

**HEAVY METALS IN THE CHRISTCHURCH RESIDENTIAL
RED ZONE AND IMPLICATIONS FOR COMMUNITY
GARDENS**

A dissertation submitted in partial fulfilment for the degree

of

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By

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In loving memory of my Father:

Michael Kim (김신)

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“Spread love everywhere you go. Let no one ever come to you without leaving happier.”

- Mother Teresa -

Abstract

Following the 2010-11 Christchurch earthquakes, a total of 8060 residential buildings in the greater Christchurch area were demolished and removed. After removal, most of this land was levelled and planted with grass as the land was uninhabitable and deemed unsuitable for rebuilding on. This area of unoccupied land is known as the Christchurch Residential Red Zone (RZ) and covers an area of 630-hectares. The establishment of community gardens has been proposed for this area. Community gardens are becoming increasingly important as urban centres expand. They provide healthy produce while also benefiting the socio economic wellbeing of individuals who are disconnected from where and how their food is produced. However, as urban soils are a natural sink for anthropogenically released heavy metal (HM) contaminants, there is an increased risk of HM exposure through working in and eating produce grown in this area. Exposure to high concentrations of HMs has an adverse effect on human health. Therefore, it is essential to gain an understanding of the HM contaminants in the RZ to avoid potential human health risks. In-situ XRF screening of surface soils in the RZ was used to measure 313 soil samples from the RZ. Elevated levels of soil Pb and Zn concentrations were observed. Some 20% of RZ soil samples had Pb concentrations exceeding the New Zealand soil Pb guideline of 210 mg/kg, with one site containing a Pb concentration of 3289 mg/kg. Zn concentrations exceeded the New Zealand soil Zn guideline of 400 mg/kg in 5% of samples, with a maximum Zn concentration of 1894 mg/kg. Samples taken in areas of bare soil with visible debris and rubble had significantly higher concentrations than areas without. The mean Zn concentrations in these areas were 217.88 mg/kg compared to 113.42 mg/kg in areas without, while the mean Pb concentrations in these areas were 226.88 mg/kg compared to 75.44 mg/kg in areas without. Soil HM concentrations should be a key factor in deciding on the future land use of RZ land. The likelihood of human exposure to these HMs in soils would be reduced if these RZ areas were redeveloped into nature reserves or native forests, rather than community gardens where produce is grown and bare soil is exposed.

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1. Introduction

Heavy metals (HMs) are elements with atomic weights between 63.5–200.6 g/mol and densities greater than 5 g/cm³ (Srivastava & Majumder, 2008). HMs are present at low concentrations in soils, plants, and animals (including humans), where they are tolerated (Robinson et al., 2009). Exposure to high concentrations of HMs has an adverse effect on human health (Robinson et al., 2009). Even essential nutrients such as copper (Cu) and zinc (Zn) can become environmental contaminants when present in high concentrations. Common HM contaminants are lead (Pb), cadmium (Cd), Zn, mercury (Hg), Cu, metalloid arsenic (As), and nickel (Ni) (Srivastava & Majumder, 2008). HMs are persistent in the environment. Therefore, they can accumulate to toxic levels (Robinson et al., 2009; Sharma et al. 2007). The total concentration of HMs in soils is a function of the natural background concentration and anthropogenic contributions (Guagliardi et al., 2012, as cited in Ashrafzadeh et al., 2018).

Humans are exposed to HMs in contaminated soils through the consumption of food grown on contaminated soils, dermal contact, ingestion, and inhalation of dust and vapours (Nathanail & Earl, 2001). Organ failure, cancer, and death can result from the accumulation of these HMs in the human body (Martin & Griswold, 2009). Pb in soils is of particular concern to developing children as they are more sensitive to Pb exposure than adults. Historical use of Pb in leaded petrol, paint, piping, and roofing has elevated Pb concentrations in urban soils (Carr et al., 2008) and other HMs such as As, Cu and Zn have increased due to mining, transportation, agriculture, and industrial production (Robinson et al., 2009).

The Christchurch City district, which covers an area of 1539 km², is the largest South Island population centre and New Zealand's third-largest city, with ~370,000 inhabitants according to the 2018 census (Statistics New Zealand, n.d.). After the 2010 and 2011 Christchurch earthquakes, hundreds of hectares of land in Christchurch's eastern suburbs were deemed unsuitable for rebuilding. As a result, roughly 8000 buildings were demolished (Brand & Nicholson, 2016). After removal, most of this land was levelled and planted with grass. However, indigenous vegetation and exotic trees over 4 meters tall were retained for ecological

reasons (Brown et al., 2012). This area of unoccupied land is known as the Christchurch Residential Red Zone (RZ).

Different land uses for this area have been proposed by different community organisations in Christchurch. Community gardens are one of the many land uses that have been proposed. Community gardens provide healthy produce while also improving the ecological, cultural, social, and educational aspects of the community (Cheng et al., 2015). But, because urban soils are a natural sink for contaminants, there is an elevated risk of human exposure to HMs through working in contaminated soils and eating produce grown there.

Given that the RZ consists mainly of suburbs built before the 1960s, such as Avonside, Wainoni, Bexley, New Brighton, and Brooklands, it is hypothesized that RZ soils will contain high concentrations of HMs. A single study conducted in the flatland Ōtākaro Avon River Corridor area of the Christchurch Residential RZ by Gilmour (2013), found that Pb was the only element exceeding the residential land use guideline among As, Cd, Cu, and Pb. Similarly, Ashrafzadeh et al. (2018) found that the mean Pb concentration in Christchurch garden soils in neighbourhoods developed before the 1950s exceeded the guideline values (282 mg/kg).

Soils contaminated with HMs can be remediated through a variety of methods. Types of remediation include dig and dump, covering with topsoil, covering with impermeable surfaces, in situ stabilization, or changing land use (e.g. playing fields or native forest instead of community gardens). Some remediation has already occurred in the RZ. Topsoil from Lincoln has been spread over soils in the RZ to reduce exposure to the underlying soil which may be contaminated with HMs.

To avoid potential environmental consequences and human health risks, the concentration of HMs in RZ soils must be quantified before the establishment of community gardens.

1.1 Research aims and objectives

The objectives of this research were to conduct in-situ XRF screening of RZ soils to gain a quantitative understanding of HM concentrations and determine the nature of HM distribution in Christchurch residential RZ soils. Exposure to high concentrations of HMs has an adverse effect on human health. Therefore, it is essential to gain an understanding of the HM contaminants in the RZ to avoid potential environmental consequences and human health risks and to gain a better understanding of the suitability and implications of different types of proposed land uses, specifically community gardens. While many studies have been conducted regarding the common HM contaminants in soils, the health effects of HMs, and the pathways of exposure (Assi et al., 2016; Laidlaw et al., 2017; Kandic et al., 2019), none have specifically focused on what key HM contaminants are present in RZ soils, the concentration of these HM contaminants, and the nature of HM spatial distribution. This research will complement the regeneration work that is currently underway in the RZ by providing data and recommendations for land use that minimizes human exposure to HMs. Furthermore, the results from this research project will contribute to the development of risk management strategies and potentially lead the way for future research projects in the RZ.

The aim of this study is to:

1. Identify the key contaminants in RZ soils that pose a threat to humans and ecosystems by using in-situ screening analysis.
2. Determine the nature of the spatial distribution of HMs in RZ soils.
3. Determine the implications of community gardens.
4. Compare and contrast remediation methods or management strategies that can minimize and mitigate the exposure to these HM contaminants.

2. Literature Review

2.1 Sources of lead and zinc in soils

The total concentration of HMs in the soil is determined by the background concentration as well as anthropogenic contributions, which include the use of soil conditioners such as compost, fertilizers, and manures, paints, vehicle emissions, agrichemicals (herbicides, insecticides, and fungicides), heating, and local industries (Ashrafzadeh et al., 2018). Elevated HM concentrations have been found in urban soils around the world (Ashrafzadeh et al., 2018).

Soils are the largest sink for environmental Pb, absorbing 60-70% of annual worldwide atmospheric Pb emissions (Rooney, 2002). Batteries (Assi et al., 2016), Pb-based paints, solders from food packaging, plumbing, and leaded gasoline were historically the primary sources of Pb exposure globally (Mason et al., 2014). Soils in urban and suburban areas are more likely to have contaminated soils than compared to rural soils as they are more influenced by anthropogenic activities (Ashrafzadeh et al., 2018).

Pb contamination of soil is an issue of environmental justice since it disproportionately affects urban, poor, and minority populations (Clark et al., 2006). A study by Clark et al. (2006) found that 30% of soil mass and 32% of soil Pb was represented by soils with size fractions between 0.5 and 0.25mm. Clark et al. (2006) also found that soils <0.044mm represented 5% of soil mass but contained a disproportionate amount of soil Pb (10%). Because leaded gasoline combustion produces fine particulate matter (PM), the Pb observed in these size fractions is most likely from this source (Clark et al., 2006). Fine particles, notably PM less than 100 µm, are often considered to be wind-transferable. Because wind can transfer these particles into neighbouring gardens, they pose the greatest risk of inhalation or ingestion (Clark et al., 2006).

Soil Pb concentrations were found to be greater in older buildings and neighbourhoods (Tong, 1998). Pb contamination of surface soils has an impact on human and environmental health, and food quality (Rooney, 2002). The concentration of Pb contaminants in soils is influenced by a number of different variables. Distance from the nearest arterial road, building age, and the use

of Pb-based paints were the main variables that explained 75% of Pb variability in garden soils (Kandic et al., 2019). Pb concentrations in backyard garden soils were found to have a significant correlation to the distance from arterial roads (Kandic et al., 2019). Kandic et al. (2019), discovered that Pb concentrations in backyard garden soils were found to decrease with increased distance to the nearest arterial road. Zn

Pb concentrations in backyard garden soils are influenced by building characteristics such as age and construction materials. Jordan and Hogan (1975) and Kandic et al. (2019) discovered that the concentration of soil Pb increases with the age of the building. Buildings over 35 years old had much higher backyard soil Pb concentrations than newer dwellings (Kandic et al., 2019). Kandic et al. (2019) showed that the distance from arterial roads shows a larger link with backyard garden soil Pb concentrations than building age. In backyard garden soils, the median Pb concentration increased from 960 mg/kg in buildings 20-100 years old to 1040 mg/kg in buildings over 100 years old (Kandic et al., 2019). As the majority of the buildings in the RZ were constructed between 1940-1970, HM soil contamination is more likely as HMs accumulate over time.

Kandic et al. (2019) also found that wooden buildings had higher Pb concentrations in garden soils than brick and concrete ones, while Jordan and Hogan (1975) discovered a significant correlation between high Pb concentrations in soils and painted wooden buildings. Pb levels were found to be significantly lower in locations where buildings were made of asbestos, brick, concrete, or coloured concrete (Jordan & Hogan, 1975).

Vehicle emissions were formerly a major source of Pb exposure, but with the development of Pb-free fuels, this is no longer an issue (Shukla et al., 2018). Following the ban on leaded gasoline, the US concentrated on paints, with Pb-based paint in old buildings now being the primary source of Pb poisoning in children (CDC, 2005).

Industrial activities such as steel processing, waste combustion, mining, and heating are thought to be the leading sources of anthropogenically produced Zn (Garba & Abubakar, 2018). The

corrosion of galvanized metals, tire wear, engine oil, brake dust and automotive grease also contribute to soil Zn concentrations (Garba & Abubakar, 2018).

2.2 Human exposure

It is necessary to understand the concentration of Pb in urban soils to minimize human exposure to Pb in soil and to produce and implement remediation strategies (Clark et al., 2006). Exposure pathways include the inhalation of dust, ingestion of soil, physical contact, or eating unpeeled or unwashed vegetables (Ashrafzadeh et al., 2018; Ministry of Health, 2018). Pb is most commonly absorbed through the respiratory and gastrointestinal systems (Shukla et al., 2018). Pb poisoning is a public health concern, especially in developing countries (Assi et al., 2016). Children are the most vulnerable population, particularly in urban and suburban areas, as they are more susceptible to the adverse effects of Pb and more vulnerable to inadvertent ingestion of soils than adults (Ashrafzadeh et al., 2018; Day, 1977). Children are often encouraged to participate in community gardening, even though they are the most vulnerable to contaminants (Cheng et al., 2015). In cities with Pb-contaminated soils, childhood Pb poisoning is a major environmental health concern (Ashrafzadeh et al., 2018). Efforts to reduce Pb exposure would benefit community gardeners.

2.3 Health effects of lead exposure

There is no safe level for Pb exposure (Shukla et al., 2018). Low levels of Pb exposure can have a negative impact on people's health (Shukla et al., 2018). The health effects of Pb have been the subject of several detailed reviews in recent years (Laidlaw et al., 2017). Because Pb has no biological function in the body, it has serious health consequences when it enters the body (Assi et al., 2016). Immunological deficiencies, anaemia, decreased brain function, hearing loss, and changes in behaviour that can lead to delinquency are some of the side effects that can be experienced (Assi et al., 2016; Carroll & McDonald, 2018). Excessive exposure to Pb can also

harm the reproductive systems in both men and women (Shukla et al., 2018). These effects include reduced sperm motility and activity in men, and pre-eclampsia, pregnancy-induced hypertension, premature membrane rupture, infertility, and premature delivery for women (Shukla et al., 2018). The most dangerous neurological impact of Pb poisoning is lead encephalopathy, which is a reaction to high levels of Pb that can lead to death (Mason et al., 2014).

The amount of Pb absorbed through the intestine is estimated to be between 10-15% of what is ingested, however, if there is a deficit of iron (Fe), calcium (Ca), or Zn, this amount increases (Shukla et al., 2018). And 30-40% of Pb that is inhaled is absorbed in the blood (Shukla et al., 2018). Once the Pb is absorbed through the gastrointestinal tract or respiratory system, it is stored in soft tissues as well as the skeleton (Shukla et al., 2018). Therefore, if there is evidence of Pb or other HM contamination in soils, vigilance should be exercised in gardening practices and the types of produce to be cultivated on such soil.

2.4 Lead contamination in Christchurch

Pb concentrations in Christchurch soils have been elevated due to the anthropogenic use of Pb in roofing materials, leaded gasoline, domestic heating, insecticides, Pb-based paints, and plumbing (Jordan & Hogan, 1975). The weathering of paint and atmospheric deposition are the two principal sources of Pb in Christchurch soils (Day, 1977). Day (1977) discovered that the combustion of leaded gasoline was responsible for 99% of all atmospheric/airborne Pb in Christchurch. New Zealand began phasing out leaded gasoline in 1986, and it was ultimately banned in 1996 (Wilson & Horrocks, 2008).

Pb-based paint, which was widely used until 1965 was outlawed in New Zealand in 1979, however, it can still be found in some older buildings (Hill Laboratories, 2018; Level, 2021). Buildings constructed before the 1980s are likely to have been painted with Pb-based paints (Ministry of Health, 2021). Flakes of old paint can enter soils as a result of natural weathering or

during the demolition or renovation of buildings (Jordan & Hogan, 1975). Pb plumbing can also be found in buildings built before 1940 (Level, 2021; Mason et al., 2014).

Several studies in Christchurch and around the world have indicated that Pb concentrations in urban soils are significantly above natural background concentrations, and are substantially greater in older neighbourhoods than in newly built areas (Ashrafzadeh et al., 2018; Cheng et al. 2015; Davies et al. 1987). Ashrafzadeh et al. (2018) found Pb concentrations in urban Christchurch soils that were 4000% greater than the urban background soil Pb concentration (level 1) of 23.3-57.3 mg/kg from Tonkin and Taylor (2007), and more than 1200% greater than the New Zealand Soil Contaminant Standards for Health for Inorganic Substances of 210 mg/kg. Most urban Pb soil samples exhibited concentrations greater than the Canterbury background soil concentrations (Ashrafzadeh et al., 2018).

In another study, Day (1977) found that Pb levels dropped towards the outskirts of Christchurch and increased in high-traffic regions. Background concentrations decreased from 3000 mg/kg in the city centre, to 1800 mg/kg, 6km away from the centre, and 500 mg/kg at the edge of the urban area at 9km (Day, 1977).

2.5 Community gardens

As urban centres expand, urban agriculture is becoming increasingly important. Urban agriculture has the potential to benefit communities, the local economy, and the wellbeing of those who are disconnected from where and how their food is produced. The quality of food grown in urban gardens is influenced by soil, water, and air quality. A community garden is a parcel of land that is collaboratively gardened by a group of individuals who live in an urban area (Al-Delaimy & Webb, 2017). Community gardens are commonly built on vacant properties with historically elevated levels of HM contamination, such as former parking lots and areas where old buildings have been demolished (Al-Delaimy & Webb, 2017). Community gardens on previously abandoned lands can provide a variety of benefits, including inexpensive and nutritious food, decreased airborne dust, and carbon sequestration (Cheng et al., 2015). Urban

agriculture not only provides nutritious food, but also promotes urban environmental sustainability, social equality and justice, and educational benefits (Cheng et al., 2015). According to Alaimo et al. (2008), community gardeners consume more fresh fruits and vegetables than non-gardeners, and a diet rich in these products can lower the risk of stroke, diabetes, heart disease, obesity, and some forms of cancer.

However, urban agriculture and gardening increase the risk of exposure through ingestion and inhalation of HM contaminants in soils (Cheng et al., 2015; Hunter et al., 2019; Kandic et al., 2019). Several studies have found that urban garden soils can contain high concentrations of HMs (Cheng et al., 2016; Clark et al., 2006). A study by Litt et al. (2002) in Boston, USA, found Pb levels of 12,875 mg/kg in yard soils. Similarly, urban garden soils in New York City, USA, also revealed extremely high soil Pb values of up to 8,912 mg/kg (Cheng et al., 2016).

High concentrations of Pb and other HMs may be present in RZ soils. This can result in produce from urban community gardens not meeting food safety standards which can put community members at risk. Therefore, it is crucial to monitor the contaminant levels in the soil and produce to make sure that they are at safe levels (Al-Delaimy & Webb, 2017). The types of produce grown in the community gardens and gardening practices implemented can also influence the exposure to HMs. Sangster et al. (2012) discover that vegetables grown in community gardens contaminated with Pb, in Omaha, Nebraska (USA), had elevated Pb concentrations. Pb concentrations in leafy greens, eggplant, and tomatoes grown in soils containing more than 100 mg/kg of Pb, exceeded the US Food and Drug Administration's (FDA) Pb standard of 0.5 mg/kg (Sangster et al., 2012). However, onions, and tomatoes grown in soils containing less than 100 mg/kg of Pb did not exceed the FDA Pb standards (Sangster et al., 2012). Similarly, Luo et al. (2012) found that the concentrations of Pb in the edible parts of vegetables in most samples exceeded the maximum threshold approved for consumption in China. Root vegetables and green leafy vegetables are thought to be more prone to absorbing and storing contaminants from contaminated soil (Al-Delaimy & Webb, 2017). Sangster et al. (2012) mentioned that the high Pb levels observed in the leafy greens may be explained, at least in part, by the lack of washing before testing, as soil particles remaining on the greens could be a source of Pb.

Although evidence suggests that produce grown in urban soils may be contaminated with HMs, limited research has been done to try to correlate community garden produce or working in such gardens with individual levels of exposure (Al-Delaimy & Webb, 2017). Similarly, limited research has been done to measure the levels and effects of HM exposure from various edible plants in urban community gardens (Al-Delaimy & Webb, 2017).

2.6 Research gap

Previously, urban agricultural research has concentrated on three key issues: 1) soil contamination in urban agricultural locations, 2) contamination absorption and presence in and on produce, and 3) gardeners' safety concerns about contaminants (Moller, 2016). However, no study to date has comprehensively examined the key HM contaminants in RZ soils, the concentration of these contaminants, and how these HM contaminants in RZ soils are spatially distributed. Little is known about the current levels of HM contaminants present throughout the RZ soils. Throughout the literature, there is consistent evidence that older neighbourhoods have significantly higher Pb concentrations than newly built areas. However, limited research on HM concentrations in RZ soils has been undertaken. With only one study by Gilmour (2013) being publicly available. Gilmour (2013) found soil Pb concentrations above the Soil Contaminant Standard guideline in the Ōtākaro Avon River Corridor area of the Residential RZ. Pb concentrations in RZ soils ranged from 39-260 mg/kg and had a mean of 123 mg/kg (Gilmour, 2013). However, this study only had a small sample size (n=16) which increases the likelihood of a Type II error and decreases the statistical power of the study (does not represent the true concentration of Pb in RZ soils) (Button et al., 2013). Additionally, several studies have used a Field-portable X-ray fluorescence (XRF) spectrometer to test soil for contamination (Clark et al., 2006), but none of these studies has specifically focused on the distribution of HM contaminants in the RZ.

Because high concentrations of HMs are harmful to human health, it's crucial to learn about the HM contaminants in the RZ, their concentrations, and distribution to avoid negative environmental consequences and human health risks, as well as to better understand the

suitability and implications of community gardens. Given the changed nature of the land in the RZ, it is hypothesised that RZ soils will contain elevated concentrations of HMs such as Pb, and Zn, as concentrations of these HMs in Christchurch soils have been elevated due to anthropogenic activities. This study will provide information on the spatial distribution and concentration of contaminants in the RZ, as well as suggestions for land use, which will supplement existing regeneration efforts in the RZ. In addition, the findings of this study will aid in the development of risk management strategies and may pave the way for future research initiatives in the RZ.

3. Methodology

The primary goal of this chapter is to provide an in-depth description of the methods utilized in the field as well as the subsequent analysis of the collected data. This chapter will also outline the rationale for choosing these methods and why the methods suit the objective. The methods outlined in this chapter have allowed for multiple in-situ measurements of HMs in RZ soils to be taken and proved to be the most effective in gaining a better understanding of multiple areas in the RZ. This section begins with information on the research area, as well as photos taken during fieldwork and the main pieces of equipment used. Following the introduction of the research area, the rationale, field methods and analysis used will be given.

3.1 Study area

The Christchurch Residential RZ itself stretches from the city to the sea and has an area of 630-hectares (6.3 km²) (Scott & Carville, 2016). The Christchurch Residential RZ was formed as a result of the 2010/11 Christchurch earthquakes and includes parts of the Port Hills, Kaiapoi, Brooklands, as well as the flatland area of the RZ located in the Ōtākaro Avon River Corridor (Scott & Carville, 2016). Figure 3.1 shows the extent of the Christchurch Residential RZ and Figure 3.2 shows the Ōtākaro Avon River Corridor area of the Christchurch Residential RZ. The

fieldwork occurred across 8 sites in the Christchurch Residential RZ. The sites had a combined total area of approximately 11.01-hectares (0.1101 km²) (Figure 3.3).

Following the 2010-11 Christchurch earthquakes, the government offered to purchase insured RZ properties in August 2011, and by December 2015, 5,442 property owners in the RZ had accepted the offer (Regenerate Christchurch, 2019). To date, a total of 8060 residential buildings in the Christchurch area have been 'red zoned' by the Crown (Brand & Nicholson, 2016; LINZ, 2021). This meant that the land was uninhabitable and could not be built on (Davis, 2018; Nielsen, 2016; Vallance & Tait, 2013).

The residential buildings in the RZ were demolished and grass was planted. Indigenous vegetation and exotic trees over 4 meters tall were retained for aesthetic and ecological reasons (Brown et al., 2012). Figure 3.4 illustrates the landscape and vegetation that exists in the Ōtākaro Avon River Corridor RZ area. On behalf of the Crown, Land Information New Zealand (LINZ) took over responsibility for these areas in 2015 and the Waimakariri RZ land was transferred to the Waimakariri District Council and Te Kōhaka o Tūhaitara Trust in 2018, while ownership of the remaining property is gradually transferring to the Christchurch City Council (CCC) (LINZ, 2021). The CCC owns the Port Hills RZ and manages the flatland areas in the Ōtākaro Avon River Corridor and the Port Hills RZ (LINZ, 2021).

As residential buildings in the RZ were cleared away and replaced with open parkland, remaining communities were faced with a loss of community connections and infrastructure, depopulation, and uncertainty about the future of this area (Regenerate Christchurch, 2019). Native habitats, trails and walks, recreation facilities, agriculture, and communal spaces such as community gardens are among the future plans for this area, which may increase human exposure to HMs as soils in the RZ may be contaminated with HMs and other toxic agents. Ashrafzadeh et al. (2018) reported Pb levels in residential Christchurch soils that were in excess of the residential land use guideline values (210 mg/kg).

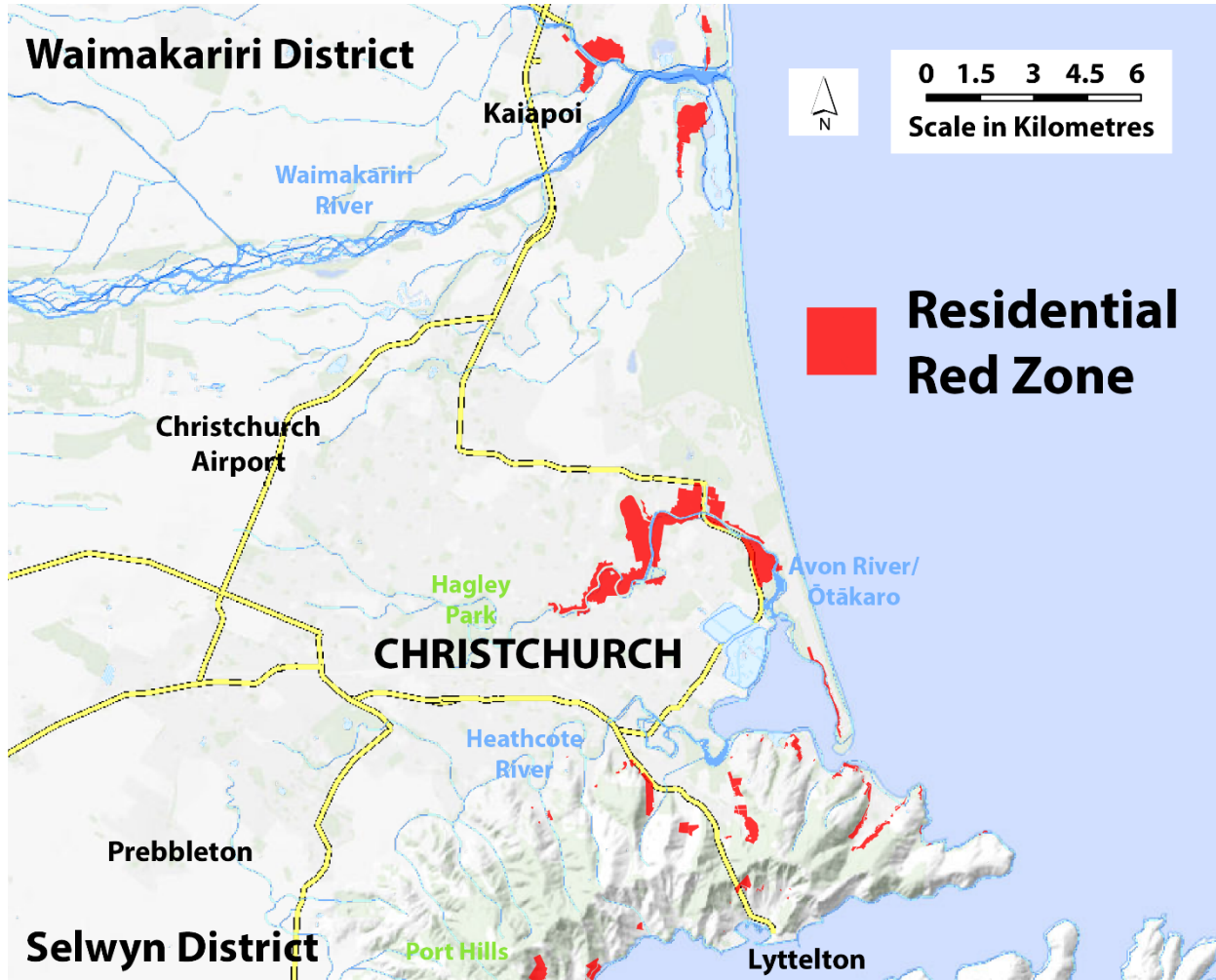


Figure 3.1. Map of the Residential Red Zone and the greater Christchurch area (New Zealand Government, 2020). CC BY-SA 4.0.

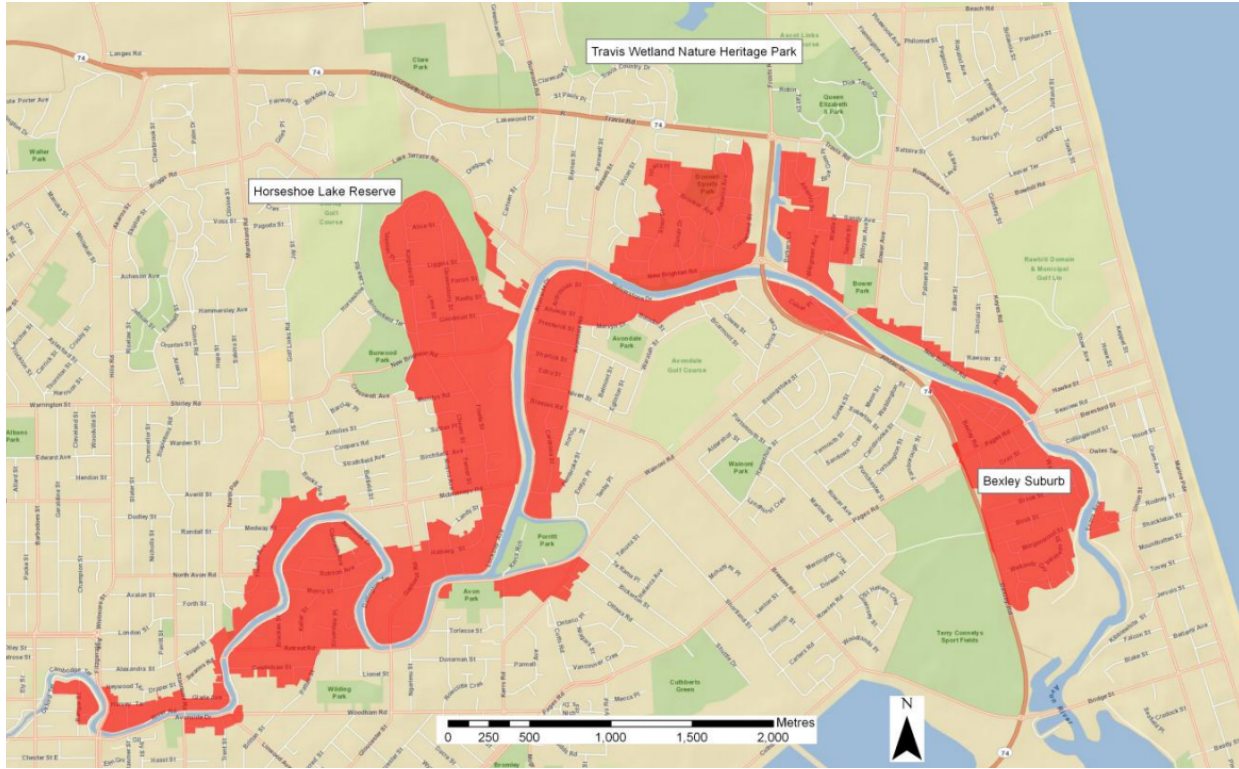


Figure 3.2. Map of the Ōtākaro Avon River Corridor area of the Christchurch Residential Red Zone (shown in red). (Gilmour, 2013).



Figure 3.3. Map of the Ōtākaro Avon River Corridor red zone area which shows the locations of study sites 1-8. *Note.* The red dots represent the sample locations and the red lines represent the perimeter of the sample sites. Made using ArcMap 10.8.1 and Paint 3D on a base map of NZ 10m Satellite Imagery (2018-2019).



Figure 3.4. Photograph of two red zoned sites that have been planted with grass. (Top) off River Road, Richmond, and (Bottom) off Breezes Road, Avondale.

3.11 Soils

The majority of the Canterbury Plains is made up of free-draining gravelly materials, whereas less permeable silty sands and clays are more predominant closer to the shore (Begg et al., 2015). Most of the soil parent materials come from basement rocks in the Canterbury foothills and

Southern Alps (Begg et al., 2015). Since its establishment in the 1850s, the soils and geomorphology of Christchurch's urban area have been significantly affected through drainage, the moving of waterways, the infilling of hollows, and urban land development (Christchurch City Council, 2003). Water tables at or near the ground surface, combined with lower permeability within the fine-textured deposits, result in imperfectly drained soils over most of the Christchurch lowland urban area (Begg et al., 2015; Christchurch City Council, 2003). Ōtākaro Avon River Corridor land is mostly composed of poorly consolidated silts, which are especially prone to the effects of earthquakes (Regenerate Christchurch, 2019). Figure 3.5 shows the soil drainage characteristics at the study site.

Study sites 5 and 8 have imperfectly drained soils (Kaiapoi_16a.1 and Kaiapoi_17a.1) and sites 1-4 and 6-7 have well-drained soils (Waimakariri_3b.1 and Waimakariri_4b.1) a description of these soils can be found in Appendix E. Generally, both of these soil types are well-drained with very low vulnerability to waterlogging in non-irrigated conditions and have high soil water holding capacity.

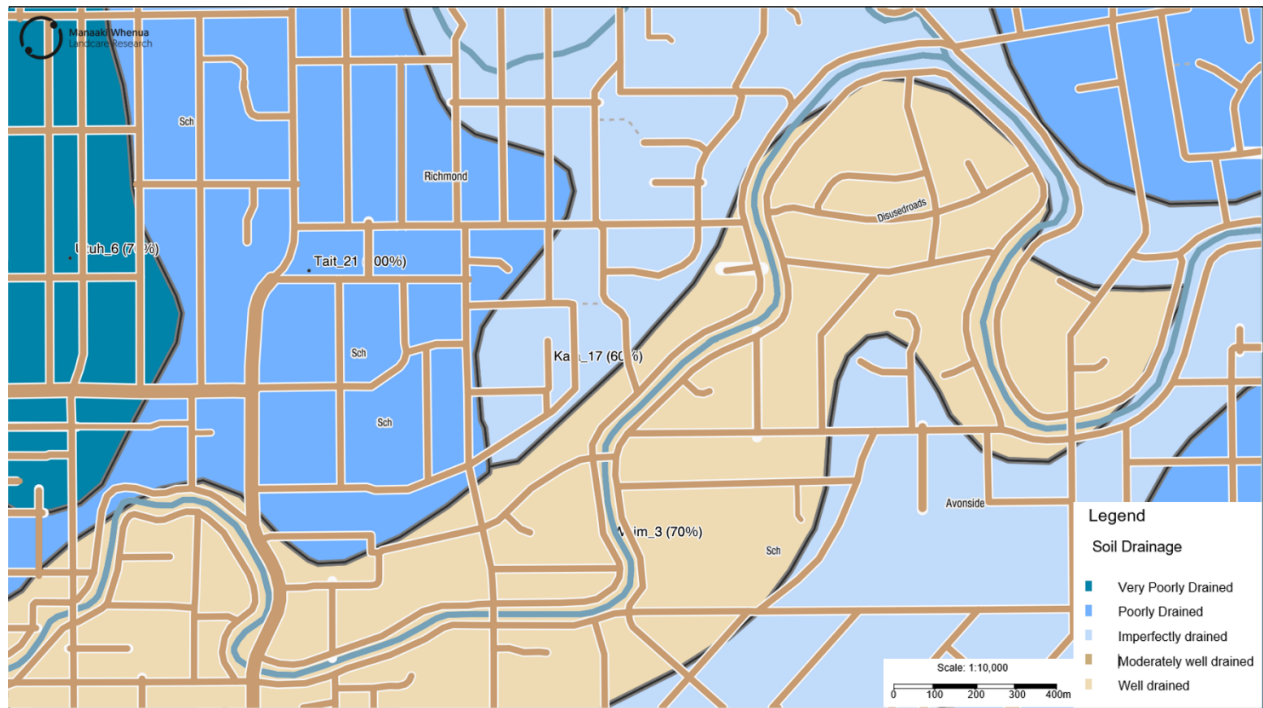


Figure 3.5. Map of the different soil drainage types in the Ōtākaro Avon River Corridor (Landcare Research NZ Limited, 2021). CC BY-SA 3.0.

3.2 Field Portable X-ray Fluorescence Spectrometry

Typically, HM concentrations in soils are determined using atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP–MS), or inductively coupled plasma optical emission spectrometry (ICP-OES), all of which require lengthy and costly digestions (Blaylock et al., 1997; Clevenger et al., 1991). The turnaround times associated with these methods are generally insufficient to ensure the optimal utilization of data (Kalnicky & Singhvi, 2001). This limits the number of samples that can be processed, making large-scale, in-situ research challenging (Clark et al., 2006). The use of Field portable X-ray fluorescence (FP-XRF) technology has become a well-established analytical method for in-situ screening over the past 30 years (Kalnicky & Singhvi, 2001; Shackley, 2018).

FP-XRF Spectrometers are an effective tool for rapidly determining the total elemental composition of surface layers of in-situ soils (detectable elements typically range from sodium

(11) to uranium (92) in most instruments), which can be used to conduct contaminated site investigations and guide site remediation (Olympus, 2021; Rumsby, 2013, 2015). It is extremely cost-effective and quickly identifies areas of interest that require further extensive sampling and research (Clark et al., 2006). However, as FP-XRF is susceptible to a variety of sampling and analytical errors, it is only used as a screening or semi-quantitative assessment tool (Rumsby, 2013, 2015). The primary causes of error impacting this technique's accuracy are sampling errors caused by variations in sample moisture content and variability in the elemental distribution in the soil (Rumsby, 2013, 2015).

Although FP-XRF is less accurate and has a larger measurement bias than AAS, ICP-MS, and ICP-OES, increasing sample density with in-situ measurements can help to effectively identify the level of contamination, with the added benefit of lowering the probability of incorrectly identifying a site due to poor site characterization (Rumsby, 2015). Even with precise data points, a small sample size makes it difficult to obtain an assessment that accurately characterizes and locates site contamination (Crumbling, 2001). Small sample sizes can also produce erroneous project decisions and misleading conclusions (Crumbling, 2001). When many samples are evaluated, a far more accurate image of the site emerges, even if the analytical method is less accurate (Crumbling, 2001). FP-XRF is a better method for soil screening. Figure 3.6 illustrates that many lower quality data points taken using the FP-XRF can offer a more precise characterization of contamination than a small number of more accurate laboratory analyses (Crumbling, 2001; Rumsby, 2015).

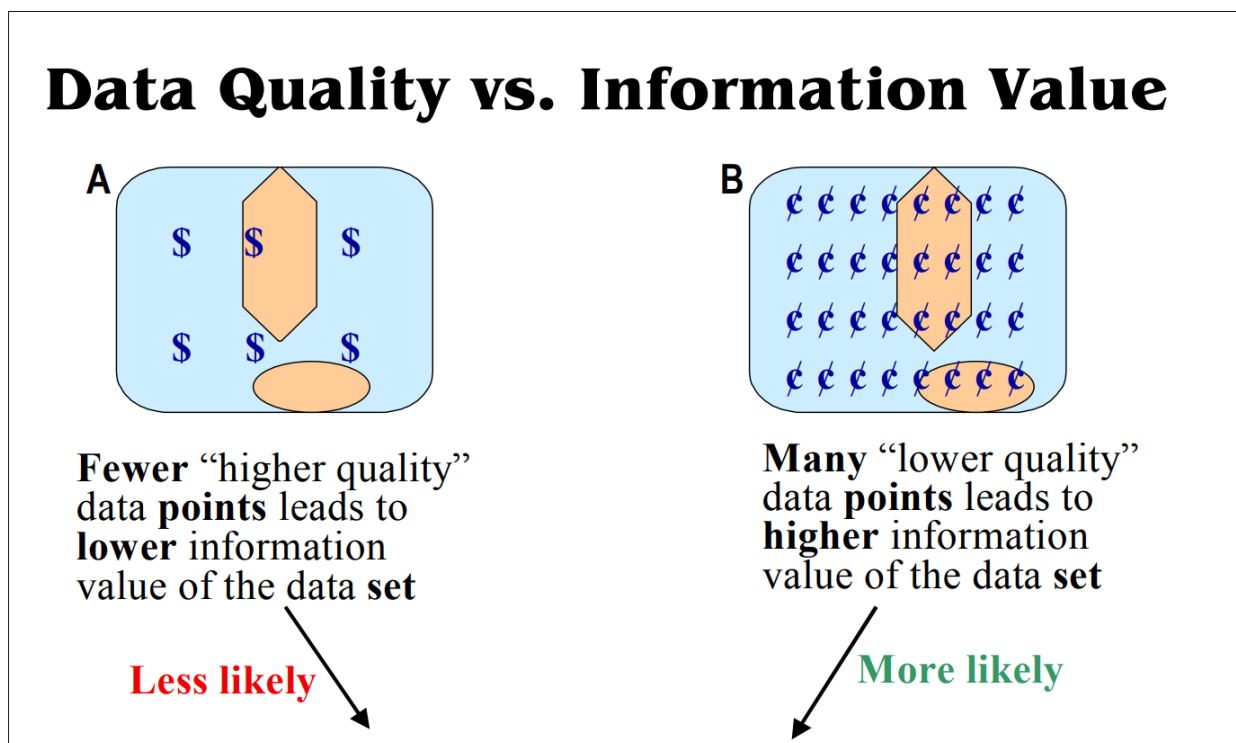


Figure 3.6. Two different sampling and analysis scenarios for a site. *Note.* The orange shapes depict hot spot locations (areas where contamination levels are much greater than in the surrounding area) (Crumbling, 2001).

3.3 Sampling

The optimal strategy for any research study is to investigate the whole population. However, this is not always possible due to practicality. Sampling is the process of selecting a subset of individuals from the total population that aims to represent and estimate the properties and/or parameters of the larger population (Acharya et al., 2013; Pennock et al., 2008). Taking a representative sample of the population can reduce the expenses, time taken, and labour required to conduct the study (Acharya et al., 2013). Sampling is a necessary part of any field research programme in soil science due to the impracticability of measuring the whole population (Pennock et al., 2008).

Designing a sampling strategy involves determining the most efficient strategy for selecting the samples that will be used to estimate the properties of the population (Pennock et al., 2008). Many extensive guides exist for various sampling designs and the statistical procedures that are suitable for each design. This section will detail in situ and discrete sampling as well as targeted and systematic sampling and the concerns that should be taken into account when selecting a sampling design.

When analyzing soil samples with an FP-XRF, there are two sample preparation methods to consider: in-situ and discrete sampling (Kalnicky & Singhvi, 2001). Discrete samples are a small mass of soil (usually 100-200g) collected from a single spot within a study area, and in-situ sampling is a sampling approach that allows measurements to be taken at the original site without the need to remove physical samples. The number of analyses required, the site/contaminant history, allocated time, and the intended sampling design are all factors that influence which method is used (Kalnicky & Singhvi, 2001). For the in-situ analysis of

contaminated soils, an FP-XRF can be placed directly on the soil surface to measure HM contamination. When using an FP-XRF, in-situ analysis offers more flexibility by enabling the rapid collection of data for multiple sample points, eliminating physical sampling and the chain of custody concerns, and providing real-time data that can be used to make quick field decisions (Kalnicky & Singhvi, 2001).

Significantly more preparation time is required for discrete sampling as this requires samples to be taken to a lab to be analyzed. Discrete sampling does not provide a complete understanding of the contamination; however, in-situ sampling using a FP-XRF allows one to identify small levels of contamination to build an accurate map of the contamination (Bosco, 2013). This limits the number of samples that can be taken in the given timeframe. The benefits of the discrete sampling method include increased analytical accuracy and precision when compared to in-situ samples (Kalnicky & Singhvi, 2001).

Targeted sampling is often used when the properties of a specific area are being investigated. However, it can only be used if there is a strong understanding of the site's history and the location of site activities (Rumsby, 2015). The number of samples taken depends in part on the number of target areas that have been selected for sampling. The number of samples taken at each target location and the number of different sites will be determined by the use of potentially contaminating activities on the site, the contamination mechanism, and the aim of the study (Rumsby, 2015). If the target area is large or anticipated to be extremely diverse, additional measurements will be required (Rumsby, 2015).

Systematic sampling is appropriate for level and near-level landscapes and allows for quantitative conclusions to be made about the area of interest (Pennock et al., 2008). For many field studies, the most common sampling designs consist of systematic sampling using transects or grids (Pennock et al., 2008). It is advised that more than 20 samples are taken for sites between 400 m² and 2000 m² when the site history indicates that HM concentrations are expected to be relatively uniform (Rumsby, 2015). More than 20 samples may be required for sites that are larger than 2000 m² and/or sites with complex histories, where spatially diverse contamination is more likely (Rumsby, 2015). Although statisticians frequently criticize systematic sampling

designs, they are popular in the field of earth sciences because of their ease of use and efficiency in collecting data (Pennock et al., 2008). The transects starting point and/or orientation should ideally be chosen at random (Pennock et al., 2008). The most important point to remember when using systematic sampling with constant spacing is that the objects to be sampled should not be organized in an orderly fashion that aligns with the transect spacing (Pennock et al., 2008). Figure 3.7 shows the layout of a transect sampling campaign.

Although In-situ XRF analysis requires minimal sample preparation, it is only a screening level technique (Rumsby, 2013, 2015). Screening can be used to provide preliminary identification of HM contaminants, identify hot spot locations within a site, provide the spatial extent and spatial variability of HM contaminants, and assist with remediation (Rumsby, 2015).



Figure 3.7. Layout of a transect sampling campaign. *Note.* The red dots represent the transect sample locations and the red line represents the ideal path to take when transect sampling. Adapted from a base map of NZ 10m Satellite Imagery (2018-2019) and Paint 3D.

3.4 Methods

This section describes the methods used to collect data from the field to achieve the project's objectives. This study's research approach utilizes unique environmental science methods to

determine the threat to humans and ecosystems, mitigation strategies, and spatial distribution of HMs in RZ soils. Section 3.41 will describe the equipment used for sampling. Section 3.42 describes the calibration process and requirements. Section 3.43 details the methods used for in situ soil sampling in the RZ. This includes the use of FP-XRF technology to analyze a large number of samples in a short period. And section 3.44 details the methods used for the statistical analysis of data gathered using the FP-XRF.

3.41 Equipment

An M series Vanta XRF handheld analyzer (Figure 3.8), was used to test for HM contaminant concentrations in the soils around the Christchurch Residential RZ. The M series Vanta XRF analyzer is a handheld energy-dispersive XRF spectrometer. The Vanta XRF analyzer delivers rapid and accurate chemical analysis for environmental testing and element identification and analysis (Olympus, 2021). The XRFs ultra-rugged waterproof/dustproof construction allows for a wide range of analytical testing in harsh environments (Olympus, 2021). A description of the Vanta XRF analyzer components can be found in Appendix x.



Figure 3.8. M series Vanta XRF analyzer that was used for in-situ field testing of soils in the RZ.

3.42 Calibration

For the quantitative use of XRF methods for environmental applications, the XRF analyzer must be calibrated using standards with known compositions (Kalnicky & Singhvi, 2001). Analysis of certified reference material (CRM) should provide findings that are within 20% of the certified values to ensure that the FP-XRF calibration is acceptable (Kalnicky & Singhvi, 2001; Rumsby, 2015). Only then can this data be used for quantitative environmental applications. While this criterion is less strict than that used in traditional laboratory XRF analysis, it is a suitable option for most FP-XRF environmental applications (Kalnicky & Singhvi, 2001). Each time the XRF analyzer is turned on, an energy calibration check should be performed (Rumsby, 2013).

Calibration was undertaken by analyzing standard reference material (SRM) from NIST. This was done using the Vanta workstation (Figure 3.9), the M series Vanta XRF analyzer and the CRM (NIST 2710a). The results from the analysis of the NIST 2710a Montana I Soil SRM were compared to the certified data. As seen in Appendix F, the values for Pb and Zn were well within the 20% limit at 1.83% and -1.99%, respectively.



Figure 3.9. Photograph of the Vanta workstation that was used for calibration (XRF analyzer is connected underneath).

3.43 Field sampling

A combination of both systematic and targeted sampling was used in this study to gain a better understanding of hot spots and background concentrations. Targeted sampling was undertaken in areas where elevated contaminant concentrations were likely to occur, such as along fence lines, under trees, near roads and footpaths, and in bare patches of soil and rubble. And systematic sampling using transects was taken across the whole study site in roughly equal increments of 5m to get a good understanding of HM distribution in the sites. The transects starting point and orientation were chosen at random, mostly out of convenience. The locations of the study sites were chosen randomly. These locations were convenient to sample as they had easy access and open ground. Figure 3.10 demonstrates how the sample locations of targeted samples were chosen. Measurements were mostly taken in areas of rubble, exposed soil, near rows of trees, and

on the border of the property, rather than in the middle of the property where it is less likely to find high concentrations of HMs. Figure 3.11 shows an area of interest for targeted sampling.



Figure 3.10. Aerial map of a Red Zone property in Avondale that shows the areas of interest when conducting targeted sampling. *Note.* The red highlighting represents the areas of high priority when measuring HM concentrations in RZ soils. The highest concentration of HMs is expected to occur in the areas highlighted in red. Adapted from a base image from Google Earth Pro using Paint 3D.



Figure 3.11. Photograph of an area of interest for targeted sampling in the RZ off Harvey Terrace, Richmond. *Note.* This area is an example of an area that can be targeted for sampling as it has a higher likelihood of having elevated soil HM concentrations (bare patch of soil that is next to vegetation and has visible brick fragments).

XRF spectrometry is a common analytical technique that is used for in situ screening with faster turnaround times than conventional methods of soil analysis (Kalnicky & Singhvi, 2001). However, as the FP-XRF is not capable of measuring the concentration of every HM (Rumsby, 2015), Pb concentrations will be used as a proxy to identify areas of soil contamination as it is often correlated with other contaminants such as Hg (Ashrafzadeh et al., 2018), that cannot be measured (at biologically relevant concentrations) using FP-XRF. Screening level analysis is useful for identifying potential hot spots in a given site and for determining the extent of contamination (Rumsby, 2013, 2015).

Soil HM concentration measurements were taken using the M series Vanta XRF handheld analyzer at eight sites in the RZ. Initially, it was planned to collect soil HM concentration measurements from multiple suburbs including Brooklands, Bromley and New Brighton,

however, it was decided to focus on the flatland areas in the Ōtākaro Avon River Corridor due to time constraints and unsatisfactory weather conditions. A total of 313 samples were taken using the FP-XRF spectrophotometer over three different sampling campaigns in the RZ. The first of the three sampling campaigns was conducted on the 24th of June, 2021. On this day a total of 117 samples were taken from sites 1, 2 and 3. Subsequent campaigns occurred on the 5th and 8th of July, 2021 where another 105 (sites 4-5) and 91 (sites 6-8) samples were taken, respectively. Each sample took roughly 5 minutes to take and a total of 24 hours were spent out in the field collecting these samples. Figure 3.12 shows the XRF handheld analyzer in action. Originally a separate handheld GPS unit was used to log the location of each measurement, however, this data was scrapped as the M series Vanta XRF handheld analyzer had a built-in GPS that logged each sample point automatically. The steps of the sampling technique and the initial pre-checks before undertaking XRF investigations are listed below.

Steps to sampling:

1. Switch the XRF handheld analyzer on and allow sufficient time to warm up.
2. Conduct an energy calibration check (usually done in the lab before getting to the field site).
3. Select a suitable XRF programme (Geochem (2) 50 kV three-beam).
4. Select analysis times (10 seconds).
5. Locate an area to sample that is not inundated with water or has lots of vegetation cover.
6. Clear away any grass or large rocks that might damage the lens on the XRF analyzer.
7. Level the surface area and pack down the soil
8. Place a clear plastic Ziplock bag over the soil that is going to be sampled.
9. Point the XRF analyzer toward the ground.
10. Hold the XRF analyzer and keep the nose of the probe flush with the ground.
11. Press the trigger on the XRF analyzer to fire the beams.
12. Wait for the beams to finish (2x 10-second beams).
13. Record the sample number and other relevant information.
14. Remove any dirt or organic matter from the measurement window after use (Make sure that the window is not ripped or punctured).

15. Move on to the next sample. Repeat steps 5-14.



Figure 3.12. Photograph of the XRF handheld analyzer in action, at site 1 (Oxford Terrace, Christchurch Central City).

3.44 Quality assurance

During collection, there was a risk of sampling error and cross contamination between samples due to the large number of samples taken. To limit the risk of sampling errors, various quality control measures were undertaken. The FP-XRF was cleaned after taking samples from each site by brushing and wiping away any remaining traces of soil, and the clear plastic Ziplock bag was also replaced after each site to limit the transfer of soils between different sites.

3.45 Statistical treatment and analysis

Field data collected using the XRF analyzer was extracted and put into an Excel spreadsheet. Repeated data was excluded from the data set for statistical analysis. The data set was then split

into two groups; targeted and transect samples (Appendix 1). Only Pb and Zn samples were statistically analyzed as other HM concentrations had large gaps in data due to the limits of detection (LOD) of the XRF analyzer. LOD is the smallest concentration of an element that can be identified with accuracy (Rumsby, 2015).

Basic statistical calculations such as the geometric mean and STDEV-range were calculated and then the data was log-transformed for statistical analyses. The R-values were calculated for each element and its correlation to Pb was calculated. Statistical analyses were conducted using the statistical software IBM SPSS Statistics 27. The significance of differences between the targeted and transect soil Pb concentrations, targeted and transect soil Zn concentrations, targeted soil Pb and Zn concentrations, and transect soil Pb and Zn concentrations was tested by one-way analysis of variance (ANOVA) followed by a Post-Hoc test (Tukey's Honest Significant Difference test), at the 95% confidence level ($p < 0.05$). Pearson correlation coefficient was used to determine the correlations between concentrations of targeted and transect Pb and Zn samples.

An ANOVA is a type of omnibus test statistic that examines the means of multiple samples to see if one group's mean is statistically different from the others. The null hypothesis for the test is that the two means are equal. As a result, a statistically significant result shows that the two means are not equal. While ANOVA can aid in analysing the differences in means between two independent variables, it cannot tell you which statistical groups were different. If the ANOVA test produces a significant F-statistic, a Post-Hoc analysis such as Tukey's Honest Significant Difference (Tukey's HSD) test is needed to determine which groups have different means. The Tukey's HSD test gives a p-value, which is used to determine whether or not the relationship between variables is significant.

Despite the fact that the test is robust when dealing with non-normally distributed data, the ANOVA test is based on the assumption that each sampled population's observations are normally distributed.

4. Results

4.1. Soil lead and zinc summary statistics

The summary statistics for soil Pb and Zn concentrations in the Christchurch Residential RZ are presented in Tables 4.1 and 4.2. Of the 313 samples collected from the field, 55% (171) were targeted samples and 45% (142) were transect samples.

The Pb samples in the RZ had a mean of 158.18 mg/kg. However, soil Pb concentrations were significantly higher in targeted samples (mean=226.88 mg/kg) than in transect samples (mean=75.44 mg/kg) (Table 4.1). The mean targeted Pb sample value greatly exceeded the upper background values of soils in Canterbury, as well as the New Zealand soil Pb guideline of 210 mg/kg, while the mean transect Pb sample value also exceeded the background values of soils in Canterbury, but was well below the New Zealand soil Pb guideline value. Of the 171 targeted Pb soil samples, 52 samples (~30%) exceeded the New Zealand soil Pb guideline of 210 mg/kg. While, in the transect Pb soil samples, only 10 (~6%) out of the 142 samples were above guideline values. All sites except site 8 had at least one sample that exceeded the guideline values for soil Pb. One site contained a Pb concentration of 3289 mg/kg, compared to its respective upper background concentration of 57.3 mg/kg.

Table 4.1. Summary statistics of targeted and transect soil lead samples from the Ōtākaro Avon River Corridor area in the Christchurch Residential Red Zone.

Groups	Method	Count	Sum	Mean	Median	Variance	Standard Error	Minimum	Maximum	Above Guidelines
Site 1 Pb	Targeted	28	5236	187.00	88.00	44920.30	40.05	20	797	9
	Transect	18	617	34.28	18.50	1400.80	8.82	5*	129	0
Site 2 Pb	Targeted	11	7173	652.09	286.00	976656.69	297.97	35	3289	6
	Transect	12	350	31.82	26.00	401.36	6.04	5*	73	0
Site 3 Pb	Targeted	22	5349	243.14	191.50	28247.36	35.83	22	680	10
	Transect	26	2958	113.77	60.50	31581.06	34.85	5*	931	3
Site 4 Pb	Targeted	34	6358	187.00	93.50	102737.21	54.97	17	1678	6
	Transect	20	559	27.95	21.50	394.58	4.44	5*	96	0
Site 5 Pb	Targeted	20	2338	116.90	83.00	10465.46	22.88	29	362	4
	Transect	32	3470	108.44	73.00	16550.58	22.74	5*	611	5
Site 6 Pb	Targeted	23	3618	157.30	136.00	6701.22	17.07	52	402	5
	Transect	11	753	68.45	61.00	3109.07	16.81	5*	157	0
Site 7 Pb	Targeted	19	8006	421.37	287.00	253851.69	115.59	45	2361	12
	Transect	12	1548	129.00	86.00	16093.82	36.62	27	411	2
Site 8 Pb	Targeted	14	718	51.29	32.50	2198.53	12.53	5	140	0
	Transect	11	458	41.64	29.00	1363.05	11.13	5*	142	0
Total	Targeted	171	38796	226.88	129.00	-	-	-	-	52
	Transect	142	10713	75.44	35.50	-	-	-	-	10
All Pb	-	313	49509	158.18	71.00	-	-	5*	3289	62

Note. * = <LOD.

The Zn samples in the RZ had a mean of 170.07 mg/kg. However, soil Zn concentrations were significantly higher in targeted samples (mean=217.88 mg/kg) than in transect samples (mean=113.42 mg/kg) (Table 4.2). The mean targeted Zn sample value greatly exceeded the urban background soil Zn concentration in Canterbury (level 1) of 55.5-91.7 mg/kg from Tonkin and Taylor (2007). However, it was still well below the New Zealand soil Zn guideline of 400 mg/kg. Similarly, the mean transect Zn sample value slightly exceeded the background values of soils in Canterbury, but not the New Zealand soil Zn guideline value. Of the 171 targeted Zn soil samples, 14 samples (~8%) exceeded the New Zealand soil Zn guideline of 400 mg/kg. While, in the transect Zn soil samples, only 3 (~2%) of the 142 samples were above guideline values. All sites had at least one sample that exceeded the guideline values for soil Zn. One site contained a Zn concentration of 1894 mg/kg, compared to its respective upper background concentration of 91.7 mg/kg.

Table 4.2. Summary statistics of targeted and transect soil zinc samples from the Ōtākaro Avon River Corridor area in the Christchurch Residential Red Zone.

<i>Groups</i>	<i>Method</i>	<i>Count</i>	<i>Sum</i>	<i>Mean</i>	<i>Median</i>	<i>Variance</i>	<i>Standard Error</i>	<i>Minimum</i>	<i>Maximum</i>	<i>Above Guidelines</i>
Site 1 Zn	Targeted	28	6356	227.00	174	53763.63	43.82	47	974	3
	Transect	18	1475	81.94	68.50	1194.76	8.15	49	170	0
Site 2 Zn	Targeted	11	2850	259.09	236	20713.29	43.39	55	482	3
	Transect	12	1177	98.08	100.00	699.17	7.63	48	136	0
Site 3 Zn	Targeted	22	4915	223.41	191	10346.25	21.69	67	421	1
	Transect	26	4271	164.27	113.00	17161.32	25.69	80	690	1
Site 4 Zn	Targeted	34	7285	214.26	135	97526.93	53.56	54	1894	2
	Transect	20	1349	67.45	59.50	720.58	6.00	40	150	0
Site 5 Zn	Targeted	20	3225	161.25	138.5	10220.93	22.61	51	489	1
	Transect	32	4482	140.06	115.50	8654.19	16.45	46	411	2
Site 6 Zn	Targeted	23	5383	234.04	174	75754.50	57.39	90	1464	1
	Transect	11	831	75.55	75.00	1078.07	9.90	42	143	0
Site 7 Zn	Targeted	19	4169	219.42	170	11670.48	24.78	75	419	1
	Transect	12	1438	119.83	103.50	4666.52	19.72	48	286	0
Site 8 Zn	Targeted	14	2943	210.21	119.5	42002.95	54.77	70	795	2
	Transect	11	1082	98.36	72.00	6090.85	23.53	43	320	0
<i>Total</i>	Targeted	171	37126	217.11	165.00	-	-	-	-	14
	Transect	142	16105	113.42	87.50	-	-	-	-	3
<i>All Zn</i>	-	313	53231	170.07	117.00	-	-	40	1894	17

4.2. Significance between targeted and transect samples for soil lead and zinc

Figure 4.1a shows the difference between the average concentration of targeted and transect soil Pb samples in the RZ. Sites 5 and 8 showed no significant difference between targeted and transect samples, while sites 1 and 7 showed high significance between targeted and transect samples, and sites 2, 3, 4, and 6 showed very high significance between targeted and transect samples. The table of significance can be found in Appendix H.

Figure 4.1b shows the difference between the average concentration of targeted and transect soil Zn samples in the RZ. Site 5 was the only site that showed no significant difference between targeted and transect samples. Sites 3 and 8 showed significant differences, sites 1 and 7 showed highly significant differences and sites 2, 4, and 6 showed very highly significant differences between targeted and transect samples. The table of significance can be found in Appendix X.

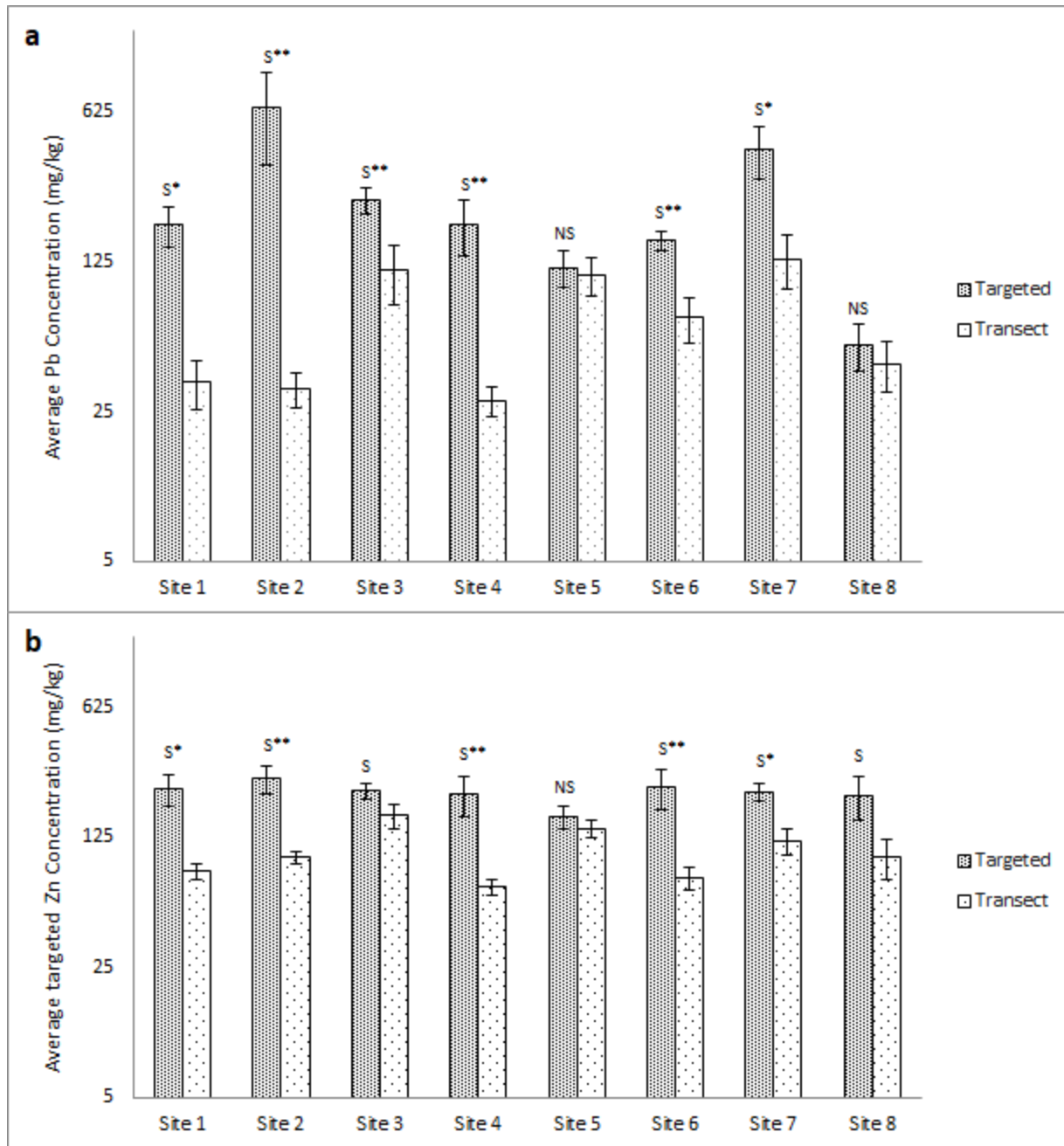


Figure 4.1. Geometric means and standard deviation ranges of targeted and transect lead (a) and zinc (b) samples. *Note.* P-values are given as follows; $p < 0.05$ NS (Not Significant), $0.05 < p < 0.01$ S (Significant), $0.01 < p < 0.001$ S* (Highly Significant), $p < 0.001$ S** (Very Highly Significant).

4.3. Targeted soil lead and zinc samples

Figure 4.2a shows that the average concentration of targeted soil Pb samples from site 1-7 in the RZ, was higher than the upper background soil Pb concentration of 57.3 mg/kg. Site 8 was the only site that did not exceed the upper background concentration. Three of the sites (sites 2, 3, and 7) exceeded the New Zealand soil Pb guideline value (210 mg/kg). Site 8 had significantly lower soil Pb concentration values compared to sites 1, 2, 3, 4, 6, and 7.

Figure 4.2b shows that the average concentration of all targeted soil Zn samples in the RZ was higher than the upper background soil Zn concentration of 91.7 mg/kg, while no sites exceeded the New Zealand soil Zn guideline value (400 mg/kg). No significant difference was found between Zn samples at the different site locations.

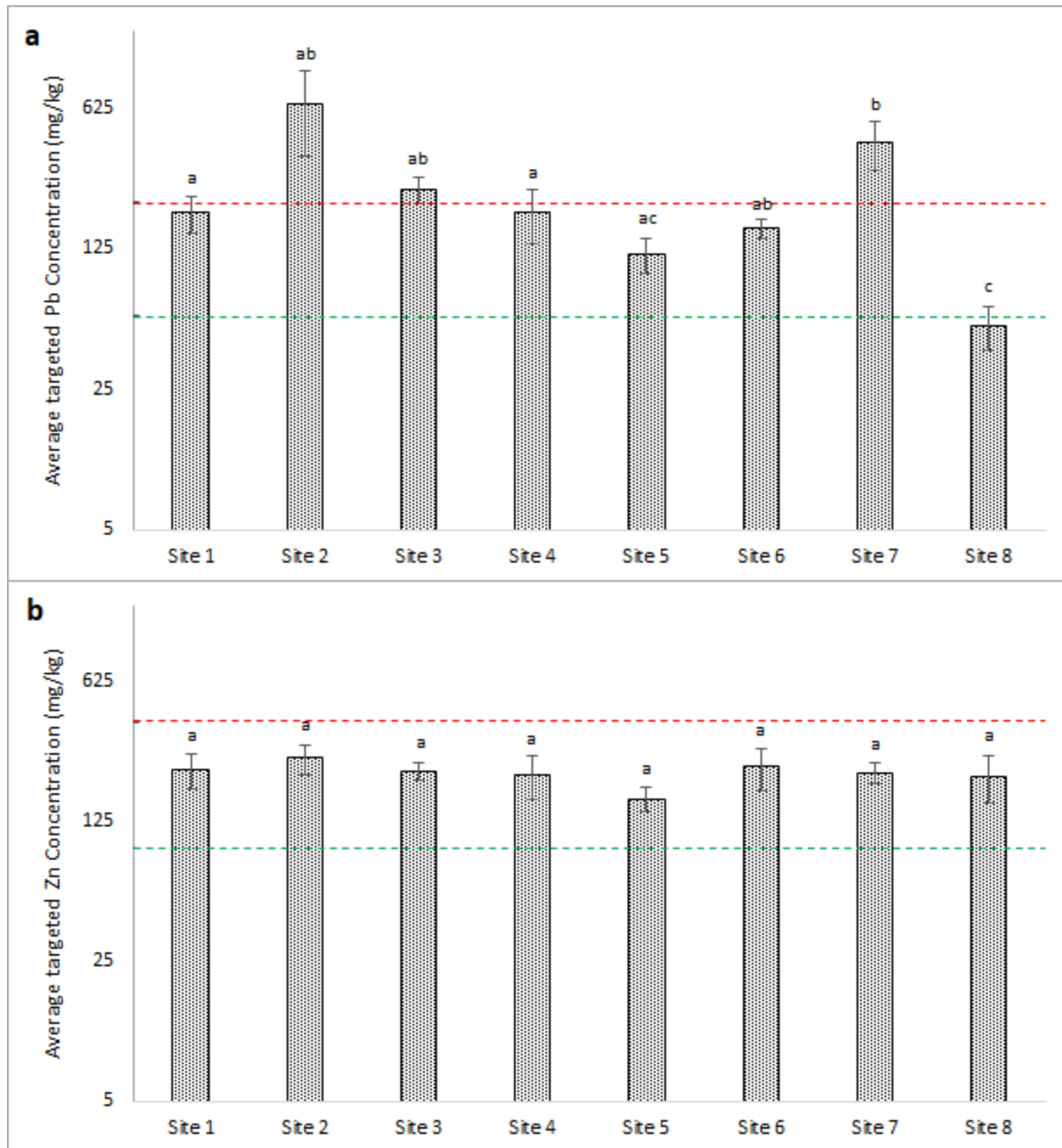


Figure 4.2. Geometric means and standard deviation ranges of targeted lead (a) and zinc (b) samples. *Note.* The red dashed horizontal lines reflect the New Zealand contaminant standards for Pb (210 mg/kg) and Zn (400 mg/kg), while the green dashed horizontal line reflects the upper background soil Pb (57.3 mg/kg) and Zn (91.7 mg/kg) concentrations in Canterbury (Tonkin and Taylor, 2007). The bars labelled with the same letter are not significantly different ($P > 0.05$,

Tukey's Test). Site 1 (n=28), site 2 (n=11), site 3 (n=22), site 4 (n=34), site 5 (n=20), site 6 (n=23), site 7 (n=19), and site 8 (n=14).

4.4. Transect soil lead and zinc samples

Figure 4.3a shows that the average concentration of transect soil Pb samples at sites 3, 5, 6, and 7 was higher than the upper background soil Pb concentration of 57.3 mg/kg. No sites exceeded the New Zealand soil Pb guideline value (210 mg/kg). The average soil Pb concentration at sites 1, 2, 4, 6, and 8 was not significantly different from each other, and the average soil Pb concentration at sites 3, 5, and 7 was also not significantly different from each other.

Figure 4.3b shows that the average concentration of transect soil Zn samples at sites 2, 3, 5, 7, and 8 was higher than the upper background soil Zn concentration of 91.7 mg/kg. No sites exceeded the New Zealand soil Zn guideline value (400 mg/kg). The average soil Zn concentration at sites 2, 7, and 8 was not significantly different from all other sites. The average soil Zn concentration at sites 4 and 6 was significantly different from sites 1, 3 and 5. The average soil Zn concentration at sites 1 and 3 was also significantly different from each other.

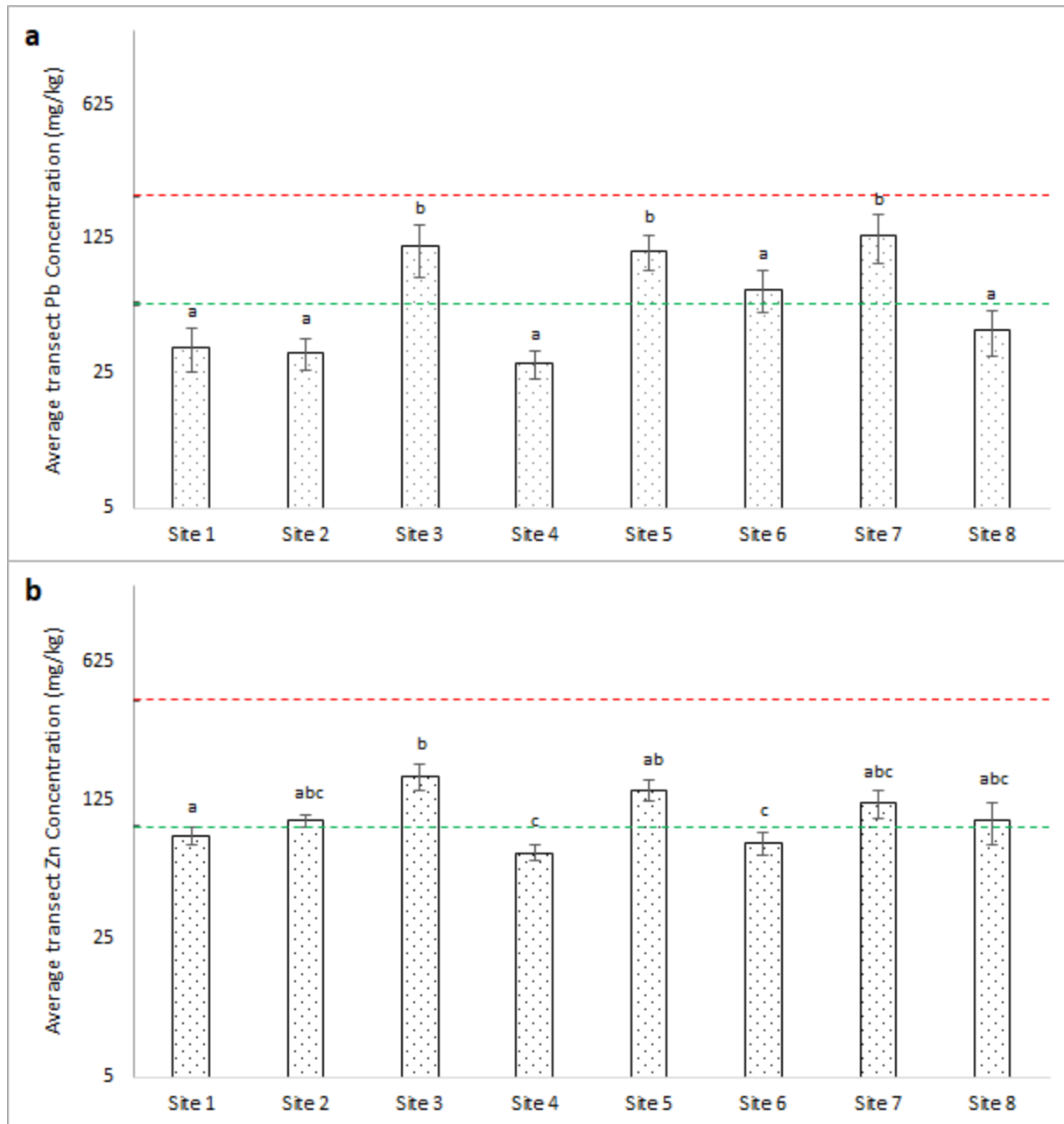


Figure 4.3. Geometric means and standard deviation ranges of transect lead (a) and zinc (b) samples. Note. The red dashed horizontal lines reflect the New Zealand contaminant standards for Pb (210 mg/kg) and Zn (400 mg/kg), while the green dashed horizontal line reflects the upper background soil Pb (57.3 mg/kg) and Zn (91.7 mg/kg) concentrations in Canterbury (Tonkin and Taylor, 2007). The bars labelled with the same letter are not significantly different ($P > 0.05$),

Tukey's Test). Site 1 (n=18), site 2 (n=12), site 3 (n=26), site 4 (n=20), site 5 (n=32), site 6 (n=11), site 7 (n=12), and site 8 (n=11).

4.5. Correlation between soil lead and zinc samples

Figure 4.4 shows the correlation between targeted Pb and Zn samples. The coefficient of determination (R^2) value of 0.5877 (58.77%) represents a significant positive relationship between targeted Zn and Pb concentrations for RZ soils. This shows that 58.77% of the variation in targeted soil Zn concentrations can be explained by variations in targeted soil Pb concentrations in the RZ.

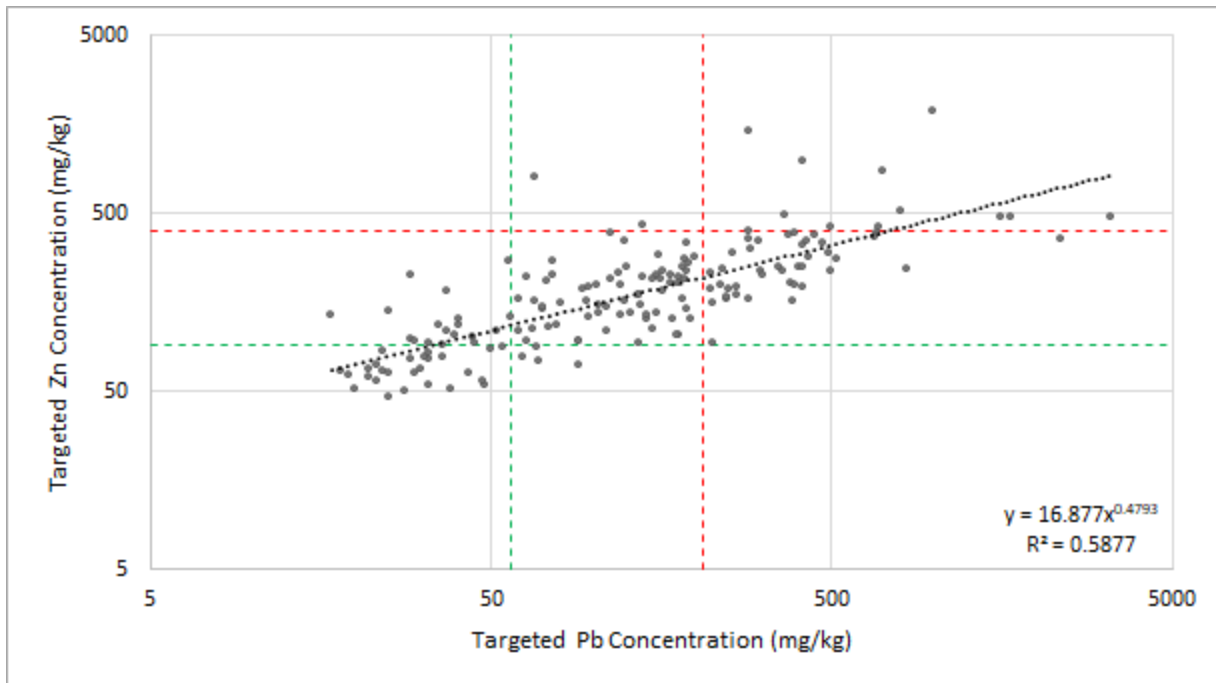


Figure 4.4. Correlation between targeted lead and zinc samples. *Note.* The red dashed vertical line reflects the New Zealand contaminant standards for Pb (210 mg/kg), while the green dashed vertical line reflects the background soil Pb concentration in Canterbury (57.3 mg/kg) (Tonkin and Taylor, 2007). The red dashed horizontal line reflects the New Zealand contaminant standards for Zn (400 mg/kg), while the green dashed horizontal line reflects the background soil Zn concentration in Canterbury (91.7 mg/kg) (Tonkin and Taylor, 2007).

Figure 4.5 shows the correlation between targeted Pb and Zn samples. The coefficient of determination (R^2) value of 0.562 (56.2%) represents a significant positive relationship between transect Zn and Pb concentrations for RZ soils. This shows that 56.2% of the variation in transect soil Zn concentrations can be explained by variations in transect soil Pb concentrations in the RZ.

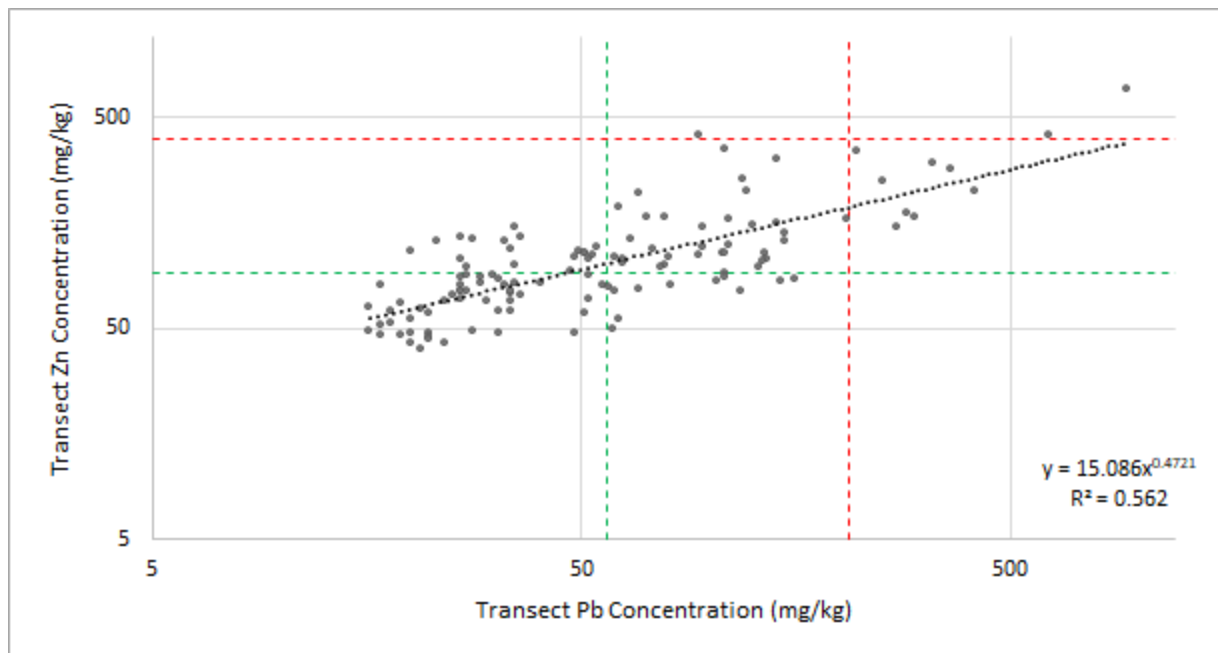


Figure 4.5. Correlation between transect lead and zinc samples. *Note.* The red dashed vertical line reflects the New Zealand contaminant standards for Pb (210 mg/kg), while the green dashed vertical line reflects the upper background soil Pb concentration in Canterbury (57.3 mg/kg) (Tonkin and Taylor, 2007). The red dashed horizontal line reflects the New Zealand contaminant standards for Zn (400 mg/kg), while the green dashed horizontal line reflects the upper background soil Zn concentration in Canterbury (91.7 mg/kg) (Tonkin and Taylor, 2007).

5. Discussion

This section reviews and discusses the observable trends, unexpected results, and implications of the results while comparing the results from this study to the results of other researchers, as well as giving a potential explanation for these results. Section 5.2 outlines the methods of exposure reduction. This section ends with the research limitations and future research suggestions.

5.1 Trends and unexpected results

HMs such as Pb and Zn were expected to be found in high concentrations in RZ soils, and the concentrations of these HMs were expected to be much higher in targeted samples than in transect samples.

The soil Pb and Zn samples taken in the RZ had a mean of 158.18 mg/kg and 170.07 mg/kg respectively (Table 4.1 & 4.2). These elevated levels of soil Pb and Zn concentrations were consistent with the concentrations observed by Ashrafzadeh et al. (2018) in Christchurch soils (Pb=137 mg/kg, Zn=189 mg/kg), only showing a difference of -15.46% for Pb and 10.02% for Zn. The average concentration of soil Pb in the RZ is also similar to those found in Baltimore, Boston, Chicago, Naples, Palermo, and Rome (Ajmone-Marsan & Biasioli, 2010).

The results are also consistent with what was hypothesized. They show that the average soil Pb and Zn concentrations in the RZ had significantly higher concentrations than the background soil concentrations in Canterbury, and that soil samples taken from the RZ (once urban/suburban land) generally had significantly higher Pb and Zn concentrations than rural Pb and Zn soil concentrations as reported by Ashrafzadeh et al. (2018). This suggests that HM concentrations in urban soils have been elevated from previous land uses and anthropogenic activities such as industrial discharges, vehicle emissions, and the demolition of buildings.

The maximum concentrations of Pb and Zn at all sites were significantly higher than their respective background concentrations (Table 4.1 & 4.2). The highest soil Pb concentration observed (3289 mg/kg) was >57 times greater than the Pb soil background concentration in Canterbury, and >15.5 times greater than the national soil Pb standard (210 mg/kg). While the

highest soil Zn concentration observed (1894 mg/kg) was >20.5 times greater than the Zn soil background concentration in Canterbury, and >4.5 times greater than the national Zn standard (400 mg/kg). These elevated concentrations of soil Pb greatly exceeded the maximum findings of Seeley and Smy (2021) in community garden soils in Christchurch (462 mg/kg) by >711% and exceeded the maximum findings of Ashrafzadeh et al. (2018) (2615 mg/kg) by >125%. However, they were similar to the maximum soil Pb values in Jakobstad, Finland of 3439 mg/kg (Ajmone-Marsan & Biasioli, 2010). The elevated concentrations of Pb found in this study may be due to the widespread historical use of Pb-based paint in Christchurch.

The maximum levels of soil Zn concentrations found in this study also greatly exceeded the findings of Ashrafzadeh et al. (2018) (799 mg/kg) by >237% and exceeded the maximum findings of Seeley and Smy (2021) (946 mg/kg) by > 200%. However, they were similar to the maximum soil Zn values in Tallin (1560 mg/kg), Wrocław (1640 mg/kg), Osnabrück (1660 mg/kg), Richmond upon Thames (1810 mg/kg), and Avilés (1959 mg/kg), (Ajmone-Marsan & Biasioli, 2010). This may be due to the widespread use of galvanised steel in building materials and vehicle components.

Some ~30% of targeted Pb samples and ~6% of transect samples were above the national soil Pb guideline values, while ~8% of targeted Zn samples and ~2% of transect samples were above national soil Zn guideline values. These results suggest that targeted sampling is more likely to find higher Pb and Zn concentrations in soils than transect sampling. This also indicates that areas of bare soil with visible debris and rubble are more likely to have elevated Pb and Zn soil concentrations (are hotspots for HMs).

The differences between targeted and transect samples were much lower in Zn samples than Pb samples (Figure 4.1). This shows that some very high levels of soil Pb contamination were found in this study. This may also indicate point source contamination which can lead to areas of increased Pb concentrations and may explain the increased range of Pb concentrations that was observed in this study.

Site 8 had significantly lower soil Pb concentration values compared to all other sites (Figures 4.2 & 4.3). Site 8 had an unusually low mean soil Pb concentration of 51.29 mg/kg in targeted

samples (Table 4.1) and did not exceed the upper background concentration of 57.3 mg/kg for urban Canterbury soils, the reason as to why was not quantified. The variations in concentration between the sites could be related to seasonal fluctuations, sample collection, as well as historical land use and traffic density (Garba & Abubakar, 2018). However, it is possible that this site was remediated with topsoil which would explain the low soil Pb concentrations observed at this site.

The correlation between Pb and Zn soil concentrations across both targeted and transect samples at all sites showed that Pb was significantly positively correlated to Zn concentrations (Figures 4.4 & 4.5). This may be associated with vehicle emissions and wear from tires which can contain both these HMs (Garba & Abubakar, 2018), or more broadly indicate the impact of anthropogenic activities on soil contamination. Gulan et al. (2017) found a significant positive correlation (0.838) between Zn and Pb for urban soils in Priština, Kosovo. And in another separate study, Lu et al. (2003) also found a significant positive correlation (0.814) between Zn and Pb for urban soils in Nanjing, China. The lack of a normal distribution and high SD values are frequently used as indicators of anthropogenic activity. This strong correlation between Pb and Zn in RZ soils suggests that these HMs may have come from similar anthropogenic sources such as industrial discharges, vehicle emissions, and building materials, rather than from original parent materials (Gulan et al., 2017).

5.2 Implications

There are multiple implications that can be considered from the findings of this research. The positive relationship between soil Pb and Zn, may allow Zn, which is often measured in soil nutrient analyses (Mitchell et al., 2014), to act as an indicator for anthropogenically elevated concentrations of Pb and other HMs in RZ soils. Community gardeners may use this information to help guide efforts to minimise exposure to Pb and other HM contaminants in RZ soils (Mitchell et al., 2014). This research also provides new insight into the relationship between targeted and transect Pb and Zn soil contaminations in the RZ as no other studies in Christchurch, New Zealand have conducted research with targeted and transect FP-XRF sampling. This information can allow for targeted remediation in the RZ, which may be a more

economically viable option for remediation as less work is necessary if specific areas of bare soil and visible rubble are targeted. Community members may use this information to help minimise their exposure to HM contaminants in RZ soils by avoiding contact with these hotspot areas.

A large percentage of urban/suburban soils from the Christchurch Residential RZ, like those from other cities, had Pb and Zn concentrations that exceeded national standards. This will have pronounced implications for the future land use of this area. Whilst the concept of community gardens in the RZ has good intentions for the socioeconomic well being of community members, if remediation measures are not taken the possible implications of HM exposure on human health pose a great threat to vulnerable populations, especially children. Using this RZ land for other uses such as nature reserves and native forests may limit human exposure to HM contaminants that are present in RZ soils.

5.21 Exposure reduction

Community members may be directly exposed to soil Pb and Zn while gardening and indirectly exposed through airborne particles and consuming produce that has been contaminated with HMs. Direct and indirect exposure to soil Pb and Zn can be reduced through various methods. These can be split into protective measures (exposure prevention) and remediation methods. Protective measures to reduce community exposure to HMs in community garden soils include using raised garden beds, the addition of clean topsoil and compost, untreated timber for garden beds and fencing, minimising soil resuspension by reducing disturbance of dry soil, changing land use (e.g. playing fields or native forest instead of community gardens), limiting interaction with soil through appropriate hygiene and food preparation, crop selection, keeping the pH of the soil near neutral, regular soil testing and monitoring, and by maintaining beds and adding clean compost regularly (Mitchell, et al., 2014). While remediation methods include the excavation and dumping of contaminated soils, covering with uncontaminated topsoil, covering with impermeable surfaces, covering with other ground barriers such as grass, in situ stabilization, as well as the use of chelating agents or biosolids to remove or sequester Pb (Clark et al., 2008).

Soil treatments, such as grass seed or sod, may not last if people do not maintain their lawns (Ashrafzadeh et al., 2018).

While this study did not evaluate HM accumulation in food crops from RZ soils, it is likely that such crops may contain HM concentrations exceeding food safety standards, that may be caused by the uptake from plants, or from soil particles that are attached to the plant. HM accumulation, absorption, and distribution patterns differed significantly amongst vegetable crops grown on HM contaminated soils, and so did the HM concentrations in various plant parts (Singh et al., 2012). Singh et al. (2012) also found that HMs generally accumulated most in the edible parts of root and leafy green vegetables. Tree-borne fruits accumulated the least amount of HMs, while leafy green vegetables accumulated the most HMs (Singh et al., 2012). Ashrafzadeh et al. (2018) described that tree-borne fruits, as well as fruits and vegetables that are peeled or enclosed within a capsule or pod, are less likely to have significant amounts of attached soil than low-growing leafy vegetables and unpeeled root vegetables. Selecting crops that are unlikely to have significant concentrations of HMs in soils can minimize human exposure to HMs in soils.

Ground cover and barriers were used in the soil intervention programme provided by Dixon et al. (2006), and soil Pb concentrations were reduced by 1815 mg/kg. Another study by Aschengrau et al. (1994) found that soil Pb was reduced by 2060 mg/kg and the blood Pb levels (BLLs) in children decreased when the top 6 inches of soil were removed. These studies show that in-situ remediation can significantly and quickly reduce Pb exposure. However, Dixon et al. (2006) reported a cost range of \$1095–\$5643 USD (~\$1500-\$8000 NZD) for soil intervention, with an average cost of \$2798 USD (~\$4000 NZD) for each yard (the average yard was 360 m²). Large-scale ground cover and barriers which are needed for the RZ are impractical due to this cost aspect. The cost to remediate the 8 sites through soil intervention works out to be \$855,721 USD (~\$1,220,000 NZD), and \$48,965,000 USD (~\$69,840,000 NZD) for the whole RZ area (6.3 km²).

Raised garden beds can be a cheap and effective method of exposure reduction that allows gardeners to continue growing produce on contaminated lands, while also introducing community education and awareness, which can have a significant influence on exposure

reduction (Clark et al., 2008). Mitchell et al. (2014) found that concentrations of Pb, Zn, and Ba were lower in samples taken from garden beds rather than non-bed samples. However, as raised garden beds only cover/contain a small percentage of contaminated soil, using them as a remediation or soil intervention programme does not address the principal routes of Pb exposure (e.g., ingestion of soil) (Clark et al., 2008). Therefore, raised garden beds should be considered as an exposure reduction approach rather than a remediation method (Clark et al., 2008).

Strong seasonal winds and low precipitation are frequent in Christchurch, which encourage the development of airborne soil particles (Ashrafzadeh et al, 2018). Furthermore, following the 2010/2011 Christchurch earthquakes, there was a lot of demolition and rebuilding in the Christchurch area, which may have led to more dust formation in some areas (Ashrafzadeh et al, 2018). Clark et al. (2008) reported that Pb is redistributed in gardens by soil particles transported by wind. Therefore, it is crucial to keep maintaining raised garden beds by adding clean compost or mulch regularly, as airborne soil particles from outside the beds can pollute garden beds over time. Clark et al. (2008) recommended that the top 3–5 cm of soil be removed and replaced with compost or new topsoil once a year to maintain low Pb concentrations. These are economically viable and practical strategies that nonprofits and community organisations can implement for exposure reduction (Clark et al., 2008).

Rahman et al. (2004) reported that raised garden beds made from CCA treated timber diffused Cu, Cr, and As into adjacent garden soils. Therefore the use of untreated timber for raised beds, fencing, and posts in proximity to gardens is crucial in minimizing further sources of contamination and exposure.

The approaches mentioned in this section should be promoted among urban gardeners. Furthermore, widespread adoption of healthy gardening practices, such as keeping soil pH near neutral and washing and peeling produce, is a critical strategy for reducing human exposures to soil contaminants, especially if resources for a thorough site evaluation are insufficient (Mitchell, et al., 2014).

5.3 Limitations

Although using the FP-XRF for screening has many benefits, it also has many limitations. Apart from Pb and Zn, this study was unable to find consistent values of other HMs such as Hg, Cd, and As in RZ soils due to the LOD of the FP-XRF which are listed in Appendix G.

Seeley and Smy (2021) compared soil HM contaminant results from data collected through FP-XRF sampling and ICP-MS analysis to find similarities between the observed results. They found that both Pb and Zn concentrations in soils were underestimated by the FP-XRF when compared to results from ICP-MS analysis as water molecules increased the bulk of the soil without adding to the HM concentration. The concentrations obtained by in-situ XRF analysis were on average 25–50% lower than those obtained by ICP-MS (Seeley & Smy, 2021). This shows that FP-XRF can produce incorrect readings of HM contaminants in soils, which can impact the decision quality of the data.

Research also found that screening analytical methods such as FP-XRF had greater LOD (Crumbling, 2001; Kalnicky & Singhvi, 2001; Rumsby, 2015), were more biased, less precise, and more sensitive to interferences than compared to definitive methods such as ICP-MS (Crumbling, 2001). This makes it more difficult to get an accurate picture of HM distribution in the RZ, especially for Hg, and Cd, which have extremely low background concentrations of 0.04-0.08 mg/kg and 0.073-0.14 mg/kg respectively (Tonkin and Taylor, 2007).

Determining the sources of HM contaminants in RZ soils was also made more difficult due to the fact that the FP-XRF could not detect organic contaminants, such as organochlorine pesticides and polycyclic aromatic hydrocarbons (PAHs) which can be indicators of HM contaminants (Rumsby, 2015).

5.4 Future research

Concentrations of HMs in the Christchurch Residential RZ soils are not well understood and require further investigations to understand the nature of HMs in the RZ and how they are distributed. Future research that aims to expand on the findings of this study should include

gathering more data from different sites in the Christchurch Residential RZ rather than just the flatland Ōtākaro Avon River Corridor area of the RZ. This will allow for a better representation of the distribution and concentrations of HMs in RZ soils. Although FP-XRF is only used as a method of screening analysis, it can still provide evidence of hotspot locations. However, future research should combine the use of FP-XRF screening with ICP-MS analysis as this will allow for more accurate and reliable soil contaminant results.

As this study was unable to address the reason as to why site 8 had significantly lower concentrations of soil Pb than the other seven sites, future work at this site is needed to determine the reason for this. This can include digging down beneath the surface of the top soil for evidence of contaminated soils which will prove that this site was previously remediated.

Finally, future research could also examine the HM concentrations in fruits and vegetables grown in urban/suburban gardens in Christchurch, to quantify the levels of exposure for community gardeners and to aid in future crop selection.

6. Conclusion

In-situ XRF screening of RZ soils was conducted to gain a better understanding of the types of HMs in RZ soils, the concentrations of HMs, and the nature of HM distribution in Christchurch residential RZ soils. This study found elevated concentrations of Pb and Zn in the flatland Ōtākaro Avon River Corridor area of the Christchurch Residential RZ that exceed the urban background concentrations in Canterbury soils, suggesting that HM concentrations in these soils have been elevated from previous land uses and anthropogenic activities such as industrial discharges, vehicle emissions, and the demolition of buildings. These elevated levels of soil Pb and Zn concentrations were consistent with the finding of other researchers. Importantly, targeted samples had a significantly higher mean concentration than non-targeted transect samples. This suggests that areas of bare soil with visible debris and rubble such as brick fragments can indicate the presence of contaminated soils, which may be useful for targeted remediation or in helping community members minimize their exposure to HM contaminants in RZ soils. Exposure to high

concentrations of these HMs has an adverse effect on human health. This is why soil HM concentrations should be a key factor in deciding on the future land use of RZ land. The likelihood of human exposure to these HMs in soils would be reduced if these RZ areas were redeveloped into nature reserves or native forests, rather than community gardens where produce is grown and bare soil is exposed. This research can be used to complement the regeneration work that is currently underway in the RZ. Furthermore, the results from this research could contribute to the development of new risk management strategies and potentially lead the way for future research projects in the RZ.

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8. References

Acharya, A. S., Prakash, A., Saxena, P., & Nigam, A. (2013). Sampling: Why and how of it. *Indian Journal of Medical Specialties*, 4(2), 330-333.
<https://doi.org/10.7713/ijms.2013.0032>

- Ajmone-Marsan, F., & Biasioli, M. (2010). Trace elements in soils of urban areas. *Water, Air, & Soil Pollution*, 213(1), 121-143. <https://doi.org/10.1007/s11270-010-0372-6>
- Al-Delaimy, W. K., & Webb, M. (2017). Community gardens as environmental health interventions: Benefits versus potential risks. *Current environmental health reports*, 4(2), 252-265. <https://doi.org/10.1007/s40572-017-0133-4>
- Alaimo, K., Packnett, E., Miles, R. A., & Kruger, D. J. (2008). Fruit and vegetable intake among urban community gardeners. *Journal of nutrition education and behavior*, 40(2), 94-101. <https://doi.org/10.1016/j.jneb.2006.12.003>
- Aschengrau, A., Beiser, A., Bellinger, D., Copenhafer, D., & Weitzman, M. (1994). The impact of soil lead abatement on urban children's blood lead levels: Phase II results from the Boston Lead-In-Soil Demonstration Project. *Environmental research*, 67(2), 125-148. <https://doi.org/10.1006/enrs.1994.1069>
- Ashrafzadeh, S., Lehto, N. J., Oddy, G., McLaren, R. G., Kang, L., Dickinson, N. M., ... & Robinson, B. H. (2018). Heavy metals in suburban gardens and the implications of land-use change following a major earthquake. *Applied Geochemistry*, 88, 10-16.
- Assi, M. A., Hezme, M. N. M., Abd Wahid Haron, M. Y. M., & Sabri, M. A. R. (2016). The detrimental effects of lead on human and animal health. *Veterinary world*, 9(6), 660. <https://doi.org/10.14202/vetworld.2016.660-671>
- Begg, J. G., Jones, K. E., & Barrell, D. J. A. (2015). Geology and geomorphology of urban Christchurch and eastern Canterbury. *GNS Science Geological Map*, 3(1).
- Blaylock, M. J., Salt, D. E., Dushenkov, S., Zakharova, O., Gussman, C., Kapulnik, Y., ... & Raskin, I. (1997). Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents. *Environmental Science & Technology*, 31(3), 860-865. <https://doi.org/10.1021/es960552a>

- Bosco, G. L. (2013). Development and application of portable, hand-held X-ray fluorescence spectrometers. *TrAC Trends in Analytical Chemistry*, 45, 121-134. <https://doi.org/10.1016/j.trac.2013.01.006>
- Brand, D., & Nicholson, H. (2016). Public space and recovery: learning from post-earthquake Christchurch. *Journal of Urban Design*, 21(2), 159-176.
- Brown, M., Robinson, D., & Kamo, A. (2012). *RESIDENTIAL RED ZONE Interim Land Clearance Treatment Methodology – Version 1.1*. Canterbury Earthquake Recovery Authority.
- Button, K. S., Ioannidis, J. P., Mokrysz, C., Nosek, B. A., Flint, J., Robinson, E. S., & Munafò, M. R. (2013). Power failure: why small sample size undermines the reliability of neuroscience. *Nature reviews neuroscience*, 14(5), 365-376. <https://doi.org/10.1038/nrn3475>
- Carr, R., Zhang, C., Moles, N., & Harder, M. (2008). Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS. *Environmental Geochemistry and Health*, 30(1), 45-52.
- Carroll, J., & McDonald, L. (2018, October 9). Christchurch Properties contaminated with lead top of Environment Ministry's priority list. *Environment*. <https://www.stuff.co.nz/environment/107630704/christchurch-properties-contaminated-with-lead-top-environment-ministrys-priority-list>
- Centers for Disease Control and Prevention (CDC). (2005). Blood lead levels--United States, 1999-2002. *MMWR. Morbidity and mortality weekly report*, 54(20), 513-516.
- Cheng, Z., Paltseva, A., Li, I., Morin, T., Huot, H., Egendorf, S., ... & Shaw, R. (2015). Trace metal contamination in New York City garden soils. *Soil Science*, 180(4/5), 167-174. <https://doi.org/10.1097/SS.000000000000126>
- Christchurch City Council. (2003). *Soils and Geomorphology of Christchurch*. Waterways, Wetlands and Drainage Guide - Part B: Design. 4.1-4.8

- Clark, H. F., Brabander, D. J., & Erdil, R. M. (2006). Sources, sinks, and exposure pathways of lead in urban garden soil. *Journal of environmental quality*, 35(6), 2066-2074. <https://doi.org/10.2134/jeq2005.0464>
- Clark, H. F., Hausladen, D. M., & Brabander, D. J. (2008). Urban gardens: Lead exposure, recontamination mechanisms, and implications for remediation design. *Environmental Research*, 107(3), 312-319. <https://doi.org/10.1016/j.envres.2008.03.003>
- Clevenger, T. E., Saiwan, C., & Koirtyohann, S. R. (1991). Lead speciation of particles on air filters collected in the vicinity of a lead smelter. *Environmental science & technology*, 25(6), 1128-1133. <https://doi.org/10.1021/es00018a017>
- Crumbling, D. M. (2001). Applying the concept of effective data to environmental analyses for contaminated sites. *USEPA Office of Solid Waste and Emergency Response*. EPA.
- Davies, D. J. A., Watt, J. M., & Thornton, I. (1987). Lead levels in Birmingham dusts and soils. *The Science of the Total Environment*, 67(2), 177-185. [https://doi.org/10.1016/0048-9697\(87\)90210-5](https://doi.org/10.1016/0048-9697(87)90210-5)
- Davis, A. H. (2018). *A Commemorative Landscape in the Christchurch Residential Red Zone*. [Master's thesis, Unitec Institute of Technology]. Research Bank.
- Day, J. P. (1977). Lead pollution in Christchurch. *New Zealand Journal of Science*, 20(4), 395-406.
- Dixon, S. L., McLaine, P., Kawecki, C., Maxfield, R., Duran, S., Hynes, P., & Plant, T. (2006). The effectiveness of low-cost soil treatments to reduce soil and dust lead hazards: The Boston lead safe yards low cost lead in soil treatment, demonstration and evaluation. *Environmental research*, 102(1), 113-124. <https://doi.org/10.1016/j.envres.2006.01.006>

- Garba, S. T., & Abubakar, M. A. (2018). Source and distribution of the heavy metals: Pb, Cd, Cu, Zn, Fe, Cr, and Mn in soils of bauchi metropolis, Nigeria. *American Journal of Engineering Research*, 7(2), 13-23.
- Gilmour, D. (2013). *Community food resilience in the Avon-Otakaro residential red-zone: Christchurch and its future for community food security*. UC Sustainability Office Student Research Project. Draft, pp. 1-33.
- Grzebisz, W., Ciesla, L., Komisarek, J., & Potarzycki, J. (2002). Geochemical assessment of the heavy metals pollution of urban soils. *Polish Journal of Environmental Studies*, 11(5), 493-500.
- Gulan, L., Milenkovic, B., Zeremski, T., Milic, G., & Vuckovic, B. (2017). Persistent organic pollutants, heavy metals and radioactivity in the urban soil of Priština City, Kosovo and Metohija. *Chemosphere*, 171, 415-426. <https://doi.org/10.1016/j.chemosphere.2016.12.064>
- Hough, R. L., Breward, N., Young, S. D., Crout, N. M., Tye, A. M., Moir, A. M., & Thornton, I. (2004). Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations. *Environmental health perspectives*, 112(2), 215-221. <https://doi.org/10.1289/ehp.5589>
- Hill Laboratories. (2018, November 7). *Assessing Lead Contamination in Properties*. <https://www.hill-laboratories.com/about-us/news/lead-contamination-in-properties>
- Jordan, L. D., & Hogan, D. J. (1975). Survey of lead in Christchurch soils. *New Zealand Journal of Science*, 18(2), 253-260.
- Kalnicky, D. J., & Singhvi, R. (2001). Field portable XRF analysis of environmental samples. *Journal of hazardous materials*, 83(1-2), 93-122. [https://doi.org/10.1016/S0304-3894\(00\)00330-7](https://doi.org/10.1016/S0304-3894(00)00330-7)
- Kandic, S., Tepe, S. J., Blanch, E. W., De Silva, S., Mikkonen, H. G., & Reichman, S. M. (2019). Quantifying factors related to urban metal contamination in vegetable garden soils

of the west and north of Melbourne, Australia. *Environmental Pollution*, 251, 193-202. <https://doi.org/10.1016/j.envpol.2019.04.031>

Kim, S. M., & Choi, Y. (2019). Mapping heavy metal concentrations in Beach Sands using GIS and Portable XRF data. *Journal of Marine Science and Engineering*, 7(2), 42. <https://doi.org/10.3390/jmse7020042>

Laidlaw, M. A., Mohammad, S. M., Gulson, B. L., Taylor, M. P., Kristensen, L. J., & Birch, G. (2017). Estimates of potential childhood lead exposure from contaminated soil using the US EPA IEUBK Model in Sydney, Australia. *Environmental research*, 156, 781-790. <https://doi.org/10.1016/j.envres.2017.04.040>

Land Information New Zealand (LINZ). (2021). *Christchurch residential red zone areas*. Retrieved October 10, 2021, from <https://www.linz.govt.nz/crown-property/types-crown-property/christchurch-residential-red-zones/christchurch-residential-red-zone-areas>

Land Information New Zealand (LINZ). (2017). *Information for Canterbury surveyors*. Retrieved October 10, 2021, from <https://www.linz.govt.nz/land/surveying/earthquakes/canterbury-earthquakes/information-for-canterbury-surveyors>

Landcare Research NZ Limited. (2021, November 15). *Map of the different soil drainage types in the Ōtākaro Avon River Corridor* [Map]. S-Map. <https://smap.landcareresearch.co.nz/maps-and-tools/app/>

Level. (2021, October 4). *Lead paint*. Retrieved October 10, 2021, from <https://www.level.org.nz/health-and-safety/airborne-and-other-pollutants/lead-paint/>

Li, Y., Li, H. G., & Liu, F. C. (2017). Pollution in the urban soils of Lianyungang, China, evaluated using a pollution index, mobility of heavy metals, and enzymatic

activities. *Environmental monitoring and assessment*, 189(1), 1-13.
<https://doi.org/10.1007/s10661-016-5740-2>

Litt, J. S., Hynes, H. P., Carroll, P., Maxfield, R., McLaine, P., & Kawecki, C. (2002). Lead safe yards: a program for improving health in urban neighborhoods. *Journal of Urban Technology*, 9(2), 71-93. <https://doi.org/10.1080/1063073022000016487>

Lu, Y., Gong, Z., Zhang, G., & Burghardt, W. (2003). Concentrations and chemical speciations of Cu, Zn, Pb and Cr of urban soils in Nanjing, China. *Geoderma*, 115(1-2), 101-111. [https://doi.org/10.1016/S0016-7061\(03\)00079-X](https://doi.org/10.1016/S0016-7061(03)00079-X)

Luo, C., Liu, C., Wang, Y., Liu, X., Li, F., Zhang, G., & Li, X. (2011). Heavy metal contamination in soils and vegetables near an e-waste processing site, south China. *Journal of hazardous materials*, 186(1), 481-490.
<https://doi.org/10.1016/j.jhazmat.2010.11.024>

Mason, L. H., Harp, J. P., & Han, D. Y. (2014). Pb neurotoxicity: neuropsychological effects of lead toxicity. *BioMed research international*, 2014.
<https://doi.org/10.1155/2014/840547>

Martin, S., & Griswold, W. (2009). Human health effects of heavy metals. *Environmental Science and Technology briefs for citizens*, 15, 1-6

Ministry of Health. (2018, July 5). *Soil contaminants and health*. Retrieved July 9, 2021, from <https://www.health.govt.nz/your-health/healthy-living/environmental-health/hazardous-substances/soil-contaminants-and-health>

Ministry of Health. (2021, September 22). *Removing lead-based paint*. Retrieved September 30, 2021, from <https://www.health.govt.nz/your-health/healthy-living/environmental-health/hazardous-substances/removing-lead-based-paint>

Mitchell, R. G., Spliethoff, H. M., Ribaud, L. N., Lopp, D. M., Shayler, H. A., Marquez-Bravo, L. G., ... & McBride, M. B. (2014). Lead (Pb) and other metals in New York City community garden soils: Factors influencing contaminant distributions.

Environmental Pollution, 187, 162-169.
<https://doi.org/10.1016/j.envpol.2014.01.007>

Moller, K. M. (2016). *Soil Contamination Analyses of Urban Agricultural Sites and Health Risk Assessments of the Urban Agricultural Community in New Orleans, Louisiana* (Doctoral dissertation, Tulane University, School of Public Health and Tropical Medicine).

Nathanail, C. P., & Earl, N. (2001). Human health risk assessment: guideline values and magic numbers. In *Assessment and Reclamation of Contaminated Land* (pp. 85-102). Thomas Telford Publishing.

Nielsen. (2016). *Residential Red Zone Survey- of those who accepted the crown offer*. Canterbury Earthquake Recovery Authority. Retrieved from <https://www.dPMC.govt.nz/sites/default/files/2017-03/cera-rrz-surveyreport-feb2016.pdf>

New Zealand Government. (2020, January 20). *Map of residential red zone in and around Christchurch, New Zealand* [Map]. Wikipedia. https://en.wikipedia.org/wiki/Residential_red_zone#/media/File:Red_Zone_map_first_upload.png

Pennock, D., Yates, T., & Braidek, J. (2008). Soil sampling designs. *Soil sampling and methods of analysis*, 2, 25-37. <https://doi.org/10.1201/9781420005271.ch1>

Rahman, F. A., Allan, D. L., Rosen, C. J., & Sadowsky, M. J. (2004). Arsenic availability from chromated copper arsenate (CCA)-treated wood. *Journal of environmental quality*, 33(1), 173-180. <https://doi.org/10.2134/jeq2004.1730>

Regenerate Christchurch. (2019). *Otakaro Avon River Corridor Regeneration Plan*. Department of the Prime Minister and Cabinet. 5-84.

- Robinson, B. H., Bañuelos, G., Conesa, H. M., Evangelou, M. W., & Schulin, R. (2009). The phytomanagement of trace elements in soil. *Critical Reviews in Plant Sciences*, 28(4), 240-266.
- Rooney, C. P. (2002). *The fate of lead in soils contaminated with lead shot*. [Doctoral dissertation, Lincoln University]. Research@Lincoln.
- Rumsby, A. (2015). *Guidance for Analysis of Soil Contamination Using a Portable X-Ray Fluorescence Spectrometer* (Waikato Regional Council Technical Report 2016/22). Pattle Delamore Partners Ltd.
- Rumsby, A. (2013). *Analysis of Soil Samples Using a Portable X-Ray Fluorescence Spectrometry (XRF)*. Pattle Delamore Partners Ltd.
- Sangster, J. L., Nelson, A., & Bartelt-Hunt, S. L. (2012). The occurrence of lead in soil and vegetables at a community garden in Omaha, Nebraska. *International Journal for Service Learning in Engineering, Humanitarian Engineering and Social Entrepreneurship*, 7(1), 62-68. <https://doi.org/10.24908/ijlse.v7i1.4231>
- Scott, M., & Carville, O. (2016). Christchurch earthquake: Eerie images of city's red-zone, five years on. *New Zealand Herald*, 17. <https://www.nzherald.co.nz/nz/christchurch-earthquake-eerie-images-of-citys-red-zone-five-years-on/OFFLWHHL2TKHPNTYAUDCZL5PGA/>
- Scullion, J. (2006). Remediating polluted soils. *Naturwissenschaften*, 93(2), 51-65. <https://doi.org/10.1007/s00114-005-0079-5>
- Seeley, R. T., & Smy, T. J. (2021). *Assessment of heavy metal contamination in community garden soils - a case study from Christchurch, New Zealand*. Dept. of Civil and Natural Resources Engineering. University of Canterbury.
- Shackley, M. S. (2018). X-Ray Fluorescence Spectrometry (XRF). *The encyclopedia of archaeological sciences*, 1-5. <https://doi.org/10.1002/9781119188230.saseas0620>

- Sharma, R. K., Agrawal, M., & Marshall, F. (2007). Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. *Ecotoxicology and environmental safety*, 66(2), 258-266.
- Shukla, V., Shukla, P., & Tiwari, A. (2018). Lead poisoning. *Indian Journal of Medical Specialities*, 9(3), 146-149. <https://doi.org/10.1016/j.injms.2018.04.003>
- Singh, S., Zacharias, M., Kalpana, S., & Mishra, S. (2012). Heavy metals accumulation and distribution pattern in different vegetable crops. *Journal of Environmental Chemistry and Ecotoxicology*, 4(4), 75-81. <https://doi.org/10.5897/JECE11.076>
- Srivastava, N. K., & Majumder, C. B. (2008). Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *Journal of hazardous materials*, 151(1), 1-8.
- Statistics New Zealand. (n.d.). *Christchurch City*. Retrieved November 20, 2021, from <https://www.stats.govt.nz/tools/2018-census-place-summaries/christchurch-city>
- Tong, S. T. Y. (1998). Indoor and outdoor household dust contamination in Cincinnati, Ohio, USA. *Environmental Geochemistry and Health*, 20(3), 123-133. <https://doi.org/10.1023/A:1006561832381>
- Tonkin and Taylor (2007). *Background Concentrations of Selected Trace Elements in Canterbury Soils*. Environment Canterbury. Report No. R07/1
- Vallance, S. A., & Tait, P. R. (2013). *A Community-led, Science-Informed Conversation around the Future Use of the Avon River Residential Red Zone*. Lincoln University.
- Wilson, N., & Horrocks, J. (2008). Lessons from the removal of lead from gasoline for controlling other environmental pollutants: A case study from New Zealand. *Environmental health*, 7(1), 1-10. <https://doi.org/10.1186/1476-069X-7-1>

Appendix A: Data from FP-XRF

Line	Sample Type	Date	Time	Notes	Latitude	Longitude	Pb	Bi	U	Ca	Fe	Al	Si	Mg	K	Na	Cl	S	Other
1	Targeted	24/06/2022	10:47:22	test 001	43.5297	172.6474	22	60	4300	3911	5266	5977	1141	69	362	12	129	7	387
1	Targeted	24/06/2022	10:48:37	test 001	43.5297	172.6474	16	56	2467	3811	5438	6094	56	267	9	113	6	363	363
1	Targeted	24/06/2022	10:50:41	test 001	43.5298	172.6474	20	59	2394	4102	5103	6446	1232	60	172	12	136	7	442
1	Targeted	24/06/2022	10:51:51	test 001	43.5298	172.6473	138	230	2378	3811	5855	4606	12996	56	386	14	111	9	414
1	Targeted	24/06/2022	11:00:20	test 001	43.5297	172.6474	14	49	402	3702	5263	74	362	11	118	10	109	8	339
1	Targeted	24/06/2022	11:00:23	test 001	43.5298	172.6474	188	218	3608	4628	4319	6985	12175	38	177	9	128	8	313
1	Targeted	24/06/2022	11:01:51	test 004	43.5296	172.6475	67	362	2471	5515	5793	4425	14023	69	394	19	145	7	393
1	Targeted	24/06/2022	11:03:26	test 005	43.5296	172.6474	24	50	2162	4123	5266	7531	12965	69	242	11	118	10	339
1	Targeted	24/06/2022	11:05:19	test 006	43.5296	172.6475	23	50	400	3997	5112	5438	12935	38	189	15	163	9	332
1	Targeted	24/06/2022	11:06:38	test 007	43.5296	172.6476	20	51	2762	5566	6060	4522	12292	66	343	12	110	5	375
1	Targeted	24/06/2022	11:08:30	test 008	43.5296	172.6481	705	875	3110	5560	3920	13789	60	240	12	116	11	413	
1	Targeted	24/06/2022	11:10:38	test 009	43.5296	172.64815	297	358	400	4264	5870	4711	13975	57	177	17	113	8	442
1	Targeted	24/06/2022	11:12:34	test 010	43.5296	172.64811	25	64	2563	3067	3474	3380	9543	56	138	10	102	6	306
1	Targeted	24/06/2022	11:14:40	test 011	43.5297	172.64814	230	396	438	425	6261	4641	10810	69	295	11	123	9	425
1	Targeted	24/06/2022	11:17:35	test 012	43.5296	172.64827	188	202	400	4062	5956	3812	13853	55	206	17	168	7	423
1	Targeted	24/06/2022	11:20:36	test 013	43.5295	172.64831	25	47	400	3529	6150	4340	12899	64	159	11	124	6	389
1	Targeted	24/06/2022	11:22:14	test 014	43.5293	172.64829	43	64	2035	3122	5984	3998	14628	76	368	7	110	12	320
1	Targeted	24/06/2022	11:26:30	test 016	43.5295	172.64852	28	50	2065	3243	6361	4329	13246	72	361	14	127	6	400
1	Targeted	24/06/2022	11:27:43	test 017	43.5293	172.64853	82	76	2025	3694	6407	4605	13498	76	157	11	129	5	374
1	Targeted	24/06/2022	11:29:59	test 018	43.5297	172.64873	74	116	2456	4825	6827	4822	14696	79	178	17	147	7	393
1	Targeted	24/06/2022	11:30:47	test 019	43.5297	172.6487	472	118	3046	3908	6056	5451	17124	72	399	16	114	8	417
1	Targeted	24/06/2022	11:31:26	test 020	43.5297	172.64868	409	182	400	4105	5624	5589	15737	61	231	13	104	7	371
1	Targeted	24/06/2022	11:31:11	test 022	43.5297	172.64842	797	336	400	4256	5348	8922	15382	66	239	10	111	10	476
1	Targeted	24/06/2022	11:38:52	test 023	43.5297	172.64847	187	188	2365	4596	5183	30152	12866	57	178	13	109	7	321
1	Targeted	24/06/2022	11:41:02	test 024	43.5298	172.64862	235	296	2616	4221	5385	8607	13621	51	175	11	117	7	357
1	Targeted	24/06/2022	11:42:55	test 025	43.5291	172.6489	153	82	2981	3828	6711	4225	14868	74	179	15	117	6	389
1	Targeted	24/06/2022	11:43:51	test 026	43.5294	172.64856	434	974	1312	4185	6516	5176	17942	81	219	13	120	11	424
2	Targeted	24/06/2022	11:38:49	test 045	43.5295	172.6523	48	55	2066	3702	6349	3813	13248	69	362	15	151	6	410
2	Targeted	24/06/2022	11:39:22	test 046	43.5295	172.6525	15	24	400	3676	5825	4826	13863	74	362	16	166	6	386
2	Targeted	24/06/2022	11:39:54	test 047	43.5297	172.65218	39	104	400	3297	5300	3570	10330	65	159	9	159	5	359
2	Targeted	24/06/2022	11:41:59	test 048	43.5297	172.65263	73	211	2328	3465	5077	4285	13430	67	349	13	113	6	383
2	Targeted	24/06/2022	11:42:55	test 049	43.5297	172.65215	183	245	2425	4128	5946	4733	12242	59	212	12	118	6	407
2	Targeted	24/06/2022	11:46:58	test 051	43.5295	172.65177	286	400	3775	5673	6311	14383	52	202	9	128	11	477	
2	Targeted	24/06/2022	11:48:59	test 051	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670	6450	5153	14999	68	379	5	114	8	479
2	Targeted	24/06/2022	11:51:58	test 053	43.5295	172.65215	289	473	2701	3670									

Site	Sample Type	Date	Time	Notes	Latitude	Longitude	Pb	In	Al	Si	Ca	Fe	Mg	K	V	Cr	Ni	Cu	Zn	Mn	Sr	Ba	
1	Transect	24/09/2021	13:04-40	text	027	-43.5238	172.64704	5	361	2390	2096	3320	6244	4612	42	104	6	77	5	251			
1	Transect	24/09/2021	13:06:07	text	028	-43.5238	172.64711	19	66	400	2925	5988	4028	12454	84	143	11	122	8	327			
1	Transect	24/09/2021	13:07:02	text	029	-43.5238	172.64719	5	193	401	3126	6410	515	1421	10	143	10	143	10	143			
1	Transect	24/09/2021	13:08:12	text	030	-43.5238	172.64728	18	60	2563	2807	5674	4225	12710	60	146	8	105	6	247			
1	Transect	24/09/2021	13:09:22	text	031	-43.5238	172.64735	36	49	2311	3005	5320	4236	10221	50	122	8	91	5	228			
1	Transect	24/09/2021	13:10:30	text	032	-43.5239	172.64741	129	98	2375	3330	5372	4318	12287	58	148	14	136	4	314			
1	Transect	24/09/2021	13:11:31	text	033	-43.5239	172.64749	58	78	1976	3271	6253	4416	13343	86	156	13	120	7	343			
1	Transect	24/09/2021	13:12:34	text	034	-43.5238	172.64757	26	76	1847	3161	5793	4355	11400	60	150	12	107	5	263			
1	Transect	24/09/2021	13:13:46	text	035	-43.5239	172.64763	15	115	3285	3284	6224	4742	12363	65	130	7	104	8	325			
1	Transect	24/09/2021	13:14:54	text	036	-43.5239	172.64779	108	51	2834	3277	6579	4381	11313	53	135	11	106	6	302			
1	Transect	24/09/2021	13:16:10	text	037	-43.5239	172.64802	17	170	2836	3367	5650	4524	11706	52	156	11	120	5	303			
1	Transect	24/09/2021	13:17:10	text	038	-43.5239	172.64809	34	74	2561	3274	5707	4236	10398	58	137	14	91	4	342			
1	Transect	24/09/2021	13:18:14	text	039	-43.5239	172.64822	5	66	2151	3200	5823	4368	11426	60	153	10	109	7	260			
1	Transect	24/09/2021	13:19:27	text	040	-43.5239	172.64833	5	63	1963	3447	5742	4502	12107	63	128	10	98	7	259			
1	Transect	24/09/2021	13:21:20	text	041	-43.5239	172.64851	52	69	2810	3390	5511	4289	10000	50	136	12	86	5	244			
1	Transect	24/09/2021	13:22:19	text	042	-43.5239	172.64863	5	56	2138	3436	5830	3800	11341	55	121	11	92	6	300			
1	Transect	24/09/2021	13:23:52	text	043	-43.5239	172.64871	5	68	2611	4503	6424	4029	13700	81	150	17	121	6	315			
1	Transect	24/09/2021	13:25:14	text	044	-43.5239	172.64883	5	68	2607	4428	7345	5308	11172	40	152	10	93	5	353			
2	Transect	24/09/2021	13:57:30	text	056	-43.5253	172.65257	73	118	2236	4058	6306	4375	10875	57	140	9	106	5	321			
2	Transect	24/09/2021	13:58:46	text	057	-43.5253	172.65245	5	110	400	3388	4744	4320	6545	35	104	9	81	4	268			
2	Transect	24/09/2021	14:00:41	text	058	-43.5253	172.65232	23	133	1594	3918	5303	4425	8389	35	92	5	87	5	367			
2	Transect	24/09/2021	14:02:02	text	059	-43.5253	172.65238	26	107	2871	3920	4852	4533	6385	35	95	11	79	5	361			
2	Transect	24/09/2021	14:03:14	text	060	-43.5253	172.65235	49	117	2775	4269	6232	4881	12301	67	152	13	138	7	368			
2	Transect	24/09/2021	14:04:29	text	061	-43.5253	172.65235	40	83	400	3713	5612	4401	9312	42	134	8	90	5	263			
2	Transect	24/09/2021	14:05:30	text	062	-43.5253	172.65238	36	136	400	4677	5177	5280	10389	57	146	9	100	6	367			
2	Transect	24/09/2021	14:06:55	text	063	-43.5253	172.65232	47	93	3057	3571	5801	4047	10308	52	138	8	124	5	200			
2	Transect	24/09/2021	14:08:09	text	064	-43.5253	172.65231	24	101	3926	3483	5813	3491	9483	34	128	10	127	6	239			
2	Transect	24/09/2021	14:11:05	text	065	-43.5254	172.65255	22	48	400	4053	6003	3933	10393	62	158	9	143	6	403			
2	Transect	24/09/2021	14:12:26	text	066	-43.5253	172.65246	5	77	3254	3549	5777	4042	10173	71	163	9	144	6	332			
2	Transect	24/09/2021	14:13:20	text	067	-43.5254	172.65235	27	80	400	3712	5838	4200	11318	65	158	5	138	5	389			
3	Transect	24/09/2021	15:21:06	text	090	-43.5240	172.65796	270	150	2387	4424	6916	6752	7746	73	207	15	127	9	444			
3	Transect	24/09/2021	15:22:18	text	091	-43.5240	172.65792	80	139	2391	4427	5859	4823	11237	63	149	12	127	9	389			
3	Transect	24/09/2021	15:24:37	text	092	-43.5246	172.65744	106	115	2827	5610	7842	5381	11553	64	136	11	115	7	399			
3	Transect	24/09/2021	15:26:06	text	093	-43.5246	172.65751	108	113	400	4752	7851	4725	15118	86	176	14	153	10	474			
3	Transect	24/09/2021	15:27:13	text	094	-43.5246	172.65749	85	103	2383	4302	6239	4930	11958	72	172	11	149	8	293			
3	Transect	24/09/2021	15:28:26	text	095	-43.5246	172.65746	26	87	400	3388	4744	4320	6545	35	104	9	81	4	268			
3	Transect	24/09/2021	15:30:52	text	096	-43.5246	172.65797	26	80	400	3802	5155	5260	9638	58	123	8	129	5	303			
3	Transect	24/09/2021	15:31:52	text	097	-43.5246	172.65811	5	112	400	4405	6530	5266	11845	68	146	14	129	7	393			
3	Transect	24/09/2021	15:33:26	text	098	-43.5247	172.65837	33	80	2401	3788	6455	3982	9938	63	142	10	143	5	367			
3	Transect	24/09/2021	15:35:26	text	099	-43.5246	172.65844	54	122	2385	4350	6724	6648	10969	56	134	10	138	5	307			
3	Transect	24/09/2021	15:36:49	text	100	-43.5246	172.65862	31	60	2345	3686	5984	4021	11269	58	140	10	137	5	365			
3	Transect	24/09/2021	15:38:03	text	101	-43.5246	172.65878	53	111	400	4005	6761	4456	11915	67	150	130	130	5	344			
3	Transect	24/09/2021	15:39:32	text	102	-43.5246	172.65893	28	132	400	4070	6133	5277	8657	57	121	9	94	6	346			
3	Transect	24/09/2021	15:40:53	text	103	-43.5247	172.65905	218	350	2301	4407	6669	5399	13453	57	172	14	129	4	352			
3	Transect	24/09/2021	15:46:04	text	104	-43.5247	172.65915	108	256	400	4436	6217	5385	11292	53	127	8	96	5	299			
3	Transect	24/09/2021	15:46:40	text	105	-43.5247	172.65923	81	201	2384	4431	4957	4384	11843	62	142	8	124	5	291			
3	Transect	24/09/2021	15:51:19	text	106	-43.5246	172.65939	68	220	2896	4570	5800	5677	9639	76	144	5	134	7	339			
3	Transect	24/09/2021	15:52:58	text	107	-43.5246	172.65939	51	113	2840	3991	5558	4325	10668	69	164	8	106	7	375			
3	Transect	24/09/2021	15:54:26	text	108	-43.5246	172.65953	143	159	2049	3887	6219	4605	11389	53	158	12	124	6	378			
3	Transect	24/09/2021	15:55:38	text	109	-43.5246	172.65996	125	154	400	4700	7410	5552	13951	80	168	11	127	6	346			
3	Transect	24/09/2021	15:56:03	text	110	-43.5246	172.65992	101	101	2765	3954	6303	4295	11894	64	145	6	127	5	356			
3	Transect	24/09/2021	15:59:08	text	111	-43.5246	172.65992	60	110	400	3350	6878	4959	12774	74	168	8	157	9	411			
3	Transect	24/09/2021	16:00:13	text	112	-43.5246	172.65996	29	83	2330	4151	6837	3660	13381	84	156	15	160	11	427			
3	Transect	24/09/2021	16:01:31	text	113	-43.5																	

Appendix C: Results From IBM SPSS Statistics Analysis

Descriptives

Log Concentration								
	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	28	1.983877930	.5300744402	.1001746532	1.778336520	2.189419340	1.301029996	2.901458321
2	11	2.382037765	.6706330660	.2022034774	1.931500341	2.832575190	1.544068044	3.517063873
3	22	2.269517070	.3554743401	.0757873840	2.111908577	2.427125563	1.342422681	2.832508913
4	34	1.970445948	.4775020295	.0818909225	1.803837614	2.137054283	1.230448921	3.224791956
5	20	1.926229274	.3536065269	.0790688232	1.760736325	2.091722223	1.462397998	2.558708571
6	23	2.143694493	.2219715994	.0462842780	2.047706776	2.239682211	1.716003344	2.604226053
7	19	2.455783183	.3809007288	.0873846202	2.272194909	2.639371458	1.653212514	3.373095987
8	14	1.496923043	.5005374240	.1337742536	1.207921339	1.785924748	.6989700043	2.146128036
Total	171	2.070888287	.4973175797	.0380308258	1.995814802	2.145961773	.6989700043	3.517063873

Tests of Homogeneity of Variances

		Levene Statistic	df1	df2	Sig.
Log Concentration	Based on Mean	4.496	7	163	<.001
	Based on Median	4.343	7	163	<.001
	Based on Median and with adjusted df	4.343	7	133.294	<.001
	Based on trimmed mean	4.507	7	163	<.001

ANOVA

Log Concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	10.455	7	1.494	7.707	<.001
Within Groups	31.590	163	.194		
Total	42.045	170			

Robust Tests of Equality of Means

Log Concentration

	Statistic ^a	df1	df2	Sig.
Welch	7.129	7	58.409	<.001
Brown-Forsythe	7.158	7	78.838	<.001

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: Log Concentration

Tukey HSD

(I) Site	(J) Site	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.398159835	.1566527294	.186	-.879195798	.0828761276
	3	-.285639140	.1254225617	.312	-.670776143	.0994978637
	4	.0134319818	.1123462010	1.000	-.331551238	.3584152017
	5	.0576486563	.1288865580	1.000	-.338125294	.4534226069
	6	-.159816563	.1238862694	.901	-.540236050	.2206029235
	7	-.471905253 [*]	.1308501225	.010	-.873708752	-.070101755
	8	.486954887 [*]	.1440995526	.020	.0444661582	.9294436154
	2	1	.3981598354	.1566527294	.186	-.082876128
3		.1125206958	.1625662200	.997	-.386673915	.6117153062
4		.4115918172	.1527043738	.131	-.057319869	.8805035037
5		.4558084917	.1652534470	.113	-.051637828	.9632548116
6		.2383432723	.1613839045	.819	-.257220784	.7339073282
7		-.073745418	.1667894225	1.000	-.585908282	.4384174457
8		.885114722 [*]	.1773742878	<.001	.3404487488	1.429780696
3		1	.2856391396	.1254225617	.312	-.099497864
	2	-.112520696	.1625662200	.997	-.611715306	.3866739145
	4	.2990711214	.1204548345	.210	-.070811405	.6689536478
	5	.3432877959	.1360126580	.193	-.074368380	.7609439718
	6	.1258225764	.1312840661	.979	-.277313439	.5289585922
	7	-.186266114	.1378747723	.878	-.609640313	.2371080855
	8	.772594026 [*]	.1505070740	<.001	.3104296224	1.234758430
	4	1	-.013431982	.1123462010	1.000	-.358415202
2		-.411591817	.1527043738	.131	-.880503504	.0573198693
3		-.299071121	.1204548345	.210	-.668953648	.0708114051
5		.0442166745	.1240576198	1.000	-.336728980	.4251623294
6		-.173248545	.1188543475	.828	-.538216431	.1917193414
7		-.485337235 [*]	.1260964025	.004	-.872543412	-.098131058
8		.473522905 [*]	.1397971002	.020	.0442457836	.9028000265
5		1	-.057648656	.1288865580	1.000	-.453422607
	2	-.455808492	.1652534470	.113	-.963254812	.0516378283
	3	-.343287796	.1360126580	.193	-.760943972	.0743683801
	4	-.044216674	.1240576198	1.000	-.425162329	.3367289804
	6	-.217465219	.1345972952	.740	-.630775219	.1958447802
	7	-.529553910 [*]	.1410332539	.006	-.962626907	-.096480912
	8	.4293062305	.1534056883	.103	-.041758993	.9003714542
	6	1	.1598165631	.1238862694	.901	-.220602924
2		-.238343272	.1613839045	.819	-.733907328	.2572207836
3		-.125822576	.1312840661	.979	-.528958592	.2773134393
4		.1732485449	.1188543475	.828	-.191719341	.5382164310
5		.2174652194	.1345972952	.740	-.195844780	.6307752191
7		-.312088690	.1364787221	.307	-.731176017	.1069986361
8		.646771450 [*]	.1492292468	<.001	.1885308900	1.105012010
7		1	.471905253 [*]	.1308501225	.010	.0701017550
	2	.0737454180	.1667894225	1.000	-.438417446	.5859082816
	3	.1862661138	.1378747723	.878	-.237108085	.6096403131
	4	.485337235 [*]	.1260964025	.004	.0981310584	.8725434119
	5	.529553910 [*]	.1410332539	.006	.0964809120	.9626269072
	6	.3120886902	.1364787221	.307	-.106998636	.7311760166
	8	.958860140 [*]	.1550590691	<.001	.4827178545	1.435002426
	8	1	-.486954887 [*]	.1440995526	.020	-.929443615
2		-.885114722 [*]	.1773742878	<.001	-1.42978070	-.340448749
3		-.772594026 [*]	.1505070740	<.001	-1.23475843	-.310429622
4		-.473522905 [*]	.1397971002	.020	-.902800026	-.044245784
5		-.429306231	.1534056883	.103	-.900371454	.0417589931
6		-.646771450 [*]	.1492292468	<.001	-1.10501201	-.188530890
7		-.958860140 [*]	.1550590691	<.001	-1.43500243	-.482717854

*. The mean difference is significant at the 0.05 level.

Log Concentration

Tukey HSD^{a,b}

Site	N	Subset for alpha = 0.05			
		1	2	3	4
8	14	1.496923043			
5	20	1.926229274	1.926229274		
4	34		1.970445948	1.970445948	
1	28		1.983877930	1.983877930	
6	23		2.143694493	2.143694493	2.143694493
3	22		2.269517070	2.269517070	2.269517070
2	11			2.382037765	2.382037765
7	19				2.455783183
Sig.		.059	.244	.082	.363

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 19.092.

b. The group sizes are unequal. The harmonic mean of the group sizes is used.
Type I error levels are not guaranteed.

Descriptives

Log Concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	18	1.264425651	.5222753192	.1231014733	1.004704245	1.524147057	.6989700043	2.110589710
2	12	1.392718181	.3601523658	.1039670327	1.163888285	1.621548077	.6989700043	1.863322860
3	26	1.826511899	.4296534817	.0842619803	1.652971102	2.000052696	.6989700043	2.968949681
4	20	1.358874276	.2935197648	.0656330147	1.221502798	1.496245755	.6989700043	1.982271233
5	32	1.748409140	.5597764312	.0989554276	1.546588215	1.950230065	.6989700043	2.786041210
6	11	1.617498707	.5408905264	.1630846299	1.254123507	1.980873907	.6989700043	2.195899652
7	12	1.948913088	.3815314885	.1101386538	1.706499546	2.191326631	1.431363764	2.613841822
8	11	1.492660546	.3597835448	.1084788204	1.250954672	1.734366420	.6989700043	2.152288344
Total	142	1.603428705	.4995357294	.0419201072	1.520555525	1.686301885	.6989700043	2.968949681

Tests of Homogeneity of Variances

		Levene Statistic	df1	df2	Sig.
Log Concentration	Based on Mean	2.685	7	134	.012
	Based on Median	2.141	7	134	.044
	Based on Median and with adjusted df	2.141	7	115.603	.045
	Based on trimmed mean	2.641	7	134	.014

ANOVA

Log Concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	7.334	7	1.048	5.041	<.001
Within Groups	27.851	134	.208		
Total	35.185	141			

Robust Tests of Equality of Means

Log Concentration

	Statistic ^a	df1	df2	Sig.
Welch	5.836	7	46.886	<.001
Brown-Forsythe	5.444	7	100.571	<.001

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: Log Concentration

Tukey HSD

(I) Site	(J) Site	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.128292530	.1699033801	.995	-.651493850	.3949087902
	3	-.562086248*	.1397885754	.002	-.992551888	-.131620608
	4	-.094448626	.1481183328	.998	-.550564962	.3616677107
	5	-.483983489*	.1343204158	.010	-.897610451	-.070356527
	6	-.353073056	.1744755881	.470	-.890354057	.1842079442
	7	-.684487438*	.1699033801	.002	-1.20768876	-.161286118
	8	-.228234895	.1744755881	.894	-.765515896	.3090461055
	8	.1282925301	.1699033801	.995	-.394908790	.6514938504
2	3	-.433793718	.1591046119	.124	-.923741257	.0561538213
	4	.0338439044	.1664706347	1.000	-.478786603	.5464744114
	5	-.355690959	.1543224087	.299	-.830912158	.1195302398
	6	-.224780526	.1903028181	.936	-.810799978	.3612389256
	7	-.556194908	.1861198278	.064	-1.12933324	.0169434228
	8	-.099942365	.1903028181	1.000	-.685961817	.4860770869
	8	.562086248*	.1397885754	.002	.1316206084	.9925518877
	8	.4337937179	.1591046119	.124	-.056153821	.9237412572
3	4	.467637622*	.1355955732	.017	.0500839347	.8851913099
	5	.0781027589	.1203706486	.998	-.292567220	.4487727376
	6	.2090131916	.1639781992	.907	-.295942097	.7139684800
	7	-.122401190	.1591046119	.994	-.612348729	.3675463495
	8	.3338513530	.1639781992	.462	-.171103935	.8388066414
	8	.0944486257	.1481183328	.998	-.361667711	.5505649622
	8	-.033843904	.1664706347	1.000	-.546474411	.4787866026
	8	-.467637622*	.1355955732	.017	-.885191310	-.050083935
4	5	-.389534863	.1299510976	.062	-.789706925	.0106371978
	6	-.258624431	.1711345801	.800	-.785617114	.2683682531
	7	-.590038812*	.1664706347	.012	-1.10266932	-.077408305
	8	-.133786269	.1711345801	.994	-.660778953	.3932064144
	8	.483983489*	.1343204158	.010	.0703565274	.8976104509
	8	.3556909590	.1543224087	.299	-.119530240	.8309121578
	8	-.078102759	.1203706486	.998	-.448772738	.2925672198
	8	.3895348634	.1299510976	.062	-.010637198	.7897069247
5	6	.1309104327	.1593423299	.992	-.359769137	.6215900022
	7	-.200503949	.1543224087	.898	-.675725147	.2747172501
	8	.2557485941	.1593423299	.747	-.234930975	.7464281635
	8	.3530730564	.1744755881	.470	-.184207944	.8903540571
	8	.2247805263	.1903028181	.936	-.361238926	.8107999781
	8	-.209013192	.1639781992	.907	-.713968480	.2959420968
	8	.2586244307	.1711345801	.800	-.268368253	.7856171145
	8	-.130910433	.1593423299	.992	-.621590002	.3597691367
6	7	-.331414381	.1903028181	.660	-.917433833	.2546050704
	8	.1248381613	.1943958201	.998	-.473785301	.7234616240
	8	.684487438*	.1699033801	.002	.1612861175	1.207688758
	8	.5561949077	.1861198278	.064	-.016943423	1.129333238
	8	.1224011898	.1591046119	.994	-.367546349	.6123487290
	8	.590038812*	.1664706347	.012	.0774083051	1.102669319
	8	.2005039487	.1543224087	.898	-.274717250	.6757251475
	8	.3314143814	.1903028181	.660	-.254605070	.9174338333
7	8	.4562525427	.1903028181	.251	-.129766909	1.042271995
	8	.2282348951	.1744755881	.894	-.309046106	.7655158957
	8	.0999423650	.1903028181	1.000	-.486077087	.6859618168
	8	-.333851353	.1639781992	.462	-.838806641	.1711039355
	8	.1337862694	.1711345801	.994	-.393206414	.6607789532
	8	-.255748594	.1593423299	.747	-.746428163	.2349309754
	8	-.124838161	.1943958201	.998	-.723461624	.4737853013
	8	-.456252543	.1903028181	.251	-1.04227199	.1297669091

*. The mean difference is significant at the 0.05 level.

Log Concentration

Tukey HSD^{a,b}

Site	N	Subset for alpha = 0.05		
		1	2	3
1	18	1.264425651		
4	20	1.358874276	1.358874276	
2	12	1.392718181	1.392718181	
8	11	1.492660546	1.492660546	1.492660546
6	11	1.617498707	1.617498707	1.617498707
5	32	1.748409140	1.748409140	1.748409140
3	26		1.826511899	1.826511899
7	12			1.948913088
Sig.		.074	.095	.113

Means for groups in homogeneous subsets are displayed.

- a. Uses Harmonic Mean Sample Size = 15.274.
- b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Descriptives

Log Concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	28	2.185488748	.3820288505	.0721966666	2.037353425	2.333624072	1.672097858	2.988558957
2	11	2.336766240	.2931557046	.0883897707	2.139821558	2.533710922	1.740362689	2.683047038
3	22	2.303096159	.2111875031	.0450253269	2.209460866	2.396731453	1.826074803	2.624282096
4	34	2.173637283	.3191690727	.0547370444	2.062273929	2.285000637	1.732393760	3.277379975
5	20	2.142206850	.2390263439	.0534479153	2.030339077	2.254074622	1.707570176	2.689308859
6	23	2.264955784	.2496417807	.0520539096	2.157002582	2.372908985	1.954242509	3.165541077
7	19	2.289526917	.2213723837	.0507863079	2.182828844	2.396224991	1.875061263	2.622214023
8	14	2.183277994	.3375444265	.0902125426	1.988385644	2.378170343	1.845098040	2.900367129
Total	171	2.224999533	.2930607907	.0224109188	2.180760005	2.269239061	1.672097858	3.277379975

Tests of Homogeneity of Variances

		Levene Statistic	df1	df2	Sig.
Log Concentration	Based on Mean	2.881	7	163	.007
	Based on Median	2.527	7	163	.017
	Based on Median and with adjusted df	2.527	7	147.466	.018
	Based on trimmed mean	2.795	7	163	.009

ANOVA

Log Concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.682	7	.097	1.142	.340
Within Groups	13.918	163	.085		
Total	14.600	170			

Robust Tests of Equality of Means

Log Concentration

	Statistic ^a	df1	df2	Sig.
Welch	1.356	7	59.677	.241
Brown-Forsythe	1.186	7	123.329	.316

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: Log Concentration

Tukey HSD

(I) Site	(J) Site	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.151277492	.1039807833	.830	-.470572894	.1680179107
	3	-.117607411	.0832512543	.850	-.373248327	.1380335054
	4	.0118514651	.0745716084	1.000	-.217136728	.2408396582
	5	.0432818985	.0855505380	1.000	-.219419464	.3059832608
	6	-.079467035	.0822315155	.978	-.331976624	.1730425533
	7	-.104038169	.0868538856	.932	-.370741741	.1626654034
	8	.0022107546	.0956484092	1.000	-.291498297	.2959198065
	2	1	.1512774916	.1039807833	.830	-.168017911
3		.0336700806	.1079059584	1.000	-.297678418	.3650185789
4		.1631289567	.1013599985	.744	-.148118761	.4743766743
5		.1945593901	.1096896488	.639	-.142266314	.5313850941
6		.0718104564	.1071211774	.998	-.257128203	.4007491155
7		.0472393229	.1107091774	1.000	-.292717063	.3871957091
8		.1534882462	.1177350530	.896	-.208042605	.5150190973
3		1	.1176074110	.0832512543	.850	-.138033505
	2	-.033670081	.1079059584	1.000	-.365018579	.2976784177
	4	.1294588761	.0799538451	.738	-.116056635	.3749743868
	5	.1608893095	.0902806020	.633	-.116336734	.4381153529
	6	.0381403758	.0871419227	1.000	-.229447676	.3057284280
	7	.0135692423	.0915166106	1.000	-.267452232	.2945907162
	8	.1198181656	.0999015052	.931	-.186950934	.4265872653
	4	1	-.011851465	.0745716084	1.000	-.240839658
2		-.163128957	.1013599985	.744	-.474376674	.1481187610
3		-.129458876	.0799538451	.738	-.374974387	.1160566346
5		.0314304334	.0823452520	1.000	-.221428408	.2842892746
6		-.091318500	.0788914959	.943	-.333571839	.1509348384
7		-.115889634	.0836985271	.863	-.372903998	.1411247300
8		-.009640711	.0927925868	1.000	-.294580344	.2752989234
5		1	-.043281898	.0855505380	1.000	-.305983261
	2	-.194559390	.1096896488	.639	-.531385094	.1422663140
	3	-.160889310	.0902806020	.633	-.438115353	.1163367339
	4	-.031430433	.0823452520	1.000	-.284289275	.2214284078
	6	-.122748934	.0893411321	.868	-.397090132	.1515922649
	7	-.147320067	.0936131038	.765	-.434779275	.1401391410
	8	-.041071144	.1018255073	1.000	-.353748307	.2716060189
	6	1	.0794670352	.0822315155	.978	-.173042553
2		-.071810456	.1071211774	.998	-.400749115	.2571282026
3		-.038140376	.0871419227	1.000	-.305728428	.2294476763
4		.0913185003	.0788914959	.943	-.150934838	.3335718389
5		.1227489337	.0893411321	.868	-.151592265	.3970901322
7		-.024571134	.0905899597	1.000	-.302747126	.2536048591
8		.0816777898	.0990533267	.991	-.222486795	.3858423746
7		1	.1040381687	.0868538856	.932	-.162665403
	2	-.047239323	.1107091774	1.000	-.387195709	.2927170634
	3	-.013569242	.0915166106	1.000	-.294590716	.2674522316
	4	.1158896338	.0836985271	.863	-.141124730	.3729039976
	5	.1473200672	.0936131038	.765	-.140139141	.4347792753
	6	.0245711335	.0905899597	1.000	-.253604859	.3027471262
	8	.1062489233	.1029229656	.969	-.209798222	.4222960682
	8	1	-.002210755	.0956484092	1.000	-.295919807
2		-.153488246	.1177350530	.896	-.515019097	.2080426050
3		-.119818166	.0999015052	.931	-.426587265	.1869509341
4		.0096407105	.0927925868	1.000	-.275298923	.2945803445
5		.0410711439	.1018255073	1.000	-.271606019	.3537483067
6		-.081677790	.0990533267	.991	-.385842375	.2224867951
7		-.106248923	.1029229656	.969	-.422296068	.2097982216

Log Concentration

Tukey HSD^{a,b}

Site	N	Subset for alpha = 0.05 1
5	20	2.142206850
4	34	2.173637283
8	14	2.183277994
1	28	2.185488748
6	23	2.264955784
7	19	2.289526917
3	22	2.303096159
2	11	2.336766240
Sig.		.447

Means for groups in homogeneous subsets are displayed.

- a. Uses Harmonic Mean Sample Size = 19.092.
- b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Descriptives

Log Concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	18	1.884989178	.1530275097	.0360689299	1.808890387	1.961087968	1.690196080	2.230448921
2	12	1.974903872	.1311031253	.0378462123	1.891604920	2.058202823	1.681241237	2.133538908
3	26	2.139843659	.2317876491	.0454572979	2.046222602	2.233464717	1.903089987	2.838849091
4	20	1.803716458	.1436281674	.0321162346	1.736496406	1.870936509	1.602059991	2.176091259
5	32	2.071307731	.2520641149	.0445590612	1.980428926	2.162186535	1.662757832	2.613841822
6	11	1.842315660	.1839989891	.0554777826	1.718703457	1.965927862	1.623249290	2.155336037
7	12	2.026255362	.2141300847	.0618140310	1.890203597	2.162307127	1.681241237	2.456366033
8	11	1.916789645	.2418877007	.0729318859	1.754287276	2.079292013	1.633468456	2.505149978
Total	142	1.980887226	.2338901039	.0196276215	1.942084763	2.019689689	1.602059991	2.838849091

Tests of Homogeneity of Variances

		Levene Statistic	df1	df2	Sig.
Log Concentration	Based on Mean	1.710	7	134	.112
	Based on Median	1.376	7	134	.220
	Based on Median and with adjusted df	1.376	7	106.727	.223
	Based on trimmed mean	1.637	7	134	.130

ANOVA

Log Concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.993	7	.285	6.671	<.001
Within Groups	5.720	134	.043		
Total	7.713	141			

Robust Tests of Equality of Means

Log Concentration

	Statistic ^a	df1	df2	Sig.
Welch	7.155	7	47.068	<.001
Brown-Forsythe	7.270	7	97.909	<.001

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: Log Concentration

Tukey HSD

(I) Site	(J) Site	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.089914694	.0769973241	.940	-.327020640	.1471912519
	3	-.254854482*	.0633498064	.002	-.449934193	-.059774770
	4	.0812727201	.0671247109	.927	-.125431451	.2879768913
	5	-.186318553	.0608717295	.053	-.373767262	.0011301556
	6	.0426735182	.0790693710	.999	-.200813099	.2861601357
	7	-.141266184	.0769973241	.598	-.378372130	.0958397612
	8	-.031800467	.0790693710	1.000	-.275287085	.2116861505
	2	1	.0899146938	.0769973241	.940	-.147191252
3		-.164939788	.0721035059	.308	-.386975685	.0570961094
4		.1711874139	.0754416622	.318	-.061128019	.4035028467
5		-.096403859	.0699362927	.865	-.311766029	.1189583108
6		.1325882120	.0862420026	.786	-.132985843	.3981622672
7		-.051351491	.0843463425	.999	-.311088041	.2083850593
8		.0581142268	.0862420026	.998	-.207459828	.3236882820
3		1	.254854482*	.0633498064	.002	.0597747703
	2	.1649397879	.0721035059	.308	-.057096109	.3869756852
	4	.336127202*	.0614496091	<.001	.1468989676	.5253554360
	5	.0685359286	.0545499321	.913	-.099445406	.2365172628
	6	.297528000*	.0743121328	.003	.0686908457	.5263651540
	7	.1135882973	.0721035059	.764	-.108447600	.3356241946
	8	.2230540147	.0743121328	.062	-.005783139	.4518911689
	4	1	-.081272720	.0671247109	.927	-.287976891
2		-.171187414	.0754416622	.318	-.403502847	.0611280188
3		-.336127202*	.0614496091	<.001	-.525355436	-.146898968
5		-.267591273*	.0588916287	<.001	-.448942450	-.086240097
6		-.038599202	.0775552830	1.000	-.277423329	.2002249253
7		-.222538905	.0754416622	.071	-.454854337	.0097765282
8		-.113073187	.0775552830	.828	-.351897314	.1257509401
5		1	.1863185532	.0608717295	.053	-.001130156
	2	.0964038593	.0699362927	.865	-.118958311	.3117660295
	3	-.068535929	.0545499321	.913	-.236517263	.0994454056
	4	.267591273*	.0588916287	<.001	.0862400967	.4489424498
	6	.228992071*	.0722112356	.039	.0066244304	.4513597123
	7	.0450523687	.0699362927	.998	-.170309801	.2604145388
	8	.1545180862	.0722112356	.395	-.067849555	.3768857271
	6	1	-.042673518	.0790693710	.999	-.286160136
2		-.132588212	.0862420026	.786	-.398162267	.1329858432
3		-.297528000*	.0743121328	.003	-.526365154	-.068690846
4		.0385992019	.0775552830	1.000	-.200224925	.2774233291
5		-.228992071*	.0722112356	.039	-.451359712	-.006624430
7		-.183939703	.0862420026	.400	-.449513758	.0816343526
8		-.074473985	.0880968816	.990	-.345759964	.1968119935
7		1	.1412661845	.0769973241	.598	-.095839761
	2	.0513514906	.0843463425	.999	-.208385059	.3110880406
	3	-.113588297	.0721035059	.764	-.335624195	.1084476001
	4	.2225389046	.0754416622	.071	-.009776528	.4548543373
	5	-.045052369	.0699362927	.998	-.260414539	.1703098014
	6	.1839397026	.0862420026	.400	-.081634353	.4495137578
	8	.1094657175	.0862420026	.909	-.156108338	.3750397727
	8	1	.0318004670	.0790693710	1.000	-.211686151
2		-.058114227	.0862420026	.998	-.323688282	.2074598284
3		-.223054015	.0743121328	.062	-.451891169	.0057831394
4		.1130731871	.0775552830	.828	-.125750940	.3518973143
5		-.154518086	.0722112356	.395	-.376885727	.0678495548
6		.0744739852	.0880968816	.990	-.196811994	.3457599638
7		-.109465717	.0862420026	.909	-.375039773	.1561083378

*. The mean difference is significant at the 0.05 level.

Log Concentration

Tukey HSD^{a,b}

Site	N	Subset for alpha = 0.05		
		1	2	3
4	20	1.803716458		
6	11	1.842315660	1.842315660	
1	18	1.884989178	1.884989178	
8	11	1.916789645	1.916789645	1.916789645
2	12	1.974903872	1.974903872	1.974903872
7	12	2.026255362	2.026255362	2.026255362
5	32		2.071307731	2.071307731
3	26			2.139843659
Sig.		.066	.052	.065

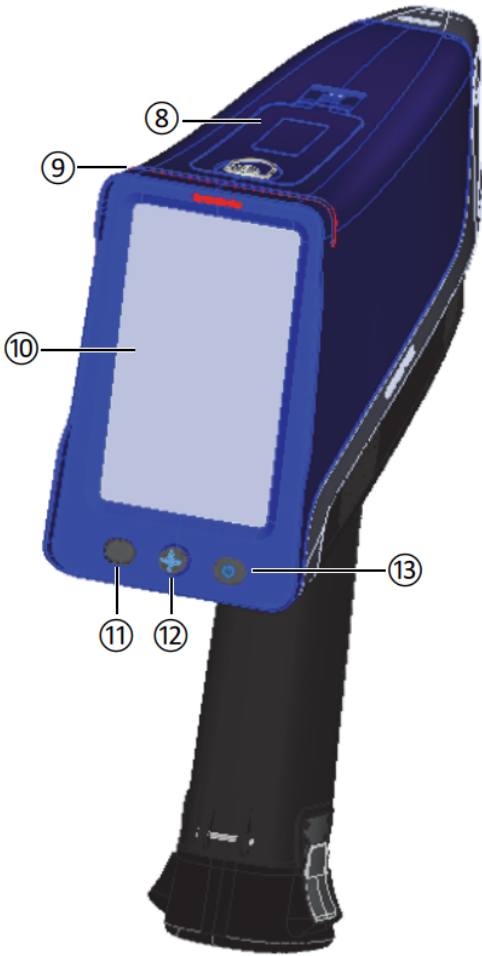
Means for groups in homogeneous subsets are displayed.


a. Uses Harmonic Mean Sample Size = 15.274.

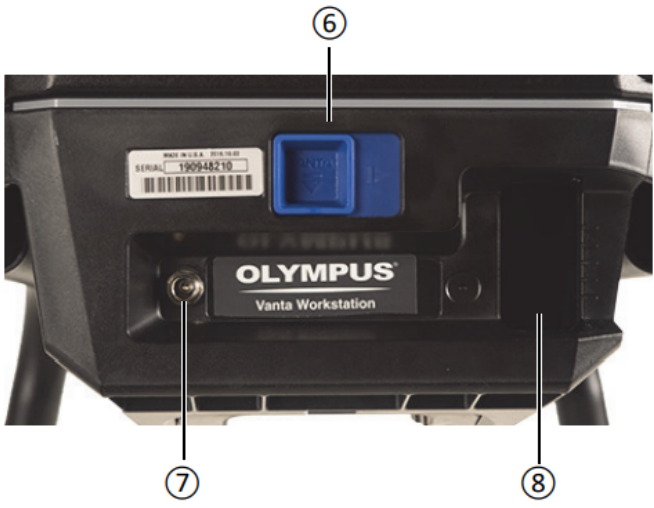
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Appendix D: Equipment components

Component key		Vanta XRF analyzer
1	Probe	
2	Measurement window	
3	Window plate	
4	Docking connector (not on the Vanta Element Series)	
5	Trigger	
6	Handle	
7	Battery	

Component key		Vanta XRF analyzer
8	Connector access cover	 <p>The diagram shows a handheld Vanta XRF analyzer. It has a blue upper housing and a black lower handle. A large rectangular touch screen is on the front. At the top, there is a connector access cover (8) and an X-ray warning indicator (9). Below the screen, there is a back button (11) and a joystick (12). At the bottom of the front panel, there is a power button (13). The handle has a trigger and a wrist strap.</p>
9	X-ray warning indicator	
10	User interface touch screen	
11	Back button	
12	Joystick	
13	Power button	

Component key		Vanta Work Station
1	Lid handle	
2	Chamber interior	
3	Stand locking lever	
4	Lid locking lever	
5	Stand	

Rear panel:		
6	Analyzer release lever	
7	DC power connector	
8	Battery receptacle	

Appendix E: Soil characteristics



SOIL REPORT

Environment Canterbury

Waimakariri_3b.1

Report generated: 18-Nov-2021 from <https://smap.landcareresearch.co.nz>

Waim_3b.1 (70% of the mapunit at location (1572959, 5181406). Confidence: Medium)

This information sheet describes the typical average properties of the specified soil to a depth of 1 metre, and should not be the primary source of data when making land use decisions on individual farms and paddocks. S-map correlates soils across New Zealand. Both the old soil name and the new correlated (soil family) name are listed below.

Capture of the base soil information in this region was funded by Environment Canterbury, Manaaki Whenua and MPI.

Soil Classification

<p>Soil Classification: Weathered Fluvial Recent Soils (RFW)</p> <p>Family Name: Waimakariri (Waim)</p> <p>Sibling Name: Waimakariri_3b.1 (Waim_3b.1)</p>	<p>Soil profile material Stoneless soil</p> <p>Profile texture loam</p> <p>Parent Material Stones/rocks not applicable</p>	<p>Depth class (diggability) Deep (> 1 m)</p> <p>Soil material hard sandstone rock</p>
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Origin
Alluvium

Soil Sibling Concept

This soil belongs to the Recent soil order of the New Zealand soil classification. Recent Soils are weakly developed, showing limited signs of soil-forming processes although a distinct topsoil is present, a B horizon is either absent or only weakly expressed. It is formed in alluvial sand silt or gravel deposited by running water, from hard sandstone parent material.

The topsoil typically has loam texture and is stoneless. The subsoil has dominantly loam textures, with gravel content of less than 3%. The plant rooting depth extends beyond 1m.

Generally the soil is well drained with very low vulnerability of water logging in non-irrigated conditions, and has high soil water holding capacity. Inherently these soils have a high structural vulnerability and a low N leaching potential, which should be accounted for when making land management decisions.



Allan Hewitt ©

Fluvial Recent

About this publication

- This information sheet describes the typical average properties of the specified soil.
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Waimakariri_4b.1

Report generated: 18-Nov-2021 from <https://smap.landcareresearch.co.nz>

Waim_4b.1 (30% of the mapunit at location (1572959, 5181406), Confidence: Medium)

This information sheet describes the typical average properties of the specified soil to a depth of 1 metre, and should not be the primary source of data when making land use decisions on individual farms and paddocks. S-map correlates soils across New Zealand. Both the old soil name and the new correlated (soil family) name are listed below.

Capture of the base soil information in this region was funded by Environment Canterbury, Manaaki Whenua and MPI.

Soil Classification

Soil Classification:

Weathered Fluvial Recent Soils (RFW)

Family Name:

Waimakariri (Waim)

Sibling Name:

Waimakariri_4b.1 (Waim_4b.1)

Soil profile material

Moderately deep soil

Depth class (diggability)

Moderately deep (45 - 90 cm)

Profile texture

loam

Parent Material

Stones/rocks
hard sandstone rock

Soil material

hard sandstone rock

Origin

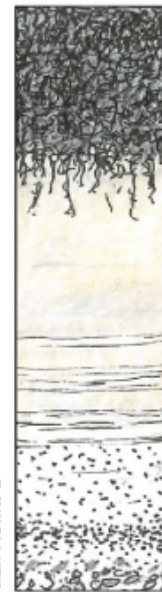
Alluvium

Soil Sibling Concept

This soil belongs to the Recent soil order of the New Zealand soil classification. Recent Soils are weakly developed, showing limited signs of soil-forming processes although a distinct topsoil is present, a B horizon is either absent or only weakly expressed. It is formed in alluvial sand silt or gravel deposited by running water, from hard sandstone parent material.

The topsoil typically has loam texture and is stoneless. The subsoil has dominantly loam textures, with a very gravelly layer that starts at or below 45 cm soil mineral depth and extends continuously to 100 cm. The plant rooting depth extends beyond 1m.

Generally the soil is well drained with very low vulnerability of water logging in non-irrigated conditions, and has high soil water holding capacity. Inherently these soils have a high structural vulnerability and a low N leaching potential, which should be accounted for when making land management decisions.



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Fluvial
Recent

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Kaiapoi_17a.1

Report generated: 18-Nov-2021 from <https://smap.landcareresearch.co.nz>

Kaia_17a.1 (60% of the mapunit at location (1572895, 5182016), Confidence: Medium)

This information sheet describes the typical average properties of the specified soil to a depth of 1 metre, and should not be the primary source of data when making land use decisions on individual farms and paddocks. S-map correlates soils across New Zealand. Both the old soil name and the new correlated (soil family) name are listed below.

Capture of the base soil information in this region was funded by Environment Canterbury, Manaaki Whenua and MPI.

Soil Classification

Soil Classification:

Mottled-weathered Fluvial Recent Soils (RFMW)

Family Name:

Kaiapoi (Kaia)

Sibling Name:

Kaiapoi_17a.1 (Kaia_17a.1)

Soil profile material

Stoneless soil

Profile texture

loam

Parent Material

Stones/rocks

not applicable

Depth class (diggability)

Deep (> 1 m)

Soil material

hard sandstone rock

Origin

Alluvium

Soil Sibling Concept

This soil belongs to the Recent soil order of the New Zealand soil classification. Recent Soils are weakly developed, showing limited signs of soil-forming processes although a distinct topsoil is present, a B horizon is either absent or only weakly expressed. It is formed in alluvial sand silt or gravel deposited by running water, from hard sandstone parent material.

The topsoil typically has loam texture and is stoneless. The subsoil has dominantly loam textures, with gravel content of less than 3%. The plant rooting depth extends beyond 1m.

Generally the soil is imperfectly drained with low vulnerability of water logging in non-irrigated conditions, and has high soil water holding capacity. Inherently these soils have a high structural vulnerability and a low N leaching potential, which should be accounted for when making land management decisions.



Fluvial Recent

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Kaiapoi_16a.1

Report generated: 18-Nov-2021 from <https://smap.landcareresearch.co.nz>

Kaia_16a.1 (40% of the mapunit at location (1572895, 5182016), Confidence: Medium)

This information sheet describes the typical average properties of the specified soil to a depth of 1 metre, and should not be the primary source of data when making land use decisions on individual farms and paddocks. S-map correlates soils across New Zealand. Both the old soil name and the new correlated (soil family) name are listed below.

Capture of the base soil information in this region was funded by Environment Canterbury, Manaaki Whenua and MPI.

Soil Classification

<p>Soil Classification: Mottled-weathered Fluvial Recent Soils (RFMW) Family Name: Kaiapoi (Kaia) Sibling Name: Kaiapoi_16a.1 (Kaia_16a.1)</p>	<p>Soil profile material Moderately deep soil</p> <p>Profile texture loam</p> <p>Parent Material Stones/rocks hard sandstone rock</p>	<p>Depth class (diggability) Moderately deep (45 - 90 cm)</p> <p>Soil material hard sandstone rock</p> <p>Origin Alluvium</p>
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Soil Sibling Concept

This soil belongs to the Recent soil order of the New Zealand soil classification. Recent Soils are weakly developed, showing limited signs of soil-forming processes although a distinct topsoil is present, a B horizon is either absent or only weakly expressed. It is formed in alluvial sand silt or gravel deposited by running water, from hard sandstone parent material.

The topsoil typically has loam texture and is stoneless. The subsoil has dominantly loam textures, with a very gravelly layer that starts at or below 45 cm soil mineral depth and extends continuously to 100 cm. The plant rooting depth extends beyond 1m.

Generally the soil is imperfectly drained with low vulnerability of water logging in non-irrigated conditions, and has high soil water holding capacity. Inherently these soils have a high structural vulnerability and a low N leaching potential, which should be accounted for when making land management decisions.



Fluvial
Recent

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Appendix F: Calibration data

Element	2710a**	XRF %	XRF	Errors	Difference	% Difference	% of Certified Value
	Montana I Soil	10s Beams	10s Beams	1 Standard Deviation			
Aluminium (Al)	5.95%	5.96%	59551	1161	-51	0.09%	100.09%
Antimony (Sb)	52.5	0.00%	45	8	7.5	14.29%	114.29%
Arsenic (As)	0.15%	0.13%	1332	73	208	13.51%	113.51%
Barium (Ba)	792	0.06%	610	30	182	22.98%	122.98%
Cadmium (Cd)	12.3	0.00%	25	7	-12.7	-103.25%	-3.25%
Calcium (Ca)	0.96%	0.70%	6970	92	2670	27.70%	127.70%
Copper (Cu)	0.34%	0.33%	3276	104	144	4.21%	104.21%
Iron (Fe)	4.32%	4.04%	40402	613	2798	6.48%	106.48%
Lead (Pb)	0.55%	0.54%	5419	97	101	1.83%	101.83%
Manganese (Mn)	0.21%	0.18%	1829	218	311	14.53%	114.53%
Phosphorus (P)	0.11%	0.09%	876	65	174	16.57%	116.57%
Potassium (K)	2.17%	2.11%	21063	234	637	2.94%	102.94%
Rubidium (Rb)	177	0.01%	109	7	68	38.42%	138.42%
Silicon (Si)	31.10%	25.59%	255917	2688	55083	17.71%	117.71%
Silver (Ag)	40	0.00%	39	4	1	2.50%	102.50%
Strontium (Sr)	255	0.03%	253	9	2	0.78%	100.78%
Zinc (Zn)	0.42%	0.43%	4263	100	-83	-1.99%	98.01%
Zirconium (Zr)	200	0.02%	204	8	-4	-2.00%	98.00%

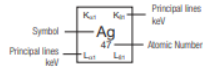
Appendix G: XRF handheld analyzer Limits of Detection



Your Vision, Our Future

Vanta™ Handheld XRF Analyzers

Limits of Detection



For alloy LODs, please see the separate alloy analysis LOD specifications.

Detection limits are a function of testing time, sample matrix, and presence of interfering elements. Detection limits are estimates based on 2 minutes test times and detection confidence of 3σ (99.7% confidence). Interference-free detection limits are intended as guidelines; please contact Olympus to discuss your specific application. Rare earth element (REE) LODs are calculated using L lines in the absence of any transition-metal elements.

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PHOTON ENERGIES, IN ELECTRON VOLTS, OF PRINCIPAL K- AND L-SHELL EMISSION LINES

Element	Symbol	Atomic #	K _{K₁}	K _{K₂}	L _{L₁}	L _{L₂}
Actinium	Ac	89	90.88	102.85	12.65	15.71
Aluminum	Al	13	1.49	1.56	0	0
Antimony	Sb	51	26.36	29.73	3.6	3.84
Argon	Ar	18	2.96	3.19	0	0
Arsenic	As	33	10.54	11.73	1.28	1.32
Astatine	At	85	81.52	92.3	11.43	13.88
Barium	Ba	56	32.19	36.38	4.47	4.83
Beryllium	Be	4	0.11	0	0	0
Bismuth	Bi	83	77.11	87.34	10.84	13.02
Boron	B	5	0.18	0	0	0
Bromine	Br	35	11.92	13.29	1.48	1.53
Cadmium	Cd	48	23.17	26.1	3.13	3.32
Calcium	Ca	20	3.69	4.01	0.34	0.34
Carbon	C	6	0.28	0	0	0
Cerium	Ce	58	34.72	39.26	4.84	5.26
Cesium	Cs	55	30.97	34.99	4.29	4.62
Chlorine	Cl	17	2.62	2.82	0	0
Chromium	Cr	24	5.41	5.95	0.57	0.58
Cobalt	Co	27	6.93	7.65	0.78	0.79
Copper	Cu	29	8.05	8.91	0.93	0.95
Dysprosium	Dy	66	46	52.12	6.5	7.25
Erbium	Er	68	49.13	55.68	6.95	7.81
Europium	Eu	63	41.54	47.04	5.85	6.46
Fluorine	F	9	0.68	0	0	0
Francium	Fr	87	86.1	97.47	12.03	14.77
Gadolinium	Gd	64	43	48.7	6.06	6.71
Gallium	Ga	31	9.25	10.26	1.1	1.12
Germanium	Ge	32	9.89	10.98	1.19	1.22
Gold	Au	79	68.8	77.98	9.71	11.44
Hafnium	Hf	72	55.79	63.23	7.9	9.02
Holmium	Ho	67	47.55	53.88	6.72	7.53
Indium	In	49	24.21	27.28	3.29	3.49
Iodine	I	53	28.61	32.29	3.94	4.22
Iridium	Ir	77	64.9	73.56	9.18	10.71
Iron	Fe	26	6.4	7.06	0.71	0.72
Krypton	Kr	36	12.65	14.11	1.59	1.64
Lanthanum	La	57	33.44	37.8	4.65	5.04
Lead	Pb	82	74.97	84.94	10.55	12.61
Lithium	Li	3	0.05	0	0	0
Lutetium	Lu	71	54.07	61.28	7.66	8.71
Magnesium	Mg	12	1.25	1.3	0	0
Manganese	Mn	25	5.9	6.49	0.64	0.65
Mercury	Hg	80	70.82	80.25	9.99	11.82
Molybdenum	Mo	42	17.48	19.61	2.29	2.39
Neodymium	Nd	60	37.36	42.27	5.23	5.72

Element	Symbol	Atomic #	K _{K₁}	K _{K₂}	L _{L₁}	L _{L₂}
Neon	Ne	10	0.85	0	0	0
Nickel	Ni	28	7.48	8.26	0.85	0.87
Niobium	Nb	41	16.62	18.62	2.17	2.26
Nitrogen	N	7	0.39	0	0	0
Osmium	Os	76	63	71.41	8.91	10.36
Oxygen	O	8	0.52	0	0	0
Palladium	Pd	46	21.18	23.82	2.84	2.99
Phosphorus	P	15	2.01	2.14	0	0
Platinum	Pt	78	66.83	75.75	9.44	11.07
Polonium	Po	84	79.29	89.8	11.13	13.45
Potassium	K	19	3.31	3.59	0	0
Praseodymium	Pr	59	36.03	40.75	5.03	5.49
Promethium	Pm	61	38.72	43.83	5.43	5.96
Protactinium	Pa	91	95.87	108.43	13.29	16.7
Radium	Ra	88	88.47	100.13	12.34	15.24
Radon	Rn	86	83.78	94.87	11.73	14.32
Rhenium	Re	75	61.14	69.31	8.65	10.01
Rhodium	Rh	45	20.22	22.72	2.7	2.83
Rubidium	Rb	37	13.4	14.96	1.69	1.75
Ruthenium	Ru	44	19.28	21.66	2.56	2.68
Samarium	Sm	62	40.12	45.41	5.64	6.21
Scandium	Sc	21	4.09	4.46	0.4	0.4
Selenium	Se	34	11.22	12.5	1.38	1.42
Silicon	Si	14	1.74	1.84	0	0
Silver	Ag	47	22.16	24.94	2.98	3.15
Sodium	Na	11	1.04	1.07	0	0
Strontium	Sr	38	14.17	15.84	1.81	1.87
Sulfur	S	16	2.31	2.46	0	0
Tantalum	Ta	73	57.53	65.22	8.15	9.34
Technetium	Tc	43	18.37	20.62	2.42	2.54
Tellurium	Te	52	27.47	31	3.77	4.03
Terbium	Tb	65	44.48	50.38	6.27	6.98
Thallium	Tl	81	72.87	82.58	10.27	12.21
Thorium	Th	90	93.35	105.61	12.97	16.2
Thulium	Tm	69	50.74	57.52	7.18	8.1
Tin	Sn	50	25.27	28.49	3.44	3.66
Titanium	Ti	22	4.51	4.93	0.45	0.46
Tungsten	W	74	59.32	67.24	8.4	9.67
Uranium	U	92	98.44	111.3	13.61	17.22
Vanadium	V	23	4.95	5.43	0.51	0.52
Xenon	Xe	54	29.78	33.62	4.11	4.42
Ytterbium	Yb	70	52.39	59.37	7.42	8.4
Yttrium	Y	39	14.96	16.74	1.92	2
Zinc	Zn	30	8.64	9.57	1.01	1.03
Zirconium	Zr	40	15.78	17.67	2.04	2.12

Appendix H: Table of significance

Degrees of Freedom	Probability, p		
	0.05	0.01	0.001
1	0.997	1.000	1.000
2	0.950	0.990	0.999
3	0.878	0.959	0.991
4	0.811	0.917	0.974
5	0.755	0.875	0.951
6	0.707	0.834	0.925
7	0.666	0.798	0.898
8	0.632	0.765	0.872
9	0.602	0.735	0.847
10	0.576	0.708	0.823
11	0.553	0.684	0.801
12	0.532	0.661	0.780
13	0.514	0.641	0.760
14	0.497	0.623	0.742
15	0.482	0.606	0.725
16	0.468	0.590	0.708
17	0.456	0.575	0.693
18	0.444	0.561	0.679
19	0.433	0.549	0.665
20	0.423	0.457	0.652
25	0.381	0.487	0.597
30	0.349	0.449	0.554
35	0.325	0.418	0.519
40	0.304	0.393	0.490
45	0.288	0.372	0.465
50	0.273	0.354	0.443
60	0.250	0.325	0.408
70	0.232	0.302	0.380
80	0.217	0.283	0.357
90	0.205	0.267	0.338
100	0.195	0.254	0.321

$p > 0.05$ NS (not significant), $0.05 < p < 0.01$ S (significant), $0.01 < p < 0.001$ S* (highly significant), $p < 0.001$ S** (very highly significant).

Appendix I: Canterbury soil background concentrations

	Soil Group	No. Samples	B	Mn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Regional Data	BGC/BGL	4	4 - 20	629 - 1780	1.13 - 5.1	0.06 - 0.2	4.6 - 22.5 (110.1)	10 - 27.3 (48.9)	0.02 - 0.04	4.5 - 20.7 (158.6)	3.63 - 17.2	50 - 116
	Gley	6	2 - 8	135 - 758	0.9 - 8.7	0.03 - 0.24	6.4 - 16.8	2.1 - 15.5	0.02 - 0.06	2.9 - 13.4	7.72 - 17.8	18.8 - 65.6
	Intergrade	8	4 - 6	255 - 573	1.6 - 6.1	0.04 - 0.12	9.8 - 24.5	6.2 - 15.2	0.03 - 0.6 (0.12)	7.3 - 15.3	8.25 - 27.5 (133)	35.2 - 69.8 (134)
	Organic	3	5 - 7	66 - 114	2.2 - 2.9	0.28 - 0.34	5.8 - 13.8	6.8 - 18.4	0.08 - 0.1 (0.35)	5.8 - 7.2	9.37 - 25.9	12.1 - 53.5
	Recent	13	2 - 8 (29)	244 - 536 (1210)	2.7 - 8.4 (11.5)	0.03 - 0.07 (0.18)	8.3 - 20	6.6 - 18.8	0.01 - 0.09	8.3 - 19	8.48 - 21.4	37.6 - 84
	Rendzina	4	16 - 41	157 - 372	2.1 - 36.9	0.12 - 0.31	16.9 - 26.4	6.2 - 9.5	0.03 - 0.05	10.4 - 15.9	4.27 - 16.7	39.7 - 57.4
	Saline gley recent	4	6 - 19	82 - 251	2.2 - 6.8	0.01 - 0.09	6.6 - 13.2	3.3 - 12.2	0.03 - 0.07	5.4 - 9.6	6.21 - 44.4	14.7 - 47.3
	Yellow brown sand	4	2 - 9	148 - 1110	2.6 - 3.4	0.01 - 0.06	6.9 - 11	2.3 - 7.1	0.02 - 0.04	4.6 - 8.7	5.89 - 31.9	20.3 - 50.7
	Yellow brown stony	10	2 - 6	195 - 651	2.3 - 4.6	0.02 - 0.1	8.9 - 18.3	3 - 10.2	0.01 - 0.07	5.2 - 11.9	7.23 - 18.7	36.9 - 62.8
	Yellow grey earth	15	2 - 5	196 - 877	2.1 - 4.6	0.03 - 0.11 (0.18)	8.2 - 15.6	4 - 11.5	0.01 - 0.1	5.2 - 11.6	8.89 - 18.8	28.8 - 62.4
Yellow Brown Earth	2	5 - 5	435 - 489	2.9 - 4.2	0.03 - 0.04	15.5 - 18.9	9.5 - 10.1	0.07 - 0.09	11 - 16.1	11.1 - 11.9	42.3 - 43.1	
Urban Data	Gley	5	3 - 6	200 - 602	3.5 - 9.6	0.07 - 0.15	11 - 17.5	7 - 12.9	0.05 - 0.1	8.7 - 15.6	20.3 - 34.9	41.7 - 90.3
	Organic	2	4 - 7	142 - 310	5.7 - 13.2	0.09 - 0.11	11.2 - 12.4	7.5 - 13.3	0.09 - 0.18	6.3 - 11.7	15.3 - 40.9	26.9 - 63.3
	Recent	4	3 - 5	310 - 529	4.1 - 6.1	0.073 - 0.14	10.2 - 15.8	6 - 10.4	0.04 - 0.08	8.2 - 13.56	23.3 - 57.3	55.5 - 91.7
	Saline Gley Recent	2	9 - 20	164 - 355	3.3 - 7.5	0.01 - 0.06	9.1 - 22.1	3.3 - 10.2	0.03 - 0.08	6.9 - 14.1	11 - 31.2	26.6 - 87.7
	Yellow Brown Sand	3	2 - 5	193 - 336	4.9 - 5.6	0.03 - 0.08	8.2 - 15.4	3.1 - 8.8	0.02 - 0.07	7 - 11.7	9.48 - 22.3	33.2 - 54.9

NB Remaining outlier values are indicated by brackets