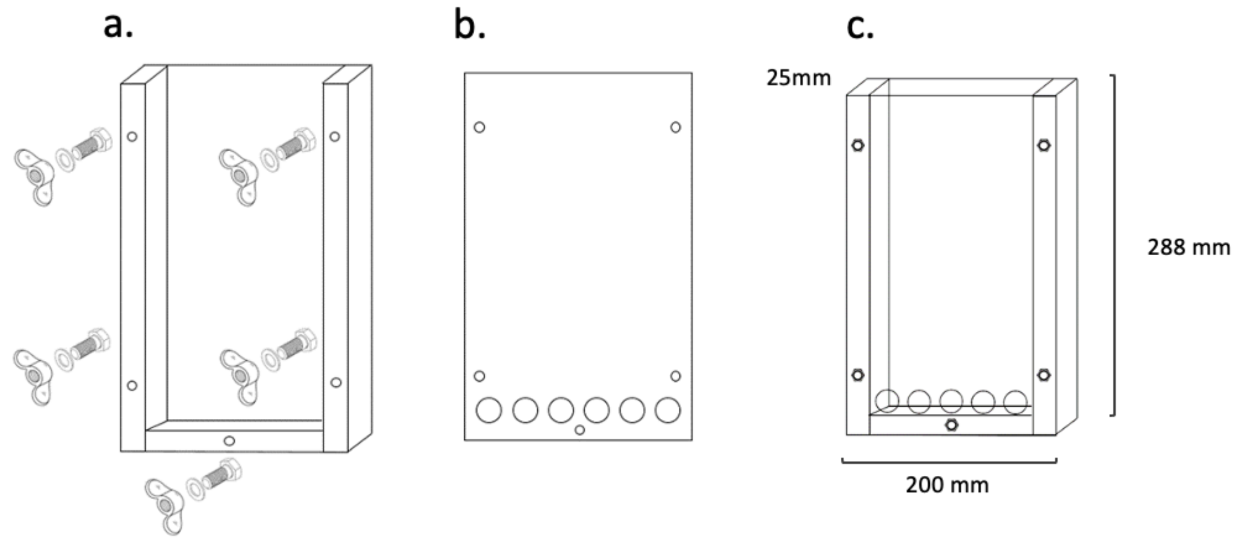

Figure 4.1. A conceptual drawing of the rhizotron design. Fig 4.1a. Shows the design without the removable face. Fig 4.1b. Shows the removable face plate with drainage holes. Fig 4.1c. Shows built rhizotron with height, width, and depth measurements.

4.4.3 Australian Native Grasses

Four Australian native grass species were chosen for their ability to survive in nutrient poor or metal contaminated environments similar to legacy mine sites. *Astrebla lappacea, Themeda triandra, Imperata cylindrical, Chloris truncata, and Dichanthium sericeum* seeds were sourced from Nindethana Australian seeds and kept refrigerated until use.

Curly Mitchell Grass (*Astrebla lappacea* (Lindl.))

Long-lived perennial species growing up to (0.9 m) in height that forms dense tussocks with deep root systems. A common grass with a wide distribution across QLD, NSW, South Australia, Western Australia, it is considering tolerant of heavy grazing and drought making it an attractive option for mine site rehabilitation (Jacobs & Hastings, 1993). *Astrebla* species have also been shown to tolerate heavy metal contamination, and in some cases accumulate significant amounts of Pb and Zn inside above ground tissues (Lottermoser et al., 2009).

Kangaroo Grass (*Themeda triandra Forssk.*)

A very common native grasses species found all across Australia, *T. triandra* is a tall tussock forming perennial species. The species is easily recognised due to its distinct spiked flower (Jacobs et al., 2008). Within the literature the species is also commonly used in revegetation and rehabilitation studies, due to its ability to grow under low nutrient/rainfall conditions (Dell'Acqua et al., 2013; Roberts et al., 2015; Windsor & Clements, 2001).

Cogon Grass (*Imperata cylindrica* (L.) P.Beauv)

A perennial grass found along the east coast of Australia (Jacobs & Wall, n.d.-b). Growing in areas prone to fire with poor nutrient soils, *I. cylindrica* has been shown to colonise quickly after disturbance (MacDonald, 2004). This ability has led to the species being classified a weed in several countries. Studies conducted in China have shown *I. cylindrica* to have phytomanagement potential (Fu et al., 2016; McNamara et al., 2006; Zhang et al., 2009) with suggestions it may be a hyperaccumulator of lead (Adejumo et al., 2018) and zinc (Ng et al., 2016).

Windmill Grass (*Chloris truncata* R.Br)

A small tussock forming, short-lived perennial (2-3 years), often considered good for colonising when conditions are right. Well distributed across temperate mainland Australia and a common species in areas of NSW associated with mining (Jacobs & Hastings, 1994). *Chloris truncata* is considered a weed species in northern and sub-tropical grain areas of Australia (Chauhan et al., 2018). Farley et al. (2013) found that compared with a range of other species including *T. triandra*, *Astrebla lappacea* and *Dichanthium sericeum*, *C. truncata* had much higher levels of germination percentage in mine site rehabilitation project. However, results were mixed with Huxtable et al. (2005) finding the species did not persist when sown on mining overburden. While *C. truncata* has been suggested as a candidate for hydrocarbon remediation (Hoang et al., 2021), little information is available for it use as a metal remediator.

Queensland Blue Grass (*Dichanthium sericeum* (R.Br.) A.Camus)

An erect tussock forming perennial species up to 1.2m high with a range that covers all states of Australia, *D. sericeum* is the dominant species of the endangered Bluegrass Tussock communities (Jacobs & Wall, n.d.-a; Ladouceur & Mayfield, 2017). While intolerant to grazing and disturbance, studies have shown the species may be suitable for revegetation of low nutrient, low contaminated mine spoils and tailings with good emergence percentage and biomass recorded (Ashley et al., 2004). Further research indicates while moderately impacted by metals and metalloids in contaminated soils, *D. sericeum* is reasonably tolerant and may be a suitable remediator species under certain conditions (Lamb et al., 2010; Mahbub et al., 2017).

4.4.4. Diffusive Gradients in Thin-films (DGT)

DGT pistons with a Chelex binding layer were prepared following the procedures recommended by DGT Research (Lancaster, UK) as outlined in (Davison, 2016). The binding resin was a 0.4 mm thick Chelex-100 (Bio-Rad, mesh 200-400) impregnated polyacrylamide gel. During the binding resin synthesis, gravitational settling resulted in the Chelex-100 beads concentrating towards at the bottom of the gel. This concentrated side was placed towards the window of the DGT, in contact with the 0.8 mm thick polyacrylamide diffusive layer. A 0.13 mm thick, 0.45 µm pore size polyethersulfone filter paper was placed on top of the diffusive layer. The three layers were sandwiched on the piston base by a housing with a 2 cm diameter window. Prior to deployment, assembled pistons were conditioned for 24 h in a 0.12 M NaCl solution (Suprapur, Merck Millipore). Prepared DGT were stored moist in low-density polyethylene bags at 4°C.

Following deployment, DGT devices were disassembled, and the binding resin placed in 1 mL of 1 M HNO3 (Suprapur grade, Merck Millipore) for ≥12 h on an orbital shaker. The eluants were diluted to a final concentration of 0.2% HNO3 before metal analysis. Equation 1 was used to calculate the mass (M) of metal accumulated by the DGT binding layer. Ce is the concentration of eluent (nmol L -1) which is multiplied by the dilution factor of 10. HNO^3 eluent volume (0.001 L) is denoted by V_e and V_{gel} represents volume of resin gel (0.002 L), Fe is the elution factor (0.85) (standard measurement).

Equation 2 was then used to convert M into DGT labile concentration (C_{DGT}) measured concentration in (nmol ml $^{-1}$), Δg is the thickness of the diffusion layer (0.0094 cm), D is the diffusion coefficient taken from (ref) for each metal at average temperature of 27 c (x10−6 cm2 s−1), t is 24-hour deployment time in (s), and A represents the area of the DGT piston (3.14 cm^2)(Koppel et al., 2021).

Equation (1): Mass of metal accumulated by DGT:

$$M = \frac{10 \text{ x } C_e(V_e + V_{gel})}{fe}$$

Equation (2): DGT labile concentration:

$$C_{DGT} = \frac{M \, \Delta_g}{D \, A \, \Delta_t}$$

4.4.5. Sequential Method for Total Metal Analysis of Soils and Plant Tissues

Soil sample preparation and measurement followed General ICP-MS methods covered in detail in reference (Chapter 3.4.3 iii). Digestion of plant biomass followed EPA 3050B method outlined in (Chapter 3.4.3 iii), however, each digestion contained 1g of certified plant reference material (CRM-PINE, Choice Analytical). To account for matrices interferences while also producing samples within detection limits, different dilution factors were used for plant tissue and soil samples in glasshouse study. Root and shoot samples were measured using a dilution factor of 20, while soil samples were measured using a 150 times dilution. Spiked recoveries for shoots were within acceptable limits 100 ± 10% except arsenic which measured 84.68%. All spiked recoveries for roots and soils were within acceptable limits 100 ± 10%.

Certified reference material Loam Soil Level D for soil, and Pine needles for plants (Choice Analytical, Australia) were within acceptable limits 100% ± 10% for soils. Pine needle CRM for chromium, arsenic, and cobalt were not within detection limits, and zinc measured a 126.55% return.

4.4.6. Bioconcentration Factor and Translocation Factor

The bioconcentration factor (BCF) and translocation factor (TF) were used to determine the suitability of each plant species for use in heavy metal phytomanagement (Fig. 4.2). BCF is the ratio of metal found in the plant roots divided by the total metal within the soil (Equation 3). TF ratio compares the amount of metal found within the shoot to the amount within the root (Equation 4). These are common measurements used to determine the suitability of a species for phytostabilisation or phytoextraction. Plants with a BCF > 1 and a TF <1 are considered good candidates for phytostabilisation, where plants with both BCF and TF > 1 may be indicative of phytoextractor species.

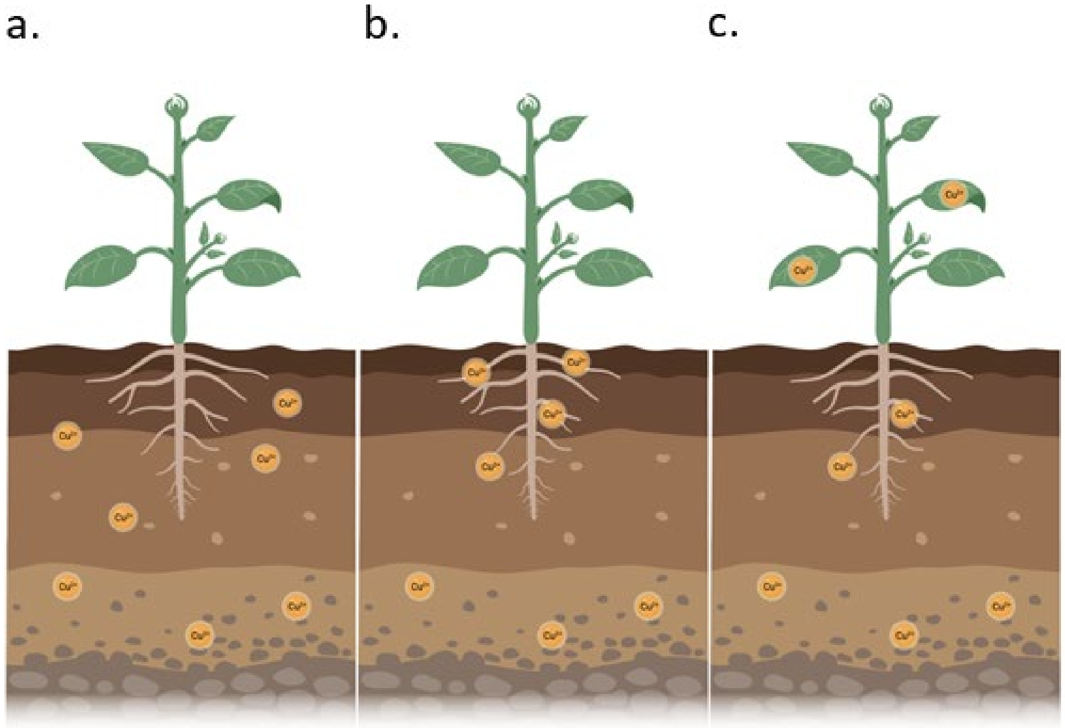

Figure 4.2. A simplified example of the processes of BCF and TF using Cu $^{2+}$ (i.e., a bioavailable form of Cu): 4.2a. A plant growing in contaminated soil; 4.2b. The bioavailable metals absorbing into the roots or adsorbing onto the root; and 4.2c. The translocation of contaminants from the root tissues into the shoot tissues. Image made using the program BioRender

Equation (3): Bioconcentration Factor:

$$\mathrm{BCF} = \frac{\mathrm{Metal}^{\mathrm{root}}}{\mathrm{Metal}^{\mathrm{soil}}}$$

Equation (4): Translocation Factor:

$$\mathrm{TF} = \frac{\mathrm{Metal}^{\mathrm{shoot}}}{\mathrm{Metal}^{\mathrm{root}}}$$

4.4.7. Data Analysis

Statistical analyses

To estimate the amounts of metals accumulated in the experimental species tissues, I fitted eight separate linear models of the ln transformed metals (ppm) using categorical factors for species (five level fixed factor), tissue (two level fixed factor; root and shoot), and a species x tissue interaction term. Terms for the bioavailability of the metals (diffusive gradient thin film [DGT]; continuous variable, ln transformed) and the total soil metal concentration (ppm; continuous variable, ln transformed) in the soils the plants were grown in were also included to control for unintended variation among replicate plants. Next, to estimate the tissue mass of the species, a linear model was fitted to the recorded tissue masses (in g, ln transformed), modelled with terms for species, tissue type, and a species x tissue type interaction. The transformed parameter estimates (i.e. transformed to the original units of g) from this model, and the transformed metal concentrations (in ppm) for each tissue type were then used to calculate the mean mass adjusted concentrations of metals for each species by tissue type (estimated metal mass by species and tissue multiplied by the respective estimated tissue mass). To determine the overall accumulation patterns of the metals for each plant species, and which species might accumulate the least metal overall in their tissues per plant, these values were then summed together (root and shoot mass adjusted accumulation) to arrive at the relative mean metal concentrations for an individual of each plant species. All analyses were conducted in 4.1.2 (R Core Team, 2020), using the packages *car* (Fox & Weisberg, 2019) for significance testing, and *emmeans* (Lenth, 2022) to provide parameter estimates.

4.5. Results

4.5.1. DGT Compared to Total Metal Analysis

Across all metals, a significant tissue metal concentration x DGT metal interaction was found ($F_{1, 76}$ = 9.558, P = 0.003; Fig. 4.3a), with shoots accumulating relatively less metal at lower DGT compared to root tissues. At higher DGT metal concentration, the differences in metal concentration between the tissues were relatively smaller, with root tissue having significantly higher tissue concentrations than shoot tissue overall ($F_{1, 76}$ = 71.944, P < 0.0001). Considering individual metals, DGT concentrations differed widely (Fig. 4.3b). When accounting for individual metals and their disparate DGT concentrations in a separate model with a three-way interaction between tissue type, the individual metals, and their DGT concentrations, the tissue metal concentration x individual metal x DGT metal concentration was non-significant ($F_{7,48}$ = 0.417, P = 0.9; Fig 4.3b), as higher concentrations of individual metals did not result in different patterns of accumulation of those metals within tissue types, or within tissue types across metals with the tissue metal concentration x DGT metal concentration term becoming non-significant (F 1,48 = 2.378, P = 0.1; Fig. 3c). Further, when consideration of the concentrations of individual metals was included in the modelling, DGT metal concentration was not significantly related to tissue accumulation overall (Fig 4.3c).

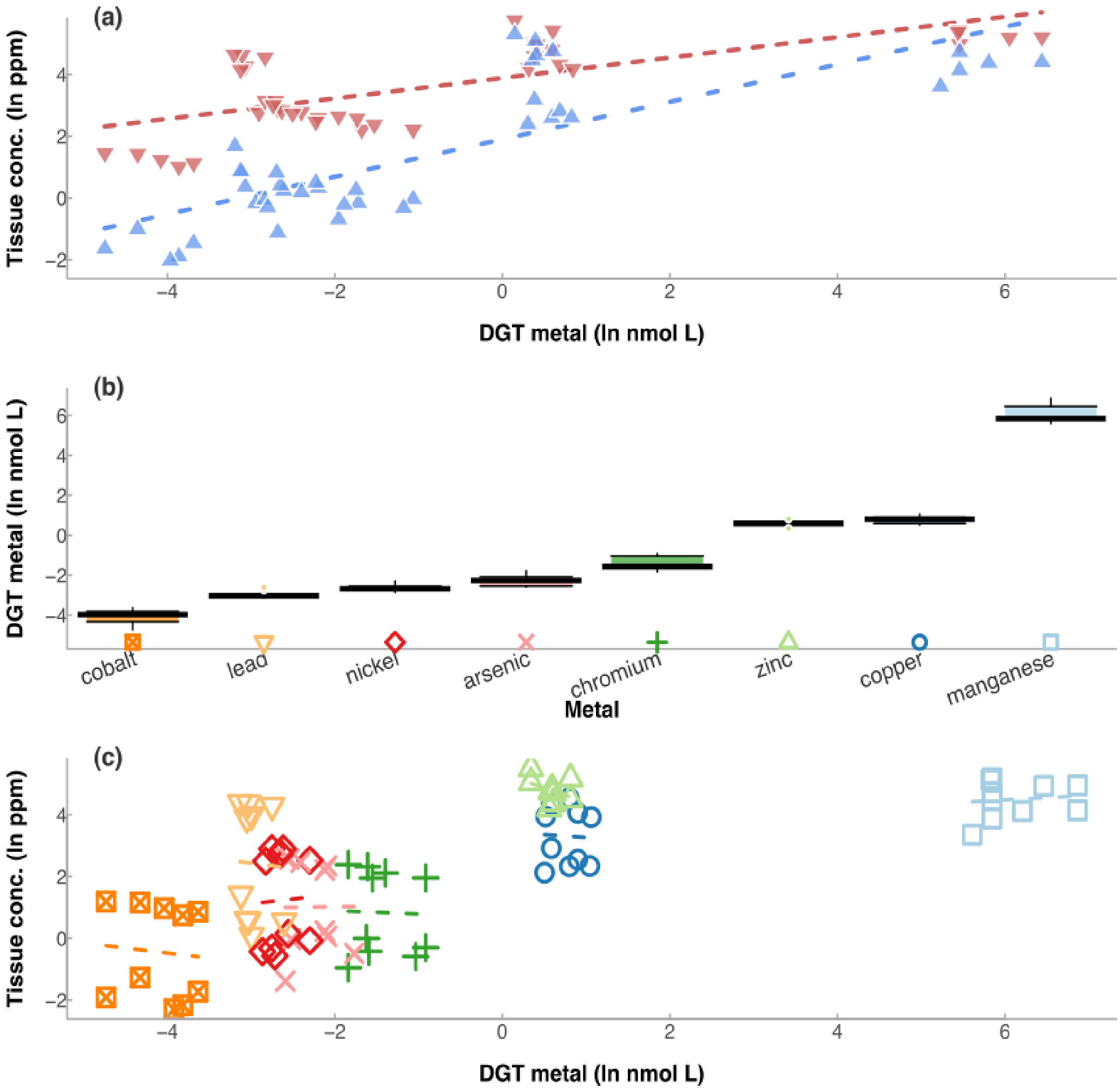

Figure 4.3. DGT metals VS tissue concentration. Red triangles indicate root samples and blue triangles indicate shoot samples. Strong correlation for both root (R^2 = 0.5699) and shoot (R^2 =0.655; Fig 4.3a) respectively. High variability in the concentrations of the eight analytes with the lowest concentration on the left following an increasing pattern to the right (Fig 4.3b). (Fig 4.3c) Breaks down the relationship between individual analytes and plant tissue (root and shoot tissue combined and labelled tissue), showing no correlation for individual metal species.

Similar overall patterns emerged when comparing tissue metal concentration to the total metal extraction method. There was a significant tissue x total metal relationship overall ($F_{1, 76,}$ = 8.43, P = 0.0048, Fig 4.4a) with again root tissue accumulating significantly more than shoot ($F_{1, 76}$ = 122.49, P = 0.000, Fig 4a). Some differences emerged when looking at individual metals. For example, in comparison to DGT, total Pb concentrations increased from second lowest to third highest concentration of all metals (Fig 4.4b). Zn and Ni also recorded higher concentrations, while concentration of As, Cr, and Cu fell in relation to other analytes (Fig 4.4b). No significant relationship was observed when examining the tissue metal concentration x individual metal x total metal concentration ($F_{7, 48}$ = 0.45, P = 0.8659; Fig 4.4b), or within tissue types across metals with the tissue metal concentration x total metal concentration term becoming non-significant ($F_{1, 48}$ = 0.39, P = 0.5351; Fig. 4.4c)

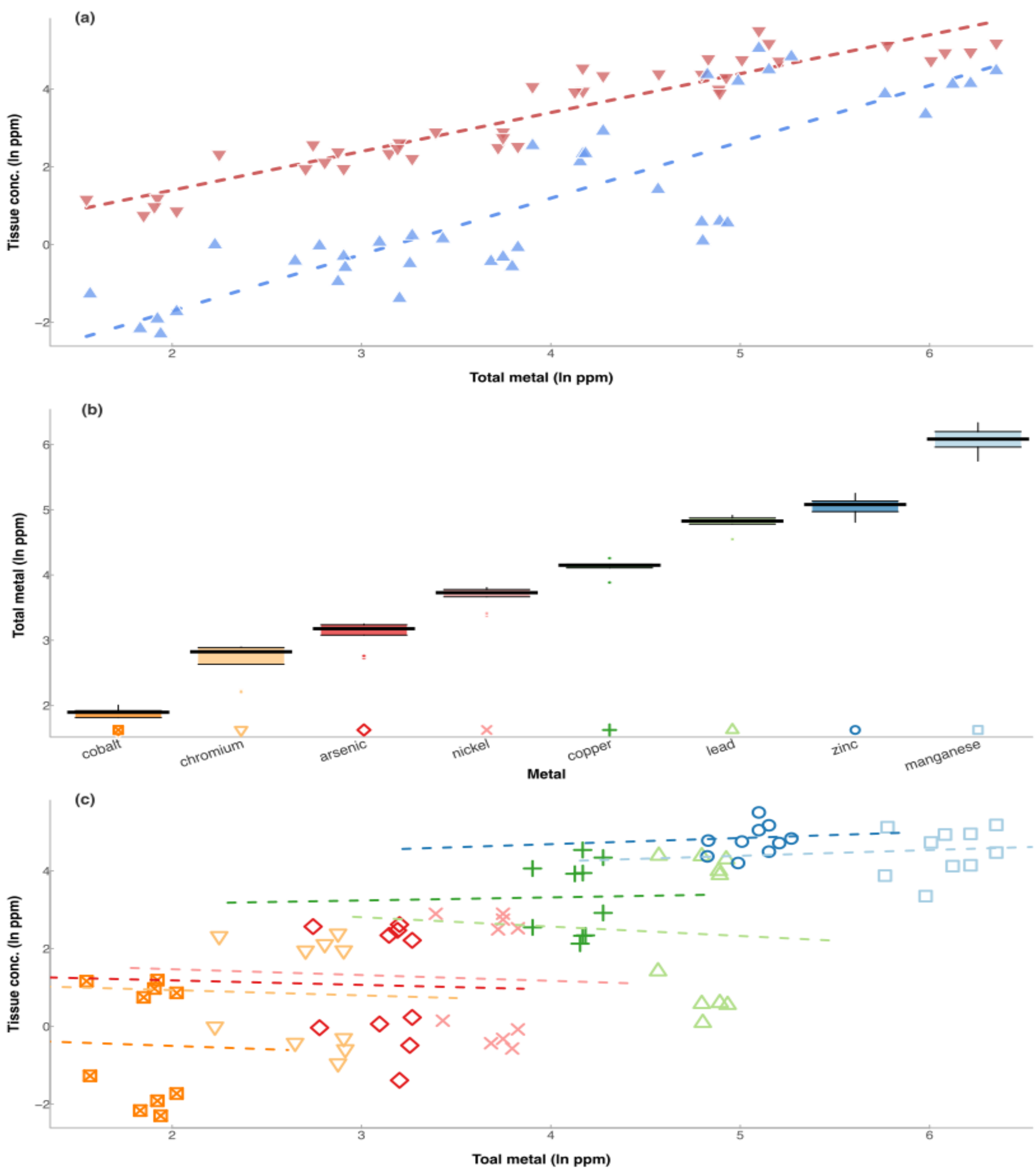

Figure 4.4. Total metals compared tissue concentration. a. Red triangles indicate root samples and blue triangles indicate shoot samples. Strong correlation for both root (R^2 = 0.8698) and shoot (R^2 = 0.7089) respectively; b. High variability in the concentrations of the eight analytes with the lowest concentration on the left following an increasing pattern to the right; c. The relationship between individual analytes and plant tissue (root and shoot tissue combined and labelled tissue), showing no correlation.

Pairwise comparison of soil samples in species and control rhizotrons found similar concentrations of metals across all total metal soil measurements as measured by the sequential method, with no significant different between the soil concentrations recorded (Table AC 13.). This is in contrast to DGT metal concentrations, where significantly higher Ni and Zn were found in the control soil samples when compared to *T. triandra* (Ni: T-ratio = 3.349, P = 0.0186 and Zn T-ratio = 3.384, P = 0.0169) and *C. truncata* (Ni: T-ratio = -3.096, P = 0.0363 and Zn: T-ratio = -3.657, P = 0.0079). All other DGT versus species pairwise comparisons were non-significant (Table AC 14.).

4.5.2. Species by Tissue Statistical Interactions

When comparing the concentration of metals in roots and shoots of each species, for As, Cr, Co, Pb, Mn and Ni, no significant species x tissue interactions emerged, and for these metals, root tissues contained significantly higher metal concentrations compared to shoot tissues (Table 4.1; Fig. 4.5). As, Cr, Co, Pb and Ni concentrations did not differ significantly among species, (Table 4.1; Fig. 4.5). Mn concentrations were significantly higher in *C. truncata* relative to *A. lappacea* (Fig. 4.5e), while the other species were not significantly different to either of these species. For Cu and Zn there was a significant species x tissue interaction (Table 4.1). Cu concentrations in root tissues were significantly higher in *C. truncata* compared to *A. lappacea*, *D. sericeum* and *T. triandra*, while *I. cylindrica* did not differ significantly to the other species (Table 1; Fig. 4.6a). There was no significant difference in Cu concentrations in shoot tissues among species (Table 1; Fig. 4.6a). *C. truncata* and *I. cylindrica* showed significantly higher concentrations of Zn in root tissues compared to *A. lappacea*, *D. sericeum* and *T. triandra* (Table 1; Fig. 4.6b). In shoot tissue, Zn concentration was significantly lower in *A. lappacea* relative to *C. truncata* and *T. triandra*, and also in *D. sericeum* compared to *C. truncata*, while *I. cylindrica* did not differ significantly to any other species (Table 1; Fig. 4.6b).

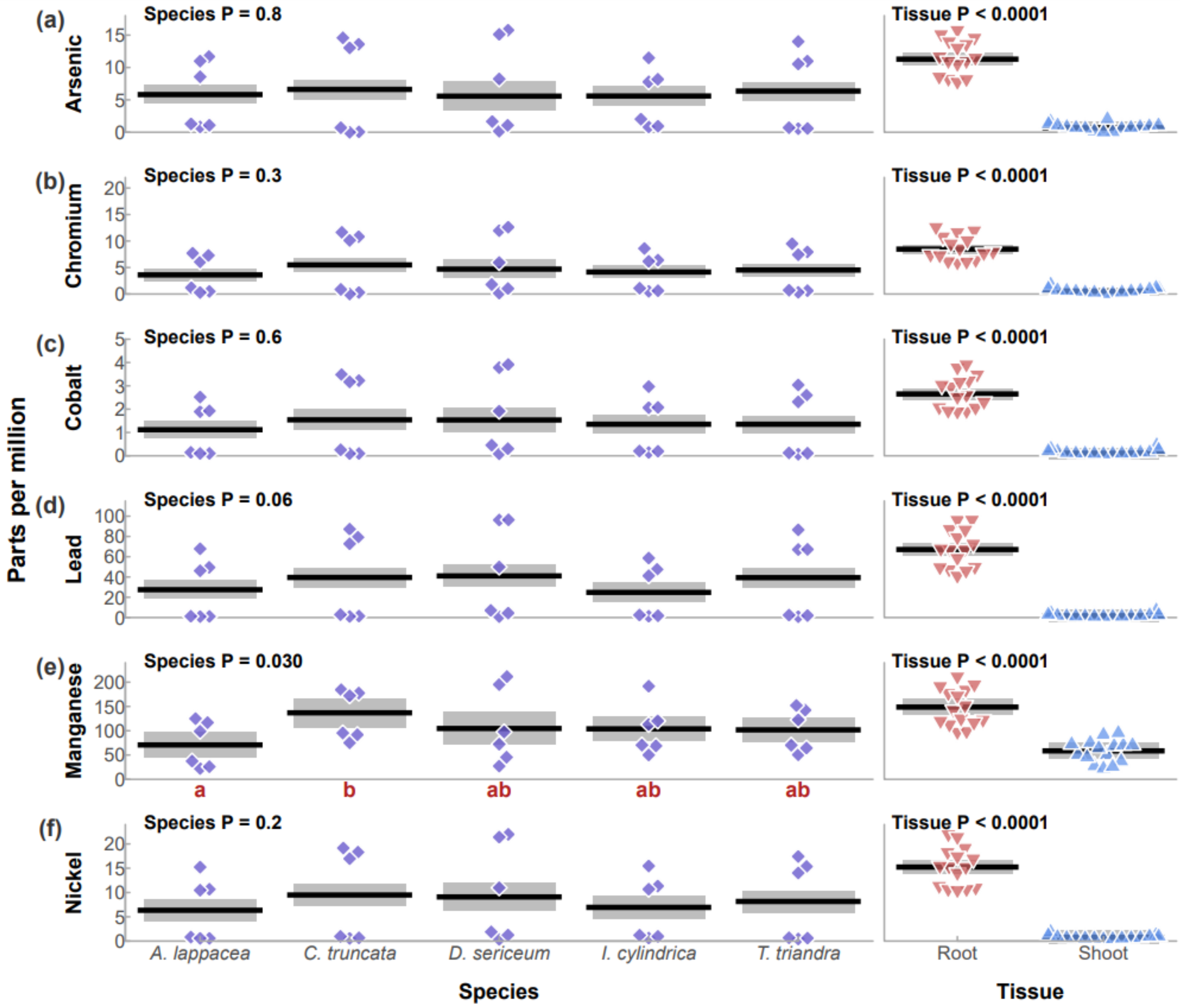

Figure 4.5. Plots of metal concentrations by species and tissue. Shaded areas indicate the 95% CI of the mean, and the black line the mean for each group, points show the data. The associated P values from the models are shown in black in each plot. In (e) the red letters below the x-axis indicate which species significantly differ.

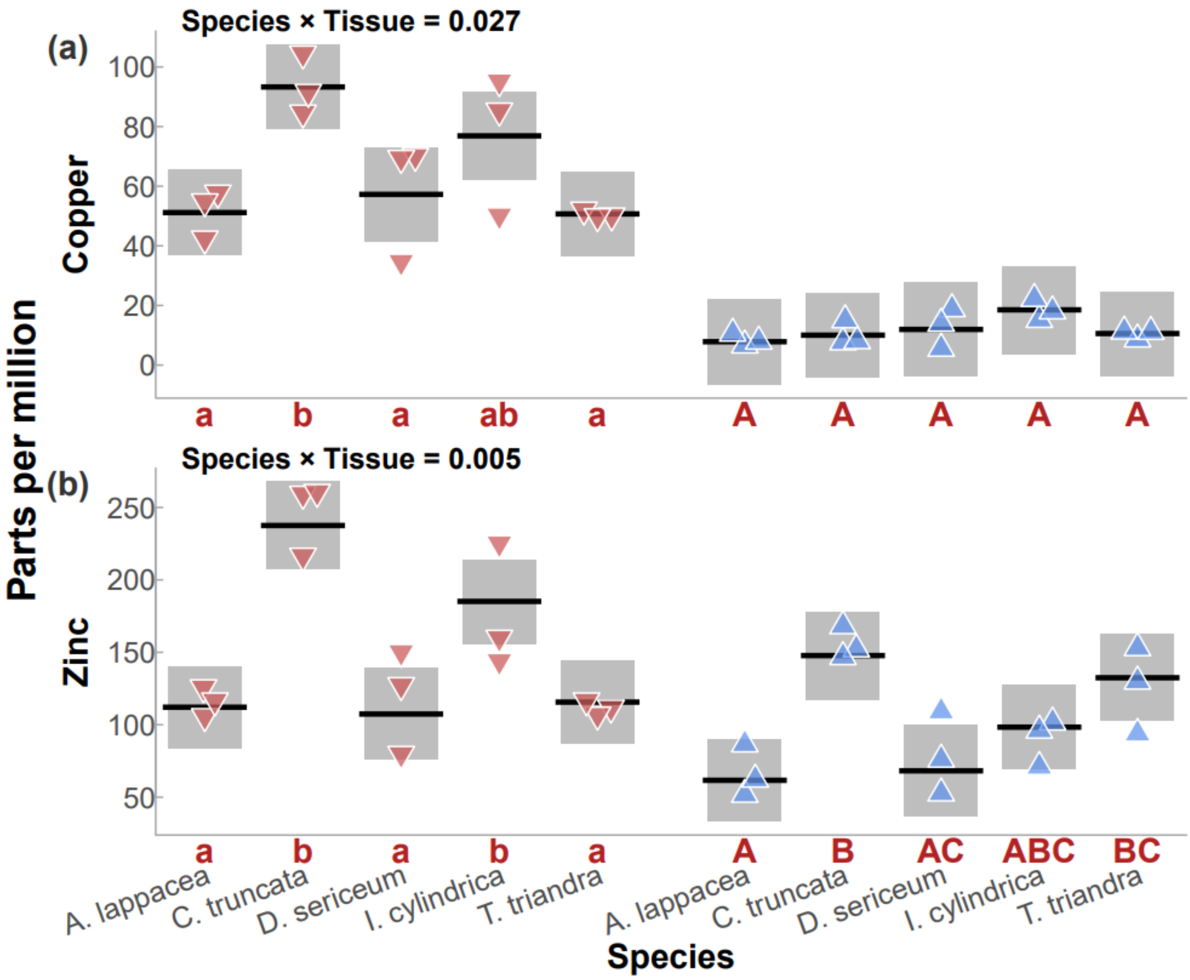

Figure 4.6: Metals showing a significant species x tissue interaction (P value shown at top right of each plot). Roots are shown on the left side (red downward pointing triangles), and shoots on the right side (blue upward pointing triangles). Red lowercase letters indicate which species significantly differ among root tissues, and red uppercase letters the significant differences among species in shoot tissue. Shaded areas indicate the 95% CI of the mean, and the black line the mean for each group, points show the data.

In modelling tissue mass, there was a non-significant tissue x species interaction ($F_{4,20}$ = 0.287, P = 0.9; Fig. 4.7a), although *A. lappacea*, *C. truncata* and *T. triandra* showed comparably larger differences in their estimated mean mass for roots and shoots than did *D. sericeum* and *I. cylindrica*. Mean tissue mass across tissue type differed among species ($F_{4,20}$ = 5.652, P = 0.003; Fig. 4.7b), with *I. cylindrica* having significantly lower tissue mass compared to *T. triandra* and *D. sericeum*, and *T. triandra* having significantly greater mass than *C. truncata* (Fig. 4.7b). No significant difference between the mass of tissue types emerged ($F_{1, 20}$ = 0.579, P = 0.1; Fig. 4.7c).

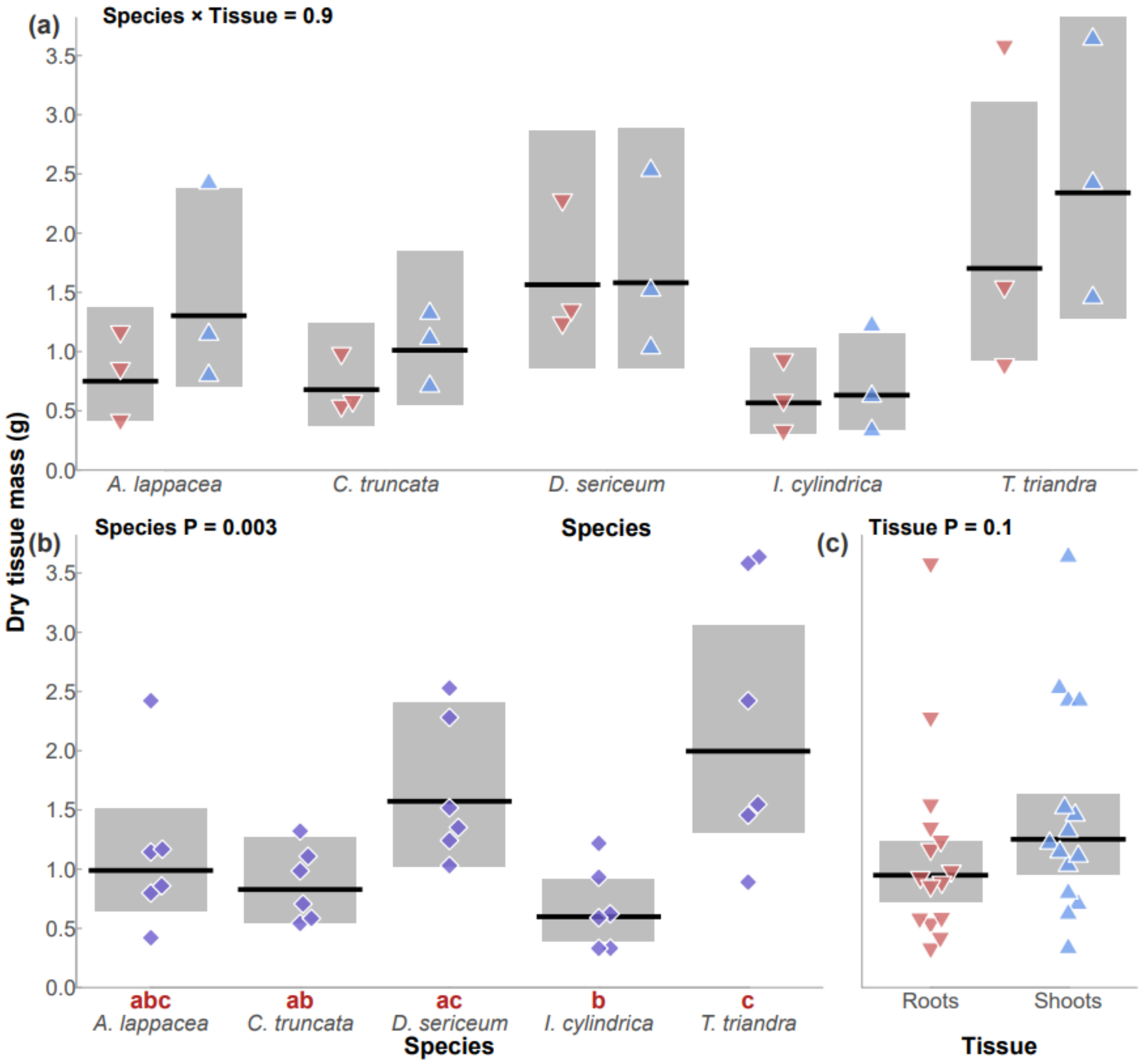

Figure 4.7: Estimated means from the model of tissue mass by species, tissue, and the species x tissue interaction. Shaded areas indicate the 95% CI of the mean, and the black line the mean for each group, points show the data. The associated P values from the model are shown in black in each plot. In (b) the red letters below the x-axis indicate which species significantly differ. The values from (a) are used to weight the model estimated metal concentrations in the subsequent mass adjusted metal accumulation calculations.

Weighted by plant mass, overall metal concentration per plant scaled with plant dry mass (Fig. 4.8). The strongest exception to this pattern was *A. lappacea*, with a lower accumulation of metal for its mass, showing similar accumulation per plant to *I. cylindrica*, which was the lightest plant overall. *I. cylindrica* showed the lowest accumulation of arsenic, chromium, cobalt, lead and nickel (Fig. 4.8), while *I. cylindrica* and *A. lappacea* were approximately equivalent in manganese accumulation (Fig. 4.8f). For copper and zinc, *A. lappacea* showed the lowest accumulation per plant. *T. triandra* emerged as having the highest accumulation per plant of arsenic, chromium, copper, lead, manganese, and zinc (Fig. 4.8) and the greatest overall dry mass, while greater amounts of cobalt and nickel were accumulated by *D. sericeum* (Fig. 4.8), the next heaviest plant species.

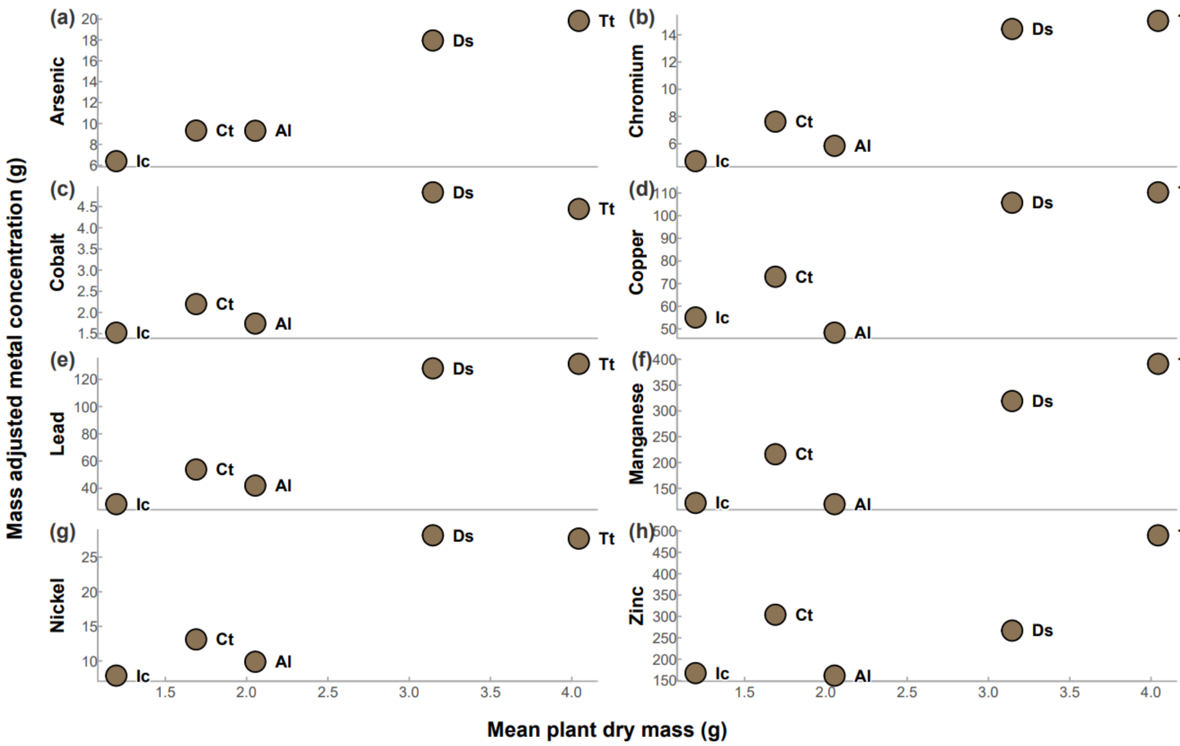

Figure 4.8: Mass adjusted metal concentration (model estimated tissue concentration multiplied by model estimated mass by tissue summed by species) vs plant total dry mass (summed model estimated mass of roots and shoots). Points are labelled with species initials.

4.5.3. Bioconcentration Factor (BCF) Compared Across Grasses

Only three species of plants displayed the ability to bioconcentrate amounts of metals, with a BCF > 1 (Table 4.2.). For *D. sericeum* Cr and Cu both had BCF > 1; Co, Ni, Zn, As, Pb between 0.5-0.99; and Mn <0.5. *Chloris truncata* recorded Zn and Cu BCF > 1; Cr, Co, As, Pb between 0.5-0.99; and Mn and Ni <0.5. Whereas *I. cylindrica* showed: Zn and Cu to have BCF > 1; no analytes between 0.5-0.99; and Cr, and Mn, Co, Ni, As, and Pb <0.5. *Astrebla lappacea* recorded no analytes with a BCF > 1; Cr, Cu, Zn As, and Pb between 0.5-0.99; and Mn, Co, Ni, <0.5. While *T. triandra* also showed no analytes with a BCF > 1; Cr, Cu, Zn, and Pb between 0.5-0.99; and Mn, Co, Ni, and As <0.5.

4.5.4. Translocation Factor (TF) Compared Across Grasses

Only one species showed the potential to translocate significant amounts of metal into the above ground biomass (Table 4.3.). *Themeda triandra* recorded a TF > 1 for Zn; no analytes recorded between 0.5-0.99 and only Mn, between 0.49-0.1. All other analytes Cr, Co, Ni, As, and Pb recorded values <0.1. *Chloris truncata* recorded no analytes with a TF > 1, or between 0.5-0.99. Three analytes, Mn, Cu, and Zn were measured between 0.49 - 0.1; and Cr, Co, Ni, As, Pb all <0.1. *Imperata cylindrica* recorded no analytes with a TF > 1; Zn between 0.5-0.99; Mn, Cr, Cu, and As between 0.49-0.1; and Co, Ni, and Pb <0.1. *Astrebla lappacea* saw no analytes with a TF > 1; Zn between 0.5-0.99; Mn, Cu, and As between 0.49-0.1; and Cr, Co, Ni, and Pb <0.1. *Dichanthium sericeum* no analytes with a TF > 1; Zn between 0.5-0.99; Mn between 0.49-0.1; and Cr, Co, Ni, As, Pb < 0.1.

Table 4.1: Results from the models of metal concentrations (in ppm) modelled by species, tissue, and a species x tissue interaction, while controlling for soil metal availability (DGT) and overall soil metal concentration. All significant results (P ≤ 0.05) have been highlighted in bold.

Metal	Terms	SS	F	DF	P
Arsenic	Species	4.875	0.446	4	0.8
	Tissue	816.538	298.964	1	**< 0.0001**
	DGT arsenic	8.847	3.239	1	0.09
	Soil arsenic	4.253	1.557	1	0.2
	Species x tissue	28.646	2.622	4	0.07
	Residuals	49.162		18	
Chromium	Species	11.033	1.469	4	0.3
	Tissue	471.04	250.856	1	**< 0.0001**
	DGT chromium	1.906	1.015	1	0.3
	Soil chromium	3.262	1.737	1	0.2
	Species x tissue	19.974	2.659	4	0.07
	Residuals	33.799		18	
Cobalt	Species	0.551	0.761	4	0.6
	Tissue	48.105	265.545	1	**< 0.0001**
	DGT cobalt	0.399	2.201	1	0.2
	Soil cobalt	0.078	0.433	1	0.5
	Species x tissue	1.387	1.915	4	0.2
	Residuals	3.261		18	
Copper	Species	2243.024	4.201	4	**0.014**
	Tissue	21908.78	164.142	1	**< 0.0001**
	DGT copper	16.791	0.126	1	0.7
	Soil copper	7.464	0.056	1	0.8
	Species x tissue	1884.838	3.53	4	**0.027**
	Residuals	2402.541		18	
Lead	Species	1293.842	2.746	4	0.06
	Tissue	31883.5	270.645	1	**< 0.0001**
	DGT lead	95.203	0.808	1	0.4
	Soil lead	1.008	0.009	1	0.9
	Species x tissue	1181.96	2.508	4	0.08
	Residuals	2120.5		18	
Manganese	Species	10569.37	3.433	4	**0.03**
	Tissue	60961.85	79.211	1	**< 0.0001**
	DGT manganese	133.889	0.174	1	0.7
	Soil manganese	132.827	0.173	1	0.7
	Species x tissue	1844.793	0.599	4	0.7
	Residuals	13853.07		18	
Nickel	Species	39.538	1.589	4	0.2
	Tissue	1564.968	251.651	1	**< 0.0001**
	DGT nickel	0.021	0.003	1	1

Metal	Terms	SS	F	DF	P
	Soil nickel	2.212	0.356	1	0.6
	Species x tissue	47.521	1.91	4	0.2
	Residuals	111.938		18	
Zinc	Species	33659.17	15.91	4	**< 0.0001**
	Tissue	18712.93	35.38	1	**< 0.0001**
	DGT zinc	1405.25	2.657	1	0.1
	Soil zinc	1007.741	1.905	1	0.2
	Species x tissue	11192.77	5.29	4	**0.005**
	Residuals	9520.376		18	

Table 4.2. Average bioconcentration factor (BCF) and standard error for the 5 species and 8 analytes. BCF>1 shows species is concentrating substantial amounts of metals in root tissue. Ratio values > 1 have been highlighted in bold.

Species	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Arsenic	Lead
Dichanthium sericeum	**1.00 ± 0.18**	0.49 ± 0.08	0.63 ± 0.18	0.56 ± 0.10	**1.17 ± 0.22**	0.92 ± 0.14	0.78 ± 0.14	0.82 ± 0.11
Themeda triandra	0.50 ± 0.06	0.33 ± 0.03	0.42 ± 0.05	0.38 ± 0.03	0.84 ± 0.03	0.62 ± 0.07	0.49 ± 0.07	0.60 ± 0.10
Chloris truncata	0.71 ± 0.11	0.38 ± 0.03	0.54 ± 0.06	0.48 ± 0.05	**1.63 ± 0.08**	**1.64 ± 0.13**	0.64 ± 0.06	0.70 ± 0.10
Imperata cylindrica	0.46 ± 0.06	0.31 ± 0.04	0.36 ± 0.05	0.30 ± 0.03	**1.23 ± 0.28**	**1.12 ± 0.16**	0.39 ± 0.04	0.36 ± 0.01
Astrebla lappacea	0.53 ± 0.11	0.30 ± 0.05	0.34 ± 0.06	0.31 ± 0.06	0.86 ± 0.17	0.83 ± 0.13	0.51 ± 0.10	0.50 ± 0.11

Table 4.3. Shows average translocation factor (TF) and standard error for 5 species and 8 analytes. TF>1 shows species is concentrating substantial amounts of metals in shoot tissue. Ratio values > 1 have been highlighted in bold.

Species	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Arsenic	Lead
Dichanthium sericeum	0.09 ± 0.03	0.29 ± 0.05	0.08 ± 0.02	0.06 ± 0.02	0.21 ± 0.03	0.68 ± 0.10	0.07 ± 0.03	0.05 ± 0.01
Themeda triandra	0.07 ± 0.01	0.45 ± 0.05	0.04 ± 0.01	0.04 ± 0.00	0.21 ± 0.02	**1.13 ± 0.17**	0.05 ± 0.00	0.02 ± 0.01
Chloris truncata	0.04 ± 0.03	0.49 ± 0.04	0.05 ± 0.02	0.02 ± 0.01	0.11 ± 0.02	0.41 ± 0.21	0.02 ± 0.02	0.02 ± 0.01
Imperata cylindrica	0.10 ± 0.01	0.46 ± 0.07	0.08 ± 0.01	0.04 ± 0.02	0.25 ± 0.03	0.51 ± 0.04	0.13 ± 0.03	0.04 ± 0.00
Astrebla lappacea	0.09 ± 0.03	0.25 ± 0.03	0.05 ± 0.00	0.03 ± 0.02	0.16 ± 0.01	0.57 ± 0.06	0.10 ± 0.00	0.02 ± 0.01

4.6. Discussion

4.6.1. Comparing DGT and Sequential Extraction Methods

In this study, both total metals and DGT available metals were measured for five native grasses species under glasshouse conditions. The overarching aim was to compare sequential and DGT soil sampling techniques, while also identifying phytostabilising grasses suitable for mine remediation and rehabilitation. Both total metals and DGT proved to be accurate predictors of metal in roots and shoots when grouped by species and metal with a significant linear relationship between DGT metal concentration and plant metal uptake. However, no relationship appears when grouped by individual metals. Within the literature, measuring total metals and DGT have reported mixed results as discussed below.

4.6.2. DGT for Phytoremediation Research

A large amount of research has been conducted on the accuracy of using DGT binding gels to predict metal bioavailability and uptake in plants. Under certain conditions, it is generally agreed that DGT provides one of the most accurate representations of heavy metal resupply from the solid phase of the soil (Dai et al., 2018; Degryse et al., 2009; Zhang & Davison, 2015).

In doing this, DGT mimics plant uptake of heavy metals, something that is not accurately accomplished by other extraction techniques. Correlation analysis grouping all plants species and all metals showed a strongly significant relationship between DGT and plant tissue uptake. Further, the DGT method, recorded significantly lower concentrations of Ni and Zn in *T. triandra* and *C. truncata* compared with control rhizotrons where there was no difference in control and species rhizotrons found using the total metal sequential extraction method. Indicating that DGT was accurately measuring the processes of plant uptake and resupply. These result are in line with other studies which measured heavy metal uptake in plants grown in contaminated soils and sediments. For example, Zn within plant tissue correlated well with DGT recording an R^2 value of 0.9 while the correlation between Zn in soil was only R^2 = 0.33 (Tandy et al., 2011) And for Cu, the correlation between Ethylene Diamine Tetra acetic Acid (EDTA) and Diethylene Triamine Pentacetate Acid (DTPA), and plant tissue was R^2 = 0.60 and 0.39 respectively, while DGT recorded a correlation of R^2= 0.90 (Tandy et al., 2011). This study was similar to Song et al. (2018), as both used highly contaminated sediments, where they found DGT correlation analysis of *Phragmites australis* recorded R^2 values of 0.76, 0.74, 0.92 for Cr, Cu, and Zn respectively. A review of a wide range of extraction techniques, found that while DTPA and EDTA were marginally better predictors of plant uptake than total metal methods, they all predicted biologically available metals poorly (Menzies et al., 2007). It should be noted that the complexity of soils must also be factored in. When Almendros et al. (2020) compared $CaCl_2$, Low Molecular Weight Organic Acids (LMWOAs), Ammonium acetate (NH_4OAc), and DTPA with DGT in a glasshouse study of tomato and bean species, they found DTPA and NH_4OAc to be accurate predictors under some soil conditions, while DGT performed well across all soil types. The soils from the mine sites studied in this thesis have shown that highly heterogeneous soils are to be expected, with vast differences in soil composition, physiochemical properties, and contaminant concentrations happening over the space of meters, requiring the flexible sampling methods offered by DGT technology.

4.6.3. Utility of Sequential Extraction Methods for Phytoremediation

While overall this study showed DGT to be a good predictor of plant uptake, when looked at as individual metal species the relationship broke down. It is not always the case that DGT is able to accurately predict heavy metals in plants, with some studies showing that for certain metals and certain conditions, total metal is a more accurate predictor. For example, while Nolan et al. (2005) showed DGT to be a good predictor of Zn, Pb, and Cd, the best predictor for Cu availability was total Cu in soil. Similarly total metal was a more accurate predictor of Cd than DGT, particularly in when soil concentrations were high (Long et al., 2022). In some instances both relationships have been recorded to break down. In mildly contaminated soils, no positive correlation between total metals in soil and extractable forms of Zn, Cd, and Pb and no significant correlation between DGT and plant metal uptake (Popovic et al., 2011). These studies show that under certain conditions, DGT may not be applicable, whereas the simpler total metal sampling may be appropriate. Under conditions which have high concentrations of metal contamination in soil, DGT will act as a "zero sink" until layer saturation (Zhang & Davison, 2015), meaning it will accumulate metals at a rate much larger than a plant. While at very low levels of heavy metal in the soil, resupply from pore waters or no available metal species, may result in little DGT uptake (Koppel et al., 2021). Simply, at very low metal concentrations, there is less available metal to be taken up by the DGT layer.

The complexity of soil and plant interaction make a one method fits all approach difficult if not impossible (Zhang & Davison, 2015), however, combining DGT with total metal extractions provides a viable and useful tool in both site assessment and the ability to predict metal uptake by plants. Comparing the two techniques in this study provides a clearer picture than looking at each individually. Comparing DGT Pb concentrations (Fig 4.3b) against total Pb (Fig 4.4b) indicates that while the total concentration in the soil is high, very little Pb is bioavailable for plant uptake. This result is supported by the depletion of DGT Zn and DGT Ni in *T. triandra* and *C. truncata* in comparison to the control. In terms of site assessment, these results tell us that regardless of the concentration, Pb is unlikely to affect plant growth, while the opposite is true for Zn and Ni. This is an important factor when examining the current standards for site assessment regarding heavy metals, and in particular highlights the need for the implementation of a wide range of techniques which will accurately represent the condition of degraded sites.

4.6.4. Bioconcentration Factor

Another successful and relatively simple measure of a plant's phytoremediation potential is through measuring bioconcentration and translocation factors. Species with potential for phytostabilisation should be: able to withstand moderate to high levels of contamination; produce large root systems; and accumulate high concentrations of heavy metals within their root zone without translocating it into above ground biomass (Garbisu et al., 2020). In this study, three species were found to offer phytoremediation potential of at least one heavy metal. *Dichanthium sericeum* was the only species to record significant Cr phytoremediation potential, recording an average BCF of 1. Cr is shown to be one the most toxic elements affecting root growth and development impacting new roots and root length, with alteration to the plant membrane causing oxidative stress (Nagajyoti et al., 2010). Average root dry weight of *D. sericeum* was the second highest of the five species, indicating that this species may warrant further investigation as a Cr phytostabiliser. In terms of Cu contamination, *D. sericeum*, along with *C. truncata* and *I. cylindrica* were shown to have a high potential for concentrating Cu within their roots. Further *C. truncata* and *I. cylindrica* offer options for phytoremediation of Zn, since they both recorded BCF > 1 for Zn. *I. cylindrica* has been previously shown to tolerant Cu, Zn, and Cd spiked soils and has been suggested as a possible candidate for Pb and Hg stabilisation (Fu et al., 2016; Ng et al., 2016) but to my knowledge this is the first time this species has shown Cu or Zn stabilisation abilities. Interestingly, the ability of *D. sericium* to restrict Cu in this study is in contrast to previous results. Lamb et al. (2012) showed *D. sericium* to be highly sensitive to Cu solution, stating that the species had little ability to regulate Cu uptake.

Both Cu and Zn are essential micronutrients and are common more mobile and in return taken up in large quantities by plants (Tran et al., 2020). While essential, both Cu and Zn can also be toxic to non-tolerant species, effecting germination, photosynthesis, growth, and biomass production (Lamb et al., 2012; Vardhan et al., 2019). In high doses, both Zn and Cu will cause reactive oxygen species (ROS) and induce oxidative stress leading to tissue chlorosis (Burkhead et al., 2009; Tiwari et al., 2002). In a study by Thounaojam et al. (2012), there was a negative relationship between Cu concentrations and shoot and root length and overall biomass. The Cu increase lead to production of ROS leading to oxidative damage within the plants (Thounajam et al., 2012), while other research has suggested that decreased growth rates in Australian native grasses are due to Cu displacing other essential micronutrients (P, Fe, Mn) (Kopittke et al., 2010). As Zn and Cu are some of the most common contaminants found on abandoned mine sites within Australia (Kavehei et al., 2021; Lei et al., 2010; Nirola, Megharaj, Aryal, Thavamani, et al., 2016) it is important to find species adapted to tolerating high concentrations of these metals.

4.6.5. Translocation Factor

Translocation is a less common process than bioconcentration. It relates to the ability of a plant to transfer important levels of heavy metal from root to shoot (Lange et al., 2017). It is generally accepted that the translocation of metals to above ground biomass at rates higher than 1 is considered Important in terms of phytoremediation. Species with high translocation factor are interesting as in some cases they may meet the assumptions of being hyperaccumulator species (Brooks et al., 1998). It should be highlighted that hyperaccumulator species are extremely rare, accounting for only 0.2% of known plants, and are unlikely to be viable options for wider scale phytoremediation due to slow growth and lack of plants biomass (Rascio & Navari-Izzo, 2011; Reeves, 2003). For example, one species from Queensland, Australia, *Stackhousia tryonii*, has been shown to accumulate 13.7 ppm of Ni in aerial parts, more than 1% of total dry biomass, however, due to being a small and rare herbaceous species endemic to ultramafic soils, it is unlikely to even grow outside of its natural habitat (Bhatia et al., 2005; Bhatia et al., 2004). In this study, *T. triandra* showed a TF > 1 with Zn, while also recording the highest total amount of Zn, Cr, Cu, As, Pb and Mn per predicted dry mass in comparison to all other species. *Dichanthium sericeum* had the second largest biomass and largest accumulation of Co and Ni. However, neither species accumulated significantly high levels of heavy metals when compared to Australian or international standards. It should be stated that soil contamination levels were low and the ability of these species to survive in highly contaminated soil could only be taken from previous studies (Adejumo et al., 2018; Mahbub et al., 2017; Ng et al., 2016). While arguments can be made against the intentional use of phtyoextracting plant species as high levels of metal in shoot, stems, and leaves can be risky for humans and other animals if these plants are consumed (Bleeker et al., 2002; Robinson et al., 2009; Tibbett et al., 2021; Vongdala et al., 2019), in cases like this, phytoextraction paired with cropping technologies may be a viable alternative. This research shows that these five Australian native grasses may be a potential option for the remediation of the thousands of legacy mines sites found across the continent. They not only fulfil the necessary requirements for phytoremediation (Venkateswarlu et al., 2016) but may also be a pivotal step in returning ecosystem function as plants tolerant of post mining conditions are helpful at improving soil total organic carbon, N and P overall accelerating ecological restoration (Zhu et al., 2022) while also preventing erosion, and in the process limiting movement of metals from surface soils to overland flows and ground water (Ashraf et al., 2019). Mine site remediation is a difficult and lengthy process, in many cases extremely expensive. While current and recently active mine sites are difficult to manage due to metal rich tailings and nutrient poor soils (Bleeker et al., 2002), many older legacy mines have over time become more manageable in this respect.

4.7 Conclusion

This study has shown that both DGT and total metal sampling can be used together as accurate predictors for soil contamination levels in legacy mines. Further, Australian native grasses are able to grow in relatively unmodified soil from a legacy mine in NSW. *Chloris truncata*, and *I. cylindrica* showed potential for phytostabilisation of copper and zinc. While *D. sericeum* showed phytostabilisation potential for copper and chromium. *Themeda triandra* was the only species studied to record a TF > 1 for zinc, indicating that it may have potential as phytoextractor. Further research on the grass species used in this study, in particular the use of DGT in combination with dose response curves.

Chapter 5: Synthesis of Research Findings

5.1. Findings Relative to Original Aims

This thesis aims to address knowledge gaps on the prevalence, impacts, and potential remediation outcomes for legacy coal mines within the Greater Sydney region. As shown in Chapter 2, many coal mines which closed before the 1990s are not recorded on databases or online mapping tools for the state of NSW. Identifying and sharing accurate locations of abandoned mines is an essential first step for a full understanding of the extent of this environmental problem, while also ensuring these legacy sites are appropriately accounted for in state planning decisions. With no location information, the condition of abandoned coal mines cannot be assessed, making the environmental management of current and future impacts all but impossible. In Chapter 3, I completed comprehensive soil analyses of three large abandoned mines, all featuring heavy metal concentrations greatly exceeding national safety guidelines. I also examined the spatial movement of surface contaminants, which have been shown to move from largely un-vegetated sites into local waterways and rivers. Several detailed studies have been previously conducted within the western and southern coal fields showing that both abandoned and operational mines are a persistent source of water contamination, with the findings from Chapter 3 further strengthening this research body. In Chapter 4, different metal extraction techniques were contrasted against heavy metal uptake in five Australian native grasses. The overall aim of this chapter was to strengthen the current knowledge surrounding site assessment and sampling, while also exploring management techniques to mitigate heavy metal contamination identified in Chapter 3. Comparison of DGT bioavailable metals and sequential total metal techniques showed a strong positive correlation between heavy metals in soils and plant tissues concentrations (root, shoot), however, positive correlations broke down for most metals when examined as individually. In this chapter, I offer some suggestions for overcoming this problem in future research.

Through a combination of statistical modelling and heavy metal transfer coefficients, four potential phytoremediators were identified. The metal tolerance of (5 species) has been studied before using a combination of germination and spiked soil experiments, but to my knowledge no other study has examined the ability of these species to phytoremediate complex real world mine soils using the combination of DGT and total metal extraction techniques. I will now synthesise these results and explore future research directions. Much of the work conducted in this thesis was exploratory and may now be used as a baseline to be expanded on further.

5.2. Aim 1: Develop and Test a Framework for Locating Abandoned Mines

Accurate online mapping and database creation should be considered the first step in managing and prioritising abandoned mines in Australia. Using relatively simple techniques, I have developed a functional tool for identifying and mapping legacy coal mines across the greater Sydney region. The next step in this research should be geared towards updating the current databases using this tool. In Australia, important foundational research by Unger et al. (2012) listed 410 abandoned or legacy mines in NSW. Since then, this number has been updated by Werner et al. (2020) who identified over 26,000 inactive mine sites in the state. This is a significant improvement over 8 years, however, it should also be noted that this data was collated using government databases on already-identified sites, which this thesis has shown to greatly underestimate the number of mines. For example, the research by Werner et al. (2020) indicated zero inactive coal mines within in supplementary dataset for NSW. It is apparent that important research relies upon the information provided by government databases and inventories. Ensuring these information resources are up to date and reliable is a critical first step in abandoned mine site management. Following this, abandoned mine sites can then be prioritised based on their level of risk. Doing this would inevitably flow into the second area where I believe this research needs to flow, which is prioritising abandoned mines by risk.

While it is clear there is a substantial problem with abandoned mines in NSW it is unlikely that all sites possess the same level of risk to the health and safety of humans and the environment. Similar to the Canadian NOAMI program, future research should classify sites and prioritise those with a high potential risk. The Canadian model ranks sites from A. (high risk) through to D. (low risk) in regard to the likelihood and potential to cause harm (NOAMI, 2018). Adopting a similar system to NOAMI would provide the NSW government and other relevant stakeholders the ability to focus remediation work on the sites that need it most. In a recent paper published by (Salmi et al., 2022) the importance of creating a national standard for mine site risk assessment is covered in detail stating that through a focus on national standardisation, all current databases could be amalgamated into one national database, accompanied by clear definitions for classifying risk and therefore designating remediation goals.

5.3. Aim 2: Identify the Ongoing Risks of Soil Contamination in Abandoned Mines

Soil pollution from abandoned mine sites has been comprehensively discussed in Chapters 2 and 3. My research adds more important information to this body of work by exploring the risks of soil contamination directly from the surface of mines, and has highlighted a number of important considerations for abandoned mine management as well as future research opportunities. Satellite image analysis of the 61 sites found in Chapter 2, reveals a high proportion to have little to no vegetative cover, similar to the Neath and Abermain collieries, or underdeveloped vegetation, similar to Canyon. When comparing the three mine sites, we found significant differences between individual metals in the upper and lower profile, however, when grouping upper and lower profiles, metal concentrates were similar between mine sites. The three sites were similar in a large range of contamination concentrations and wide variability of the spatial spread across the sites. These results may be used to inform the assessment of other legacy coal mines in Australia. While this research has shown maximum concentrations well above EIL's, only Abermain colliery recorded mean levels of zinc in ranges above these levels.

Metal soil samples did not record homogenously high samples across the sites, but spatial mapping conducted in Chapter 3 showed movement of metal in soil samples corresponded with erosive processes was migrating towards local water bodies. If the conditions of these sites could be used to infer the likely conditions of similar legacy mines mapped in Chapter 2, then it is highly likely that other unmarked mines are contaminating some of the state's most important water sources. Two unmarked legacy mines Brimstone number 1 (-33.9960, 150.4902) and Brimstone number 2 (-33.9837, 150.4885) may be of particular concern. Both of these unmarked mines are located in the Nattai region, 70 km southwest of the Sydney CBD, and sit only 3.5 km and 2.5 km respectively upstream of Burragorang Dam, Sydney's main drinking water catchment. Both sites are un-vegetated with coal waste rock visible from satellite image data. If these mines are in similar condition to the ones profiled in my thesis, the soil on these sites is likely contaminated with heavy metals and, due to a lack of vegetation, likely increasing contamination to surrounding areas through the weathering processes and surface water runoff. This links to Chapter 4 of my thesis, which aimed to provide some solution to the problems associated with soil heavy metal contamination in the legacy coal mines of NSW.

5.4. Aim 3: Compare DGT and Sequential Extraction using Native Grasses in Mined Soils

As covered in the introduction of this thesis, the bioavailable fraction of heavy metals in soils is an important but complex issue with the processes of clay content, CEC, pH, age of contaminants, and organic content all interacting within the rhizosphere (Antoniadis, Levizou, et al., 2017; Antoniadis, Shaheen, et al., 2017; Liu et al., 2018). Due to such complexities, sampling and analysis of bioavailable metals has largely been overlooked during mine soil assessments. It is common for sites assessments to use only simple methods of measuring total metals in soil (Gao et al., 2020). Quick and relatively easy, total metal sampling will only provide a general picture of soil condition, and while informative to a degree, more detailed information on bioavailable fractions in soils is necessary, for an informed revegetation remediation plan.

In this thesis, I aimed to compare one total metal sequential extraction technique against the newer technology of DGT. The mathematics and process are complex, and only the general mechanisms have explained in the thesis, however, the attractiveness for DGT in this study comes from the ability of DGT measure bioavailable metals to a degree that accurately mimics plant heavy metal uptake. As the DGT sample is taken over a period of time, the depletion of heavy metals from the soil solution into the binding layer has been shown to follow similar patterns to plant uptake (Ahumada et al., 2014; Tandy et al., 2011) To my knowledge no other study has used DGT to predict the uptake of Australian native grasses species in mine contaminated soil. One of the main aims in chapter 4 was to compare the accuracy of a total extraction technique and DGT techniques in Australian native grasses grown in “real world” contaminated soils.

Previous to this study, several other glasshouse studies were conducted using soils spiked with cationic salt solutions. This was with the aim of using dose response curves to more accurately identify the predictability of the two chosen techniques. Original experimental work was conducted with Co, Pb, Mn, and NI nitrates added as aqueous solutions to grass pot experiments. In these original experiments, several problems arose in regards to accurately answering my studies questions: (1) the higher concentrations of bioavailable metals where not representative of real world data collected from the field; (2) leaching of heavy metal solutions meant inaccurate response curves; (3) using conventional pots gave no non-destructive access to the rhizosphere. To overcome the problems with metal availability and leaching, it was decided that a more stable or aged contaminant would be used, taken from a legacy mine site identified in Chapter 2 and sampled in Chapter 3. To answer the overall question regarding the phytoremediation options for these sites, using real mine soil appeared as more representative option, minimising problems with leaching and providing a stable soil sample. The third problem was address by building rhizotrons with a removable faceplate, resulting in rhizosphere access with little to no disturbance of the soil or roots. This method also resulted in less soil bound to the root tissue when conducting final analysis.

The changes to original methods for this experiment overall resulted in more representative results to better answer my study questions and aims, although did create other issue which I will discuss here. The first was the general low concentration of metals in the soils collected from Abermain colliery. Results from Chapter 3 showed the most contaminated points at the site to be around the now sealed mine entry shafts. Five bulk soil samples were taken from a transect which crossed this area. Small amendments were added to encourage plants growth and water infiltration, however, in doing so the total metal concentration within the soils measured much lower than first anticipated. In some ways this is a positive result, as it shows that with very little inputs the remediation outcomes of sites similar to Abermain would likely be successful. Regardless, the ability to test the five chosen species in highly contaminated mine soil was limited. The second problem in using real world soil is the inability to conduct dose curve experiments. In my study, both DGT and total metals accurately predicted plant root and shoot up take when pooled as all species and all metals, a relationship that broke down when examined as individual metals (Fig 4.3c; 4.4c). This breakdown is not to be unexpected, as the soil samples used contained similar concentrations of each analyte. As already mentioned, spiked soils were replaced with real world soil data as I believed it would more accurately answer the questions posed in this thesis. While overall this is true, the ability to test DGT and sequential extraction method as a predictor for individual analytes was limited. I see two ways to rectify this in future studies: using real world soils with higher original concentrations and creating a step-down dilution factor; or addressing the problems with the original spiked soil experiment by letting spike solutions settle in the soil for between four and eight weeks before planting (Hussain et al., 2019; Yang et al., 2022). In making either of these changes, plants could be grown in soils consisting of an increasing range of each contaminant, providing a clearer picture of the ability of DGT and total metal techniques to predict plant up take. This would also build on the knowledge of toxicity thresholds for these five native grass species.

Figure 5.1. *Themeda triandra* growing in the rhizotron. Face plate has been removed to see the soil and root architecture.

Regardless of these problems, the results collected in Chapter 4 add important knowledge to the current body of work, in particular I highlight the importance of using a combination of different metal analysis methods when conducting site assessments. For example, when looking at the differences in Pb concentrations between the two sampling methods, my results showed that regardless of the total amount of metal in the sample, only a small fraction was available for uptake. A result further supported by the BCF and TF calculations. Again, the small but important difference found in the soil concentrations of Ni and Zn when comparing *C. truncata* and *T. triandra* to the control plots, further supports the idea of using a combination of soil sampling methods. By using both methods, a clearer picture of the mechanisms acting on the plants was established, showing that Ni and Zn were being removed from the bioavailable fraction of soil at a significant rate, while not significantly impacting the total metal concentration in the soil. To focus on this with the lens of a site assessment, using both methods would provide detailed information necessary for choosing the correct remediation options. I believe this chapter filled the identified knowledge gap, proving both methods have utility in predicting the uptake of metals under ex-situ mine site conditions, with a combination of DGT and total soils techniques used together to paint a clear picture of the complex processes acting on the rhizosphere.

5.4.1. Aim 4: Assess the Phytoremediation Potential of Australian Native Grasses Grown in Contaminated Mine Soils

The second component of Chapter 4 focused on the individual plant species and the movement of metals in root and shoot tissue. Throughout this thesis, I have examined a range of different problems associated with legacy coal mines in NSW. The conversation will now shift towards using plants as a solution to these problems. The history and viability of plants as phytoremediators has already been covered earlier in this thesis. In Chapter 1, the rareness of hyperaccumulators, and the limited amount of research being conducted on Australian native phytoremediators in general was shown. While there has been some promising results (see Chapter 1), research on Australian native phytoremediators is still in its infancy. This chapter set out to measure the phytostabilisation and phytoextraction potential of five Australian native grasses. In doing so, *D. sericium, C. truncta*, and *I. cylindra* were identified as potential stabilisers of Cr, Zn, and Cu and T. triandra a possible phytoextractor of Zn. In

Chapter 3, these contaminants were all shown to be present in high levels, with concentrations above NEPM EIL guidelines. Zn in particular was consistently found in much higher levels, between 3 and 41 x higher than the EIL's across the three mine sites sampled (Table AB 1.) Chapter 3, also identified Zn and other contaminants are leaving these sites and entering local waterways and rivers.

The damaging effects of this movement have been covered in detail within this thesis and elsewhere, but here I would like to take these results and offer a possible solution. In 1.8 of this thesis, the long term viability of mine remediation has been briefly discussed, with soil quality, low quality tailings, and soil contamination cited as limiting factors. These studies have focused on open-cut mines, which are larger in size with recently disturbed top soils. While open-cut mines and legacy mines share some similarities, the nuanced differences could mean with the right species and a tailored plan that many of these legacy sites could be returned to some level of ecosystem functionality reasonable quickly. Size is one major difference between an open-cut mine and a legacy coal mine sites. As seen in Chapters 2 and 3, the total surface area impacted by underground mines is much smaller. For reference the surface disturbance caused by Neath Colliery comes to a total of 0.11 km^2 which is dwarfed by the size of one of the closest neighbouring open-cut coal mines, Mount Thorley, which measures 68.25 km^2 of visible disturbance. While they share similar characteristics, the sheer size difference makes remediating Neath colliery a more achievable task. This is true for most legacy mines in the region, as the aboveground footprint of underground mines are inherently smaller by nature.

Other limiting factors such as soil quality and heavy metal contamination have been covered more directly in this thesis. The glasshouse study conducted in Chapter 4 showed that the five species chosen were all able to grow well in soil consisting of soil amendments similar to site ripping and the instillation of new soil top layer. *Dichanthium sericium, C. truncta*, and *I. cylindrica* showed they were successful excluders, and warrant further research for their phytostabilising potential. Low cost but resilient species, proven to exclude heavy metals while also binding them within the rhizosphere may prevent the large scale movement seen across the mine sites sampled. The Canyon colliery can be used as an example of this work in action, while concentrations of heavy metals in soil were still high, my research has shown much of this was been contained within the lower profile of the site. It would appear that the thick vegetative cap of grasses and their fibrous root systems is helping to prevent spread of contaminants off site. While this is a promising option for the management of this 1000s of legacy mines found across Australia, it does lead to the final discussion point of this thesis.

5.5. The Impacts of Bushfires on Contaminants Generated from Abandoned Mine Sites

The high levels of vegetation found at the Canyon colliery presented a unique opportunity to assess the in-situ phytoremediation processes of Australian native grasses. Predominantly covered in mature *Poa labillardierei* tussocks, and a range of smaller Australian native eucalyptus species, the uptake and exclusion of heavy metals on site was to be one of the main questions of this thesis. Unfortunately, the large scale Black Summer Bush Fires of 2019 and 2020 directly impacted the Canyon colliery, removing the vegetation completely. The link between a warming climate and increases in wildfire frequency and intensity is well known, with these events predicted to increase globally in the coming years (Goss et al., 2020; Mueller et al., 2020). While outside of the scope of this thesis, as these events increase it is important to know the likely impacts on contaminated sites such as legacy mines.

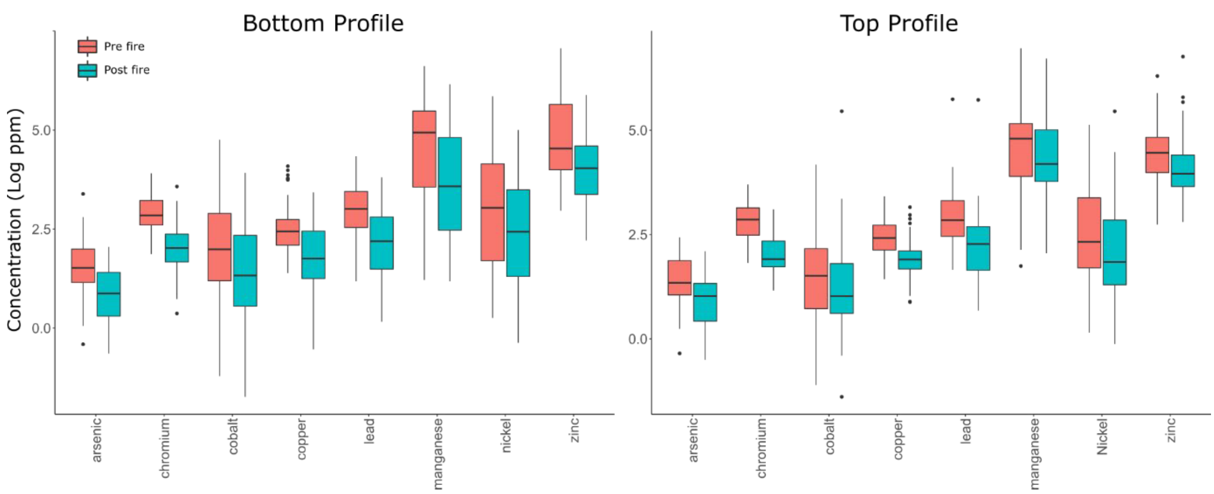

Figure 5.2. Total metal concentration (data natural log transformed parts per million) taken from Canyon colliery before and after the 2019-2020 Black Summer Bushfire. Both bottom and top profiles saw a decrease in all metal concentrations post-fire.

Using the same methods seen in Chapter 3, Canyon colliery was resampled post-fire and post-rainfall event with the aim of quantifying the impact of a large wildfire on soil metal concentrations. Previously, studies have shown that cationic soil concentrations decrease post-fire, driven by a combination of the loss of the stabilising vegetative layer and an increase in erosive processes during rainfall events (Abraham et al., 2017a, 2017b; Vieira et al., 2018). Increased erosion then leads to sedimentation in local waterways for months preceding a wildfire, often bringing with it increases in toxic trace elements previously contained to soils (Pelletier et al., 2020; Rust et al., 2022). While still in early stages of analysis, these results appear to be in line with the data collected from the Canyon site post fire. Both top and bottom profiles saw decreases in metal concentrations for all metals (Fig. 5.2). Similar to Chapter 3 of this thesis, I plan to compile heatmaps with the aim of identifying spatial patterns in the movement of metals post-fire, highlighting further risks posed by legacy mine sites left unmanaged in the environment.

5.6. General Conclusion

In summary, this research highlights the importance of strengthening current practices around legacy mine site assessment and management, while also offering simple but effective ways to do so. While I have shown significant contamination is present on legacy mine sites, high heavy metal concentration are not heterogeneously distributed, making revegetation in targeted areas an achievable goal. I demonstrate that phytoremediation of legacy mine sites using Australian native grasses is a viable and cost effective solution to mitigate future pollution risks impacting soils and nearby waterways. Finally, while only briefly stated in this work, I touch on the future risks more frequent and intense wildfires will likely have on the condition of legacy mines and the environments they are found in. This is an area of research where I aspire to build knowledge in the future.

Appendix A

Supporting evidence for Chapter 2

Table A1. Coordinates and year of closure for the unmarked mines in the Southern Coalfield.

Mine	Longitude	Latitude	Year Closed
Austinmer Extended	150.93163	−34.29657	1904
Blackball	150.89704	−34.34471	1884
Brokers Nose	150.88073	−34.36724	1947
Bulli Main	150.94851	−34.2799	1967
Dombarton	150.79524	−34.45335	1905
Excelsior no 1.	150.90854	−34.30884	1914
Excelsior no. 2	150.91283	−34.30416	1857
Hales	150.89412	−34.34201	1910
Haywards Block	150.82374	−34.44429	1952
Huntley	150.72589	−34.50089	Unknown
Kemira	150.85945	−34.40804	Unknown
Model	150.89429	−34.34045	1909
Mount Kembla	150.82477	−34.41852	1861
Mt Pleasant 1	150.86168	−34.39883	1886
Mt Pleasant 2	150.86391	−34.38339	Unknown
North Illawarra No. 2 and 3	150.92657	−34.30203	Unknown
Owens Balgownie	150.86357	−34.38467	Unknown
Port Kembla No. 2/Nebo	150.82099	−34.4474	1975
South Bellambi	150.88485	−34.36185	1912
South Clifton	150.96402	−34.2634	Unknown
South Kembla/Wongawilli	150.78563	−34.46269	1967
Tom Thumb	150.83473	−34.40804	1904

Table A2. Coordinates and year of closure for the unmarked mines in the Newcastle Coalfield.

Mine	Longitude	Latitude	Year Closed
Hebburn No 1 Colliery	151.45572	−32.82045	1958
Pelaw Main	151.47537	−32.82758	1955
Hebburn No 2 Colliery	151.43661	−32.85136	1972
Aberdare Main	151.37871	−32.84811	1961
Aberdare South	151.40081	−32.88881	1927
Ayrfield No 1 Colliery	151.50986	−32.78526	1933
Ayrfield No 2 Colliery	151.51036	−32.78808	1928
Ayrfield No 3 Colliery	151.34948	−32.67392	Unknown
Bellbird Colliery	151.32291	−32.85902	1976
Abermain No 2 Colliery	151.40191	−32.86083	1964
Abermain No 3 Colliery	151.41408	−32.84003	1960
Cessnock No 1 Colliery	151.32705	−32.90522	1964
Cessnock No 2 Colliery	151.33973	−32.84873	1955
East Greta No 1 Colliery	151.52305	−32.76086	1929
East Greta No 2 Colliery	151.52318	−32.75725	1929
Elrington Colliery	151.41887	−32.87571	1962
Glen Ayr Colliery	151.51086	−32.778	1930
Greta Colliery	151.38516	−32.67736	1931
Hebburn No 2 Tunnel	151.43629	−32.82601	1908
Maitland Main Colliery	151.27915	−32.88517	1972
Millfield Greta Colliery	151.27537	−32.88538	1955
Neath Colliery	151.40925	−32.82066	1961
Stanford Main No 2 Colliery	151.27907	−32.90418	1961
Richmond Vale Main Colliery	151.47468	−32.86023	1967
Seaham No 2 Colliery	151.55334	−32.91308	1945
Seaham Colliery	151.58216	−32.89169	1932
Killingworth Colliery	151.54505	−32.93312	Unknown
West Wallsend	151.58172	−32.89896	Unknown
John Darling	151.6743	−33.0251	Unknown
Burwood	151.705	−33.014	1982
Dudley	151.7188	−32.9914	1944
Lambton Colliery	151.711	−33.0081	1936

Table A3. Coordinates for the unmarked mines in the Western Coalfield.

Mine	Longitude	Latitude	Year Closed
Cal Colliery	150.0804	−33.3745	Unknown
Commonwealth Colliery	150.078	−33.38	Unknown
Wallerawang Colliery	150.0575	−33.3643	Unknown
Irondale Colliery	150.0119	−33.3772	Unknown
State Coal Mine	150.168477	−33.46306	Unknown
Lithgow Valley Colliery	150.155398	−33.48591	Unknown
Eskbank Colliery	150.1618	−33.48129	Unknown

Appendix B

Supporting evidence for Chapter 3

Table AB 1. Summary table of mean, minimum, and maximum values of 8 analytes of the top (0-50mm) and bottom (250-300mm) profiles of Abermain, Canyon, and Neath Collieries. The standard deviation (SD) from the mean and NEPM ecological investigation levels have been included for comparison.

Mine	Profile	Metal	Mean (ppm)	SD	Min (ppm)	Max (ppm)	NEPM (2013)
Abermain	Bottom	Arsenic	5.45	4.55	0.21	**22.43**	20
		Cobalt	5.86	5.55	0.15	31.50	50
		Chromium	22.26	9.61	1.47	43.81	400
		Copper	23.14	26.64	0.00	**180.27**	100
		Manganese	218.63	482.29	2.16	**2936.87**	500
		Nickel	39.94	33.16	0.86	**158.59**	60
		Lead	52.94	107.66	1.80	**636.59**	600
		Zinc	**293.77**	1218.70	9.31	**8330.23**	200
Abermain	Top	Arsenic	6.45	9.81	0.38	**54.90**	20
		Cobalt	4.57	2.97	0.32	11.96	50
		Chromium	21.60	12.08	2.69	70.55	400
		Copper	16.75	10.86	1.77	58.79	100
		Manganese	209.79	371.29	1.61	**1875.88**	500
		Nickel	30.27	24.26	1.83	**109.38**	60
		Lead	53.13	106.91	2.53	541.10	600
		Zinc	187.58	426.67	28.37	**2719.46**	200
Canyon	Bottom	Arsenic	6.33	4.86	1.05	**29.62**	20
		Cobalt	17.40	21.50	0.30	**116.42**	50
		Chromium	20.06	8.54	6.50	49.74	400
		Copper	17.39	13.89	4.01	59.68	100
		Manganese	194.32	188.57	3.38	**748.38**	500
		Nickel	50.48	62.16	1.29	**347.73**	60
		Lead	25.20	15.97	3.26	86.47	600
		Zinc	189.18	197.20	19.42	**1170.14**	200
Canyon	Top	Arsenic	5.13	2.73	1.60	12.38	20
		Cobalt	7.27	9.86	0.33	**65.13**	50
		Chromium	18.28	8.46	6.15	40.48	400
		Copper	12.26	5.49	4.18	30.50	100
		Manganese	166.72	185.71	5.73	**1056.75**	500
		Nickel	19.70	26.38	1.16	**168.79**	60
		Lead	28.72	44.72	5.25	311.94	600
		Zinc	104.73	89.14	22.44	**544.09**	200
Neath	Bottom	Arsenic	6.60	4.84	1.07	**29.34**	20

Mine	Profile	Metal	Mean (ppm)	SD	Min (ppm)	Max (ppm)	NEPM (2013)
		Cobalt	3.01	3.13	0.59	19.54	50
		Chromium	21.24	10.92	8.48	60.98	400
		Copper	21.23	33.83	4.53	**236.53**	100
		Manganese	29.17	48.36	2.94	293.10	500
		Nickel	18.91	18.08	3.67	**103.42**	60
		Lead	24.44	57.56	5.25	418.84	600
		Zinc	86.00	363.24	6.06	**2692.02**	200
Neath	Top	Arsenic	6.50	3.27	2.25	18.25	20
		Cobalt	5.13	4.45	1.21	22.90	50
		Chromium	23.41	8.00	12.55	52.77	400
		Copper	13.19	6.19	6.89	36.93	100
		Manganese	102.35	141.49	10.30	**727.15**	500
		Nickel	21.06	16.81	5.09	**85.56**	60
		Lead	16.57	5.20	8.75	41.93	600
		Zinc	66.92	96.29	23.62	**721.38**	200

Table AB 2. Quality control values for tissue and soil samples for glasshouse study.

	Cr (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	As (%)	Pb (%)
Shoot	101.46	96.62	90.88	101.85	98.40	100.95	84.68	102.78
Root	100.97	101.41	100.84	101.33	101.42	101.86	98.63	100.95
Soil	106.56	101.77	99.31	100.82	101.29	112.15	105.32	101.48
Soil	106.51	104.40	104.87	101.55	103.04	109.14	106.52	103.03

Table AB 3. Quality control percentage return values for soil samples of Neath colliery.

	Cr (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	As (%)	Pb (%)
QC1	100.01	101.36	92.56	100.02	106.45	106.80	95.34	99.00
QC2	101.16	99.80	88.59	96.49	107.81	129.55	96.75	99.90
QC3	92.43	95.35	90.52	94.57	94.19	95.82	82.69	91.63

Table AB 4. Quality control percentage return values for soil samples of Abermain number 2 colliery.

	Cr (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	As (%)	Pb (%)
QC1	92.07	92.65	86.37	90.54	92.88	95.35	82.30	94.47
QC2	99.02	94.26	93.35	93.47	96.37	102.40	94.42	93.54
QC3	98.17	93.66	94.13	91.38	86.48	92.31	94.63	94.63

Table AB 5. Quality control percentage return values for soil samples of Canyon colliery.

	Cr (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	As (%)	Pb (%)
QC1	94.95	100.66	94.99	103.40	94.73	101.64	95.99	94.99
QC2	101.25	100.47	98.69	106.27	100.71	101.05	95.90	99.56
QC3	98.44	101.30	94.13	97.66	95.63	101.97	100.19	96.79

Table AB 6. Certified reference material percentage return values for loam (CRM-LO) and pine needles (CRM-PINE).

	Cr (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	As (%)	Pb (%)

CRM-LO	92.77	93.39	90.69	85.50	101.70	97.10	120.13	91.15
CRM-PINE	150.93	104.43	3420.97	93.51	102.85	126.55	201.23	95.13

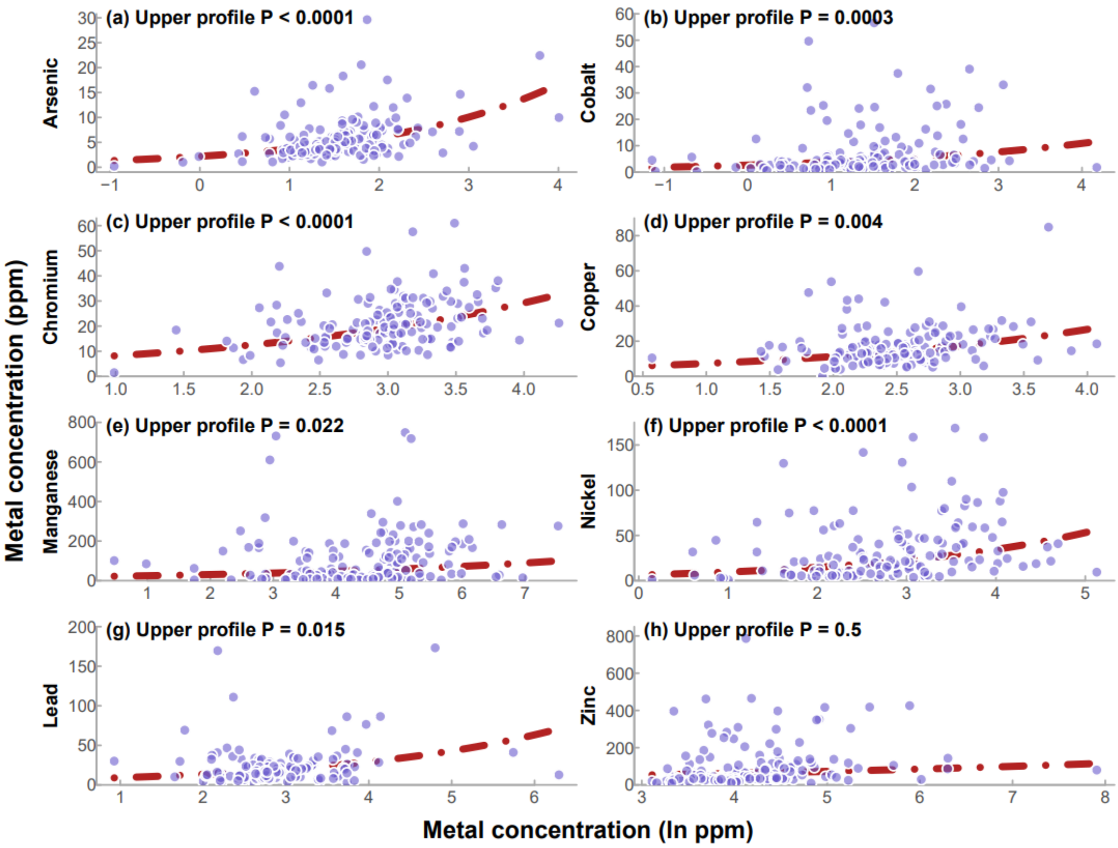

Figure AB 1: Plots show the lower profile metal concentration (y-axis) compared to the upper profile metal concentration (x-axis; ln transformed). The broken red line shows the modelled relationship between the variables averaged across the three mines.

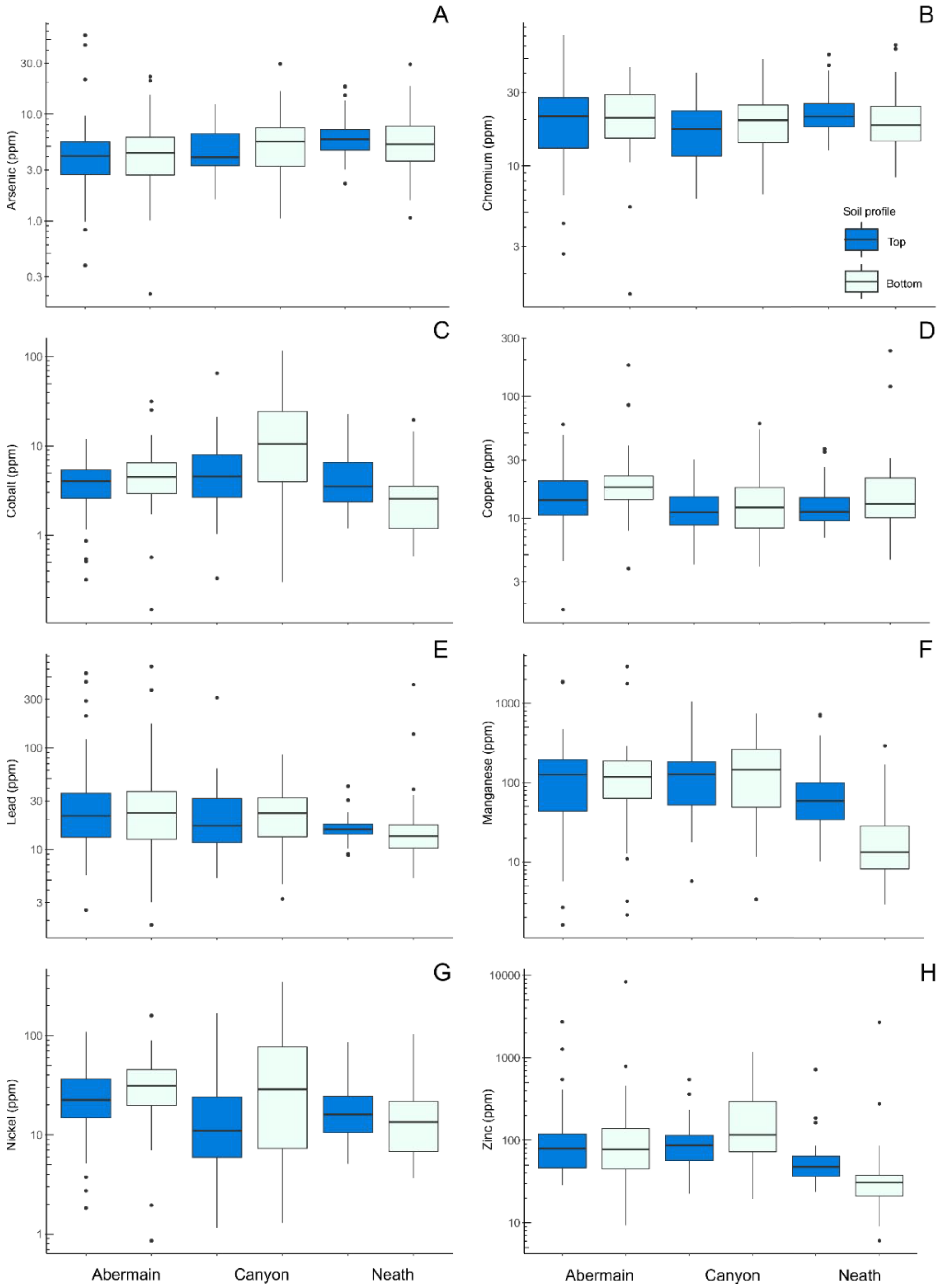

Figure AB 2. Box and whisker plot of metal concentrations at three mines. Soil samples taken from top profile (0-50mm) shown in dark blue, and bottom profile (250-300mm) shown in light blue. Y-axis scale logarithmic due to large variation in the range of concentrations.

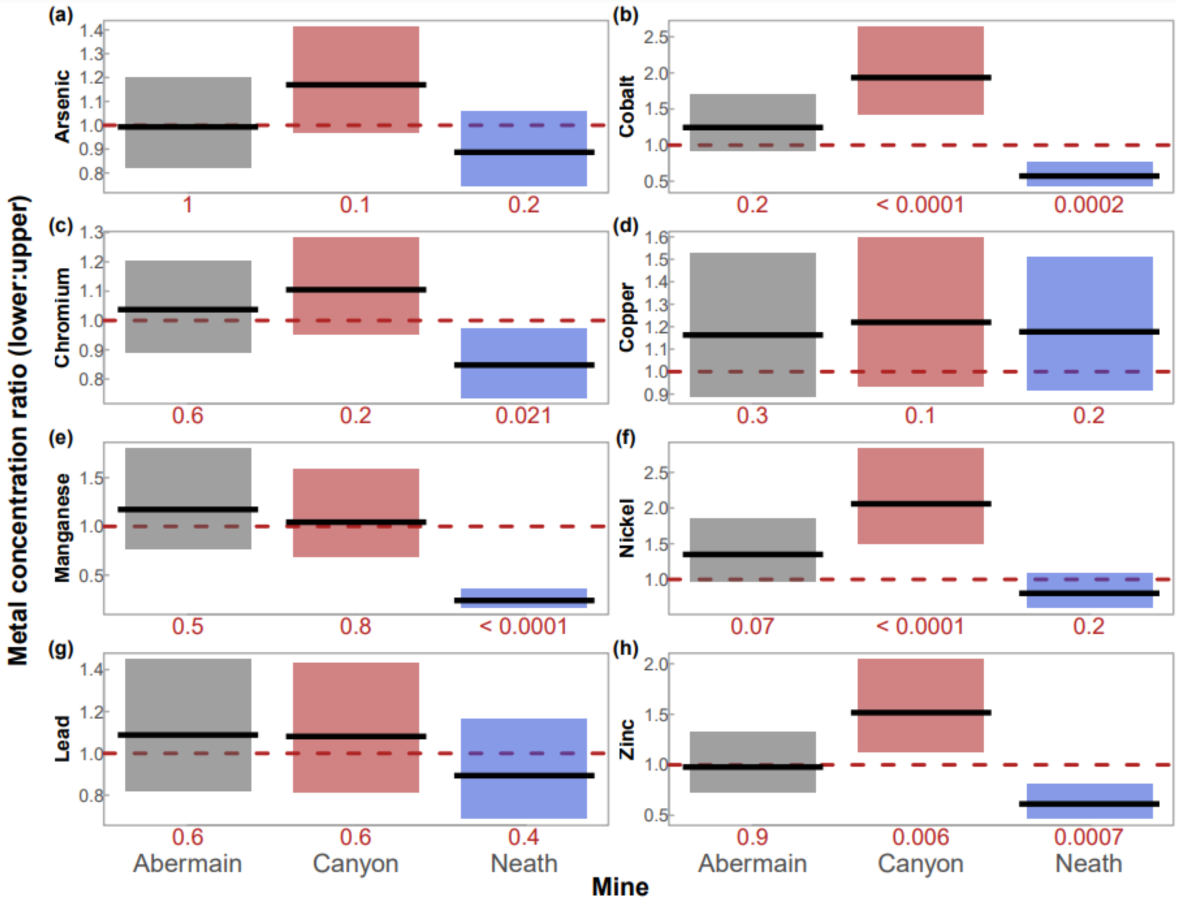

Figure AB 3: Model estimated mean ratios of upper to lower profile metal concentrations. The black lines show the means, the shaded area the 95% confidence interval of the mean.

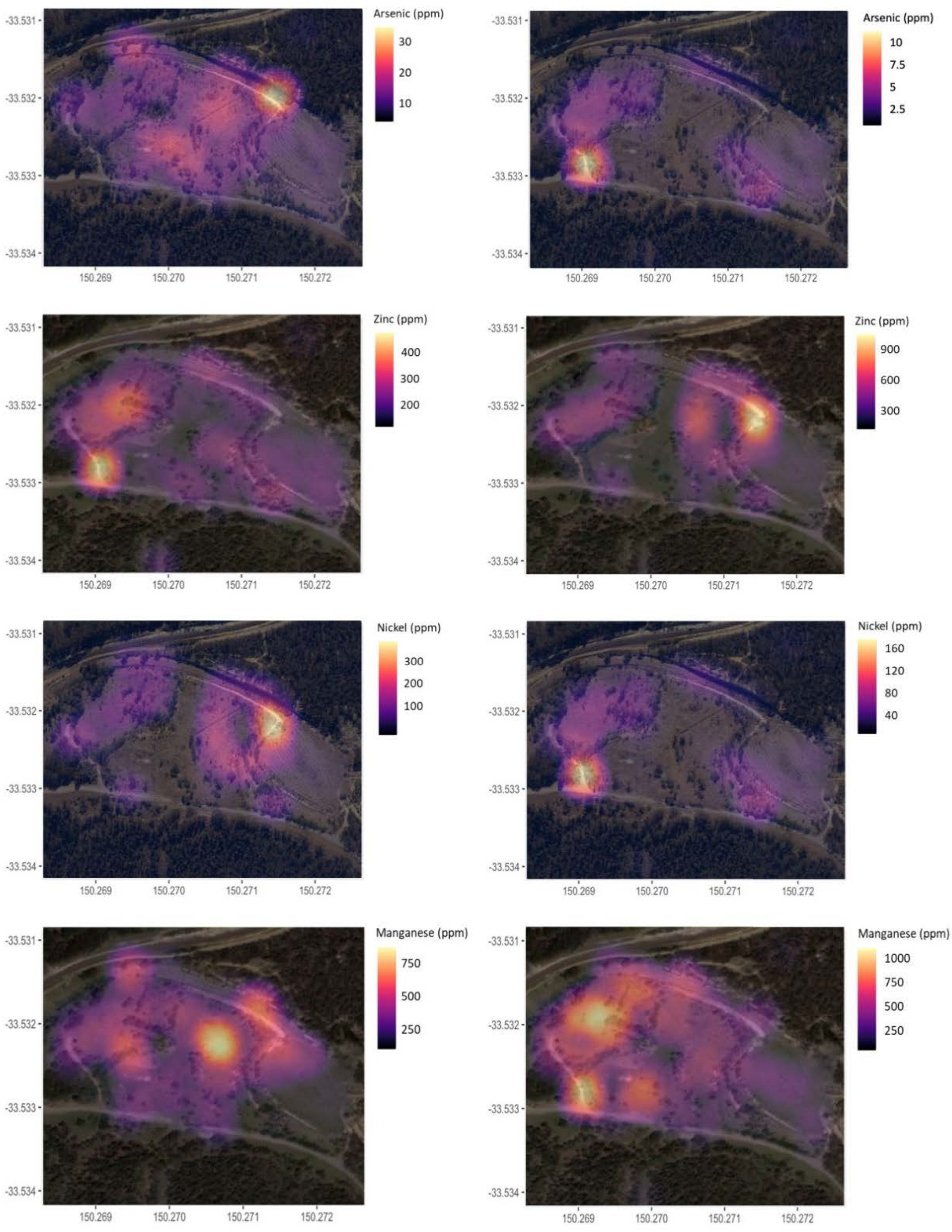

Figure AB 4. Canyon colliery heatmaps showing As, Zn, Ni, and Mn (Bottom profile on the left, top profile on the right) Note difference in scale between top and bottom profiles.

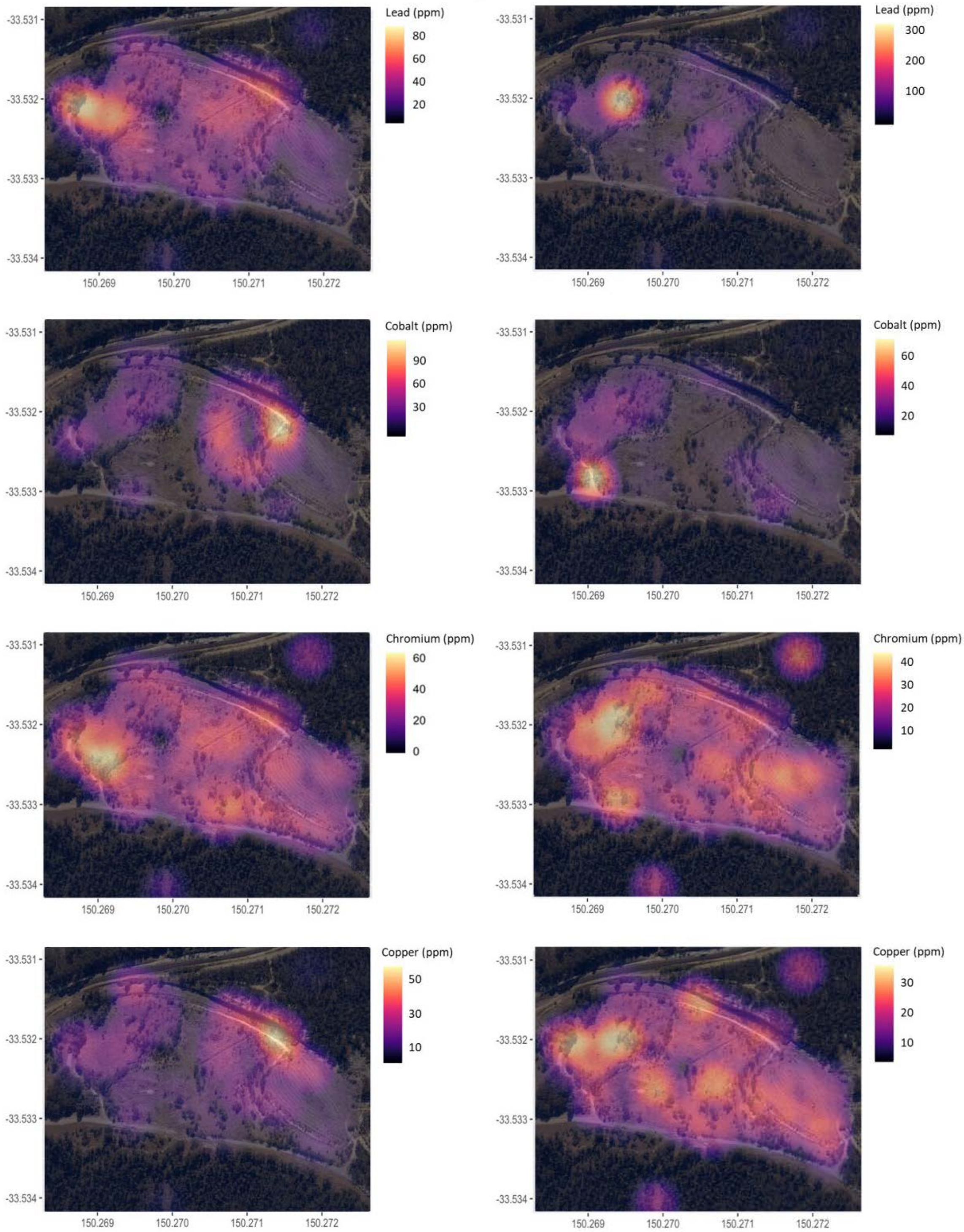

Figure AB 5. Canyon colliery heatmaps showing Pb, Co, Cr, and Cu (Bottom profile on the left, top profile on the right). Note difference in scale between top and bottom profiles.

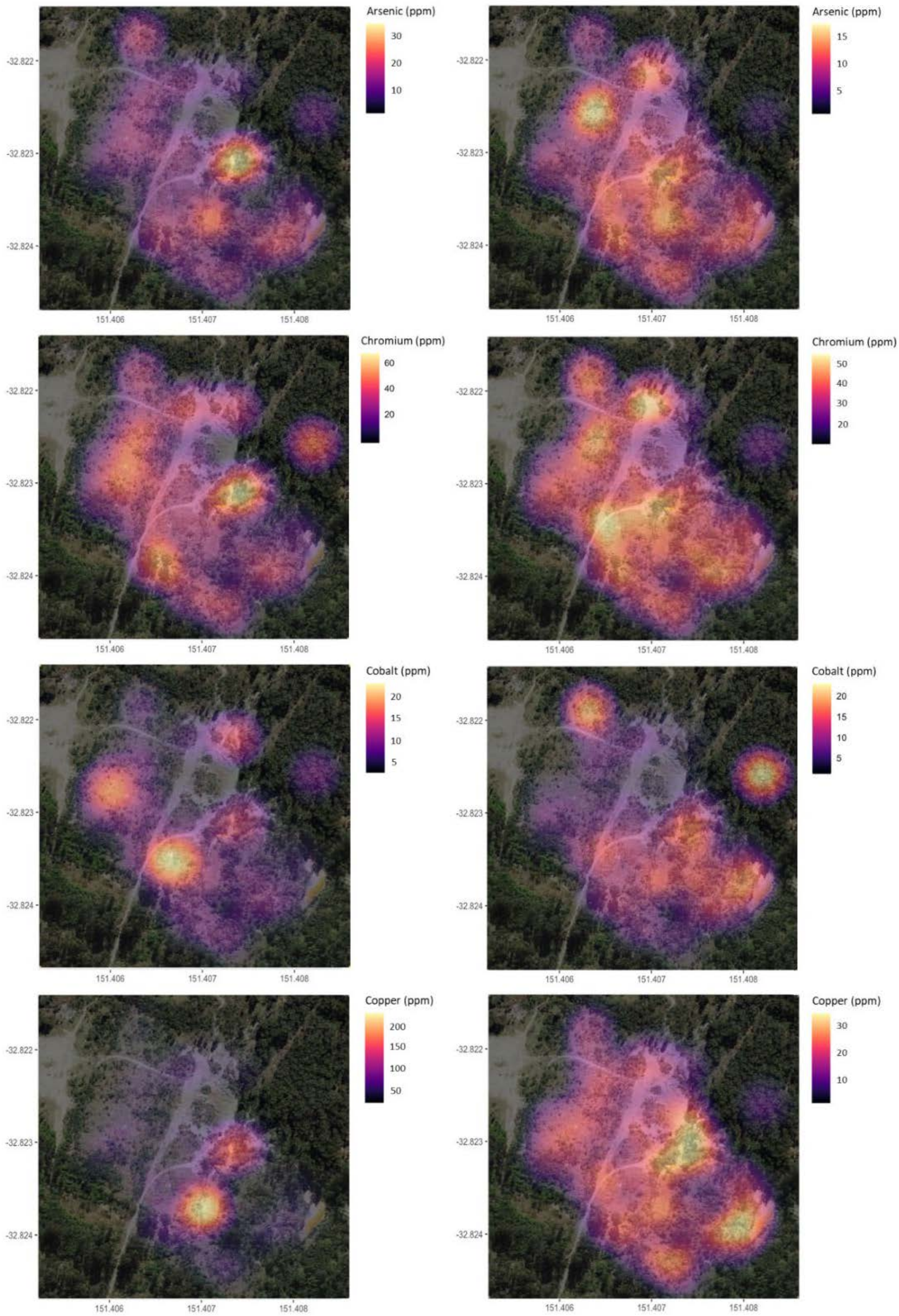

Figure AB 6. Neath colliery heatmaps showing As, Co, Cr, and Cu (Bottom profile on the left, top profile on the right). Note difference in scale between top and bottom profiles.

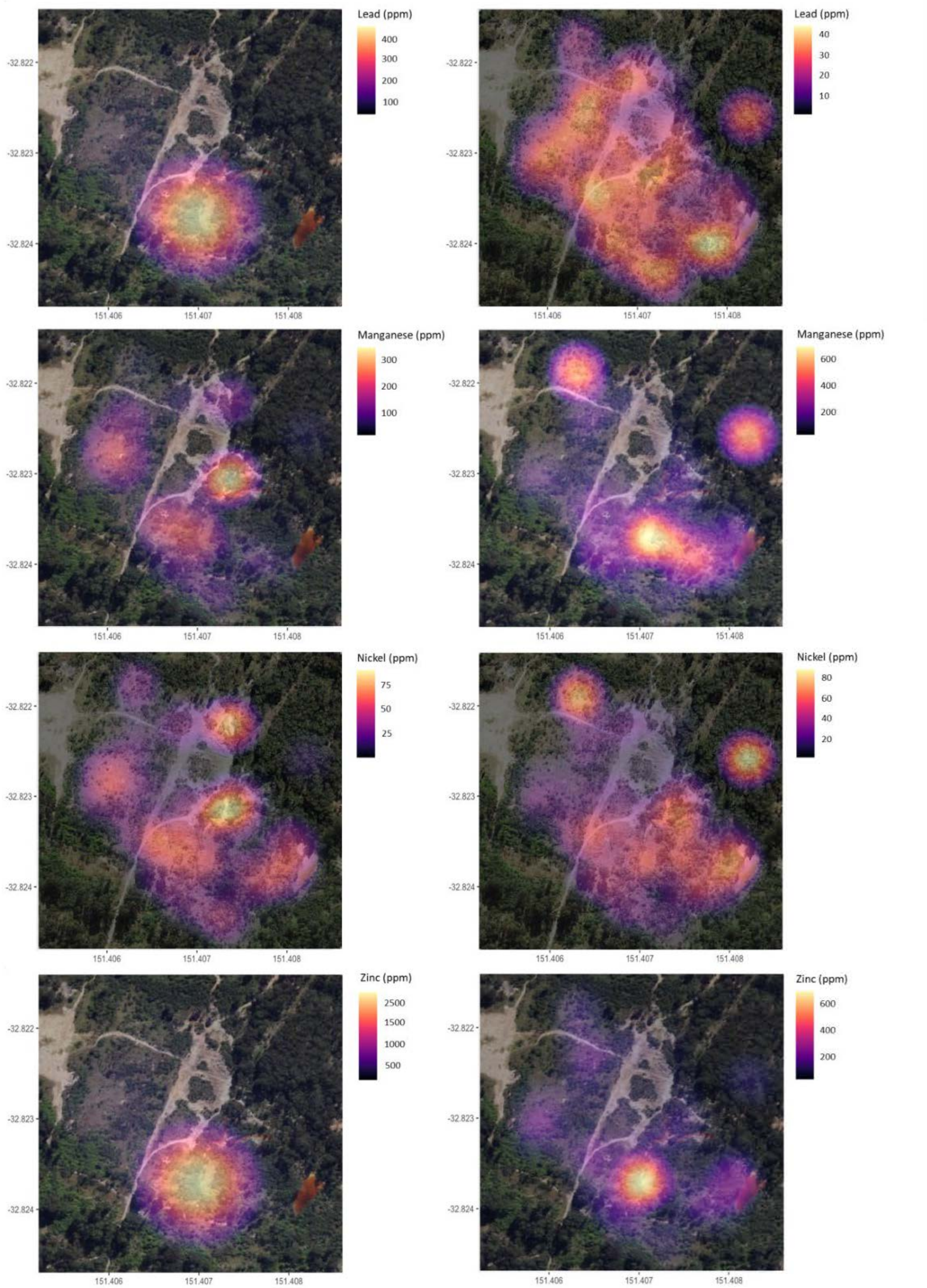

Figure AB 7. Neath colliery heatmaps showing Pb, Mn, Ni, and Zn (Bottom profile on the left, top profile on the right). Note difference in scale between top and bottom profiles.

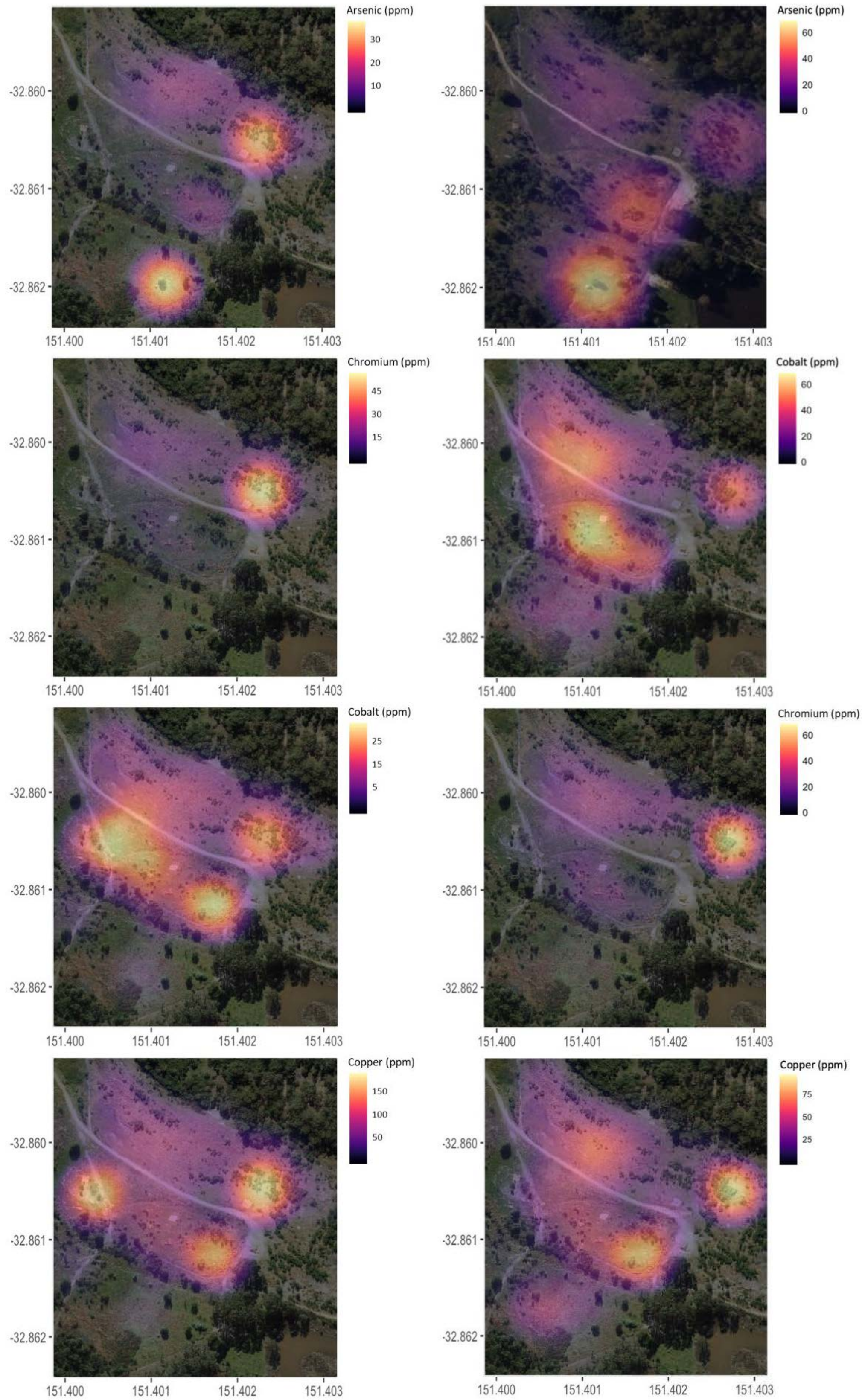

Figure AB 8. Abermain colliery heatmaps showing As, Cr, Co, and Cu (Bottom profile on the left, top profile on the right). Note difference in scale between top and bottom profiles.

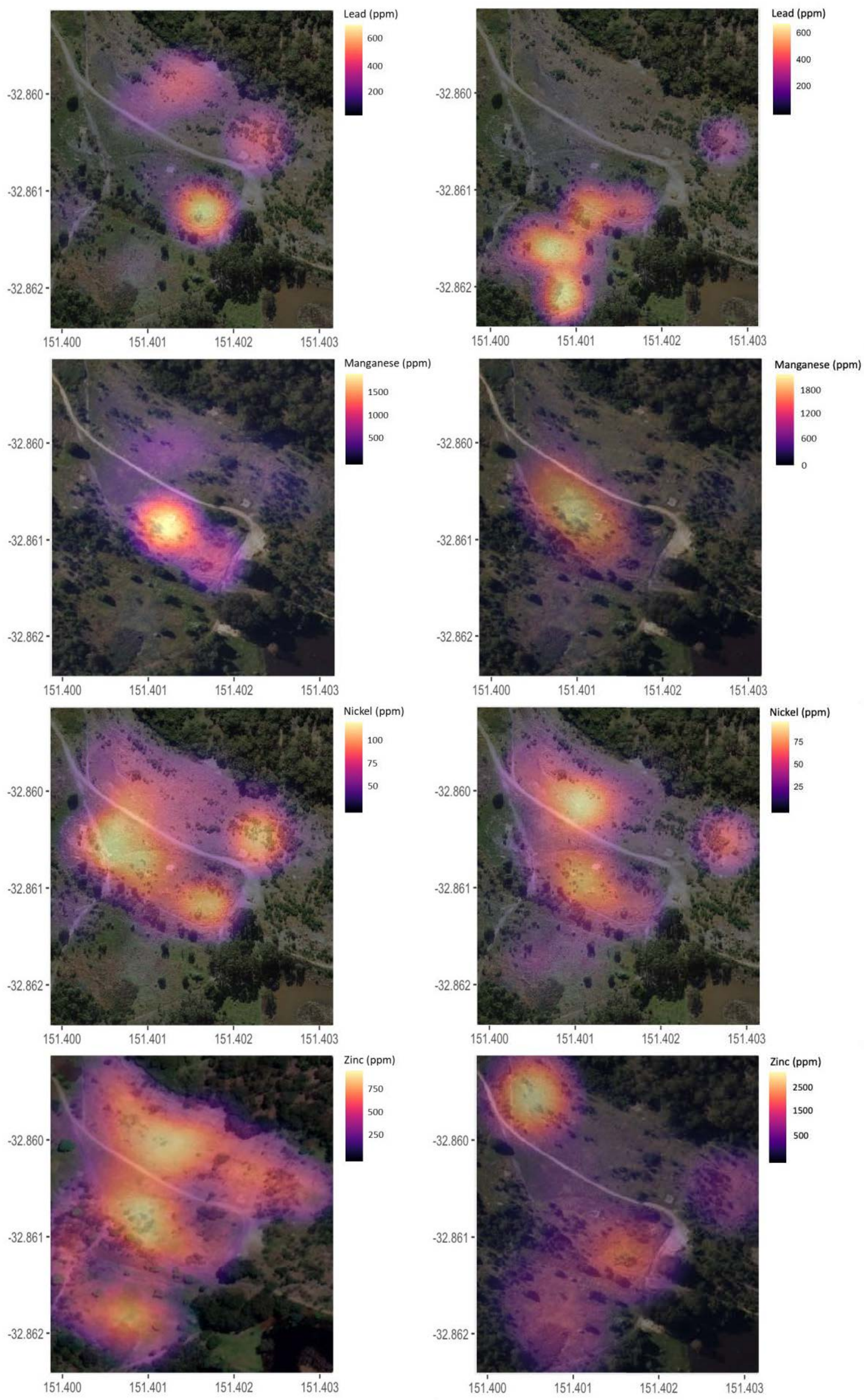

Figure AB 9. Abermain colliery heatmaps showing Pb, Mn, Ni, and Zn (Bottom profile on the left, top profile on the right). Note difference in scale between top and bottom profiles.

Figure AB 10. Red discolouration indicating AMD affected water at Neath Colliery. Photo taken October 2019.

Table AB 7. Ecological investigation levels soils (EIL) and Ecological Soil Screening Levels (Eco-SSLs) for Australia, New Zealand, The United States of America, Canada, China, and Sweden.

Governing body	Region	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Arsenic	Lead	Reference
NEPM (2013)	Australia	(III) 400 (VI) 1	500	50	60	100	200	20	600	
	NZ	100				F= 25 A= 45	Fresh 50 Aged 120	6	55	
Eco-SSLs for plants (mg/kg dry weight in soil	USA	Not enough data to derive	220	13	38	70	160	18	120	
CCME (2015) Residential/parkland	Canada	64	-	50	45	63	250	12	300	Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health
Environmental quality standards for soil level I (GB 15618-1995)	China	(III) 90			40	35	100	15	35	Chen (2018)
Swedish guideline values for contaminated soils (sensitive land use)	Sweden	(III) 120 (VI) 5	-	30	35	100	350	15	80	Swedish EPA report 4639, (SEPA, 1996). https://esdac.jrc.ec.europa.eu/ESDB_Archive/eusoils_docs/other/EUR22805.pdf

Table AB 8. Ecological investigation levels fresh waters for Australia and New Zealand, The United States of America, Canada, China, and the United Nations.

Governing body	Region	Chromium (ug/L)	Manganese	Cobalt	Nickel	Copper	Zinc	Arsenic	Lead	Reference
ANZECC Trigger values for freshwater (µgL-1) 95% species level protection	Australia and NZ	(vi) 1	1900	-	11	1.4	8	24 (III) 13 (V)	3.4	Trigger values for freshwater (µgL-1) 95% species level protection
EPA national recommended water quality guidelines for aquatic life (µg/L)	USA	(III) 570 (VI) 16	-	-	470	-	120	340	65	https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table
CCME (2018) Long-term guideline (ug/L)	Canada	(vI) 1.0 (III) 8.9	430	-	-	-	7.0	5.0	-	
The Environmental Quality Standards for Surface Water mg/L	China	(VI) 0.01	< 0.1			< 0.01	0.05	0.05	0.01	https://english.mee.gov.cn/SOE/soechina1997/water/standard.htm
WHO drinking water guidelines ((mg/L)	EU	0.05	0.4		0.02	2.0		0.01	0.01	WHO. (2004). *Guidelines for drinking water quality* (3rd ed.). Geneva: World Health Organization.

Appendix C

Supporting evidence for chapter 4

Table AC 1. Average Root area of five species in contact with DGT window

Species	Total root area (mm2) ± standard error	Total percent root cover (%) ± standard error
Dichanthium sericeum	42.03 ± 9.26	13.38 ± 2.95
Themeda triandra	92.99 ± 9.70	29.61 ± 3.09
Chloris truncata	78.34 ± 10.05	24.95 ± 3.20
Imperata cylindrica	70.29 ± 16.90	22.38 ± 5.38
Astrebla lappacea	90.66 ± 12.97	28.87 ± 4.13

Table AC 2. Average heavy metal concentration of five species (root and shoot) ± standard error

Species	Sample	arsenic average (ppm)	chromium average (ppm)	cobalt average (ppm)	copper average (ppm)	lead average (ppm)	manganese average (ppm)	nickel average (ppm)	zinc average (ppm)
Dichanthium sericeum	Root	13.03 ± 2.41	10.17 ± 2.12	3.20 ± 0.65	58.06 ± 11.71	80.82 ± 15.48	168.03 ± 35.55	18.11 ± 3.57	119.04 ± 20.72
	Shoot	0.77 ± 0.37	0.79 ± 0.39	0.23 ± 0.09	10.97 ± 3.28	3.33 ± 1.48	43.05 ± 10.68	0.96 ± 0.37	72.66 ± 14.19
Themeda triandra	Root	11.62 ± 0.85	8.20 ± 0.49	2.63 ± 0.16	50.53 ± 0.95	71.98 ± 5.29	139.83 ± 6.71	15.54 ± 0.78	111.72 ± 4.29
	Shoot	0.61 ± 0.10	0.61 ± 0.16	0.09 ± 0.01	9.96 ± 0.66	1.49 ± 0.29	59.40 ± 4.65	0.54 ± 0.06	115.74 ± 11.58
Chloris truncata	Root	13.73 ± 0.45	10.86 ± 0.44	3.29 ± 0.10	93.55 ± 5.81	79.69 ± 4.17	177.97 ± 3.54	18.14 ± 0.64	245.46 ± 14.46
	Shoot	0.37 ± 0.23	0.58 ± 0.29	0.15 ± 0.05	10.29 ± 2.41	1.79 ± 0.56	87.44 ± 6.20	0.72 ± 0.12	155.70 ± 6.40
Imperata cylindrica	Root	9.15 ± 1.17	7.05 ± 0.77	2.37 ± 0.30	76.88 ± 13.65	49.10 ± 5.09	141.54 ± 25.13	12.49 ± 1.50	176.35 ± 24.85
	Shoot	1.26 ± 0.39	0.74 ± 0.18	0.18 ± 0.02	18.52 ± 2.04	1.83 ± 0.36	63.09 ± 6.53	0.93 ± 0.17	89.58 ± 9.44
Astrebla lappacea	Root	10.41 ± 0.95	7.02 ± 0.49	2.11 ± 0.20	51.65 ± 4.72	54.47 ± 6.74	113.54 ± 7.39	12.12 ± 1.56	116.05 ± 5.75
	Shoot	1.00 ± 0.12	0.61 ± 0.23	0.11 ± 0.01	7.96 ± 0.94	1.10 ± 0.12	26.98 ± 3.74	0.63 ± 0.07	63.13 ± 8.41

Table AC 3. Average total metal concentration (ppm) of five species and NEPM (2013) soil guidelines ± standard error. Total metals range: chromium 4.33-23.90; manganese 248.08-677.19; cobalt 3.60- 8.37; nickel 23.14- 54.72; copper 38.92 - 81.92; zinc 84.04 - 242.03; arsenic 10.53 - 28.69; lead 12.12 - 217.99 ppm.

	arsenic average (ppm)	chromium average (ppm)	cobalt average (ppm)	copper average (ppm)	lead average (ppm)	manganese average (ppm)	nickel average (ppm)	zinc average (ppm)
NEPM (2013)	20	400	50	100	600	500	60	200
Dichanthium sericeum	16.94 ± 2.03	10.21 ± 1.57	5.01 ± 0.45	49.55 ± 3.72	100.14 ± 14.67	335.39 ± 27.55	32.31 ± 2.70	128.83 ± 9.51

Themeda triandra	24.41 ± 1.93	16.77 ± 2.09	6.43 ± 0.47	60.13 ± 5.35	127.72 ± 17.31	424.76 ± 6.43	41.07 ± 3.32	184.40 ± 18.59
Chloris truncata	21.49 ± 1.61	15.90 ± 1.63	6.16 ± 0.40	58.04 ± 5.03	116.12 ± 6.89	474.61 ± 51.63	38.41 ± 2.41	150.50 ± 6.98
Imperata cylindrica	23.54 ± 1.93	15.96 ± 1.86	6.62 ± 0.54	64.85 ± 5.50	139.81 ± 18.00	450.22 ± 33.70	41.16 ± 3.13	159.62 ± 14.26
Astrebla lappacea	21.31 ± 2.06	14.22 ± 1.69	6.27 ± 0.42	63.27 ± 5.10	113.94 ± 16.43	396.54 ± 28.56	39.86 ± 2.70	144.93 ± 10.30
Control	19.19 ± 2.27	13.48 ± 2.20	5.72 ± 0.56	54.36 ± 5.00	104.45 ± 28.01	406.75 ± 35.43	35.56 ± 3.47	151.58 ± 21.57

Table AC 4. Average DGT concentration (ppb) of five species.

Species	arsenic average (ppb)	chromium average (ppb)	cobalt average (ppb)	copper average (ppb)	lead average (ppb)	manganese average (ppb)	nickel average (ppb)	zinc average (ppb)
Dichanthium sericeum	6.37 ± 1.23	10.42 ± 1.94	0.87 ± 0.24	162.14 ± 24.90	9.88 ± 0.37	23777.78 ± 6571.78	5.63 ± 0.93	138.89 ± 17.08
Themeda triandra	12.93 ± 6.00	19.31 ± 6.34	1.21 ± 0.26	182.74 ± 39.47	15.79 ± 3.97	33222.22 ± 10458.62	4.47 ± 0.63	126.34 ± 11.59
Chloris truncata	6.00 ± 1.22	10.01 ± 2.25	0.69 ± 0.24	153.04 ± 27.72	9.69 ± 1.02	22888.89 ± 5175.92	4.83 ± 0.46	118.88 ± 12.24
Imperata cylindrica	9.93 ± 0.50	13.89 ± 3.72	1.47 ± 0.16	121.61 ± 7.13	12.64 ± 1.21	42222.22 ± 15050.63	7.24 ± 0.94	172.97 ± 14.16
Astrebla lappacea	9.84 ± 0.78	10.93 ± 0.87	1.39 ± 0.11	118.21 ± 8.05	12.38 ± 1.76	25555.56 ± 7390.14	5.45 ± 1.04	145.84 ± 14.75
Control	11.71 ± 5.41	14.92 ± 5.60	1.39 ± 0.73	153.04 ± 18.95	13.92 ± 4.18	20222.22 ± 3361.46	9.21 ± 1.60	218.76 ± 35.27

Table AC 5. Raw data showing the bioconcentration factors of each of the 5 species and 8 heavy metals

Species	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Arsenic	Lead
1 *Dichanthium sericeum*	0.68	0.33	0.44	0.38	0.78	0.65	0.59	0.72
2 *Themeda triandra*	0.51	0.35	0.41	0.39	0.88	0.49	0.41	0.43
3 *Chloris truncata*	0.93	0.45	0.65	0.57	1.71	1.75	0.76	0.91
4 *Imperata cylindrica*	0.35	0.24	0.28	0.26	0.69	0.81	0.32	0.34
5 *Astrebla lappacea*	0.32	0.21	0.26	0.24	0.54	0.63	0.34	0.37
7 *Dichanthium sericeum*	1.32	0.60	0.81	0.74	1.54	1.10	1.04	1.04
8 *Themeda triandra*	0.39	0.27	0.34	0.32	0.79	0.69	0.44	0.57
9 *Chloris truncata*	0.58	0.34	0.50	0.45	1.70	1.79	0.60	0.62

10 *Imperata cylindrica*	0.47	0.38	0.44	0.35	1.38	1.29	0.45	0.35
11 *Astrebla lappacea*	0.69	0.38	0.45	0.43	1.11	1.07	0.70	0.72
13 *Dichanthium sericeum*	0.99	0.54	0.65	0.56	1.19	1.02	0.70	0.69
14 *Themeda triandra*	0.59	0.36	0.50	0.44	0.86	0.68	0.63	0.79
15 *Chloris truncata*	0.62	0.36	0.47	0.41	1.48	1.38	0.57	0.58
16 *Imperata cylindrica*	0.55	0.32	0.35	0.30	1.62	1.26	0.39	0.38
17 *Astrebla lappacea*	0.57	0.30	0.32	0.27	0.92	0.79	0.49	0.40

Table AC 6. Raw data showing the translocation factors of each of the 5 species and 8 heavy metals

Species	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Arsenic	Lead
1 *Dichanthium sericeum*	0.03	0.28	0.04	0.03	0.16	0.66	0.02	0.02
2 *Themeda triandra*	0.08	0.36	0.03	0.03	0.17	0.84	0.05	0.01
3 *Chloris truncata*	0.02	0.41	0.03	0.03	0.09	0.59	0.00	0.02
4 *Imperata cylindrica*	0.08	0.44	0.07	0.05	0.30	0.49	0.10	0.03
5 *Astrebla lappacea*	0.08	0.23	0.05	0.05	0.16	0.49	0.10	0.02
7 *Dichanthium sericeum*	0.15	0.37	0.12	0.09	0.27	0.86	0.11	0.07
8 *Themeda triandra*	0.04	0.53	0.05	0.04	0.22	**1.43**	0.06	0.04
9 *Chloris truncata*	0.00	0.52	0.03	0.04	0.09	0.65	0.00	0.01
10 *Imperata cylindrica*	0.13	0.36	0.06	0.08	0.23	0.45	0.18	0.04
11 *Astrebla lappacea*	0.15	0.30	0.06	0.05	0.18	0.69	0.11	0.01
13 *Dichanthium sericeum*	0.08	0.21	0.08	0.06	0.20	0.51	0.07	0.05
14 *Themeda triandra*	0.08	0.46	0.04	0.04	0.23	**1.11**	0.05	0.02
15 *Chloris truncata*	0.09	0.55	0.08	0.00	0.14	0.00	0.05	0.04
16 *Imperata cylindrica*	0.10	0.59	0.10	0.00	0.21	0.60	0.11	0.04

17 *Astrebla lappacea*	0.04	0.22	0.05	0.00	0.14	0.53	0.10	0.03

Table AC 7. Average shoot height (mm), shoot dry weight (g) and root dry weight (g), and root to shoot ration for 5 species.

Sample	Average shoot height (mm)	Shoot dry weight (g)	Root dry weight (g)	Root: shoot ratio
1 *Dichanthium sericeum*	540	2.53	2.28	0.90
2 *Themeda triandra*	740	3.64	3.58	0.98
3 *Chloris truncata*	256.67 ± 20.28	1.32	0.99	0.75
4 *Imperata cylindrica*	390 ± 30	1.22	0.93	0.76
5 *Astrebla lappacea*	340 ± 28.87	2.42	1.17	0.48
7 *Dichanthium sericeum*	510 ± 40	1.03	1.24	1.21
8 *Themeda triandra*	420 ± 50	1.46	0.89	0.61
9 *Chloris truncata*	303.33 ± 46.31	0.71	0.54	0.77
10 *Imperata cylindrica*	430	0.33	0.33	1.00
11 *Astrebla lappacea*	280 ± 20	1.14	0.86	0.75
13 *Dichanthium sericeum*	413.33 ± 98.38	1.52	1.35	0.89
14 *Themeda triandra*	353.33 ± 21.86	2.42	1.54	0.64
15 *Chloris truncata*	213.33 ± 3.33	1.11	0.58	0.53
16 *Imperata cylindrica*	450	0.62	0.59	0.95
17 *Astrebla lappacea*	295 ± 35	0.80	0.42	0.53

Table AC 8. Physiochemical properties for all 18 rhizotrons. Total nitrogen and carbon were both measured at the end of the experiment and showed no difference between replicates and control. Nitrogen % of the soil was low (0.48- 0.77%), while total carbon % ranged between (16.08- 28.04 %). pH was slightly acidic but stable ranging between (6.13- 6.59). Cation exchange capacity (CEC) ranged between 13 and 23 c mol kg−1.

Sample	Nitrogen (%)	Carbon (%)	pH	Conductivity	CEC µS cm –1)
1 *Dichanthium sericeum*	0.56	19.81	6.20	98	19
2 *Themeda triandra*	0.77	24.12	6.31	47	18
3 *Chloris truncata*	0.58	28.04	6.40	110	15

4 *Imperata cylindrica*	0.58	22.80	6.21	100	16
5 *Astrebla lappacea*	0.50	27.78	6.27	54	17
6 *Control*	0.57	21.21	6.28	50	17
7 *Dichanthium sericeum*	0.53	17.94	6.28	66	19
8 *Themeda triandra*	0.48	24.80	6.24	130	13
9 *Chloris truncata*	0.55	22.79	6.33	96	17
10 *Imperata cylindrica*	0.56	17.71	6.57	58	18
11 *Astrebla lappacea*	0.55	19.72	6.25	99	20
12 *Control*	0.55	16.97	6.19	58	21
13 *Dichanthium sericeum*	0.58	18.90	6.32	40	18
14 *Themeda triandra*	0.53	21.62	6.32	170	22
15 *Chloris truncata*	0.60	20.03	6.27	200	22
16 *Imperata cylindrica*	0.54	16.08	6.16	140	20
17 *Astrebla lappacea*	0.64	16.65	6.13	64	16
18 *Control*	0.54	19.89	6.59	65	23

Table AC 9. Analysis of variance table for total metal concentration x tissue concentration for individual metals

Response	Metal	terms	Df	Sum sq	F-value	P-value
Total metal vs shoot	All	shoot	1	142.90	282.53	**0.00**
		Residuals	116	58.67		
	Chromium	shoot	1	0.00	0.00	0.95
		Residuals	12	0.92		
	Manganese	shoot	1	0.06	2.29	0.15
		Residuals	13	0.35		
	Cobalt	shoot	1	0.01	0.27	0.61
		Residuals	13	0.30		
	Nickel	shoot	1	0.00	0.09	0.76
		Residuals	13	0.27		
	Copper	shoot	1	0.01	0.49	0.50
		Residuals	13	0.39		

	Zinc	shoot	1	0.00	0.04	0.84
		Residuals	13	0.44		
	Arsenic	shoot	1	0.03	0.76	0.40
		Residuals	12	0.48		
	Lead	shoot	1	0.00	0.05	0.82
		Residuals	13	0.73		
Total metal vs root	All	shoot	1	176.63	788.39	**0.00**
		Residuals	118	26.44		
	Chromium	root	1	0.00	0.03	0.87
		Residuals	13	1.00		
	Manganese	root	1	0.02	0.64	0.44
		Residuals	13	0.39		
	Cobalt	root	1	0.01	0.34	0.57
		Residuals	13	0.30		
	Nickel	root	1	0.01	0.53	0.48
		Residuals	13	0.26		
	Copper	root	1	0.00	0.00	0.95
		Residuals	13	0.40		
	Zinc	root	1	0.00	0.04	0.84
		Residuals	13	0.44		
	Arsenic	root	1	0.01	0.22	0.65
		Residuals	13	0.50		
	Lead	root	1	0.00	0.02	0.88
		Residuals	13	0.73		

Table AC 10. Analysis of variance table for DGT x tissue concentration for individual metals

Response	Metal	terms	Df	Sum sq	F-value	P-value
DGT x shoot	All	shoot	1	640	216	**0.00**
		Residuals	114	337		
	Chromium	shoot	1	0.13	0.49	0.50
		Residuals	12	3.26		
	Manganese	shoot	1	0.61	1.21	0.29
		Residuals	13	6.57		
	Cobalt	shoot	1	0.02	0.18	0.68
		Residuals	11	1.50		
	Nickel	shoot	1	0.52	5.81	**0.03**
		Residuals	13	1.16		
	Copper	shoot	1	0.11	0.54	0.47
		Residuals	13	2.68		
	Zinc	shoot	1	0.03	0.57	0.46
		Residuals	13	0.69		
	Arsenic	shoot	1	0.00	0.00	0.98

		Residuals	12	3.72		
	Lead	shoot	1	0.10	1.14	0.31
		Residuals	13	1.17		
DGT x root	All	shoot	1	565.28	153.70	**0.00**
		Residuals	116	426.62		
	Chromium	root	1	0.66	1.78	0.20
		Residuals	13	4.81		
	Manganese	root	1	0.17	0.31	0.59
		Residuals	13	7.02		
	Cobalt	root	1	0.63	7.75	**0.02**
		Residuals	11	0.90		
	Nickel	root	1	0.00	0.00	0.99
		Residuals	13	1.68		
	Copper	root	1	0.01	0.05	0.83
		Residuals	13	2.78		
	Zinc	root	1	0.02	0.44	0.52
		Residuals	13	0.70		
	Arsenic	root	1	1.86	6.88	**0.02**
		Residuals	13	3.51		
	Lead	root	1	0.20	2.49	0.14
		Residuals	13	1.07		

Table AC 11. Total metal concentration in five species vs control plots. No significant result was found for any analyte.

Response	Metal	Terms	Df	Sum Sq	F-value	P-value
	Chromium	Species	5	172.40	1.67	0.17
		Residuals	30	619.70		
	Manganese	Species	5	69617	1.86	0.13
		Residuals	30	224561		
	Cobalt	Species	5	10.28	1.51	0.22
		Residuals	30	40.83		
	Nickel	Species	5	368	1.38	0.26
		Residuals	30	1598		
	Copper	Species	5	979.00	1.31	0.29
		Residuals	30	4471		
	Zinc	Species	5	10122	1.61	0.19
		Residuals	30	37784		
	Arsenic	Species	5	228.20	1.94	0.12

		Residuals	30	706.90		
	Lead	Species	5	6523	0.67	0.65
		Residuals	30	58233		

Table AC 12. DGT metal concentration in five species vs control plots. No significant result was found for any analyte.

Response	Metal		Df	Sum Sq	F-value	P-value
DGT	Chromium	Species	5	0.2123	0.806	0.551
		Residuals	48	2.5279		
	Manganese	Species	5	1013737	0.865	0.512
		Residuals	48	11254874		
	Cobalt	Species	5	0.001314	0.8	0.555
		Residuals	48	0.015772		
	Copper	Species	5	6.78	1.066	0.391
		Residuals	48	60.99		
	Arsenic	Species	5	0.0626	0.677	0.643
		Residuals	48	0.8867		
	Lead	Species	5	0.00577	0.847	0.523
		Residuals	48	0.0654		

Table AC 13. Pairwise comparison of soil DGT nickel concentrations from five species and control plots. P-Values were adjusted for multiple comparisons.

Response	Estimate	SE	Df	T-ratio	P-value
A.lappacea x control	-0.06397	0.0241	48	-2.654	0.1041
D. sericeum x control	-0.07463	0.0241	48	-3.096	**0.0363**
I. cylindrica x control	0.06092	0.0241	48	2.527	0.1365
T. triandra x control	0.03351	0.0241	48	1.39	0.7327
C. truncata x control	0.08072	0.0241	48	3.349	**0.0186**

Table AC 14. Pairwise comparison of soil DGT zinc concentrations from five species and control plots. P-Values were adjusted for multiple comparisons.

Response	Estimate	SE	Df	T-ratio	P-value
A. lappacea vs control	-1.115	0.418	48	-2.67	0.1005
D. sericeum vs control	1.222	0.418	48	2.924	0.0556
I. cylindrica vs control	0.7	0.418	48	1.676	0.5537
T. triandra vs control	1.414	0.418	48	3.384	**0.0169**
C. truncata vs control	-1.528	0.418	48	-3.657	**0.0079**

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