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Arsenic contamination of soil and groundwater from the leaching of CCA treated fence posts in several Hawke’s Bay vineyards

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Geography.

University of Otago, Dunedin, New Zealand.

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Abstract

Throughout the rapidly expanding area of vineyards in New Zealand, great numbers of wooden posts, treated with copper, chromium and arsenic (CCA) are used to support the vine canopy. Studies have shown that when CCA-treated wood remains in the ground, varying amounts of copper, chromium and arsenic leach into the surrounding soil. Arsenic is particularly toxic, so any contamination of soil or groundwater is of concern. Therefore, it is important to determine the extent of arsenic accumulating in soil surrounding treated posts and the mobility of arsenic in soil, to investigate the potential for groundwater contamination.

Soil samples were taken at several depths and distances from 35 post locations throughout several vineyards in the Hawke’s Bay region to determine the extent and mobility of arsenic in soil. At each vineyard and several control sites, groundwater samples were taken from existing wells to examine any groundwater contamination.

Analyses of soil samples showed all thirty five post sites to have elevated concentrations of arsenic. Arsenic was found to accumulate in greater concentrations in soils with a higher organic matter and clay content, and a lower sand content, while arsenic was found to be more mobile in the soil profile, both vertically and laterally, in the more acidic soils that contained higher sand contents and lower organic matter contents. No groundwater samples contained elevated levels of arsenic.

Results suggest that arsenic accumulation in vineyard soils is widespread, and in the right conditions can be mobile in the soil profile. While no groundwater samples contained elevated arsenic levels, it is not known how long it may take for arsenic to travel into groundwater so monitoring of groundwater quality is needed in the future. Mitigation measures such as using alternatives to CCA treated posts, and disposal methods for broken and unwanted posts, are required to reduce the possible impact on the environment.
Acknowledgements

Before you indulge into the fascinating area of arsenic contamination, soil properties, treated timber and vineyards, I would like to pay tribute to the many special people that have helped both directly and indirectly in the production of this thesis:

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1 Introduction

In the past decade the amount of land developed into vineyards in New Zealand has more than tripled from 6,610 hectares to 21,002 hectares (New Zealand Wine Institute, 2005). The increase in the amount of land used for viticulture reflects the exponential growth of viticulture in the two dominant New Zealand wine growing regions of Marlborough and Hawke’s Bay. In Hawke’s Bay alone there has been a four fold increase in land area being used for wine grape production. Future expansion is likely to continue because wines from the Hawkes Bay region are now receiving international acclaim for their premium quality and unique flavours.

The increase in vineyards in New Zealand has consequences for land and water management in these viticultural regions. Are current vineyard management practices having adverse effects on local environments? If so, how can we respond now? And for the future, what are the implications for alternative land uses of soil previously used as a vineyard? Are vineyards affecting the quality of local groundwater supplies?

The sustainability of vineyard soil can be adversely affected by a number of practices employed in viticulture. One such practice is the use of timber posts at a rate of 579 posts per hectare treated with a solution of copper-chromium-arsenic (CCA), to create a support for the vine canopy. Hawke’s Bay alone has an estimated 3 million posts over nearly 5,000 hectares of vineyards (New Zealand Wine Institute, 2005). The copper is used to control fungi and borers, arsenic to control insects and some copper resistant fungi, and chromium to fix the copper and arsenic to the wood (Read, 2003). Given a density of 579 posts per hectare, and an average post weight of 12 kg, each hectare of vineyard has a copper, chromium and arsenic loading of 12, 21 and 17 kg, respectively (Robinson et al., 2005). Because arsenic is toxic, human exposure to arsenic through contact with soils and sediments is of concern, as is the potential for arsenic migration through soils to groundwater. The purpose of this study is to examine the extent of arsenic leaching in several Hawke’s Bay vineyards, and in particular to focus on the mobility of arsenic in the soil.
Arsenic is a relatively common, toxic element that is also a known carcinogen. It is found in a wide range of chemical forms throughout the environment and can be readily transformed by microbial action, changes in geochemical conditions, and other environmental processes (Melamed, 2005). While arsenic occurs naturally, anthropogenic arsenic contamination can also be significant, resulting from a variety of activities such as the storage of mining waste, use of certain pesticides, burning of fossil fuels, and the use of certain chemicals, in particular copper chromium arsenate (CCA) which is used in timber treatment. Arsenic, chromium and copper are known environmental toxins, and their presence in CCA treated wood raises several human safety and environmental concerns.

There is evidence from several studies that under certain conditions, CCA treatment leaches out of treated timber into the soil environment (Zagury et al., 2003, Robinson et al., 2005, Hingston et al., 2001, Chirenje et al., 2003, Clothier et al., 2006). Zagury et al. (2003) showed soil Cu, Cr and As concentrations adjacent to treated posts up to 1460, 287, and 410 mg/kg, respectively. After undertaking a general survey to determine the extent of CCA leaching from treated timber posts in vineyards in Marlborough, Robinson et al. (2005) found that some 25% of the samples exceeded 100 mg/kg As, the Australian National Environment Protection Council (ANEPC) guideline level for As in agricultural soil, and 10% exceeded 100 mg/kg Cr, the ANEPC limit for chromium. Arsenic is particularly toxic and is also considered the most mobile of the CCA-cocktail, which creates the issue of potential groundwater contamination. Clothier et al. (2006) recognised this by beginning to assess the risk that the pattern dynamics of CCA, in particular the most mobile and toxic arsenic, might lead to leaching into the underlying aquifers and degrade the groundwater in the Marlborough region. However, given the physical and chemical heterogeneity of soils, there may be significant variation in the risk to groundwater from arsenic contamination across the range of viticultural soils and climates.

To establish if there is a threat of arsenic contamination to groundwater, there first needs to be an understanding of the mobility of arsenic once leached into the soil. The mobility of arsenic in the environment has been of some concern because it is relatively more water soluble than copper and chromium and less likely to be adsorbed (Lebow, 1996). In addition there are also many factors that affect the
mobility of arsenic in the soil such as soil pH, organic matter content and base saturation (Lebow, 1996). It is known that it takes more than just high arsenic concentrations in the soil for groundwater to become contaminated. The conditions that favour arsenic dissolution (becoming dissolved in the water) depend on the circumstances. Macrae (2004) states there are generally three ways that arsenic can get in to water: where pH is high, arsenic may be released from surface binding sites that lose their positive charge; when organic carbon is present in groundwater it can feed bacteria that release arsenic; or finally, arsenic trapped in sulphide minerals can be released when the sulphide minerals are exposed to oxygen (MacRae, 2004).

For the purpose of this study, arsenic mobility is defined as the movement of arsenic in soil, both vertically down the profile and laterally through the soil layers. Slightly acidic soils, with high levels of sand, and little clay or organic matter, are believed to promote the mobility of arsenic in the soil, meaning arsenic is more likely to leach down through the soil profile. If there is sufficient leaching from above ground sources, this could raise the potential for groundwater contamination underneath arsenic contaminated soils.

Grapevines are dependent on a regular supply of water and nutrients to maintain their productivity. Many viticultural regions in New Zealand are located in areas that are characterised with warmer and drier weather, and contain free-draining soils with low water holding capacity and organic matter. Therefore, many of the wine producing regions of New Zealand are located on large aquifer systems that not only provide water for irrigation and frost protection, but are also a source for local domestic use and drinking water. In Hawkes Bay, New Zealand’s second largest wine growing area, vineyards on the Gimblett gravels area are situated on top of the Heretaunga Plains unconfined aquifer system. This is the region’s largest aquifer system and provides domestic water for a population of 143,000 and the large horticultural, agricultural and food processing industries (Green et al., 2004). Thus, it is vital for the region’s economic and environmental well-being that best management practices are adopted for water, fertilizer and agrichemical use in order to reduce the risk of contamination of this important regional water resource.
The Hastings District Plan (2003), under section 12.1 has documented regional concerns by creating the Heretaunga Plains Unconfined Aquifer Resource Management Unit. The objective of the unit is to ensure that the life-supporting capacity of the Heretaunga Plains Unconfined Aquifer Water Resource is not compromised by the effects of land use activities occurring above it. Policy number two (AQP2) of section 12.1 prohibits the use of substances (with particular regard to arsenic) whose effects have the potential to cause irrevocable damage to the Heretaunga Plains Unconfined Aquifer. Activities such as timber treatment mills use toxic substances (such as arsenic) in their processing. Accidental spillage and infiltration of these toxic substances (even in minute quantities) into the unconfined aquifer could have disastrous effects on the health and safety of the community who rely on the water resource for drinking, industrial, horticultural, or other uses.

Concerns of high arsenic levels in local groundwater supplies used by local residents in Rarangi, part of New Zealand's largest wine growing region, Marlborough, has meant that research has recently been, and is still currently being, undertaken to determine the extent and consequences of CCA leaching from treated vineyard posts (Robinson, et al., 2005, Greven et al., 2005, Clothier et al., 2006, Volgeler et al., 2005). Robinson et al. (2005) conducted a general survey at six different vineyard sites, determining the extent of leaching in different vineyards. Vogeler et al. (2005) defined the risk of CCA accumulation for the major soil groups in Marlborough and then used a model to simulate CCA concentrations for years to come. Currently a CCA leaching experiment is being undertaken by Greven et al. (2005) to determine the rate of CCA leaching from treated timber posts.

1.1 Research aim and objectives

The aim of this study is to evaluate both the amount of arsenic leaching into viticultural soils, and any subsequent mobility in the soil surrounding treated posts in the Hawkes Bay region, in order to determine whether there is a risk of arsenic contamination to the Heretaunga Plains Unconfined Aquifer.
Introduction

The specific objectives are:

1. To assess whether arsenic is accumulating in vineyard soils as a result of the leaching of treated timber posts.
2. If arsenic is present in the soil, determine if it is mobile through the soil profile.
3. Establish if there is a risk of arsenic contamination to the Heretaunga Plains Unconfined Aquifer System.

Accordingly, the research comprised three main stages: determination of arsenic concentration from soil surrounding some CCA treated posts in several Hawke’s Bay vineyards; a detailed analysis of soil samples taken from different distances and depths from the posts, to examine effects soil properties may have on levels and mobility of arsenic in the soil; and analysis of groundwater samples from the underlying aquifer.
2 Arsenic in the environment

This chapter considers the role of arsenic as a part of a chemical treatment for timber, and the use of this treated timber in New Zealand vineyards. Then the focus is specifically placed on arsenic leaching into vineyard soils, the behaviour of arsenic in the soil, the effects particular soil properties have on the mobility of soil arsenic and the consequences these properties may have on the potential for arsenic contamination of underlying groundwater and aquifers. This information is used to identify specific research objectives in relation to the investigation of arsenic levels in certain Hawke’s Bay vineyards.

2.1 Chromated copper arsenate timber treatment

Chromated copper arsenate (CCA) wood preservative is primarily used by the timber industry for the control of wood destroying termites, fungi and micro-organisms. The copper is used to control fungi and borers, arsenic to control insects and some copper resistant fungi, and chromium to fix the copper and arsenic to the wood (Read, 2003). The treatment process involves impregnating wood with the CCA preservative solution using pressurized treatment cylinders (Townsend et al., 2003). During the process, chemical reactions take place that act to bind the metal compounds to the wood. Wood preservation scientists refer to this process as “fixation,” a reaction dominated by the reduction of hexavalent chromium to trivalent chromium (Townsend et al., 2003). While the metals are “fixed” to the wood from a treatment efficacy standpoint, the metals do leach over time to the surrounding environment. Most CCA products are used outdoors, and when rainfall comes into contact with treated wood structures that are located above or in soil, some arsenic, chromium and copper will dissolve into the water and travel to the underlying or adjacent soil (Townsend et al., 2003). The leached metals may then
bind to the soil causing an increase in the soil metal concentrations. Although it is clear that large amounts of preservative do remain properly fixed in the wood after prolonged exposure, even small percentage losses may be environmentally significant, due to the high concentration in the timber, and the toxicity of the component (Hingston et al., 2001).

CCA preservatives are used extensively and are readily available in several commercial formulations. Working solutions of CCA preparations commonly consist of high concentrations of copper sulphate (CUSO₄), sodium dichromate (Na₂Cr₂O₇), and arsenic acid (H₃AsO₄), all of which are potentially highly toxic to biota. Up to 250 litres of CCA solution are applied to 1 m³ of wood, resulting in arsenic, chromium and copper concentration ranges of 1000 – 5000 mg per kilogram (Chirenje et al., 2003).

Timber treated with a CCA solution has an extended working life. A CCA treated fence post is expected to last 30-50 years in the ground compared to only a few years for untreated posts (Beder, 2003). The use of CCA treated wood extends from playground equipment, public utility poles, and general purpose decks to agricultural fences and viticultural trellis support posts.

### 2.2 Treated timber use in vineyards

Viticulture is one of New Zealand's fastest growing land uses, and also one that accounts for a large number of treated fence posts. CCA treated timber posts provide the foundations and support for grapevines throughout vineyards of New Zealand at an average rate of 579 posts per hectare. With over 21,000 hectares of producing vineyard area throughout New Zealand in 2005, there are well over 12 million treated posts located throughout the wine growing region, with the majority of posts put in over the past ten years (New Zealand Wine Institute, 2005). Given a density of 579 posts per hectare, and an average post weight of 12 kg, each hectare of vineyard has an approximate copper, chromium and arsenic loading of 12, 21 and 17 kg, respectively (Robinson et al., 2005).
These specialised grape growing areas of New Zealand, containing millions of CCA treated posts throughout their vineyards, make the viticultural soils of New Zealand particularly susceptible to arsenic contamination.

2.3 Post-to-soil leaching of arsenic

Most treated timber, especially in vineyards, is used in direct contact with the soil. It has been found that over a period of time, when CCA treated timber remains in the ground in contact with soil, varying amounts of the CCA constituents leach into the surrounding soil (Hingston et al., 2001; Townsend et al., 2005; Crawford et al., 2002; Stilwell et al., 2003; Chirenje et al., 2003; Gezer et al., 2004; Solo-Gabriele et al., 2003). While many studies measure all three of the CCA components leaching into the soil, the focus of this study is on arsenic because it typically poses a greater concern when encountered at elevated levels in the soil. Compared with chromium and copper, it is harmful at lower concentrations, and is also considered the most mobile of the three chemicals. For example, the generic residential soil cleanup target level (SCTL) for arsenic in Florida is 0.8 mg/kg, compared to 210 mg/kg and 110 mg/kg for chromium and copper, respectively (Townsend, et al., 2003).

Several studies have documented the leaching of CCA components. A report by Chirenje et al. (2003) determined the distribution of arsenic, chromium and copper in soils surrounding CCA treated structures such as decks, fences and poles by collecting both profile and lateral soil samples. The results showed an elevation of all three elements close to and under the structures, with mean arsenic concentrations as high as 23 mg/kg close to utility poles compared with less than 3 mg/kg at distances of about 1.5 m away. This is also supported by Solo-Gabriele et al (2003) who found that the soil below and around CCA-treated timber decks contained an average arsenic concentration of 28.5 mg/kg, well above average background soil arsenic concentrations of 1.5 mg/kg. Cooper and Ung (1997) reported soil arsenic concentrations near CCA treated utility poles at levels as high as 550 mg/kg.
The main impacts of leaching into soil are localised. Townsend et al. (2001) found that the highest concentrations of arsenic, chromium, and copper were located within five centimetres (laterally) of the CCA-treated timber, with the soil metal levels decreasing rapidly with distance. The highest median concentrations were found in the upper 20 cm of soil. Similar results were found by Gezer et al. (2004) when assessing the distribution of Cu, Cr and As in soils adjacent to CCA treated utility poles. Cu, Cr and As concentrations in soil samples in 0-5 cm depth were higher than soil samples taken from 30-40 cm depth (Gezer et al., 2004). Eleven months after the construction of a CCA treated boardwalk, Lebow et al. (2000) found arsenic concentrations in soil underneath the edge of the boardwalk ranging from 5 to 29 mg/kg in the upper 15 cm of soil, compared to background values ranging from 1 to 3 mg/kg. They also observed decreasing arsenic concentrations in deeper soils and soils at distances greater than 15 cm from the structure. Stilwell and Graetz (2001) determined that arsenic concentrations in soil immediately adjacent to highway sound barriers ranged from 7 to 228 mg/kg, with concentrations dropping dramatically at 80 cm from the barrier.

Recently research has been undertaken in Marlborough, New Zealand's largest wine growing region, after Bourne (2003) expressed concern over the potential for arsenic contamination of local soils and groundwater supplies caused by CCA leaching from vineyard posts across the nearly 10,000 hectares of vineyards. After conducting a general survey to determine the extent of CCA leaching from treated vineyard posts, Robinson et al. (2005) established that soils surrounding the posts had significantly higher CCA concentrations than control soils, and some 25% of the samples exceeded 100 mg/kg, the Australian National Environment Protection Council (ANEPC) guideline level for arsenic in agricultural soil. The initial research by Greven et al. (2005) on a variety of soils in Marlborough and with a range of vineyard post ages, showed that leaching from CCA treated posts does occur, with the amount of leaching correlated to the type of soil and post age. Only the Rarangi gravels were found to pose a real risk due to the stony soils having a low absorption capacity and low water content because they are extremely free draining. It is these factors that may cause the arsenic to leach down through the soil profile at high concentrations (Greven et al., 2005).
As this example shows, one of the major concerns with arsenic leaching from treated fence posts into surrounding soils is the potential risk of it moving down the soil profile and making its way into groundwater and local aquifer systems. However, the ability of arsenic to contaminate groundwater is dependent upon the mobility of the arsenic in the soil concerned. Therefore, it is important to understand the behaviour of arsenic in soil and the effects different soil properties have on soil arsenic mobility to determine if there is any potential for underlying groundwater contamination.

2.4 Arsenic in the soil

The mobility of arsenic in the environment has been of some concern because it is relatively more water soluble than copper or chromium and is less likely to be adsorbed by soil constituents. Studies have also shown that once in the soil, soil composition as well as soil pH, organic matter content, and the presence of other metals and microorganisms may all affect the leaching and subsequent mobility of arsenic.

Arsenic is often described as a metalloid element, but for the purposes of describing its chemical behaviour in soil it can be thought of as a non metal, forming covalent compounds or being found in anionic species, rather than the cationic forms of chromium and copper (Alloway, 1995). For example, arsenic is known to form coordination bonds with iron and aluminium oxides in the soil, which gives it increased mobility (Chirenje et al., 2003). Soil arsenic is found mainly in two different forms according to their valence states, with associated degrees of toxicity and mobility (Table 2.1). Determining the speciation of arsenic is therefore also important when considering the potential for arsenic groundwater contamination.

Table 2.1: Different forms and properties of soil arsenic

<table>
<thead>
<tr>
<th>Form</th>
<th>Valence State</th>
<th>Common Name</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trivalent</td>
<td>As III (3+)</td>
<td>Arsenite (AsO\textsubscript{3}\textsuperscript{3-})</td>
<td>More soluble, available, and toxic</td>
</tr>
<tr>
<td>Pentavalent</td>
<td>As V (5+)</td>
<td>Arsenate (AsO\textsubscript{4}\textsuperscript{3-})</td>
<td>Less soluble, available, and toxic</td>
</tr>
</tbody>
</table>
2.4.1 Speciation

Arsenic is found throughout the environment in a wide array of chemical species that vary in toxicity and mobility. These species can be readily transformed by biological activity, or changes in redox potential or pH (Melamed, 2005). This creates the possibility that a variety of unstable arsenic species can be transformed following subtle changes in the environment.

Arsenic in soil can occur in its reduced As (III) oxidation state as trivalent arsenic (arsenite), which is more soluble, available, and more toxic than the common oxidised As (V) pentavalent form, commonly as arsenate. It has also been found that reducing environments such as saturated, anaerobic soils, or poorly oxygenated waters may favour the formation of more toxic trivalent arsenic species (Lebow, 2005). Generally, in aerobic soil environments, the As (V) ion is present, while in waterlogged soils the reduced As (III) form comprises a greater proportion of the total soluble arsenic content (Carey et al., 1996). Recent research shows that the predominant species of arsenic in CCA treated wood is chromium arsenate, or pentavalent arsenic (Read, 2003). The total arsenic content will be measured in this study, with the assumption that the majority of arsenic is in the arsenate form.

Kimber et al. (2002) reported that arsenic speciation in groundwater samples taken near a contaminated cattle dip site revealed As (V) as the dominant species, with As (III) only found in detectable quantities at one of the sites. However, the speciation of arsenic may be significantly affected by the presence of micro-organisms that can convert the arsenic to volatile methylated forms of arsenic gas (Lebow, 2005). For this study, total dissolved arsenic will be measured, again assuming that the dominant species is As (V).
2.4.2 Toxicity of soil arsenic

In soil, arsenic is the most bio-available of the three CCA elements, but unfortunately it is also the most toxic to humans (Read, 2003). Nonetheless, Belluck et al. (2003) reported that to date, nationally, there have been no cases of morbidity or mortality from exposure to either anthropogenic or natural elevated soil arsenic levels. It is, however, a concern in groundwaters worldwide. Since soils are more complex and heterogeneous than bodies of water, exposure effects are much more difficult to predict. In addition, the soil component is extremely difficult to distinguish from other components such as the soil atmosphere or soil pore water.

The chemical reactions in soil depend on the soil types and physical and chemical characteristics. Toxicity and associated mobility of arsenic in soil is largely determined by different soil characteristics such as content of clay, sand and silt (texture), organic matter, soil pH, oxides of Al, Mn, and Fe, and soil redox potential (Gezer et al., 2004). Soil constituents chemically react with arsenic in a number of ways including specific and non specific adsorption, precipitation, cation exchange, and organic complexation (Gezer et al., 2004). Therefore, the arsenic compounds are susceptible to being affected in the soil by different types of reactions that can increase or decrease their element toxicity. These are discussed further in section 2.5.

2.4.3 Bioavailability

Another important key to understanding the environmental risk from arsenic is bioavailability, defined as the measure of the amount of arsenic that can be adsorbed by a living organism (Melamed, 2005). The bioavailability or phytotoxicity of arsenic is also very dependent on the characteristics of the soil in which it exists. If the soil is very high in organic matter, then it has the ability to sorb additional arsenic which is, consequently, less harmful to plant life (Carey et al., 1996). However, if the soil is sandy, the arsenic
will not be sorbed by the soil and may be more readily available to plants, potentially causing the phytotoxicity to be higher (Carey et al., 1996). Previous studies involving the Marlborough wine growing soils have shown that plant uptake of CCA, and in particular arsenic, is low (Robinson et al., 2004).

2.5 Movement in the soil

Understanding the movement of arsenic in soil is important in determining the potential for groundwater contamination. Arsenic has often been shown to be more mobile in soil than the other CCA constituents of copper and chromium. Research by Zagury et al. (2003) showed that copper and chromium concentrations approached background levels 50 mm away radially from treated posts, whereas in the same study arsenic had been found 500 mm out from posts and to a depth of 1 m down the profile. Because of arsenic’s chemical properties, its movement in the soil seems to be largely controlled by the conditions of the soil, especially soil pH, clay content, organic matter and the presence of metals such as iron and aluminium.

Unlike most trace metals, arsenic appears to move down the soil profile and is not immobilised at the soil surface or in the cultivated layers (Morrison, 1999). This was confirmed by Merry et al. (1983) who found that the arsenic content of an arsenic-treated soil increased in the subsoil and decreased in the cultivated layer over four seasons. One possible mechanism for this behaviour was that arsenic may be leached from the profile in low pH, acidic, sandy soils or retained at greater depths on suitable adsorbing surfaces. This is supported by a statement from Lebow (2005) that generally arsenic is least mobile in organic soils, slightly more mobile in clay soils, and most mobile in sandy soils. Evidence also shows that micro-organisms may affect the mobility and fate of arsenic when it enters the environment by transforming the relatively immobile forms of arsenic into volatile alkyl arsines in the form of gas, which escape into the atmosphere (Merry et al., 1983).
2.5.1 Physical characteristics of the soil

Particle size characteristics play a major role in the number of heavy metal ions that can be sorbed and held by the soil. Fine clay particles are usually associated with the retention of heavy metals in soil, while the coarser sand particles are associated with promoting the mobility of heavy metals. The retention of heavy metals in soil is influenced largely through the ability of clay particles to express negative charges and thereby to increase the cation exchange capacity (CEC) of the soil. Townsend et al. (2000) showed that heavy metal concentrations increased with clay content in the soil, which was explained by the clay particle's ability to increase the CEC of the soil, creating more exchange sites and, therefore, greater potential for heavy metal ions to be sorbed by the soil.

In contrast to most heavy metals, arsenic is generally found in soil solution in anionic form, so cation exchange processes will not be significant. However, although most soils carry a net negative charge, reflecting the dominance of silicate clays, there will usually be individual sites on other colloid surfaces which are positively charged, especially in those soils which contain significant quantities of Fe and Al oxides and short-range order silicates such as allophone (McLaren and Cameron, 1996). These positively charged sites attract anions, such as arsenite and arsenate, through anion exchange processes, although these occur at lower levels in comparison to CEC processes.

Soils collected in a study by Chirenje et al. (2003) were very sandy, with very low levels of organic matter and clay. The lack of fine particles, especially in the topsoil, resulted in very low retention of arsenic; hence the cumulative effect of CCA leaching did not manifest itself in high arsenic concentrations in the surrounding soil. However, the mean arsenic concentration was still higher than those of the background soils, indicating leaching of arsenic from CCA treated poles was occurring. The low retention capacity of these soils was further demonstrated by the low concentration and the low variation between arsenic concentrations in the surface and subsurface samples in the profiles
taken around the poles. Elevated surface concentrations were only evident in the newer poles and the difference between arsenic concentrations in the surface and those in the lower depths seemed to disappear with the age of the poles as continued leaching moved the arsenic through the soil profile (Chirenje et al., 2003). Dagan et al. (2006) also found that arsenic was present throughout the depth of the sandy soil column ranging from 26.7 mg/kg in the top 5cm of the column down to 7.5 mg/kg at 35-40cm in depth, all well above background levels. Kimber et al. (2002) reported some vertical arsenic mobility in the soil at very sandy textured sites near some arsenic-contaminated cattle-dip locations. The vertical distribution of arsenic at the clay sites was restricted to the 0-1.5m layer, while the sandy sites were contaminated to a depth greater than 2.5-3m (figure 2.1).

Holland and Orsler's (1995) arsenic adsorption results generally agree with studies of contaminated soils, in which the highest levels of arsenic were retained in the soils with high levels of clay or organic matter. A Swedish study reported that the retention capacity of arsenic in fine sand was approximately 50 ppm; in clay soil, about 500 ppm; in an
organic marsh peat soil, about 5,000 ppm (Bergholm and Dryler, 1989). Other studies of movement of CCA constituents in soils with varying compositions support the view that, although the constituents are not highly mobile, significant movement of arsenic may occur in sandy soils (Crawford et al., 2002; Allinson et al., 2000; Gezer et al., 2004).

2.5.2 Organic matter

Colloidal soil organic matter has a major influence on the chemical properties of soils (Alloway, 1995), and in particular it plays an important role in the movement of heavy metals through the soil (Wilson, 2000). Organic matter is generally recognised to attract and adsorb most heavy metal particles. This was shown, for example, in a study by Holland and Orsler (1995) that evaluated the ability of various soil types to adsorb CCA components from a three percent solution. They found that a sandy, free draining soil adsorbed little, if any, arsenic, and sphagnum peat, containing 98 percent organic material, readily adsorbed arsenic. However, the typical organic matter content of cultivated soils is less than ten percent, and the organic matter content of soil is always highest in the surface horizons and decreases rapidly with depth, so organic matter may not play as strong a role in controlling the mobility of arsenic in cultivated viticultural soils as it does with other elements, such as copper. Alternatively, organic matter could act as a filter, removing arsenic at the surface layers of the soil, so less arsenic is directly released into the subsoil.

The strong attraction organic matter has for heavy metal cations is due to the ligands that form complex compounds with the metals (Morrison, 1999). However, arsenic may be an exception to this, because arsenic is mostly found as part of a covalent compound or in anionic form. Dagan et al. (2006) reported that the elevated mobility of arsenic and chromium compared to copper results from the fact that, in soil solutions, copper is the only cationic species of the three metals. As well as adsorbing to soil particles, copper forms strong complexes with soil organic matter. On the other hand, arsenic displays anionic sorption behaviour and requires the formation of coordination bonds with iron.
and aluminium oxides, which form bridges between oxyanions and soil organic matter (Dagan et al., 2006). In a study by O’Neil (1990) it was found that the organic-rich surface horizons contained very small amounts of arsenic compounds, while Chen and Randall (1998) also found that arsenic was leached through the soil layer in their simulation model without being significantly fixed by the soil’s humic substances. However, it was noted that this result could have been due to the short amount of time for sorption to occur and the large frequency and intensity of the simulated rainfall. The authors concluded that although a high organic content was generally associated with the capability to adsorb arsenic, other factors such as pH or inorganic constituents must play a role (Lebow, 2005).

2.5.3 Soil pH

The pH level is also a factor in preservative leaching and mobility, although in practice the effects of pH are difficult to separate from those of organic and inorganic constituents (Lebow, 2005). Arsenic is most often found as a contaminant in acidic soils because of the greater ability of such soils to absorb the metal (Wilson, 2000). When present in acidic soils, heavy metals generally become more soluble and consequently their mobility in the soil increases. Previous studies of the behaviour of arsenic in soil suggest that the mobility of CCA components, including arsenic, is a function of pH, with the lowest releases around pH 6.0 to 7.0 and increased mobility at lower pHs (Lebow, 2005). Wilson (2005) also found the maximum capacity for arsenic sorption to be around pH 5.0.

Gezer et al. (2004) looked at the influence of soil pH on the mobility of arsenic in the soil when assessing the distribution of Cu, Cr and As in soils adjacent to CCA-treated utility poles in cities in Turkey. It was established that As, Cu and Cr concentrations were much higher in soil samples taken from the city of Rize, than the other two cities sampled. This was explained by the fact that the soil in the city of Rize was more acidic than that of the other two cities, which might cause the metals to leach at a greater rate from the CCA treated posts into the soil (Gezer et al., 2004). On the other hand, Carey et al. (1996)
found arsenic sorption to be the least affected of the three CCA components by changes in soil pH, and that the maximum sorption of arsenic was found to be at around pH 6 – 7. The availability to plants of arsenic in soils is also affected by changes in pH (O’Neil, 1990). In general there is an increase in arsenic toxicity effects on plants as the soils become more acid, particularly at a pH below 5.0, when arsenic-binding species such as iron and aluminium oxy-compounds become more soluble (O’Neil, 1990).

2.5.4 Micro-organisms

Another factor that could affect the amount of arsenic in the soil after leaching is the presence of micro-organisms. Many types of micro-organisms are known to convert inorganic arsenic to other, more soluble species, although their ability to do this in the presence of high retention levels of copper and chromium has not been established (Lebow, 2005). Bauer and Blodau (2006) found that micro-organisms can oxidise arsenite for detoxification or reduce arsenate to the more soluble and toxic arsenite during respiration. Although the significance of these microbial activities in preservative leaching is unknown, evidence shows that micro-organisms affect the mobility and fate of arsenic when it enters the environment (Lebow, 2005).

2.6 Migration of soil arsenic to groundwater

There are two phases in the contamination of groundwater by surface pollutants (Thorpe et al., 1982). The first stage is movement of a contaminant through the vadose (unsaturated) zone. Understanding concentrations of a contaminant such as arsenic throughout different levels of the vadose zone is important, first, in determining whether arsenic released from the surface can reach the unconfined aquifer, and secondly, to see what changes in either concentration or composition of arsenic occur due to adsorption or chemical transformation. The second phase in the process of groundwater pollution after percolation through the vadose zone is dispersion and transport within the saturated zone.
Assuming that a pollutant has reached the water table it is of vital importance to know the direction and velocity of flow, and the rates of dispersion and adsorption, and to understand the process of decay or transformation which may reduce the pollutant to a harmless level (Thorpe *et al.*, 1982).

Earlier it was mentioned that the form of arsenic in soil affects both its toxicity and its mobility. This is also true for arsenic present in groundwater. Organic forms of arsenic are rarely found in groundwater; instead it is largely the inorganic arsenite (III) ion in the form of neutrally charged arsenious acid, or inorganic arsenate (V) in the form of arsenic acid minus one or two protons, so with a charge of -1 or -2 (MacRae, 2004). The charge on the arsenate (V) allows it to bind to sites on the surface of soil particles, if they are positive, removing it from the water. As the pH is raised, the compounds will tend to become more and more negatively charged as the arsenic and arsenious acid lose H+ groups (MacRae, 2004). So the charge of these arsenic compounds depends on the pH. MacRae (2004) goes on to explain, however, that as the pH rises and the water becomes more basic, OH- groups from the water also associate with the adsorption or ion exchange sites on the soil, neutralising them. Once they have been neutralised, they are not available to the arsenic compounds, so instead of decreasing in concentration, the arsenic concentration in high pH water can actually increase. The general relationship between pH and arsenic concentration in groundwater is that as the pH increases, the arsenic concentration also tends to rise (MacRae, 2004).

Recently in Marlborough, elevated arsenic levels were reported to have been found in a shallow aquifer, and the initial blame was placed on the abundance of vineyard posts in the area (NZ Grape Grower, 2004). Further investigation by Robinson (2003) has lead to the discovery of high arsenic levels in a large number of domestic water supply wells at Rarangi, a popular area for viticulture in Marlborough. Results were compared to the human health guideline for arsenic in the Drinking Water Standards for New Zealand of 0.01 parts per million. It was found that 68% of samples had low concentrations of arsenic, 14% had elevated levels, indicating that mean concentrations were above half the guideline, and the remaining 18% of samples had high levels of arsenic i.e. exceeded the
Arsenic in the environment

guideline (Figure 2.2). Wells that draw water from the neighbouring Wairau Aquifer were also tested for arsenic concentrations. Figure 2.2 also illustrates that while a larger percentage of samples from the Rarangi Shallow Aquifer were in the high category and had concentrations above the drinking water guideline than from the Wairau Aquifer, there is still a significant percentage of Wairau samples that had elevated or high levels of arsenic (Robinson, 2004).

Figure 2.2: Arsenic concentrations found in (a) Rarangi Aquifer, (b) Wairau Aquifer.

The presence of arsenic in Rarangi groundwater suggests a natural origin, but the potential sources such as historic sheep dips, and CCA treated vineyard posts also need to be recognised (Robinson, 2004). Small concentrations of arsenic have been found to accumulate in the soil in close proximity to posts. However, the CCA treated posts associated with recently established vineyards in Rarangi are unlikely to be responsible for the observed levels of arsenic in shallow groundwater, given the flushing effect of aquifer through flow and the young age of the existing posts (Robinson, 2004). Instead, the elevated levels of arsenic in the groundwater could largely be due to weathering of natural minerals or other historic uses of arsenic.

Although relatively little research has been undertaken into the effects on groundwater from the leaching of treated timber, some researchers have found that sampling of groundwater improves our understanding on the movement of As, Cu and Cr from CCA treated wood in soils (Chirenje et al., 2003). However, when the structures that are being investigated have been in place for a long period of time, it is extremely difficult to
extrapolate the current groundwater concentration of As, Cu and Cr input from existing structures (Chirenje et al., 2003). Factors such as dilution, lateral water movement and input from other sources, create problems for these extrapolations.

2.6.1 Mechanisms for arsenic getting into groundwater

It is recognised that it takes more than just high arsenic concentrations in the soil for groundwater to become contaminated. The conditions that favour arsenic dissolution (becoming dissolved in the water) depend on the circumstances. MacRae (2004) states there are generally three ways that arsenic can get into water: where pH is high, arsenic may be released from surface binding sites that lose their positive charge; when organic carbon is present in groundwater it can feed bacteria that release arsenic; or, finally, arsenic trapped in sulphide minerals can be released when the sulphide minerals are exposed to oxygen. Once present in underground aquifers, certain processes are responsible for controlling the mobility and fate of arsenic.

2.6.2 Processes controlling arsenic mobility in aquifers

Two categories of processes largely control the movement of arsenic in aquifers: (1) adsorption and desorption reactions and (2) solid phase precipitation and dissolution reactions (Hinkle and Polette, 1999). Attachment of arsenic to an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction, arsenic becoming detached from such a surface, is an example of desorption (Hinkle and Polette, 1999). Arsenate and arsenite adsorb to surfaces of a variety of aquifer materials, including iron oxides, aluminium oxides, and clay minerals. Adsorption and desorption reactions between arsenate and iron oxide surfaces are particularly important controlling reactions because iron oxides are widespread in the hydro-geologic environment, and because arsenate adsorbs strongly to iron oxide surfaces in acidic and near neutral pH water (Hinkle and Polette, 1999). However, desorption of arsenate from iron oxide surfaces
becomes favoured as pH values become alkaline (Hinkle and Polette, 1999).

Solid-phase precipitation is the formation of a solid phase from components present in aqueous solution. Precipitation of the mineral calcite, from calcium and carbonate present in ground water, is an example of solid-phase precipitation (Hinkle and Polette, 1999). Dissolution of volcanic glass within an aquifer is an example of solid-phase dissolution. The interplay of redox reactions and solid phase precipitation and dissolution may be particularly important with regard to aqueous arsenic and solid phase iron oxides. Iron oxides frequently dissolve under reducing conditions, but often precipitate under oxidising conditions. Therefore, as a result of the redox sensitive nature of iron oxides, transfer of large amounts of arsenic between these solid phases and neighbouring water may result from redox facilitated precipitation and dissolution reactions (Hinkle and Polette, 1999). Arsenic has the ability to move from the soil into groundwater given the right soil conditions and, taking into account these processes, has the ability to remain mobile once contained in an aquifer.

### 2.7 Specific research objectives

A conceptual model based on the theories outlined in the current chapter is presented in figure 2.3. Research objectives have been developed from this conceptual model.

1. To assess levels of arsenic in vineyards with contrasting soil properties to test the hypothesis that arsenic concentrations in soil adjacent to treated posts will be:
   - Higher in vineyard soils that are slightly acidic, characterised with low sand and high clay content, and also contain high amounts of organic matter.
   - Lower in vineyard soils that are less acidic, characterised with high sand and low clay content, and contain lesser amounts of organic matter.

2. To assess the mobility of arsenic through the soil profile of vineyards with contrasting soil properties to test the hypothesis that arsenic will be:
• Retained in the upper layers of the soil profile in vineyards with low sand and high clay content, neutral soil pH ($\approx 7$) and high organic matter.

• Leached through the soil profile in vineyards with high sand but low clay content, slightly acidic soils, pH $\approx 5-6$ and low organic matter.

3. To measure the arsenic content in groundwater from an underlying, unconfined aquifer, and taking into account any measured mobility of arsenic in the soil above, evaluate the extent to which arsenic in the soil, as a result of the leaching of treated timber posts in vineyards, may be considered a potential source for arsenic contamination of underlying groundwater in the Hawke’s Bay region.

Figure 2.3: Summary diagram showing the process of arsenic leaching into the soil from treated timber, and the effects soil properties have on soil arsenic.
3 Research Strategy and Methods

3.1 Introduction

This chapter describes the research strategy adopted for the study, followed by a description of the field methods used, including a description of the study area and site locations, the methods for collecting soil and groundwater samples, and both laboratory and statistical methods for analysis. Specific techniques used are discussed in the relevant sections.

3.2 Research strategy

The study comprises two stages. First, by sampling vineyards with contrasting soil properties in terms of soil pH, organic matter content and particle size composition, comparisons can be made about the effects soil properties may have on the amount of arsenic present in soil adjacent to treated vineyard posts and the relative mobility of the arsenic once present in the soil. Second, to evaluate whether arsenic may be leaching down into groundwater, groundwater samples from an unconfined aquifer beneath the study area are tested for arsenic levels, and compared with control levels.

The vineyard sites chosen for this study were located in the Gimblett Gravels Winegrowing District, in Hawke’s Bay, and were selected because of the predominantly free-draining soil properties and their location above the unconfined section of the local aquifer system. Given the soil’s free-draining nature and absence of any confining layers above the aquifer, this area is potentially at high risk from arsenic leaching down the profile and into the groundwater. Three vineyards with contrasting soil properties, in terms of soil pH, organic matter content and particle size, were selected for sampling. This involved collecting soil samples at different distances and depths surrounding several posts, and taking groundwater samples from
wells located on the vineyards. Two extra sites were used as groundwater sampling controls to gain an understanding of background arsenic levels in groundwater. One was located above the unconfined aquifer, on a golf course, and the other on an orchard above the confined section of the aquifer.

3.3 Study area

The Gimblett Gravels Winegrowing District is situated on the Heretaunga Plains in Hawke’s Bay, in New Zealand’s second largest winegrowing region (figure 3.1). The plains were formed during the last 250,000 years by river sediments deposited largely by flooding events from the Ngaruroro and Tukituki Rivers (Dravid and Brown, 1997). The Gimblett Gravels Winegrowing District is located in, and adjacent to, the old Omahu Channel.

The river channel gravels form one of the most important aquifer systems in New Zealand. The groundwater underlying the Heretaunga Plains is a major natural resource which provides approximately 85% of the water requirements of the Heretaunga Plains and adjacent areas, ranging from irrigation, industry, public and urban water supply (Dravid and Brown, 1997). Therefore, it is vital for the region’s economic and environmental well-being that best management practices are adopted for water, fertilizer and agrichemical use in order to reduce the risk of contamination of this important regional water resource. The aquifer system includes an inland, or western, unconfined zone, where river channel deposits provide conduits for groundwater to seep from the bed of the Ngaruroro River and flow eastward beneath the plains to the Hawke’s Bay coast (figure 3.2) (Brown et al., 1999). Vineyards on the Gimblett gravels are located on top of this unconfined aquifer system.
Figure 3.1: Location map of study area showing the Gimblett Gravels Winegrowing District, and the aquifer boundary (www.gimblettgravels.com).

Figure 3.2: Generalised cross-section of the Heretaunga Plains aquifer system, showing the location of the Gimblett Gravels Winegrowing Area above the unconfined section of the aquifer (Dravid and Brown, 1997).
Grapevines on the Gimblett Gravels are dependent on a regular supply of water and nutrients from additional irrigation to maintain their productivity. This is because the soil is free-draining gravel with little organic matter and a very low water holding capacity (Green et al., 2004), so rainfall leaches down the profile rapidly. A common route, not only for water and nutrients, but also the transport of contaminants from on or in soils to the wider environment is through the seepage of water through the soils and sub-soils in the unsaturated (vadose) zone into groundwater aquifers (Sheppard et al., 1999). The effectiveness of the subsoil in inhibiting contaminant migration determines to a large degree the rate and degree of contamination of the underlying groundwater.

The main soil in the study area is the Omahu soils. The Omahu soils have fine sand to fine loamy sand topsoil, overlying stony gravels mixed with varying proportions of sand, and horizontally bedded lenses on non-stony sand between the stony layers (www.gimblettgravels.com) (figure 3.3). The top-soils are browner and have a heavier texture (more silt and clay) in the deeper phases as follows:

Omahu (1): 3-10 cm of fine sand,
Omahu (1a): 5-10 cm of brown loamy fine sand over 5-10 cm of grey fine sand,
Omahu (1b): 15-20 cm of brown loamy fine sand over 10-15 cm of grey fine sand.

Although the same soil type is dominant in the study area, the variations at each vineyard provide sufficient contrasts to allow the effect of soil properties on arsenic accumulation and mobility in the soil to be evaluated.

Figure 3.3: Soil profile of the Omahu soil, found predominantly in the Gimblett Gravels Winegrowing Area (taken from Griffiths, 2001).
3.4 Vineyard study sites

Three vineyard sites were chosen for soil and groundwater sampling from the Gimblett Gravels Winegrowing Area. Although the vineyards are not all of the same age they contain the same full round posts treated with the same H4 concentration of CCA. Background information on each vineyard is given in table 3.1, and information on wells is given in table 3.2.

| Table 3.1: Vineyard sites with corresponding background information. |
|---|---|---|---|---|---|
| Vineyard | Size | Post Age | Post Type | Post Treatment | Soil Type |
| 1) V1 | 17 ha | 6-7 yrs | Full Rounds | CCA (H4) | Mainly Omahu 1, 1a, 1b |
| 2) V2 | 80 ha | 6-7 yrs | Full Rounds | CCA (H4) | Mainly Omahu 1 |
| 3) V3a | 24 ha | 9-10 yrs | Full Rounds | CCA (H4) | Mainly Omahu 1a, 1b |
| V3b | 14 ha | 15-16 yrs | Full Rounds | CCA (H4) | |

| Table 3.2: Locations of wells sampled with summary information. |
|---|---|---|---|
| Site Location | Well Number | Well Depth (m) | Aquifer Condition |
| 1) V1 | 4632 | 38.50 | Unconfined |
| 2) V2 | 4139 | 40.00 | Unconfined |
| 3) V3 | 2538 | 29.87 | Unconfined |
| 4) Orchard Site | 1674 | 38.00 | Flowing Confined |
| 5) Golf Course | 8521 | 30.47 | Unconfined |

As shown in table 3.1 all three vineyards contain CCA H4 treated, full round posts, at a similar density throughout the vineyard. The V1 and V2 vineyards are both of similar age, while V3a and V3b are slightly older (table 3.1).
V1 is situated at the foot of Roy’s Hill near Ngaruroro River. The 17 hectare vineyard was established in 2000-2001, making the posts 6-7 years old. The soil type is predominantly the free-draining sandy Omahu soil with pockets of the more loamy, Omahu 1a. The well used for groundwater sampling is situated in the unconfined zone of the aquifer, and is 38.50 metres deep.

The second vineyard, V2, is the largest vineyard sampled. It is located just north of the V1 and is situated on the more sandy Omahu 1 soil, and was also established at the same period, so has 6-7 year old posts. Groundwater samples were taken from a well on the vineyard site located on the unconfined section of the aquifer, 40.00 metres deep.

The final vineyard used for sampling was the V3 vineyard located on Gimblett Road. This vineyard was one of the oldest in the area, and has been developed in two stages, so consequently it has been broken up into two sections for the purpose of this research. V3a is the more recent section of the vineyard, with posts being in service for approximately 9-10 years. The soil in this portion of the vineyard is more gravelly on the surface indicating it is dominated by the more sandy Omahu 1 and 1a soils, while the other part of the vineyard is situated in the more loamy Omahu 1a and 1b soils. Posts in this older section of the vineyard (V3b) have been in service for 15-16 years. Similar to the other vineyards, the well used for groundwater sampling was located in the unconfined portion of the aquifer and is 29.87 metres deep.

Two control sites were also used for groundwater sampling. The first was a well at an orchard site which is located above the confined section of the aquifer to give background levels of arsenic in the groundwater of the confined part of the aquifer. The other control sample was taken from a neighbouring golf course, to provide an example of arsenic levels in groundwater of the unconfined section of the aquifer, but not directly beneath vineyards. This assumes that no arsenic leaches from the orchard or golf course, and they are located at a sufficient distance from the study area to minimise the chance of any lateral arsenic movement from the vineyards into these wells.
3.5 Field methods

3.5.1 Soil sampling

Within each of the three vineyards, samples were taken from soil surrounding twelve randomly selected posts. The samples were taken at five depths and at two defined distances away from the post (figure 3.4 and 3.5). Samples from close to the post were examined to gain an understanding of the amount of arsenic leaching into the surrounding soil, while the samples taken at different depths and further from the post, provide information on the movement of arsenic in the soil both vertically and horizontally. Samples A, C, E, G, and I were samples collected approximately 5 cm away from the post at depths of 10, 20, 30, 40, and 50 cm respectively. Samples B, D, F, H, and J were taken from the same depths but at a distance of approximately 50 cm away from the post. A control sample was taken at each post location in the middle of the row, halfway to the next post, to provide information on soil properties at each site and background levels of arsenic in the soil. Taking samples directly beneath the posts may have been ideal, but it is not practical to do so for this study.

Figure 3.4: Locations of soil samples taken from near each post.
3.5.2 Groundwater sampling

Groundwater samples were taken by staff from the Hawke’s Bay Regional Council from wells located at each of the vineyards used for soil sampling, as well as at two extra sites used as controls, as discussed earlier. At each well site water was purged from the well for approximately 30 minutes to eradicate any contaminants left in the well casing (figure 3.6). After water was purged, approximately 200ml was collected through filter paper into an unpreserved container. These samples were sent to the commercial Hill Laboratory for analysis.

Figure 3.5: Example of a trench dug adjacent to a post in the process of gathering soil samples.
3.6 Chemical analysis

3.6.1 Soil preparation

All soil samples were sieved down to 2 mm using a stainless steel sieve, and placed in aluminium trays ready for drying. Each sample was placed in an oven, set at 35°C for 48 hours. Once all samples were dry they were bagged and stored separately ready for analysis.

3.6.2 Soil pH

Soil pH was determined using a 1:2.5 ratio of soil in 0.01M CaCl₂ solution. CaCl₂ was used due to the higher reproducibility of the results, and because results are considered closer to field soil pH values. The pH was then measured using a pH
Research strategy and methods

electrode, adjusting for temperature, and rinsing the probe in water between buffers and samples to eliminate any contamination.

3.6.3 Organic matter content

Organic matter was determined using the loss on ignition method.

\[
\text{Organic matter content (\%) (LOI) = } \frac{(\text{Weight B} - \text{Weight C})}{(\text{Weight B} - \text{Weight A})} \times 100
\]

3.6.4 Particle size analysis

The particle size analysis method used was the pipette method. Soil samples of 20g were mixed with water and Calgon in a 1L cylinder. Two extracts were taken by pipette, at 20 seconds and 2 hours repetitively, and dried. The residue was weighed and the percentage sand, silt and clay calculated.

3.6.5 Total arsenic content

The method used to determine total arsenic content in the soil samples in this research employed an ultrasound-assisted extraction method, and then samples were analysed using atomic absorption spectrometry (AAS) in a graphite furnace. Soil samples of 500 mg (± 0.001g) were accurately weighed into 50 ml plastic screw top bottles, and 10 ml of digestion solution of (1+1) diluted aqua regia was added. The bottles were closed and placed into an ultrasonic water bath, at a temperature of approximately 40°C for 9 minutes, and every 3 minutes the bottles were shaken by hand to prevent sedimentation. After cooling, the sample solution was filtered using Whatman No. 41 filter paper into a 50 ml volumetric flask. The residue was washed three times with distilled water, and this was added to the filtrate. The filtrate was made up with distilled water to a volume of 50 ml. For analysis, 2 ml of the sample solution was
placed in the graphite furnace, and total arsenic content was measured using AAS, calibrated against standard solution.

### 3.6.6 Groundwater

Analysis of the groundwater samples was carried out by the Hills Laboratory in Hamilton. Samples from all five well locations were analysed for total dissolved arsenic, to a detectable limit of 0.001 ppm. Samples were filtered before arsenic was measured using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). More information on the method used for the analysis of the groundwater samples can be found in Eaton et al. (1998).

### 3.6.7 Statistical analysis

All statistical analyses were carried out using the MINITAB statistical package, version 14. Mann-Whitney tests were carried out to determine if there was any significant difference in arsenic concentrations of the samples compared to control samples, statistically. This nonparametric procedure is used with the assumptions that the samples are randomly drawn, and distributions have the same shape. Regression analysis is also used to investigate and model the relationship between arsenic concentration and soil properties.
The results from the analysis of soil and groundwater samples are presented in this chapter. The first section contains information on the accumulation of arsenic within each of the vineyard soils, detailing the extent of arsenic leaching from the posts (section 4.1). Section 4.2 presents the physical characteristics of the vineyard soils. The soil properties as a whole are analysed to find a value that can be used to determine which sites contain high and low proportions of each soil property, in context to this study. The categorisation of high and low proportions for each soil property is then used to explore the effect soil properties may be having on the accumulation of arsenic in the soil (section 4.3), and the mobility of arsenic in the soil (section 4.4). Finally, the results from groundwater samples taken from both unconfined and confined sections of an aquifer underlying the sample area are presented in section 4.5.

4.1 Total arsenic accumulation

Levels of arsenic were measured from samples taken at a range of depths from soil 5 to 10cm from the posts and 45 to 50cm from the posts. Results from each of these samples, at each vineyard, are displayed in table 4.1. To investigate at what depths and distances arsenic is accumulating in statistically significant quantities, the median arsenic concentration of each of the sample locations is compared against the arsenic levels of control samples taken at each post location (table 4.2). The median arsenic concentrations of soil samples at different depths for each vineyard are also displayed in figure 4.1, for samples taken close to the posts, and figure 4.2, for samples taken at a greater distance from the posts.
Table 4.1: The total soil arsenic concentration (ppm) of samples taken at five depths and two distances from each post location. The control level for each post is given in the last column.

<table>
<thead>
<tr>
<th>Sample location with depth (cm)</th>
<th>5-10cm from post</th>
<th>45-50cm from post</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Post Site</td>
<td>A (10) C (20) E (30) G (40) I (50)</td>
<td>B (10) D (20) F (30) H (40) J (50)</td>
<td></td>
</tr>
<tr>
<td>V1</td>
<td>5.57 4.24 3.48 2.55 1.78</td>
<td>0.82 2.06 1.50 1.47 0.64</td>
<td>0.71</td>
</tr>
<tr>
<td>V2</td>
<td>6.55 5.49 5.36 5.68 4.19</td>
<td>1.72 2.01 2.66 1.69 0.61</td>
<td>1.14</td>
</tr>
<tr>
<td>V3</td>
<td>29.18 23.03 5.78 1.46 1.32</td>
<td>8.34 3.06 2.42 1.10 1.06</td>
<td>0.94</td>
</tr>
<tr>
<td>V4</td>
<td>33.64 26.88 6.87 4.62 3.77</td>
<td>9.13 1.49 1.30 1.20 0.69</td>
<td>0.95</td>
</tr>
<tr>
<td>V5</td>
<td>19.69 10.58 4.92 4.81 2.94</td>
<td>2.70 3.36 0.86 1.29 1.36</td>
<td>1.72</td>
</tr>
<tr>
<td>V6</td>
<td>78.60 51.66 44.21 10.03 13.76</td>
<td>2.47 1.45 1.28 1.05 1.48</td>
<td>1.07</td>
</tr>
<tr>
<td>V7</td>
<td>72.35 21.28 10.44 18.51 30.33</td>
<td>5.07 2.00 1.48 2.10 1.74</td>
<td>2.22</td>
</tr>
<tr>
<td>V8</td>
<td>92.03 54.06 34.02 28.28 21.76</td>
<td>5.02 2.15 2.21 1.57 1.51</td>
<td>1.32</td>
</tr>
<tr>
<td>V9</td>
<td>156.56 68.34 38.19 34.38 17.54</td>
<td>2.90 4.05 3.24 1.28 2.14</td>
<td>2.58</td>
</tr>
<tr>
<td>V10</td>
<td>92.71 50.10 31.59 12.20 7.60</td>
<td>7.07 2.58 1.01 2.36 1.57</td>
<td>1.93</td>
</tr>
<tr>
<td>V11</td>
<td>26.17 21.06 17.73 24.31 10.63</td>
<td>1.91 3.78 1.98 1.37 1.24</td>
<td>1.15</td>
</tr>
<tr>
<td>V12</td>
<td>8.25 1.89 2.59 1.07 1.41</td>
<td>2.98 1.15 0.99 2.04 0.72</td>
<td>0.99</td>
</tr>
<tr>
<td>V1</td>
<td>135.77 57.56 2.17 1.90 3.59</td>
<td>3.11 2.32 1.34 0.78 0.83</td>
<td>0.96</td>
</tr>
<tr>
<td>V2</td>
<td>12.83 2.77 3.55 2.78 4.16</td>
<td>3.46 0.90 0.79 0.96 0.75</td>
<td>1.05</td>
</tr>
<tr>
<td>V3</td>
<td>39.85 5.80 1.47 1.01 1.60</td>
<td>2.12 1.73 0.93 0.72 1.43</td>
<td>1.51</td>
</tr>
<tr>
<td>V4</td>
<td>62.07 13.01 30.74 49.96 33.69</td>
<td>2.55 1.66 1.26 1.21 0.96</td>
<td>0.88</td>
</tr>
<tr>
<td>V5</td>
<td>91.67 31.23 3.89 1.38 2.76</td>
<td>2.50 1.68 0.97 0.95 0.72</td>
<td>1.21</td>
</tr>
<tr>
<td>V6</td>
<td>21.60 24.66 7.18 9.61 2.91</td>
<td>2.66 1.86 0.73 0.82 0.87</td>
<td>0.70</td>
</tr>
<tr>
<td>V7</td>
<td>45.68 20.78 6.87 1.66 1.91</td>
<td>2.59 3.15 0.87 0.79 0.69</td>
<td>0.92</td>
</tr>
<tr>
<td>V8</td>
<td>138.92 33.06 3.12 3.68 1.55</td>
<td>2.25 1.35 1.40 1.53 1.49</td>
<td>1.34</td>
</tr>
<tr>
<td>V9</td>
<td>99.30 77.98 9.98 6.65 8.64</td>
<td>2.02 1.88 2.34 1.03 1.07</td>
<td>0.82</td>
</tr>
<tr>
<td>V10</td>
<td>35.96 5.47 2.84 2.14 1.42</td>
<td>4.96 1.62 1.36 1.75 1.31</td>
<td>1.36</td>
</tr>
<tr>
<td>V11</td>
<td>9.86 4.50 3.63 1.70 n/a</td>
<td>3.73 1.90 1.63 1.44 n/a</td>
<td>1.94</td>
</tr>
<tr>
<td>V12</td>
<td>27.11 10.46 14.06 11.92 n/a</td>
<td>2.12 2.21 1.81 1.93 n/a</td>
<td>3.11</td>
</tr>
<tr>
<td>V13</td>
<td>43.74 37.89 28.71 30.93 36.69</td>
<td>2.81 2.03 1.81 2.00 1.84</td>
<td>1.45</td>
</tr>
<tr>
<td>V14</td>
<td>45.01 30.85 5.54 4.51 2.37</td>
<td>3.00 2.16 1.29 1.40 1.27</td>
<td>1.47</td>
</tr>
<tr>
<td>V15</td>
<td>13.27 6.42 4.95 4.55 4.02</td>
<td>2.98 2.23 2.26 2.22 3.01</td>
<td>1.74</td>
</tr>
<tr>
<td>V16</td>
<td>56.97 57.81 42.23 20.32 6.93</td>
<td>6.01 3.33 3.47 3.98 2.33</td>
<td>*14.55</td>
</tr>
<tr>
<td>V17</td>
<td>32.63 12.13 10.77 8.52 13.71</td>
<td>2.87 8.99 3.66 1.84 2.77</td>
<td>2.17</td>
</tr>
<tr>
<td>V18</td>
<td>51.39 34.59 9.13 6.20 3.29</td>
<td>6.25 2.90 1.35 1.33 1.27</td>
<td>1.64</td>
</tr>
<tr>
<td>V19</td>
<td>102.17 67.51 51.29 8.08 21.78</td>
<td>11.34 3.69 3.13 1.78 1.53</td>
<td>4.21</td>
</tr>
<tr>
<td>V20</td>
<td>123.86 110.54 23.73 7.33 8.19</td>
<td>13.29 8.65 3.70 2.26 1.45</td>
<td>6.22</td>
</tr>
<tr>
<td>V21</td>
<td>7.66 2.84 2.56 2.41 2.65</td>
<td>5.99 1.65 1.04 0.64 1.26</td>
<td>1.61</td>
</tr>
<tr>
<td>V22</td>
<td>26.10 25.61 24.03 49.06 21.95</td>
<td>2.69 1.89 2.00 3.96 3.14</td>
<td>2.09</td>
</tr>
<tr>
<td>V23</td>
<td>63.70 29.60 17.59 7.65 2.84</td>
<td>3.40 5.50 1.95 1.47 1.88</td>
<td>1.77</td>
</tr>
</tbody>
</table>

n/a: result not available.
*: value not used in analysis of results.
Results

Table 4.1 shows the accumulation of arsenic in the soil at different depths and distances from each post in all of the vineyards compared to the respective control concentrations. The samples are in two groups. A, C, E, G, and I are samples taken from a distance of 5 to 10cm from the post at depths of 10, 20, 30, 40, 50cm respectively, while samples B, D, F, H, and J are taken from the same depths but at a further distance of 45 to 50cm from the post.

From table 4.1 it is evident that arsenic is accumulating in the soil adjacent to the treated posts. The highest arsenic concentration of 156.56 ppm is found in sample A at post V19, and four other samples contained concentrations greater than 100 ppm, which is very high in comparison to New Zealand's interim guideline value for arsenic in agricultural soils of 30 ppm. Samples taken at a distance of 5 to 10cm from the post clearly contain higher concentrations of arsenic than samples taken 45 to 50cm from the post. It is also evident that arsenic is in higher concentration at the top of the soil profile. However, some posts have higher arsenic at all depths compared with others, which suggests that while arsenic is being released into the soil, it is variable. The arsenic concentration of the control samples are higher throughout V3b compared to the other vineyards, which may be the result of arsenic travelling further in the older vineyard, affecting the control samples. The very high arsenic concentration of 14.55 ppm present in the control sample taken at V3a4 is considered to be high due to contamination and is not included in the results analysis. Other results for post sites V211 and V212 are not available because samples were unable to be taken at the appropriate depth.

Figure 4.1 shows the arsenic concentrations of samples taken within 5 to 10cm of the posts, while figure 4.2 shows the concentrations of the samples taken 45 to 50cm from the posts. The high levels of arsenic found in the samples taken close to the posts in all the vineyards are reinforced visually in figure 4.1, especially when plotted against the New Zealand interim guideline for arsenic in agricultural soils. Also clearly shown is the decrease in arsenic concentration down the soil profile for all the vineyards. V3b contains the highest arsenic concentrations throughout the profile, and V2 has the lowest.
Results

Figure 4.1: Median arsenic concentration (ppm) of soil samples taken down the soil profile at each vineyard from a distance of 5-10cm from the post. Dashed red line represents the New Zealand interim guideline for arsenic in agricultural soils.

Figure 4.2: Median arsenic concentration (ppm) of soil samples taken down the soil profile at each vineyard from a distance of 45-50cm from the post.

Figure 4.2 illustrates the lower concentrations of arsenic found further from the post, but again with concentrations decreasing down the profile, which suggests a small degree of
Results
elevation of arsenic levels in topsoil even this far from the posts. Similar to figure 4.1, V^3_b again contains the highest arsenic concentrations throughout the soil profile, and V^2 has the lowest.

Sample A for all of the vineyards individually contained a median arsenic concentration greater than 30 ppm, which is the interim guideline set for arsenic in agricultural soils in New Zealand by the Ministry for the Environment in 1997. This value was also exceeded by V^3_a at the next sample depth (sample C), and V^3_b, sample C nearly exceeds the value with a median arsenic concentration of 29.60 ppm. Average concentrations for samples further down the profile, E, G, and I do not exceed the interim guideline value but all vineyards show clearly elevated levels of arsenic, especially sample E at V^3_b, which at a depth of 30cm still contains a median concentration of 23.73 ppm. In fact, all sample sites apart from I at V^3_b contained median arsenic concentrations significantly greater at the 95% level of confidence than that of their respective control soils.

The median arsenic concentrations found in the samples taken further away from the posts are a lot lower than samples taken close to the posts as would be expected. However, V^1 and V^2 contain samples B and D (10 and 20cm depth respectively) which have median arsenic levels significantly higher than the control medians. V^3_b also contains significantly higher arsenic levels for sample B, but not V^3_a. Samples F, H, and J further down the profile have median concentrations slightly higher or similar to control samples, but no vineyards contain significantly higher concentrations at the 95% level of confidence.

In terms of analysing all the vineyards together, it was found that the median arsenic concentration of all the samples taken near the posts was significantly greater than the corresponding control samples, at the 95% level of confidence. Also samples B and D, taken at a distance of 45 to 50cm from the posts, were significantly higher than corresponding control values at the 95% level of confidence. However, remaining samples, F, H, and J showed no difference from the control.
Table 4.2 shows the median and range of arsenic concentrations for each sample location including the control samples across each vineyard, and values for all the vineyards combined. By comparing the median arsenic concentration of sample sites with the arsenic concentrations of the controls, it is clear that arsenic is accumulating in the surrounding soil. The greatest accumulation is shown to be in samples taken close to the post and in the topsoil layers, with arsenic decreasing in concentration further down the profile. The concentration of samples further from the post are not as high, but generally still elevated in the top 20cm when compared to the control concentrations.

### Table 4.2: The median and range of arsenic concentrations (ppm) for each sample location including control samples at the different vineyards, with the results from Mann-Whitney statistical tests.

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>5-10cm</th>
<th>45-50cm</th>
<th>All Vineyards</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-10cm from post</td>
<td>( V^1 )</td>
<td>( V^2 )</td>
<td>( V^3_a )</td>
</tr>
<tr>
<td>A (10)</td>
<td>31.41 (5.57, 156.56)</td>
<td>42.77 (13.27, 56.97)</td>
<td>63.70 (7.66, 123.86)</td>
</tr>
<tr>
<td>B (20)</td>
<td>8.66 (2.03, 3.15)</td>
<td>7.66 (2.84, 11.09)</td>
<td>4.95 (1.47, 3.70)</td>
</tr>
<tr>
<td>C (30)</td>
<td>32.72 (2.77, 77.98)</td>
<td>3.76 (2.81, 6.25)</td>
<td>2.57 (2.03, 3.98)</td>
</tr>
<tr>
<td>D (40)</td>
<td>44.38 (6.42, 57.81)</td>
<td>3.27 (2.04, 2.04)</td>
<td>9.95 (2.84, 11.09)</td>
</tr>
<tr>
<td>E (50)</td>
<td>29.60 (2.84, 11.09)</td>
<td>2.09 (1.29, 3.66)</td>
<td>1.78 (1.04, 3.70)</td>
</tr>
<tr>
<td>F (60)</td>
<td>63.70 (7.66, 123.86)</td>
<td>4.95 (1.47, 3.70)</td>
<td>3.27 (2.04, 2.04)</td>
</tr>
<tr>
<td>G (70)</td>
<td>29.60 (2.84, 11.09)</td>
<td>2.09 (1.29, 3.66)</td>
<td>1.78 (1.04, 3.70)</td>
</tr>
<tr>
<td>H (80)</td>
<td>43.74 (5.57, 156.56)</td>
<td>4.95 (1.47, 3.70)</td>
<td>3.27 (2.04, 2.04)</td>
</tr>
<tr>
<td>I (90)</td>
<td>29.60 (2.84, 11.09)</td>
<td>2.09 (1.29, 3.66)</td>
<td>1.78 (1.04, 3.70)</td>
</tr>
<tr>
<td>J (100)</td>
<td>63.70 (7.66, 123.86)</td>
<td>4.95 (1.47, 3.70)</td>
<td>3.27 (2.04, 2.04)</td>
</tr>
<tr>
<td>Control</td>
<td>2.94 (0.82, 9.13)</td>
<td>2.11 (0.90, 3.15)</td>
<td>1.49 (0.73, 2.34)</td>
</tr>
</tbody>
</table>

\( \checkmark \): Soil arsenic concentration significantly greater than the respective control soil (at the 95% level of confidence).

\( \ast \): Soil arsenic concentration not significantly greater than the respective control soil (at the 95% level of confidence).
Table 4.3 presents the difference in median arsenic concentrations between the topsoil and subsoil of the vineyards at distances of 5-10cm and 45-50cm from the post. Close to the post, the topsoil consists of samples A and C, and subsoil is considered as samples G and I. Further from the post, samples B and D, and H and J are used for topsoil and subsoil, respectively.

Table 4.3 illustrates throughout the vineyards, the topsoil samples contain more arsenic than the corresponding subsoil samples. Vineyards $V^3a$ and $V^3b$ contain the highest median arsenic concentrations in topsoil taken approximately 5cm from the post, with values of 36.24 and 46.65 respectively. These are both greater than the interim guideline value of 30.00 ppm. $V^1$ and $V^2$ also contain high arsenic concentrations, but do not exceed the interim guideline value. The median arsenic concentrations of subsoil samples close to the posts range from 2.77 at $V^2$ to 7.87 at $V^3b$, and all are significantly lower than the respective topsoil concentrations at all vineyards. Topsoil concentrations are lower in samples taken approximately 50cm from the post, which is expected. However, even this far from the post, the median arsenic concentration of the topsoil is still significantly higher than subsoil concentrations.

Table 4.3: The median and range of arsenic concentrations (ppm) of the topsoil and subsoil samples taken from the different vineyards, with the results from Mann-Whitney statistical tests.

<table>
<thead>
<tr>
<th>5-10cm from post</th>
<th>45-50cm from post</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Topsoil</td>
</tr>
<tr>
<td></td>
<td>(A &amp; C)</td>
</tr>
<tr>
<td>$V^1$ n=24</td>
<td>26.53 (1.89, 156.56)</td>
</tr>
<tr>
<td>$V^2$ n=24</td>
<td>29.17 (2.77, 138.92)</td>
</tr>
<tr>
<td>$V^3a$ n=12</td>
<td>36.24 (6.42, 57.81)</td>
</tr>
<tr>
<td>$V^3b$ n=10</td>
<td>46.65 (2.84, 123.86)</td>
</tr>
<tr>
<td>All vineyards n=24</td>
<td>31.04 (1.89, 156.56)</td>
</tr>
</tbody>
</table>

$\checkmark$: Arsenic concentration of topsoil is significantly greater than the respective subsoil (at the 95% level of confidence).
4.2 Physical characteristics of the vineyards

This section looks in detail at the soil properties which characterise each post site throughout the vineyards. To be able to determine the effect soil properties may have on the accumulation and mobility of arsenic in the soil, soil properties at each post site were measured. However, because there is some variation in the age of posts between vineyards, the relationship between soil arsenic concentration and post age needs to first be considered (figures 4.3 a & b).

![Graphs showing relationship between post age and arsenic concentration](image)

**Figure 4.3: Relationship between post age and the arsenic concentration of topsoil and subsoil samples taken 5cm from the posts (a), and 50 cm from the posts (b).**

Figures 4.3 a and b show that the vineyards that have had posts in service in the ground for longer periods of time contain higher levels of arsenic in the topsoil and subsoil, both 5cm and 50cm from the posts. This relationship is shown to be particularly strong in the median topsoil arsenic concentrations where the $R^2$ values are 97.17% and 95.49% for samples taken close to the posts, and further from the posts, respectively. While the age of the posts seems to effect soil arsenic concentrations, the role of soil properties on arsenic accumulation also needs to be investigated.
Results

It was not possible in this study to carry out soil analysis for every depth and distance measured, for each post, so a simpler strategy has been used to establish the physical characteristics of each post site. Post sites are categorised on the basis of the soil characteristics of the control sample taken at each site. Sites can then be characterised as either more sandy, less acidic, etc than the average for the study. Included in the analysis of the control samples is soil pH, organic matter content and particle size analysis (PSA). A summary table of the results is shown in table 4.4. Soil characteristics of each post location can be found in appendix A.

Table 4.4: A summary table of physical soil properties present at each vineyard.

<table>
<thead>
<tr>
<th>Vineyard</th>
<th>Post Age (years)</th>
<th>Posts Sampled (n)</th>
<th>Soil pH (pH) with range</th>
<th>Organic Matter (%) with standard deviation</th>
<th>Soil Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>V¹</td>
<td>7</td>
<td>12</td>
<td>6.17 (6.05-6.32)</td>
<td>2.21 (0.5)</td>
<td>[87:10:3]</td>
</tr>
<tr>
<td>V²</td>
<td>7</td>
<td>12</td>
<td>6.38 (6.09-6.45)</td>
<td>2.21 (0.7)</td>
<td>[88:9:3]</td>
</tr>
<tr>
<td>V³a</td>
<td>10</td>
<td>6</td>
<td>6.05 (5.80-6.10)</td>
<td>2.82 (0.8)</td>
<td>[90:7:3]</td>
</tr>
<tr>
<td>V³b</td>
<td>16</td>
<td>5</td>
<td>5.86 (5.67-5.98)</td>
<td>3.80 (1.1)</td>
<td>[75:21:4]</td>
</tr>
</tbody>
</table>

* One sample taken per post.
** pH expressed as median with range in brackets.
*** Mean percentage of total dried soil mass using loss of ignition (LOI) method with standard deviation in brackets.
**** Expressed as a ratio of [Sand%: Silt%: Clay%], taken from the mean values across all 12 post locations.

From table 4.4 it is evident that all of the vineyard soils are slightly acidic, with generally low amounts of organic matter and, with the exception of V³b, are all particularly sandy soils. Soil pH values range from 5.67 to 6.45. Generally the pH of New Zealand soils range between 5.0 and 6.5 (AgResearch, 1999), therefore most of the soils sampled have pH values that are considered normal for New Zealand conditions. V² contains the least acidic soil with a median pH value of 6.38. V¹ is slightly more acidic with a value of 6.17, while V³ contains the most acidic soil with V³a having a value of 6.05 and V³b section B having a value of 5.86.
Table 4.4 also shows that all the vineyard soils have low organic matter contents, with average percentages ranging from 2.21% to 3.80%. V^1 and V^2 have the lowest average content with a value of just 2.21%, while V^3 has the highest organic matter content with V^3a containing 2.82% and V^3b containing 3.80%.

Soil composition results from table 4.4 illustrate that all the vineyard soils are particularly sandy apart of V^3b, which has a high silt fraction compared to the other soils. V^1, V^2 and section A from V^3 all have similar soil composition ratios, with all the soils containing between 87-90% sand and approximately 3% clay. Section B from V^3 contains a similar clay fraction, but less sand and more silt than the other vineyard sites.

Table 4.5 describes the statistics of the different soil properties present throughout all the different sample locations. By looking at the descriptive statistics for each property in table 4.5, and examining the statistics represented in the form of box plots in figure 4.4, a value can be given to represent which samples could be perceived as containing high or low values in the respective property in context with this study.

Table 4.5: The descriptive statistics of the soil properties present at all the sample sites.

<table>
<thead>
<tr>
<th>Soil Property</th>
<th>N</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand content (%)</td>
<td>35</td>
<td>86.21</td>
<td>9.65</td>
<td>89.09</td>
<td>(46.02, 96.02)</td>
</tr>
<tr>
<td>Clay content (%)</td>
<td>35</td>
<td>3.06</td>
<td>1.461</td>
<td>2.736</td>
<td>(1.482, 8.109)</td>
</tr>
<tr>
<td>Organic matter content (%)</td>
<td>35</td>
<td>2.539</td>
<td>0.890</td>
<td>2.243</td>
<td>(1.604, 5.577)</td>
</tr>
<tr>
<td>Soil pH</td>
<td>35</td>
<td>6.16</td>
<td>0.2022</td>
<td>6.16</td>
<td>(5.67, 6.54)</td>
</tr>
</tbody>
</table>
All samples that contained more than 85% sand, which is close to the mean and median of all samples, are said to contain high amounts of sand, and all samples with less than 85% sand are said to contain low amounts. The values of 2.75% and 2.5% are used to divide the samples with high and low clay and organic matter contents respectively. Samples with a pH of less than 6.10 represent the more acidic samples, while samples containing a pH greater than 6.10 represent the less acidic samples.

The high and low analysis is used for examining arsenic mobility and is presented in section 4.4. But before that, the effect different soil properties have on the accumulation of arsenic in the soil is explored.

4.3 Effects of soil properties on soil arsenic accumulation

The topsoil samples taken at a depth of 10cm (sample A approximately 5cm from the post, and sample B approximately 50cm from the post) are used for analysis, as the
accumulation of arsenic in the topsoil layers is potentially the most harmful in terms of coming in contact with humans and animals, and future land use change. Data from all thirty five post sites are analysed together, to consider possible relationships between the individual soil properties and the accumulation of arsenic close to the post and further from the post. Then for each soil property, arsenic levels are considered in relation to the two simple groups; posts with soil property values above a defined level, posts with values below that level. Following the analysis of individual properties, all soil properties will be considered together, to investigate the possibility of more than one soil property having an effect on soil arsenic concentration.

4.3.1 Arsenic concentration in relation to organic matter content

From all of the samples taken throughout the three vineyards organic matter contents of the soils were found to be low in comparison to typical well-drained agricultural soils in New Zealand, which average 5% organic matter (AgResearch, 1999). Values range from only 1.61% to 5.67%, with a median value across all the samples of 2.24%; most of the vineyards contain low organic matter contents, and there is comparatively little variation between the vineyards. The relationship between the organic matter content of the soils and concentrations of arsenic in soil close to, and further from, the posts is shown in figure 4.5.

Figure 4.5 shows that there is absolutely no relationship between arsenic concentration and organic matter contents of soil close to the posts (p=0.877, $R^2=0.07\%$). Although some of the soils with the higher arsenic values also contain some of the highest organic matter contents, there are also soils with lower arsenic contents which also contain relatively high organic matter contents, and vice versa (figure 4.5). An outlier to the data is post site V3b1, which contains the only reasonably high organic matter content of 5.67%, and has a high average arsenic concentration from samples taken near the post of 102.17 ppm.
4.3.1 Arsenic concentration in relation to soil organic matter content

On the other hand, figure 4.5 does suggest that there is a relationship between arsenic and organic matter levels for those samples taken at a greater distance from the post (p=0.011). However, the R^2 value of 17.83% indicates a weak relationship. The linear regression line shows that arsenic levels further from the post tend to be higher in soils with a higher organic matter content.

4.3.2 Arsenic concentration in relation to soil pH

The majority of New Zealand agricultural soils have pH values between 5.0 and 6.5. Soil pH values from all three of the vineyards sampled ranged between 5.67 and 6.54, so all have a soil pH approximately between the typical values of agricultural soils in New Zealand.
Zealand. The relationship between arsenic concentration and soil pH of the samples is shown in figure 4.6.

Figure 4.6: The relationship between arsenic concentrations and soil pH. (Dashed red line represents the New Zealand interim guideline for arsenic in agricultural soils).

There is no relationship evident between the arsenic concentration and pH of the soil samples taken close to the post (figure 4.6). In contrast, the samples 50cm from the post show a relationship between the acidity of the soil and arsenic concentration (p=0.001). The relationship is an inverse one, with arsenic levels further from the post tending to be higher in the more acidic soils, and lower in the less acidic soils. With an R² value of 27% this is a relatively weak relationship, suggesting other factors are also influencing the arsenic levels.
4.3.3 Arsenic concentration in relation to content of sand-size particles

Most of the soils sampled throughout the three vineyards contained high sand contents, which is not unexpected in most viticultural soils. The sand content values ranged from between 46.02% to 96.02%, with a median value of 89.09%. There are just two post sites that contain a very low sand content, and generally there was little variation in sand content between the samples. Figure 4.7 illustrates the relationship between the arsenic concentration and sand content of all the topsoil samples taken from all three vineyards.

Figure 4.7: The relationship between arsenic concentrations and sand content. (Dashed red line represents the New Zealand interim guideline for arsenic in agricultural soils).

Figure 4.7 shows no relationship between arsenic concentration of the samples taken close to the post and sand content (p=0.167). In terms of the arsenic concentration in samples taken further from the posts, there is a relationship with sand content (p=0.003), the regression line indicating that arsenic concentrations will tend to be higher in the less
Results

sandy soils. But as with pH, the $R^2 (23.7\%)$ indicates only a weak relationship between arsenic levels and sand content further from the post.

### 4.3.4 Arsenic concentration in relation to clay content

The clay content of the soils sampled throughout the three vineyards is very low, with levels ranging from 1.48\% to 8.11\%, and a median value of just 2.74\%. Therefore, apart from a few samples having slightly higher clay contents, the majority of samples contained very low amounts of clay, with little variation between sample sites. The relationship between the clay content and arsenic concentrations of the topsoil at all the post sites is shown in figure 4.8.

![Figure 4.8: The relationship between arsenic concentrations and clay content. (Dashed red line represents the New Zealand interim guideline for arsenic in agricultural soils).](image-url)
Results

It is evident from figure 4.8 that there is no relationship between clay content and arsenic concentration of the soil samples taken close to the post (p=0.932, R²=0.02%). There is a weak relationship between arsenic levels and clay content in the samples taken further from the post (p=0.022). The positive relationship indicates arsenic concentrations further from the post tend to be higher in soils with higher clay contents. However, the R² value is only 15%, indicating this is a very weak relationship.

Figures 4.5 to 4.8 show that, individually none of the soil properties have a relationship with the arsenic levels of samples taken close to the post, while weak relationships were found between each of the soil properties and samples taken further from the post. Multiple regression is used later on (section 4.3.6) to investigate what combinations of soil properties have the greatest influence on arsenic levels of samples taken both close to and further from the post.

4.3.5 Topsoil arsenic accumulation in relation to all soil properties

Following the examination of possible relationships between individual soil properties and the concentration of arsenic in the topsoil, the possibility of several soil properties influencing arsenic levels was investigated using stepwise multiple regression. For samples close to the post, and samples further from the post, table 4.7 shows which soil properties are important in affecting the concentration of arsenic in the topsoil.

Table 4.6 shows that the arsenic concentration of the topsoil close to the post is not affected by soil pH, but is influenced by the organic matter, sand, and clay content of the soil. The R² value (41.09%) indicates reasonable strength, but clearly other factors are affecting arsenic levels. All show an inverse relationship, so arsenic levels will tend to be higher in soils with a lower organic matter content, less sand, and lower clay content. Arsenic levels in the topsoil further from the post is shown to be moderately related (R²=34.04) to the pH and sand content of the soil (table 4.8). The relationship is again
negative, so arsenic levels further from the post will tend to be higher in more acidic soils, and soils with a lower sand content.

Table 4.6: Results from stepwise regression analysis, examining the effect of a combination of soil properties on arsenic concentration found in samples A and B.

<table>
<thead>
<tr>
<th></th>
<th>5cm from post (sample A)</th>
<th>50cm from post (sample B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>876.9</td>
<td>43.25</td>
</tr>
<tr>
<td>OM%</td>
<td>-36</td>
<td></td>
</tr>
<tr>
<td>T-Value</td>
<td>-3.41</td>
<td></td>
</tr>
<tr>
<td>Soil pH</td>
<td>-5.1</td>
<td>-2.24</td>
</tr>
<tr>
<td>T-Value</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand%</td>
<td>-7.4</td>
<td>-0.09</td>
</tr>
<tr>
<td>T-Value</td>
<td>-4.64</td>
<td>-1.85</td>
</tr>
<tr>
<td>Clay%</td>
<td>-30.4</td>
<td></td>
</tr>
<tr>
<td>T-Value</td>
<td>-3.7</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>33.8</td>
<td>2.34</td>
</tr>
<tr>
<td>R²</td>
<td>41.09</td>
<td>34.04</td>
</tr>
</tbody>
</table>

4.4 Effects of soil properties on the mobility of arsenic in soil

For the purpose of this study, mobility of arsenic is defined as the movement of arsenic both laterally and vertically in the soil profile, once it has leached from the treated vineyard posts. Vertical mobility is shown in samples A-I close to the post, and lateral mobility in samples B-J which are taken approximately 50cm from the posts.

This section assesses the effects of soil properties such as particle size, organic matter and soil pH on the mobility of arsenic in soil. In order to do this, each sample location is analysed in relation to whether it contains a comparatively high or low soil property value. This allows the comparison of arsenic concentration in soil samples taken at different depths and distances from the posts, which shows any differences in arsenic
mobility between soils with a relatively high soil property content and sites with a lower content.

Each post site has been categorised depending on whether it had relatively high or low values for each of the soil properties measured in this study (see section 4.2). The critical values, which represent the appropriate median values for each property, were: 2.5% organic matter, 85% sand, 2.75% clay or a pH greater than 6.10. For each soil property, the posts were divided into two groups – those which had values for the property above the critical value, and those that fell below that value.

The effect of soil properties on arsenic mobility is determined by comparing the median arsenic concentration of each sample for the two categories of each soil property. The median values are tested statistically to determine whether the differences in arsenic concentration are significant (table 4.8). The median concentrations for both categories are also illustrated graphically showing the differences in arsenic mobility vertically down the soil profile and laterally further from the post.

Finally, two posts with contrasting soil types are examined more closely to gain an understanding of the mobility of arsenic through two contrasting soils. While there are many variables to control for, providing difficulties in drawing any conclusions, the comparison of two contrasting soils gives an indication of how the mobility of arsenic may be affected by soil properties present in the soil.

Table 4.7 shows the median arsenic concentration of samples down the soil profile, both close to the posts and further from the posts in relation to each of the four soil properties. For the samples taken close to the post (A-I), differences in median values are observed, however, none of the differences are statistically significant. Essentially, there is no relationship at any of the sampling depths between any of the soil properties and arsenic levels.
## Results

Table 4.7: Median arsenic levels down the profile, close to the posts, and further from posts, for posts categorised by soil property.

<table>
<thead>
<tr>
<th>Sample (depth)</th>
<th>Organic matter&gt;2.5% (n=13)</th>
<th>Organic matter&lt;2.5% (n=22)</th>
<th>Significant difference</th>
<th>Soil pH &lt;6.10 (n=14)</th>
<th>Soil pH &gt;6.10 (n=21)</th>
<th>Significant difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (10)</td>
<td>56.97 (7.66, 123.86)</td>
<td>37.91 (5.57, 156.56)</td>
<td>≠</td>
<td>38.19 (7.66, 123.86)</td>
<td>45.68 (5.57, 156.56)</td>
<td>≠</td>
</tr>
<tr>
<td>C (20)</td>
<td>25.61 (8.24, 110.54)</td>
<td>17.59 (1.89, 77.98)</td>
<td>≠</td>
<td>13.95 (2.84, 110.54)</td>
<td>9.67 (1.89, 77.98)</td>
<td>≠</td>
</tr>
<tr>
<td>E (30)</td>
<td>25.61 (8.24, 110.54)</td>
<td>17.59 (1.89, 77.98)</td>
<td>≠</td>
<td>13.95 (2.84, 110.54)</td>
<td>9.67 (1.89, 77.98)</td>
<td>≠</td>
</tr>
<tr>
<td>G (40)</td>
<td>25.61 (8.24, 110.54)</td>
<td>17.59 (1.89, 77.98)</td>
<td>≠</td>
<td>13.95 (2.84, 110.54)</td>
<td>9.67 (1.89, 77.98)</td>
<td>≠</td>
</tr>
<tr>
<td>J (50)</td>
<td>25.61 (8.24, 110.54)</td>
<td>17.59 (1.89, 77.98)</td>
<td>≠</td>
<td>13.95 (2.84, 110.54)</td>
<td>9.67 (1.89, 77.98)</td>
<td>≠</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample (depth)</th>
<th>Organic matter&gt;2.5% (n=13)</th>
<th>Organic matter&lt;2.5% (n=22)</th>
<th>Significant difference</th>
<th>Soil pH &lt;6.10 (n=14)</th>
<th>Soil pH &gt;6.10 (n=21)</th>
<th>Significant difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand&gt;85% (n=22)</td>
<td>34.80 (6.55, 135.77)</td>
<td>72.35 (5.57, 156.56)</td>
<td>≠</td>
<td>45.62 (7.66, 123.86)</td>
<td>43.74 (5.57, 156.56)</td>
<td>≠</td>
</tr>
<tr>
<td>Sand&lt;85% (n=13)</td>
<td>34.80 (6.55, 135.77)</td>
<td>72.35 (5.57, 156.56)</td>
<td>≠</td>
<td>45.62 (7.66, 123.86)</td>
<td>43.74 (5.57, 156.56)</td>
<td>≠</td>
</tr>
<tr>
<td>Clay&gt;2.75% (n=10)</td>
<td>34.80 (6.55, 135.77)</td>
<td>72.35 (5.57, 156.56)</td>
<td>≠</td>
<td>45.62 (7.66, 123.86)</td>
<td>43.74 (5.57, 156.56)</td>
<td>≠</td>
</tr>
<tr>
<td>Clay&lt;2.75% (n=19)</td>
<td>34.80 (6.55, 135.77)</td>
<td>72.35 (5.57, 156.56)</td>
<td>≠</td>
<td>45.62 (7.66, 123.86)</td>
<td>43.74 (5.57, 156.56)</td>
<td>≠</td>
</tr>
</tbody>
</table>

\(\sqrt{\text{V}}\): Significant difference in median values at the 95% level of confidence.  
\(\neq\): No significant difference in median values at the 95% level of confidence.
Results

For samples taken at a greater distance from the posts, the differences in median arsenic concentration at different depths are not significantly different in relation to sand and clay content of the soil. However, the median arsenic concentration of samples with an organic matter content greater than 2.5%, for samples B, H, and J, are significantly larger than the median arsenic concentration of those samples with a lower organic matter content. For example, the median arsenic concentration for sample B is 5.02 ppm for sites with a high organic matter content, compared to 2.74 ppm for sites with a lower content. The category containing sites with a more acidic soil has median arsenic concentrations significantly greater that the less acidic soils for all samples taken at 50cm from the posts. The results from table 4.7 are shown graphically and analysed as individual soil properties in the following sections.

4.4.1 Effect of organic matter on the mobility of arsenic in soil

Thirteen sites had an organic matter content of more than 2.5%, while twenty two sites contained less than 2.5% organic matter. The relationship between arsenic concentration down the profiles and these two categories at the two sampling distances is shown in figure 4.9.

![Figure 4.9: The median arsenic concentrations of samples containing more than 2.5% organic matter compared to samples containing less than 2.5% organic matter in (a) 5cm from the post and (b) 50cm from the post. (Dashed red line represents the New Zealand interim guideline for arsenic in agricultural soils).]
There is a decrease in arsenic concentration down the soil profile, which is especially marked in samples taken in close proximity to the post (figure 4.9 a). At the top of the soil profile (sample A), the median arsenic concentration is 56.97 ppm for the sites containing higher organic matter, compared to a lesser value of 37.91 ppm for the sites with the lower organic matter contents. These two values both exceed the interim guideline value of 30.00 ppm. While these values are high for both categories, there is no significant difference between them at the 95% level of confidence. At greater depths than sample A close to the post, none of the samples show significant differences either.

At a distance of approximately 50cm from the posts, median arsenic concentrations in both categories are a lot lower than soil closer to the posts (figure 4.9 b). Although lower, concentrations found at 10 and 20cm depths are elevated compared to respective control concentrations. At a depth of 10cm, samples with higher organic matter contain significantly more arsenic than the samples containing less organic matter, when tested at the 95% level of confidence. Further down the profile concentrations between the two are more similar, however, the high organic matter category contains significantly higher arsenic in sample J than the low organic matter category, when tested at the 95% level of confidence. The control arsenic concentrations from the samples containing more than 2.5% organic matter are higher than the control samples with less than 2.5% organic matter.

4.4.2 Effect of pH on the mobility of arsenic in soil

There are fourteen post sites in the more acidic category and twenty one sites in the less acidic category. The relationship between the concentration of arsenic in the soil and these two categories is shown in figure 4.10.

In close proximity to the post and in the top 10cm of the soil profile, the less acidic soils with a pH of more than 6.10 contain a median arsenic concentration of 45.68 ppm,
compared with the more acidic soils that contain a median of 38.19 ppm (figure 4.10 a); both medians exceed the interim guideline value of 30.00 ppm. However, the differences in concentration between the two categories, for any depth close to the post, are not significantly different from each other when tested at the 95% level of confidence.

Figure 4.10: The median arsenic concentrations of samples with a soil pH of less than 6.10 compared to less acidic samples with a soil pH of more than 6.10 in (a) 5cm from the post and (b) 50cm from the post. (Dashed red line represents the New Zealand interim guideline for arsenic in agricultural soils).

For the samples taken 50cm from the posts, it is evident that the more acidic category contains higher arsenic concentrations than the less acidic category. The statistical analysis in table 4.7 shows that the higher median arsenic concentrations found in the more acidic sites, are significantly greater than that of the less acidic sites when tested at the 95% level of confidence for all depths except sample H.

4.4.3 Effect of particle size on the mobility of arsenic in soil

There are twenty two sites in the high sand category and thirteen sites in the low sand category, sixteen sites in the high clay category and nineteen sites in the low clay category. The relationship between arsenic levels at different depths in the soil and these
Results
different categories of sand and clay contents are shown in figures 4.11 and 4.12, respectively.

The difference in median arsenic concentrations between the two contrasting categories for both sand and clay content are not significantly different when tested at the 95% level of confidence. Therefore, a relationship between sand and clay contents with mobility of arsenic in the soil is not present.

![Figure 4.11](image1.png)

*Figure 4.11: The median arsenic concentrations of samples containing more than 85% sand compared to samples containing less than 85% sand in (a) 5cm from the post and (b) 50cm from the post. (Dashed red line represents the New Zealand interim guideline for arsenic in agricultural soils).*

![Figure 4.12](image2.png)

*Figure 4.12: The median arsenic concentrations of samples containing more than 2.75% clay compared to samples containing less than 2.75% clay in (a) 5cm from the post and (b) 50cm from the post. (Dashed red line represents the New Zealand interim guideline for arsenic in agricultural soils).*
4.4.4 Mobility of arsenic in two contrasting soils

This section involves investigating the vertical and lateral movement of arsenic in the soil at two post sites with known contrasting soil properties. The purpose is to give examples of how arsenic behaves in the two different soil types, one a sand-dominated, freely draining soil, and the other a more fine textured loamy soil. While there are many variables present, which limits the ability to draw conclusions, this section gives a valuable insight into the variability of arsenic mobility in the natural environment. The two post sites were selected according to their soil properties. One site (V1 11) contains a high sand content, low clay and organic matter content, with a higher pH, and the other (V3 b2), a low sand content, higher clay and organic matter content, and a lower pH. The specific soil characteristics of each location are shown in table 4.8.

Table 4.8: Soil properties of two sample locations used to compare movement of arsenic within their profiles.

<table>
<thead>
<tr>
<th>Sample location</th>
<th>V1 11</th>
<th>V3 b2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (%)</td>
<td>93.98</td>
<td>68.48</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>2.01</td>
<td>5.25</td>
</tr>
<tr>
<td>Organic Matter (%)</td>
<td>1.65</td>
<td>3.30</td>
</tr>
<tr>
<td>Soil pH</td>
<td>6.32</td>
<td>5.98</td>
</tr>
</tbody>
</table>

As shown in table 4.8, V1 11 and V3 b2 are two contrasting soil types. V1 11 contains one of the highest sand contents of the sites sampled with 93.98%, and also very low clay and organic matter contents. V3 b2 contains the second lowest sand content with 68.48%, and more than double the clay and organic matter contents of V1 11. V3 b2 is the most acidic soil with a pH of 5.98, while V1 11 is slightly less acidic with a pH of 6.32. Table 4.9 shows the arsenic concentration of samples taken down the soil profile close to and further away from the post for both soils.
Table 4.9: Arsenic concentrations of each sample location for both soils.

<table>
<thead>
<tr>
<th>Sample location (5cm from post)</th>
<th>Arsenic concentration (ppm)</th>
<th>Sample location (50cm from post)</th>
<th>Arsenic concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (10cm)</td>
<td>26.17</td>
<td>B (10cm)</td>
<td>1.91</td>
</tr>
<tr>
<td>C (20cm)</td>
<td>21.06</td>
<td>D (20cm)</td>
<td>3.78</td>
</tr>
<tr>
<td>E (30cm)</td>
<td>17.73</td>
<td>F (30cm)</td>
<td>1.98</td>
</tr>
<tr>
<td>G (40cm)</td>
<td>24.31</td>
<td>H (40cm)</td>
<td>1.37</td>
</tr>
<tr>
<td>I (50cm)</td>
<td>10.63</td>
<td>J (50cm)</td>
<td>1.24</td>
</tr>
<tr>
<td>Control</td>
<td>1.15</td>
<td></td>
<td>6.22</td>
</tr>
</tbody>
</table>

Table 4.9 shows the differences in arsenic concentration of soil close to the post and further from the post between the contrasting soils. In samples collected close to the post, \( V^{11} \) contains arsenic concentrations in the range of 10.63 ppm and 26.17 ppm. In contrast, \( V^{3b2} \) contains arsenic concentrations ranging from 7.33 ppm to 123.86 ppm, with the top two samples containing over 100 ppm arsenic, and the samples at depths of 30cm or greater contain a significantly lower concentrations. While \( V^{3b2} \) exceeds \( V^{11} \) in arsenic concentration in the top 20cm considerably, \( V^{11} \) contains higher arsenic concentrations at depths of 40 to 50cm.

Samples B-J, taken 50cm from the post show that the soil of \( V^{3b2} \) contains more arsenic further from the post than \( V^{11} \). \( V^{11} \) contains arsenic concentrations between 1.24 ppm and 3.78 ppm, while \( V^{3b2} \) ranges in arsenic concentrations of between 1.45 ppm to 13.29 ppm. The control sample of \( V^{3b2} \) contains 6.22 ppm of arsenic, which is considerably higher than 1.15 ppm found in the \( V^{11} \) control sample, and all the other post sites (table 4.1), so could possibly be the result of contamination. The contrasting arsenic concentrations between the two post locations are illustrated in figures 4.12 and 4.13.
Results

Figure 4.13: Arsenic concentrations from samples taken at post V^11.

Figure 4.14: Arsenic concentrations from samples taken at post V^3b2.
Results

The two contrasting post locations show differences in arsenic concentration at different depths and distances from the post (figures 4.13 and 4.14). Figure 4.13 shows $V^{1}11$ has a relatively constant concentration of arsenic at all depths down the profile at a distance of 5cm from the post, which shows a consistent concentration of arsenic through the whole soil profile. $V^{3}b2$ in figure 4.14 contains a very high amounts of arsenic in the topsoil layers and smaller amounts in the depths of 30-50cm. In terms of arsenic concentrations found further from the treated posts, $V^{1}11$ contains low levels, similar to background levels shown in the control (figure 4.13). $V^{3}b2$ contains elevated levels of arsenic in the top 20cm, even at a distance of 50cm from the post, but concentrations are closer to background levels further down the profile (figure 4.14).

The previous sections have found that arsenic leaches from treated timber, accumulating in the surrounding soil. Analysis also shows that arsenic can be present in elevated amounts at depths of 50cm down the soil profile and at distances of up to 50cm from the posts. Therefore if arsenic can be found down the soil profile, it is conceivable that arsenic may leach further down, potentially into groundwater. The following section looks at arsenic concentrations of groundwater taken from sites both beneath the vineyard sites and also control sites, to see whether arsenic is elevated in groundwater beneath the vineyards.

4.5 Arsenic concentrations of groundwater

Groundwater samples were taken from wells at each of the vineyard locations and also two control sites, and were analysed for total dissolved arsenic content. Results of the analysis and also background information on each of the well sites are displayed in table 4.10.
Table 4.10: Background information on wells and associated arsenic content.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Well Number</th>
<th>Well Depth (m)</th>
<th>Aquifer Condition</th>
<th>Dissolved Arsenic (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(^1)</td>
<td>4632</td>
<td>38.50</td>
<td>Unconfined</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>V(^2)</td>
<td>4139</td>
<td>40.00</td>
<td>Unconfined</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>V(^3)</td>
<td>2538</td>
<td>29.87</td>
<td>Unconfined</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Orchard</td>
<td>1674</td>
<td>38.00</td>
<td>Flowing confined</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Golf Club</td>
<td>8521</td>
<td>30.47</td>
<td>Unconfined</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

The depths of the wells used for sampling range from depths of 29.87m at V\(^1\) to 40.00m at V\(^2\) (table 4.10). Also shown in table 4.9 is the condition of the aquifer, with wells located in both the unconfined and confined sections of the aquifer. In terms of the dissolved arsenic contents, all of the samples contain less than 0.001 ppm dissolved arsenic, which is well below the New Zealand guideline for arsenic in drinking water of 0.01 ppm (Ministry for the Environment, 1997).

### 4.6 Results summary

Throughout the three vineyards sampled it has been found that arsenic levels in soil close to the posts is elevated, especially in the topsoil. Generally, arsenic concentrations decreased with depth, but were often found to still be above control levels. Further from the posts there was a marked decline in arsenic levels both in the topsoil and at depth, but still often elevated above control levels. Again, arsenic levels declined with depth, but not as marked as close to the posts. Soil properties working in combination were shown to have some effect on arsenic levels, while arsenic mobility was shown to be increased by the more sandy soils. Even though arsenic was found to be mobile both laterally and vertically in the soil profile, no groundwater samples contained elevated levels of arsenic.
Results from the analysis of soil samples taken from a number of Hawke’s Bay vineyards in the Gimblett Gravels Winegrowing Area indicate elevated levels of arsenic in soil surrounding treated posts. These findings are consistent with previous research on the effects of treated timber on the surrounding soil, which suggests that arsenic accumulates in the soil as a result of the leaching of the CCA treatment from the posts. While arsenic was found at higher levels in samples taken close to the posts, it was also found that arsenic was still accumulating in significant (although much lower) concentrations in topsoil samples taken at a distance of 50cm from the posts. Topsoil arsenic concentrations for samples taken close to the posts were related to proportions of sand and clay sized particles, and the organic matter content, while soil pH and sand content showed to have more of an effect on topsoil arsenic levels further from the posts. Arsenic appears to be more mobile in the more acidic soils containing high proportions of sand, low amounts of clay and organic matter, which would be consistent with previous studies. The concentration of arsenic in groundwater samples taken from an aquifer beneath the vineyard sites was found to be well below the New Zealand guideline for arsenic in drinking water, for all the samples.

In this chapter, the implications of these findings for land use change and viticultural practices in New Zealand will be discussed, along with the possibilities of future research into the effects of CCA treated timber on the surrounding environment.

5.1 Effects of soil properties on the accumulation of arsenic in vineyard soils

From the analysis of soil samples taken in the close vicinity of treated fence posts it can be concluded that arsenic is leaching from the posts and accumulating in the soil. Soil arsenic concentrations were higher in soils surrounding all 35 of the posts
sampled throughout the three vineyards when compared with control soils. This indicates that the occurrence of arsenic leaching from posts into soil is widespread throughout these vineyards.

As would be expected samples taken close to the posts, at a distance of approximately 5cm, have the highest level of arsenic accumulation in the soil. Median concentrations of arsenic in samples at a depth of 10cm (A) ranged from 31.41 ppm to 63.70 ppm throughout the vineyards, while samples of the same depth but 50cm from the post ranged from 2.94 ppm to 5.99 ppm. In comparison, the median arsenic concentration of the control samples ranged from only 1.13 ppm to 2.09 ppm. Arsenic concentrations, then, are significantly higher in the soil adjacent to the post, but elevated levels of arsenic can also be found at a distance of 50cm from the post. Assuming that the 50cm levels are also due to arsenic leached from posts, interesting questions are raised as to how the arsenic travels that far laterally from the posts. While it is expected that the highest concentrations of arsenic are found close to the post, the high concentrations in the surface layers next to the post, and elevated levels in topsoil samples 50cm from the post are of concern, especially as the median concentration for the A samples was found to exceed the New Zealand interim guideline value of 30 ppm for arsenic in agricultural soils (Ministry for the Environment, 1997). These results were similar to a number of studies that also found the top 20cm of the soil profile contained the highest levels of arsenic (Townsend et al., 2001, Gezer et al., 2004, Lebow et al., 2000).

The high arsenic concentration in the surface layers of the soil is consistent with previous studies. The surface layers of soil often contain higher amounts of organic matter and clay than the soil beneath. It has been found previously that soil type and conditions, especially pH, organic matter, and clay content play an important role in leaching of arsenic out of the post and its subsequent movement through soil (Carey et al., 1996b; Hingston et al., 2001). The higher organic content in the surface layers may also explain the elevated arsenic concentrations in the top 20cm of the soil close to the post, as arsenic is retained on suitable adsorbing surfaces. However, it does not explain how arsenic moves laterally to produce the comparatively high arsenic levels at a distance of 50cm from the posts.
Another possible reason for why arsenic is found in higher concentrations in the surface layers is the surface layers acting as the first point of contact for the arsenic that travels down the post section above the ground. Because the majority of the post is above ground, rainfall may act to flush the arsenic down the post, so arsenic becomes accumulated in the surface soil layers. However, Robinson et al. (2003) showed that belowground wood samples of the posts had significantly lower arsenic concentrations than the aboveground portions, which were not significantly different from new posts. This indicates leaching, but suggests that the majority of leaching comes from the belowground section of the post.

Throughout the vineyard sites variations were found in the arsenic concentration of the samples. Because all the posts sampled were full rounds and have all been treated with the same CCA “H4” treatment, the main variables are the age of the posts, and the different soil properties found at each post site. In terms of the age of the posts in this study, V1 and V2 contain posts 6-7 years old, V3a, 9-10 years old, and V3b, 15-16 years old. In relation to arsenic concentrations close to the posts at a depth of 10cm, V3b has the highest with a median of 63.70 ppm, V3a has the second highest with 44.38 ppm, followed by V2 42.77 ppm, and the lowest is V1 with 31.41 ppm. V3b sample sites also contain comparatively higher arsenic concentrations in samples taken at a greater distance from the post than the other younger sites. This indicates that there may be a relationship between the age of the post and arsenic concentration of the surrounding soil, with the soils around older posts containing higher arsenic concentrations. Robinson et al. (2003) found similar results with a significant positive correlation between post age and CCA-leaching at one site, but there was no significant age correlation within or between the other sites. Greven et al. (2005) also found that the amount of leaching correlated to soil type as well as post age. With differences in soil arsenic concentration found between the post sites, and variations in soil properties post-to-post, the effect soil properties may have on arsenic accumulation in the soil also needs to be considered.

Soil properties varied both between the vineyard sites and between the post sites in each of the vineyards. Between all the post sites, organic matter contents range from 1.6% to 5.7%, which is low in terms of New Zealand agricultural soil. All soils were acidic, with soil pH values ranging from 5.67 to 6.54. Most of the soils are sand-
dominated with the median sand content of all the samples of 89.09%, and therefore, clay contents are all relatively low with a median clay content of all the sites of only 2.74%.

Although organic matter and clay content are reasonably low throughout all the soils, there are contrasts in all soil properties. For example, V3b2 had higher organic matter content than the other vineyard sites. However, when analysing organic matter content in relation to the corresponding arsenic concentration across all sites, there was not a strong relationship. This may have been largely influenced by the generally very low organic matter contents found throughout the vineyards. Another factor that may have influenced the organic matter results was the depth at which the control samples and corresponding organic matter contents were taken from. Control samples, that were used to determine soil properties at the post site, were taken at a depth of between 20 and 30cm, a depth below the topsoil layers but at a depth which can be used to get a general understanding of the soil conditions at each post site. Because the majority of organic matter of the soil is found in the top 10cm, the organic matter content of the control samples may not be representative of the actual organic matter content contained in the upper layers of the soil profile.

Despite these issues, the results suggest that organic matter plays a role in affecting the accumulation of arsenic in soil, particularly in the upper layers of the soil profile although it may not be a dominant factor in these soils. Lebow (2005) found that high soil organic content was generally associated with the capability to absorb arsenic, while other factors such as pH or inorganic constituents also play a role. The organic matter in the upper portion of the soil profile may act as a sponge, absorbing the arsenic as it is leached into the soil. This would mean there is less arsenic available to leach down the profile and possibly make its way down to underlying groundwater. On the other hand, soils with a high organic matter content could have a negative implication for land use change. If vineyards were to be replaced with another agricultural practice or land use activity, people, animals and plants may be exposed to high levels of arsenic, in the top few centimetres of soil.

All of the post sites sampled had soils with varying degrees of acidity, with soil pH values ranging from 5.67 to 6.54. When soil pH was plotted against arsenic
concentration, no relationship was found for the samples (A) taken close to the post, and only a weak relationship for the samples (B) taken 50cm from the post. This was also shown when comparing the median arsenic concentration of the most acidic sites against the less acidic sites. This suggests that while soil pH may have little effect on arsenic accumulating close to the post, arsenic may accumulate in greater amounts in soil further from the post in more acidic soils. This could be because the soil pH may have an effect on the mobility of arsenic in the soil, which will be discussed in more depth later in this chapter. The lack of soils with a pH closer to 7, a neutral pH value, makes it hard to establish if acidic soils do contain more arsenic than more neutral soils. However, the acidic soils such as those found in this study are common in vineyards throughout New Zealand and the Hawke’s Bay (Caspari, 1996), which suggests that vineyard soils could be particularly susceptible to arsenic contamination.

The soils throughout the study, with the exception of V3b2, were characterised by high sand contents, which is typical for the Gimblett Gravels Winegrowing Area. The analysis of the sand content of the samples in comparison to their associated arsenic concentrations showed no relationship for samples taken close to the post, while there was a weak relationship for samples taken further from the post. Therefore, it is suggested that post sites with a lower sand content may accumulate more arsenic in the topsoil layers 50cm from the post than the more sandy post sites. One explanation for this pattern may be the increased pore space associated with the more sandy soils, allowing arsenic to be more easily leached down the soil profile, with the result that less arsenic spreads laterally and accumulates further from the posts. Also the more sandy soils will probably contain lower levels of organic matter and clay. Therefore, the lack of fine particles restricts the ability of absorption and could result in a low retention of arsenic (Chirenje et al., 2003).

Because of the generally high sand contents found throughout the sample sites, clay contents of the sites were all reasonably low. Similar to the analysis of the other soil properties, there was found to be no relationship between clay content and the arsenic concentration of the A samples, while there was just a weak relationship for the B samples. This could largely be due to the fact none of the sample sites contained what could be regarded as a high clay content, which makes it hard to compare samples with comparatively high and low clay contents. Previous research suggests that
arsenic absorbs to clay particles, but with low contents of clay present, this process may not be important. This suggests that the clay content of the soil, when present in low amounts, may not play an important role in affecting the accumulation of arsenic in surrounding soil.

Stepwise regression was used to explore which combination of soil properties has the most effect on arsenic accumulation. The results showed that while the concentration of arsenic in the A samples (5cm from post) was more closely related to high organic matter, low sand and high clay contents, the levels of arsenic in the B samples (50cm from post) were more related to lower soil pH and lower sand content. This suggests that a soil with a high organic matter content and low sand content (and associated higher clay content) may contain higher concentrations of arsenic in the topsoil surrounding the post. This could be due to both the higher organic matter content absorbing the arsenic, and the low sand content reducing the pore space, therefore reducing the ability of arsenic to be leached down the profile. Also, more acidic soils with a low sand content may contain higher arsenic levels in topsoil 50cm from the posts. This could possibly be due to arsenic being more mobile in an acidic soil, which is looked at in more depth in the next section.

With arsenic shown to accumulate in the topsoil up to 50cm from posts, there is potential for further soil and groundwater contamination. To address these issues, it becomes important to try and understand the movement of arsenic vertically and horizontally in the soil profile. The following section looks at arsenic mobility in the soil, and the effect soil properties may have on it.

5.2 Effects of soil properties on the mobility of arsenic in vineyard soils

The movement of arsenic, both down the soil profile and laterally through the soil, is important to an understanding of the potential for soil and groundwater contamination. This section considers how soil properties such as organic matter, soil pH, sand, and clay particles may affect the mobility of arsenic vertically and laterally once it has leached from the posts into the surrounding soil.
The sites with the higher organic matter contents showed not only higher accumulation of arsenic in the upper layers of the soil, but also greater concentrations of arsenic throughout the whole soil profile. This suggests that soils with a higher organic matter content may promote the vertical movement of arsenic down the soil profile. Laterally, more arsenic is also found at a distance of 50cm from the post at sites with higher organic matter than the sites with a lower organic matter content. This shows that soils with a higher organic matter content may promote the mobility of arsenic not just vertically, but also horizontally in the soil profile.

Previous studies differ in terms of the effects organic matter has on the mobility of arsenic in the soil. Generally it is recognised that organic matter attracts and absorbs most heavy metal particles. Studies by Holland and Orsler (1995), and also Lebow (2005) showed that organic matter, which is mostly found in the top 20cm of the soil may act as a sponge, absorbing the arsenic, therefore allowing less arsenic to move down the soil profile, decreasing arsenic mobility. In contrast, and similar to the results of this study, it has been found that unlike most trace metals, arsenic appears to move down the soil profile and is not immobilised at the soil surface (Morrison, 1999).

While the less acidic soils contained more arsenic in the top 10cm from samples taken close to the post, the more acidic soils contained greater concentrations further down the soil profile to a depth of 50cm. This would suggest that the more acidic soils promote arsenic mobility down the soil profile. Alternately, there could also be greater leaching below ground in more acidic soils. The higher arsenic concentration found in the top 10cm for the less acidic soils could be as the result of not just soil pH, but the respective organic matter and clay contents that can be found in less acidic soils. At a distance of approximately 50cm from the post, arsenic concentrations were significantly greater at several depths for the more acidic soils than the less acidic soils at the 95% level of confidence. This would imply that there is greater mobility of arsenic laterally away from the post in the more acidic soils, or there is greater movement of arsenic in the surface layers where arsenic levels are higher, and after time the arsenic is leached down the soil profile.
The results from this study are consistent with previous studies that have found heavy metals generally become more soluble in acidic soils and consequently their mobility in the soil increases. Previous studies of the behaviour of arsenic in soil suggest that the mobility of arsenic is a function of pH (Lebow, 2005; Gezer et al., 2004), with the lowest releases around pH 6.0 to 7.0 and increased mobility at lower pHs.

At a distance of just 5cm from the posts, the sites with a lower sand content contained higher arsenic concentrations in the top 20cm than the more sandy sites. However, the sites with a higher sand content contained more arsenic further down the profile than the less sandy sites. So while the less sandy soils may contain more arsenic in the upper layers of the soil, the more sandy samples possibly promote the mobility of arsenic vertically down the soil profile. Further from the posts, there is less evidence of increased arsenic mobility laterally in the more sandy sites. Overall, the results suggest that a high sand content may promote the vertical movement of arsenic but may also decrease the amount of arsenic that spreads horizontally from the posts.

In this study, arsenic was found to leach down through the soil profile. This is similar to other studies which found that a soil with a high sand content is associated with high arsenic mobility, in part because the associated low CEC of the soil means the arsenic does not tend to absorb to any soil particles (Townsend et al., 2003; Chirenje et al., 2003; Dagan et al., 2006). The increased mobility may also be due to the larger size of the sand particles creating larger pore spaces, thereby reducing capillary storage. Consequently, there is a freer flow of water, especially during periods of irrigation or rainfall events, and a greater propensity for arsenic to move down the profile.

No relationship was found between the clay content of the soil and arsenic mobility. This could be due to the low clay contents found throughout the vineyard soils as discussed previously. Other studies show that the higher the clay content of a soil, the greater the CEC of the soil, and therefore the greater the ability of soil particles to attract and demobilise arsenic within the soil. However, with clay contents likely to be low in typical free-draining vineyard soils, the effect of clay sized particles on arsenic mobility can be expected to be minimal.
Individually, soil properties seem likely to affect the mobility of arsenic vertically and horizontally in the soil profile in different ways. However, soils rarely reflect the dominance of a single property; instead, different soil types are made up of high and low proportions of a number of soil properties. A free-draining sandy soil will typically contain not just a high sand content, but also a low clay and organic matter content, whereas a more finer soil may contain a higher clay content, and also a higher organic matter content and a lower sand content. So when determining the effect soil properties have on arsenic mobility, it may be more appropriate to consider all the soil properties present in the respective soils, such as the two contrasting post sites that were investigated more closely.

The post site V\textsuperscript{1}1\textsubscript{1} is characterised with a higher sand content and soil pH, and a lower organic matter and clay content. In contrast, the V\textsuperscript{3}b\textsubscript{2} post site has a low sand content and a more acidic soil pH, and a higher organic matter and clay content. The comparison of arsenic concentrations between these two post sites illustrates the difference in arsenic mobility between the two soil types. V\textsuperscript{1}1\textsubscript{1} has a consistent concentration of arsenic throughout the 50cm soil profile close to the post, and very little arsenic in samples throughout the profile further from the post. On the other hand, V\textsuperscript{3}b\textsubscript{2} contains very high arsenic concentrations in the top 20cm of the profile close to the post, and a lot lower concentrations at greater depths. Similarly, the samples taken further from the post show elevated arsenic in the top 20cm with concentrations decreasing further down the profile.

This would suggest that the more sandy V\textsuperscript{1}1\textsubscript{1} post site promotes the vertical movement of arsenic down the profile, and reduces the movement of arsenic laterally from the post. In contrast, V\textsuperscript{3}b\textsubscript{2} seems to promote the lateral movement of arsenic away from the post, while reducing the risk of arsenic leaching further down the profile. The control sample of V\textsuperscript{3}b\textsubscript{2} also showed elevated levels of arsenic in comparison to V\textsuperscript{1}1\textsubscript{1}, which could suggest that arsenic is leaching laterally from the post at a greater distance than 50cm. It must be noted that V\textsuperscript{3}b\textsubscript{2} has been in service for longer than V\textsuperscript{1}1\textsubscript{1}. This may account for the higher arsenic concentrations in the upper layers of soil, however the greater length of time the post has been in the soil may also emphasise the idea that more acidic soils with a lower sand content, and higher
organic matter and clay content may promote the horizontal movement of arsenic and decrease the amount of arsenic able to leach vertically down the soil profile.

5.3 Potential for arsenic contamination of groundwater

With arsenic thought to be relatively more mobile, especially in predominantly sandy soils such as those in the Gimblett Gravels Winegrowing Area, and the location of an unconfined aquifer beneath a majority of the vineyards, groundwater from this aquifer was sampled to test for the potential of arsenic contamination. However, the analysis of the samples showed low concentrations of dissolved arsenic, well below the New Zealand guideline for arsenic in drinking water. This suggests that while arsenic is leaching from treated posts into surrounding soil, the arsenic is either not reaching the groundwater or if it is, not in sufficient quantities to be observable.

In comparison to arsenic levels found in aquifers in the winegrowing region of Marlborough by Robinson et al. (2005), these results are very low. However, there are a number of differences between the two sites, including soil properties, but especially the depth of the aquifers. The depth of the wells sampled for this study ranged from 29.87 to 40.00 metres, which is comparatively deep in comparison to the depth of the Rarangi shallow aquifer, which at times is known to come in contact with the bottom of the posts.

The age of vineyards in the area sampled is relatively young, with the oldest vineyards in the area only about 15 years old. While the arsenic concentration of the groundwater is very low at present, it seems there is potential for arsenic to move further down the soil profile, as more arsenic is leached from the aging posts. It will be important to monitor arsenic levels in groundwater in coming years.
5.4 Implications for viticultural practices from the accumulation of arsenic in vineyard soils

This study has shown that arsenic accumulates at levels which start to cause some concern, particularly in the topsoil surrounding treated posts in vineyards. Also, in the presence of high organic matter, low sand, and a low soil pH, arsenic has been found in elevated levels up to 50cm away from posts, and to depths up to 50cm. The leaching of arsenic from treated posts into soil is of concern because, depending on its extent, it may reduce soil fertility, contaminate groundwater, and present a human health hazard if land use changes occur and new exposure pathways develop (Robinson et al., 2005).

With viticulture continuing to expand throughout New Zealand’s farmlands, the continual use of CCA treated posts in vineyards may have adverse effects for soil and groundwater quality and implications for future land use change. If older vineyards were to be converted to another land use at some future time, such as agriculture, horticulture or residential development, then soil contaminated with arsenic could conceivably become a health hazard to animals, plants and humans.

There could be several ways to eliminate or reduce the amount of arsenic leaching into soil from treated posts. There are a number of alternatives to CCA treated *Pinus radiata* posts, including plastic, galvanised steel, concrete and other, untreated, timbers such as *Eucalyptus* or beech, which would clearly not leach any arsenic. Alternatives are seen by many viticulturalists to be not as structurally effective, and often more expensive than traditional CCA treated posts, but if alternatives were used more often, their price would probably fall (Beder, 2003). If CCA treated posts are used, then maybe reducing the ratios of Cu, Cr and As in the treatment fluid or lowering the total amount of CCA that is impregnated into the posts may decrease the rate of CCA leaching (Robinson et al., 2005). However, Lebow et al. (2004) found that wood with a lower CCA concentration may have greater leaching due to the lower concentration of chromium that fixes the preservative in the wood. Lacquering CCA treated posts may be another way of reducing CCA leaching from treated timber.
Another implication of the widespread use of treated posts in vineyards is the storage and stock piling of broken and replacement posts. Posts are often broken by tractors and other machinery and are replaced annually at a rate of approximately 5% (Clothier et al., 2006). Because of the chemicals present in the treated posts, the posts that are replaced cannot be buried or burnt, creating the issue of disposal. Currently the only method for disposing of CCA-treated wood is through local council landfills, but for only small quantities (Read, 2003). Because vineyards often store extra posts and subsequent broken posts are stock piled throughout the vineyard, this may create “hot-spots”, as large piles of posts create a greater source of arsenic that may leach into the soil. Potentially, as viticulture continues to expand, millions of posts will need to be stored or disposed of.

5.5 Limitations of the study

While the analyses of soil samples indicate that there is a relationship between arsenic accumulation and mobility with contrasting soil properties, there was not a large amount of variability for some of the soil properties. None of the post sites contained particularly high organic matter or clay contents, or high soil pH values, which possibly did not emphasise the effect the soil properties may have on arsenic in soil. A more extensive selection of post sites, possibly from some different vineyards could have solved this issue.

The depth at which samples could be taken was hindered by the stoney composition of the soils. Previously, it has been found that higher arsenic concentrations are measured directly under the posts, than laterally. However, because posts were not able to be removed, and samples could not be taken any depths greater than 50cm due to the nature of the soil, no samples beneath the posts could be taken. Therefore, the potentially higher concentrations of arsenic leaching beneath the posts could not be documented. The lack of depth of sampling also limited the ability to show how deep arsenic may be leaching down the soil profile to see whether arsenic has the ability to migrate into underlying groundwater.
Another factor that may have influenced the results was the depth at which the control samples and corresponding soil property contents were taken from. Control samples, that were used to determine soil properties at the post site, were taken at a depth of between 20 and 30cm. Because a lot of the finer silt and clay particles, and also organic matter, of this former river bed soil are found in the top 10cm, the respective organic matter and clay contents of the control samples may not be an accurate representation of the characteristics of the upper layers of the soil profile. Ideally, each of the soil properties would have been measured for each sample taken at each depth and distance. However, restrictions in time and resources meant this was not possible for this particular study.

There are also limitations in the interpretation of the groundwater results, which showed that none of the groundwater samples contained elevated levels of arsenic. Firstly, the arsenic present in the soil may not have had time to move all the way from the recharge zone to the monitoring well site. Determining the age of the groundwater at each of the sites could help to determine how long it may take for arsenic to become present in the groundwater. Secondly, the vineyards where arsenic is being leached into the soil may not encompass the aquifer’s recharge zone, so arsenic may not leach into the aquifer that was sampled.

It must also be mentioned that the results for soil and groundwater samples reflect one form of arsenic due to the analytical methods that were available. Soil samples were analysed for total arsenic and do not take into account proportions of arsenic in its reduced As (III) oxidation state (arsenite), or arsenate the oxidised As (V) pentavalent form. Groundwater samples were measured for total dissolved arsenic only.

5.6 Key areas for future research

This study identifies several areas of key research that need to be undertaken to help in understanding the issue of arsenic leaching from treated posts in vineyard soils, further. The results indicate that arsenic accumulating in soil surrounding posts may
be widespread, so there needs to be more research to ensure that the arsenic is not available to plants, and especially is not being taken up into grapes.

The higher arsenic concentrations found in the older vineyard sites suggests that arsenic continues to leach out of the posts over its lifetime. Further research, possibly analysing the soil around replacement posts in older vineyards could enhance the understanding of long term arsenic accumulation and leaching.

The distance that arsenic may leach both vertically and horizontally is still unknown. With samples in this study only taken at a maximum depth of 50cm and a distance from the post of 50cm, with the right equipment there is potential to measure the arsenic concentration both further down the soil profile beneath the post, and at distances further away from the post.
Conclusions

The overall aim of this research was to assess the accumulation and mobility of arsenic in the soil of several Hawke’s bay vineyards and examine any arsenic contamination of underlying groundwater, as a result of arsenic leaching from CCA treated posts into the surrounding soil. The study was divided into three specific objectives and from the results gained, the following conclusions can be drawn:

- Soil surrounding all thirty five posts throughout three Hawke’s Bay vineyards was found to contain elevated concentrations of arsenic. Arsenic is, therefore, accumulating in the soil. As expected, arsenic concentrations were significantly greater in samples taken 5cm from the post than samples taken 50cm from the post, although elevated concentrations of arsenic were still found at a distance of 50cm from the posts at depths of 10 and 20cm.

- Arsenic concentration was significantly greater in the topsoil compared to the subsoil. The median arsenic concentration of topsoil samples taken close to the posts from throughout the three vineyards exceeded the New Zealand interim guideline of 30 ppm for arsenic in agricultural soils.

- Soil surrounding posts that had been in service in the ground the longest contained the highest arsenic concentrations. The oldest posts used for sampling were just 16 years old, which is relatively young in terms of the life of CCA treated posts. Research using older posts or replacement posts in an older vineyard is required, to assess in more depth the effect of post age on arsenic concentrations in surrounding soil.

- Accumulation of arsenic in the soil was more closely related to the organic matter, sand and clay content of the respective soil. With arsenic found to accumulate in
Conclusions

greater concentrations in soils with a higher organic matter and clay content, and a lower sand content.

- Arsenic was found to be more mobile in the soil profile, both vertically and laterally in the more acidic soils that contained higher sand contents and lower organic matter contents.

- There were no elevated levels of arsenic in any of the groundwater samples, with all samples containing less than 0.001 ppm well below the New Zealand guideline for arsenic in drinking water of 0.01 ppm. However, the depth from which samples were taken from was significantly deeper than in similar studies which have shown elevated levels of arsenic in underlying groundwater. Because groundwater is such a valuable resource in New Zealand it is recommended that monitoring of arsenic levels in groundwater near intensive viticultural areas continues into the future.

- The use of posts treated with copper, chromium and arsenic in vineyards throughout New Zealand has implications for the wine industry of New Zealand. If the use of CCA treated posts continues with the rapid expansion of the industry then land sustainability and soil contamination issues will become apparent. Alternatives to CCA treated posts are being developed and some are being used, however, these initiatives need to be further developed and applied at a greater national scale. Currently there is no way to safely dispose of large quantities of CCA treated posts, which will become an issue in the future.

Overall this study has identified widespread leaching of arsenic into surrounding soils of CCA treated posts in several Hawke’s Bay vineyards. Along with the age of the posts, several soil properties have shown to have an effect on the accumulation and mobility of arsenic in the soil. There is no evidence of elevated levels of arsenic in underlying groundwater.
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Appendix A

Soil characteristics of each post location.

<table>
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<tr>
<th>Post Site</th>
<th>Organic matter content (%)</th>
<th>Soil pH</th>
<th>Sand content (%)</th>
<th>Silt content (%)</th>
<th>Clay content (%)</th>
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