Arsenic in Groundwater of the Waikato Region

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1.1   Rationale and scope

Arsenic is a toxic but naturally occurring chemical element, present at low levels in all soil, water, plants, animals, and foods. For members of the general population, most exposure to arsenic is through the small amounts of this element that are naturally present in food and drinking water.

Exposure to too much arsenic can result in a range of cancers, and a wide range of non-cancer effects (**Table 1**). Population-wide studies overseas have shown that the most common cancers caused by too much arsenic in drinking water are those of the bladder and lung. Susceptibility of an individual to such conditions is partly determined by genetic factors (Ghosh et al.*, 2005), and exposure while young appears to amplify risks of developing arsenic-related diseases later in life (Smith et al., 2006). In most countries, the probability of such conditions occurring is kept to a practical minimum by setting upper limits for arsenic in food and drinking water. In New Zealand, the tolerated maximum concentration of arsenic in drinking water is 10 µg/L (Ministry of Health, 2005).

In previous work on arsenic in the Waikato Region's water supplies, the focus has been on surface waters, particularly the Waikato River. To date, little has been documented about the prevalence and geographical distribution of arsenic in Waikato groundwater. However, such information is of public health significance, because groundwater comprises a major source of drinking water in the Waikato Region's rural areas. The rural population of the Waikato Region is estimated to comprise about 75,000 people.

In addition to implications for human exposure and health, there is a possibility that some agricultural practices may cause a gradual increase in concentrations of arsenic in regional groundwater over time. If it were occurring, such an effect might require development of new management approaches to safeguard the groundwater resource. However, in order to either confirm or discount the existence of a link between agricultural activities and arsenic in groundwater, there is a need for robust baseline data, against which future data can be reliably compared.

Over the last few years, arsenic analysis has been carried out on a total of 302 groundwater samples collected by Environment Waikato staff.   The aim of this report was to compile and assess these analytical results to present the first region-wide picture of arsenic concentrations in Waikato groundwater. This information can then be used for a number of purposes, from protection of human health to gaining a better understanding of arsenic geochemistry in regional groundwater. Features of this report include the following:

- Estimates of rates of compliance with drinking water standards on both a regional basis and for sub-regional areas;
- Identification of areas of the Waikato region with comparatively high arsenic concentrations in groundwater;
- Identification of mechanisms that can result in high arsenic concentrations in Waikato groundwater;
- Delineation of the chemical form (speciation) of arsenic in cases where drinking water standards are exceeded;
- Assessment of the reliability of point-in-time measurements at specific locations, in relation to variation of arsenic concentrations in groundwater with time;
- Discussion of possible links between concentrations of arsenic in Waikato groundwater and specific agricultural practices.

1.2 Technical background

1.2.1 Human exposure to arsenic in drinking water

Over recent years, arsenic in drinking water has become a matter of worldwide interest. This has come about as a result of both large scale poisonings being caused by high concentrations of arsenic in drinking water, and ongoing research to understand of the mechanisms of arsenic toxicity at low levels. A detailed toxicological profile of arsenic is available from the US Agency for Toxic Substances and Disease Registry (ASTDR, 2005). Identified and inferred effects and symptoms linked with exposure to arsenic in drinking water are listed in **Table 1**.

Table 1   **Effects and symptoms linked to various concentrations of arsenic in drinking water.**

Arsenic concentration	Type of poisoning	Identified symptoms and effects so far linked to arsenic in drinking water
Above 1200 µg/L	Acute	Abdominal pain, vomiting, diarrhoea, muscular weakness and cramping, pain to the extremities, erythematous skin eruptions (erythema is redness of the skin caused by dilatation and congestion of the capillaries), swelling of eyelids, feet and hands. Possible progressive deterioration in motor and sensory responses (depending on exposure and vulnerability), finally leading to shock and death (Mead, 2005).
Above 115 µg/L	Chronic	**Non cancerous effects**: skin lesions, diabetes mellitus (also known as type 1 diabetes and insulin-dependent diabetes), adverse effects on the digestive, respiratory, cardiovascular, and nervous systems, bronchiectasis (chronic permanent widening of the bronchial tubes), reproductive and developmental effects. A number of effects depend also on nutritional and other factors: variation between countries seen in degree of skin pigmentation, hyperkeratosis (an excessive thickening of the outer layer of the skin – appearance of thickened, horny, verruca-like scales over the entire body), respiratory stress, polyneuropathy (inflammation of multiple nerves causing loss of sensation or movement), and peripheral vascular disease. **Cancers**: skin, bladder, kidney, liver, lung, colon, uterus, prostate, and stomach. Lung cancer a leading cause of death among those exposed (Mead, 2005).
Above 50 µg/L	Chronic	Intellectual impairment in children, cancer risk significant (Mead, 2005).
20 µg/L	Chronic	Lifetime risk of bladder or lung cancer from the exposure estimated to be about 1 in 140 people (National Research Council, 2001).
10 µg/L	Chronic	Lifetime excess bladder or lung cancer risk estimated at about 1 in 300 (National Research Council, 2001). Excess skin cancer risk estimated at 1 in 1700 people (Ministry of Health, 2005).
5 µg/L	Chronic	Lifetime excess risk of bladder or lung cancer estimated at about 1 in 500 people (National Research Council, 2001).
3 µg/L	Chronic	Lifetime excess risk of bladder or lung cancer estimated at about 1 in 900 people (National Research Council, 2001).

Arsenic is classified as a known human carcinogen, but a wide range of non-cancer effects can also arise from acute or chronic exposure to arsenic in drinking water. Whether an individual exposed to a given dose of arsenic is at higher risk of developing one or more of the endpoints listed in **Table 1** depends on a range of inter-related factors. These include genetic differences in biochemical response patterns (polymorphisms between individuals), nutritional factors, exposure to cofactors such as tobacco smoke, and differences in metabolic pathways, responses and endpoints between high-dose and low-dose exposures (Mead, 2005; Ghosh et al*.,* 2005). The significance of low-level dietary arsenic is a subject of intense ongoing research (Mead, 2005; Smith et al*.,* 2006). In some countries, however, higher exposures are the problem. In West Bengal, Bangladesh and Southern India, concentrations of arsenic in well water are such that over 500 million people are at risk of chronic arsenic poisoning, in an event the World Health Organization have referred to as *'the worst mass poisoning in history'* (Mead, 2005; Tanabe et al*.,* 2001).

In New Zealand, the Provisional Maximum Acceptable Value (PMAV), or standard, for arsenic in drinking water is 10 µg/L (parts-per-billion). As evident from **Table 1**, this level of exposure, where experienced over an extended period, is still associated with a reasonably high lifetime excess cancer risk of 1 in 300 for bladder and lung cancers (National Research Council, 2001), and 1 in 1700 for skin cancers (Ministry of Health, 2005). By comparison, the usual tolerable excess cancer risk for New Zealand is regarded as 1 in 100,000 (Ministry for the Environment and Ministry of Health, 1997). The standard therefore defines a tolerated upper limit for arsenic in drinking water, but it is apparent that most protection of the general population still relies on the fact that concentrations in drinking water are usually much lower than 10 µg/L, most of the time. In addition to regulatory limits, for contaminants with no known benefit such as arsenic the As Low As Reasonably Achievable (ALARA) principle is usually adopted as the desirable policy position. The Ministry of Health define a water distribution zone as that part of the town or community receiving water of similar quality, noting that for a small supply, this means 'everywhere,' whereas for larger supplies, it may be only part of a town or city. In a review of contaminants in New Zealand drinking water, Davies et al*.* (2001) identified arsenic concentrations exceeded half-PMAV (5 µg/L) in 70 distribution zones serving a population of approximately 285,000, and exceeded the PMAV (10 µg/L) in 28 distribution zones serving a population of approximately 21,000. Arsenic was therefore considered to be of high public health significance.

In most of the previous work on arsenic in the Waikato region's water supplies, the focus is on arsenic in surface waters, and in particular, the Waikato River. The Waikato River currently receives a significant load of geothermal arsenic and its concentrations average over twice the drinking water standard before treatment. Arsenic concentrations in the Waikato River have decreased over the years due to reducing inputs from the Wairakei Geothermal Power Station. Removal of arsenic during water treatment at Hamilton appears to have also improved from approximately 80% of the total present in 1993-4 to 90% in 2002. The average arsenic concentration of Hamilton drinking water in 2002 was 2.3 µg/L (**Table 2**).

Table 2 **Arsenic in the Waikato River and Hamilton drinking water, and apparent treatment efficiency, for 1993-1994 and 2002.**

Monitoring Year	1993-1994[a]	2002[b]
River concentration (µg/L)	32	23
Treated water concentration (µg/L)	6.2	2.2
Percent removal (%)	80.6	90.4

[a]. Data for 1993-1994 from McLaren and Kim (1995).
[b]. Data for 2002 from Environment Waikato for untreated water and Maire Porter, Hamilton City Council (personal communication, 2003) for treated water.

In comparison with surface water, before the present survey, little was known about the prevalence and geographical distribution of arsenic in Waikato regional groundwater. Groundwater comprises a major source of drinking water in the Waikato region's rural areas. The rural (non-urban) population of the Waikato region is estimated to comprise about 75,000 people. In the 2005 revision of the New Zealand Drinking Water

Standards, a requirement to demonstrate compliance with standards was extended to include small water supplies serving more than 1,500 person days per year (*e.g.* 25 persons for 60 days) (Ministry of Health, 2005) (although this is not yet mandatory in law). However, most private groundwater supplies still fall below this reporting threshold because of the small populations they serve, and very few have previously been tested for arsenic.

1.2.2 Occurrence of arsenic in groundwater

Influence of lithology on occurrence of arsenic in groundwater

As arsenic is naturally occurring, it can be assumed that arsenic is present at some concentration (whether parts per million, billion, trillion or quadrillion) in all groundwater. However, the PMAV for arsenic in drinking water of 10 parts per billion (µg/L) defines a magnitude that is of particular relevance for human health, in relation to groundwater used for drinking. Specific lithologies can result in higher concentrations of arsenic in the groundwater of some areas than others. Higher-than-average arsenic occurs in greywackes (old ocean sediments), schists (the same sediments transformed with heat and pressure, and chemically similar to greywackes), Tertiary volcanics, and some coals and peats (Davies, 2001). Within the volcanic lithologies, arsenic can be particularly elevated in sulphide mineral ores.

Arsenic enters groundwater mainly through geochemical interactions between the water and rocks and minerals that it comes into contact with. Such interactions include rock and mineral dissolution and weathering, sorption/desorption processes and leaching. Rates of weathering, dissolution and leaching are increased by geothermal heating, causing concentrations of major and trace constituents to increase in associated water. The influence of geothermal sources on arsenic concentrations in ground and surface waters can be felt over large areas. As an example (for surface water), the water of Lake Taupo as a whole ($606 km^2$ in area) and the Waikato River (425 km in length) both contain arsenic at elevated concentrations as a result of a volcanic lithology accompanied by geothermal heating.

In groundwater of the Waikato region, the highest concentrations of arsenic might be expected to be found in water associated with volcanic lithologies, but particularly in areas where geothermal heating or arsenic-bearing sulphide minerals are also present. The association of arsenic with sulphide minerals is significant. Arsenic employed for industrial uses (for example CCA treatment of wood) is recovered as a by-product of copper refining (Read, 2003) – which itself is mined from sulphide ores. This association extends to sulphide inclusions in other rocks and minerals. In altered greywacke, for example, the large crystals are usually marcasite (iron sulphide, FeS_2). Arsenic is present at low but significant levels (about 0.5% or 5000 mg/kg) in some parts of marcasite crystals, particularly on edges. The Coromandel Peninsula is notable for its sulphide mineral ore deposits and history of mining sulphide metals such as lead, zinc and copper.

Most arsenic in groundwater is probably generated by weathering, dissolution and leaching chemisty occurring beneath the surface at groundwater depth, but contributions of arsenic from surface environments may also become significant in certain cases. An anthropogenic example might be arsenic in irrigation water drawn from the Waikato River (itself geothermally influenced and presently containing about 25 µg/L arsenic), most of which would be retained by surface soils, but some of which is likely to leach in to groundwater over the longer term. Some leaching and contribution to arsenic in groundwater is also likely to occur from soils and subsoils themselves, which in New Zealand (as elsewhere) typically contain about 2-10 mg/kg arsenic.

Limitations of lithology in determining the outcome at a given well

Presence of an arsenic-rich lithology (with or without geothermal heating) may be a basic prerequisite for development of high concentrations of arsenic in groundwater of a given area or region, but does not provide a complete picture when considering how much arsenic may end up in the water of any specific well. This is for the following reasons:

- Primary release of arsenic from rocks and minerals to groundwater at depth is only a first step. After release of arsenic in to the groundwater, a complex range of chemical interactions can occur in the subsurface environment, before the water reaches a given water supply well. To a first approximation, these processes can be thought of as (a) multiple instances of fixation and release of the dissolved arsenic to and from solid phases in soils and subsoils, upon which are overlayed (b) the susceptibility of some of these adsorptive phases to oxidation or reduction.

- Typical natural concentrations of arsenic in soils and subsoils (2-10 mg/kg) are already 200-1000 times higher than the limit set as the New Zealand drinking water standard.[1] Natural arsenic is soils is reasonably well fixed, but not entirely immobile, and does leach to soil porewater to some extent. Processes that might work to facilitate desorption and leaching of even small proportions of arsenic from soils and subsoils therefore have the potential to significantly increase arsenic concentrations in groundwaters, independently of whether or not underlying lithologies also happen to be arsenic-rich.

An arsenic-rich lithology is therefore 'neither necessary nor sufficient' in determining whether the water of a given well may end up with high arsenic.[2] This does not mean that lithology is unimportant, but rather that its influence would be best thought of as one of raising the probabilistic baseline for exceedances of the drinking water standard across a given area or region. Information about lithology would not be sufficient to determine the outcome at a specific water supply well.

Processes that lead to arsenic enrichment in water of a given well

In this section, an overview is provided of some key subsurface chemical processes that tend to determine whether the water of a given well is likely to contain high or low concentrations of arsenic. For the most part, these involve the adsorption and release of two inorganic forms of arsenic.

Arsenic moving in groundwater is usually present as the **arsenate** ($As^V = AsO_4^{3-}$ / $HAsO_4^{2-}$ / $H_2AsO_4^-$) form, and this is chemically analogous to phosphate (PO_4^{3-}). Over time, arsenic in groundwater often becomes adsorbed to finely divided (colloidal) iron and manganese oxyhydroxides (hydrated iron and manganese oxides) naturally present in subsoils and sediments, such as goethite (α-FeO(OH)). This process removes dissolved arsenic from the groundwater by trapping it on a solid substrate.

Recent evidence shows that arsenic concentrations in iron-pans can be particularly high (up to 480 mg/kg), and that arsenic concentrations in Waikato surface soils are highly correlated with those of iron (**Figure 1**). These associations suggest that where iron oxides have formed in a soil, they act as a trap for arsenic in groundwater, with the highest concentrations being reached in those soils with the greatest and most stable iron oxide traps available.

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[1] Soil typically contains 2000–10000 µg/kg (2-10 mg/kg) arsenic, which can be compared with the drinking water PMAV of 10 µg/L = 10 µg/kg (0.010 mg/kg).

[2] A 'sufficient cause' is defined as a set of minimal conditions and events that inevitably produces a given outcome (Rothman and Greenland, 2005).
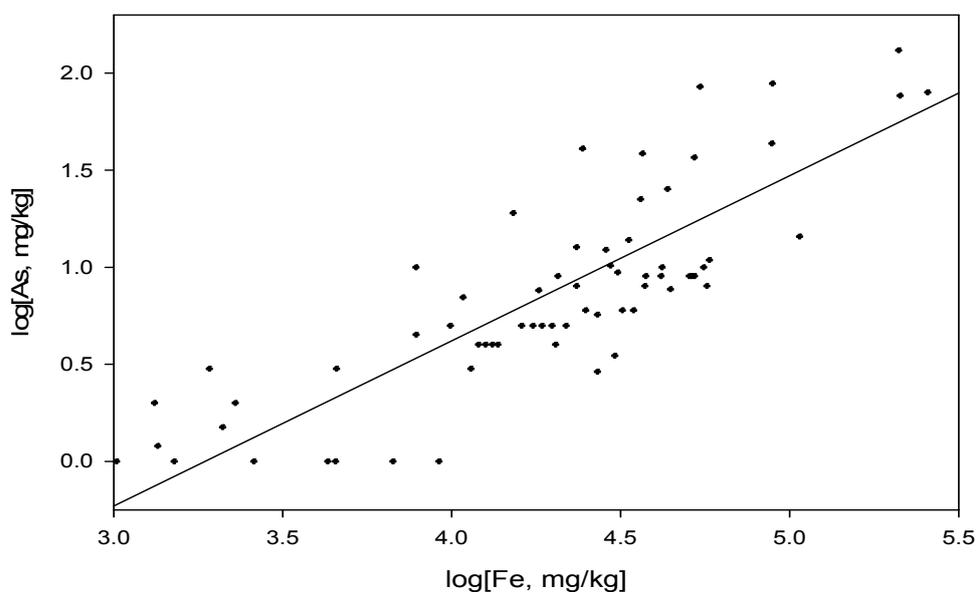
Figure 1 **Correlation between iron and arsenic in Waikato soils.**[3] **Data includes some iron-rich soils of the Hamilton basin.** N=68, R=0.841, p<0.0001. Equation of line: $\log[As] = 0.8507\log[Fe] - 2.7812$.

Colloidal iron oxides in soils and sediments are often subject to periodic dissolution and re-precipitation. Dissolution occurs when conditions become sufficiently reducing (for example, α-Fe^{III}O(OH) becomes Fe$^{II}_{aq}$), and causes release of adsorbed contaminants. This process can be biologically facilitated (Acharyya and Shah, 2004). For example, in Waikato River sediments, there is some evidence for involvement of microbes such as *Anabaena oscillaroides* using arsenate as an energy source and causing its conversion to arsenite (McLaren and Kim, 1995). However, Bose and Sharma (2002) have demonstrated that most subsurface redox reactions involving iron and arsenic are also possible through predominantly abiotic pathways.

Reductive dissolution of iron oxides is probably the main mechanism responsible for the observation that arsenic concentrations in shallow groundwater can vary with season (Frost et al., 1993; Focazio et al., 1999; Carrillo-Chavez et al., 2000). This may be abiotic or biologically-mediated. Seasonal variation can also accompany a changing water table, with a rising water table causing out-flush in areas where groundwater reaches secondarily retained arsenic (Ohlander et al., 2001).

Another concurrent change that often occurs under reducing conditions is a change in the chemical form of released and dissolved arsenic, from arsenate (AsO_4^{3-} or $HAsO_4^{2-}$) to **arsenite** (AsO_2^- or H_3AsO_3), where the oxidation state of the arsenic atom has changed from 5+ (or V) to 3+ (or III). In the environment, plants, microbes, fish and other organisms, arsenic also forms a wide range of other more complex organo-arsenical compounds. These other forms of arsenic, however, can usually be neglected in groundwater as they are not usually formed. The dominant environmental forms by mass at any given moment in groundwater are simply the two main inorganic forms – arsenate (often called 'arsenic five' due to the oxidation state of the arsenic atom) and arsenite (often called 'arsenic three').

Conversion of arsenate to arsenite is significant in terms of potential exposure and risk, because the latter is usually more mobile in the subsurface than the former (Bose and

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[3] Based on Regional Soil Quality Monitoring data for Waikato soils with horticultural sites excluded due to former use of lead arsenate sprays (N=38 remaining samples) plus a survey of arsenic in iron-rich soils of the Hamilton basin (N=30 samples). Data at the upper end of the graph relates to the iron-rich soils, but overall, the two data sets appear to be contiguous (the total data set appears to be drawn from the same underlying population). Raw data: Environment Waikato documents 844227 and 927529. Description of ironpan survey: Environment Waikato documents 988315 and 988316.

Sharma, 2002). This is due to differing adsorption characteristics (Dixit and Hering, 2003). The toxicity of arsenite has also been estimated to be between 25-50 times greater than that of arsenate (Xu et al., 2003). Presently, the 2005 New Zealand drinking water standards make no regulatory distinction between the inorganic forms of arsenic, with the 10 µg/L PMAV referring to total arsenic (Ministry of Health, 2005).

In addition to reductive dissolution of hydrated metal oxides, other mechanisms of arsenic attenuation and release are possible, depending on which solid phases the arsenic has become associated as a result of the regional and local geochemical history. In Japan, Shimada (2003) identified three main mechanisms for release of arsenic to groundwater:

Type 1:   Reductive dissolution of iron oxyhydroxides (as discussed above);

Type 2:   Oxidation of arsenic pyrite (or more generally, oxidation of an arsenic-containing sulphide mineral, as with the marcasite crystals in greywacke);

Type 3:   Decomposition of arsenic-enriched organic matter in an alluvial peat layer. This might proceed under either reducing or oxidising conditions.

Depending on circumstances, each of these mechanisms might represent the most likely last release point in cases where elevated arsenic is detected in groundwater. Two additional factors determining the final concentration of arsenic measured in a sample of groundwater are groundwater flow and time (Burgess et al., 2000). Time can also permit a change in the speciation of subsurface arsenic – arsenic released under reducing conditions as arsenite (As(III)) may move with groundwater in to an oxidising environment, where thermodynamic stability will encourage it to gradually revert to arsenate (As(V)) (**Section 4**).

Summary

Rocks and minerals of the parent geology (such as altered greywacke) and geochemical conditions (such as geothermal activity) represent a significant original source of subsurface arsenic. However, some arsenic may also be contributed through leaching from surface soils and subsoils. Over time a proportion of this released arsenic becomes attenuated on hydrated iron and manganese oxides, and other sorptive phases that may be available such as sulphide minerals and organic matter. These phases can gradually accumulate arsenic by trapping it from the groundwater, but over the longer term can begin to act as secondary reservoirs for arsenic release. Processes causing dissolution or degradation of these second-step phases may be responsible for a significant proportion of cases where arsenic is elevated in shallow New Zealand groundwater.

Under New Zealand conditions, the mechanism likely to be encountered most frequently is reductive dissolution of iron oxides, but release from organic matter and sulphides may be important in some cases. Because iron oxide dissolution is often seasonal, arsenic in shallow groundwater supplies may also vary with season. Where reductive dissolution is the release mechanism, a correlation may exist between dissolved arsenic and dissolved iron and manganese in the groundwater, and the chemical form of arsenic may have also shifted to the more toxic and mobile arsenite (also known as AsO_2^-, H_3AsO_3, As(III) or 'arsenic three').

1.2.3 Other New Zealand studies

Localised arsenic contamination in many areas of New Zealand has been found to be associated with a number of anthropogenic sources such as timber treatment plants, old sheep dip sites, old orchards (from use of lead arsenate sprays), sulphide mine drainage and most recently the leaching of arsenic from treated timber posts in orchards and vineyards. Such contamination can reach very high levels in the case of old sheep dip sites (up to 11000 mg/kg, and more typically about 2000 mg/kg as a hot-

spot), but these are relatively small areas (Kim, 2003a). In old orchards, the contamination is more diffuse and widespread, but also present at a lower concentration (typically 30-60 mg/kg) (Kim, 2003b). For the most part, although arsenic can become elevated as a result of anthropogenic activities, such effects are usually fairly localised and insufficient to cause more wide-scale changes in arsenic concentrations in groundwater.[4]

Occurrence of (mainly natural) arsenic in the Waikato region's groundwater supplies has not been systematically examined before. From work elsewhere in New Zealand, it is clear that arsenic can be naturally elevated in New Zealand groundwaters. Three examples from other regions are as follows:

1. Tangimoana township in the Manawatu-Wanganui region had groundwater from 30 bores identified with arsenic transgressing PMAV for drinking water. The cause of the contamination was initially suspected to be from an old timber treatment site, but this was dismissed as there was no pattern to the contamination. The cause of contamination was unknown (Horizons MW, 2001), but would appear is likely to be natural.

2. In the Canterbury region, several studies have examined arsenic contamination of groundwater. Locations investigated include the Woolston-Heathcote, Brighton spit and Woodend-Waikuku-Saltwater Creek areas as well as the Kaikoura Plain. In the Woodend-Waikuku-Saltwater Creek areas, arsenic contamination of groundwater was highlighted after arsenic was added to the determinands tested as part of routine sampling of groundwater in indicator bores across the Canterbury Plains. Two initial detections led to nearby wells also being tested, when the detection of elevated arsenic concentrations was found not to be isolated but more widespread than initially thought (Pattle Delamore Partners, 2001). Pattle Delamore Partners (2001), suggest that due to the wide area and range of depths where contamination was detected, the source of arsenic was most unlikely to be from near surface locations associated with human activity. As well as elevated arsenic concentrations, iron, manganese, magnesium, alkalinity and turbidity concentrations were also found to be elevated. The pattern of chemical associations coupled with soil and geological strata makes the situation similar to naturally derived occurrences of arsenic studied overseas (Pattle Delamore Partners, 2001), operating through a reductive iron oxide dissolution mechanism as described earlier.

    The occurrence of moderate to high concentrations of arsenic in the Woolston-Heathcote and Brighton spit areas was also usually associated with elevated concentrations of iron, manganese and silica (Hayward, 2002; Pattle Delamore Partners, 2001).

    Elevated arsenic was also detected in wells on the Kaikoura plain. Initially, it was thought that there might be a relationship with the location of old sheep dip sites. However, patterns of arsenic detections in groundwater from private wells did not show a relationship with the locations of sheep dips or footbaths (Hayward and Smith, 2000; Environment Canterbury, 2003). It is likely that the source of arsenic in Kaikoura wells is predominantly natural (Environment Canterbury, 2003). The original source of arsenic is thought to be from the greywacke rocks of the Southern Alps, Tertiary coal measures and/or from discrete and intermittent discharges from hydrothermal springs (Callander and Fox, 2002).

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[4]   This makes sense in relation to the mass of native arsenic naturally present in soil. At a natural concentration of 6 mg/kg, one square kilometre of Waikato soil to a depth of 50 cm would contain about 3000 kg arsenic. By contrast, an old orchard of area 3 ha containing 60 mg/kg arsenic in the surface soil (to a depth of 15 cm) would represent about 240 kg arsenic. Similarly, a 20 x 20 m sheep dip site with an average soil arsenic concentration of 1000 mg/kg to 15 cm depth would contain about 60 kg of additional arsenic.

3. Elevated arsenic has also been reported in certain groundwaters of the Marlborough region (Robinson et al*., 2004). In this case there was an initial suggestion that some of this arsenic may be leached from millions of copper-chromium-arsenic (CCA) treated posts used in Marlborough vineyards, because soil around these posts is contaminated with arsenic (Mills et al*., 2004). However, it is now thought likely that most of the arsenic detected in Marlborough groundwater is also present as a result of natural mobilisation processes (Wilson and Davidson, 2005).

2 Methodology

2.1 Sample sites

Groundwater from bores at a total of 302 sites spread throughout the Waikato region was collected and analysed for total arsenic. Initial arsenic results were aggregated from several datasets held by Environment Waikato, with subsequent results from an additional 80 sites. Sample sites are spread across a range of uses from farm supplies, domestic supplies, schools supplies and community supplies. Ninety of the boresin the survey were school water supplies, in the following districts: Franklin (11), Hauraki (3), Matamata-Piako (14), Otorohanga (4), Rotorua (2); South Waikato (5); Taupo (2); Thames-Coromandel (11); Waikato (18); Waipa (16); Waitomo (4). Sampling locations are shown in **Figure 2**.

Information about the groundwater depth was available for 109 (36%) of the 302 sites sampled. Of these, the minimum depth was 0.12 m, and the maximum 77.5 m, but these were exceptional extremes. The geometric mean and median groundwater depths were 4.42 m and was 3.61 m (respectively) and the most frequently occurring depth (the mode) was 3.65 m.

Information about the specific lithology associated with each well is not readily available. However, more general information on dominant rock types in different areas of the Waikato region is available. The potential influence of general lithology on arsenic concentrations in Waikato region groundwater are explored in the results section.

2.2 Sampling and analysis

2.2.1 General sampling and determinands

Groundwater samples were collected from bores and piezometers from across the Waikato region using the groundwater sampling protocol developed by the Institute of Geological and Nuclear Sciences Ltd (Rosen et al., 1999). The sampling protocol involved sampling as close as possible to the well-head before water passed through pipe networks, treatment systems and storage tanks. At least three annular volumes of water were pumped to purge the bores and piezometers. Most bores had existing submersible pumps as well as the occasional deep well cylinder pump. Groundwater samples were analysed for nitrate, ammonia and other 'routine' water quality determinands. Routine water quality analytes comprise pH, conductivity, total dissolved solids, alkalinity, CO_2, calcium, magnesium, hardness, sodium, potassium, chloride, sulphate, boron, total iron, manganese, copper and zinc. Groundwater samples for total and acid soluble arsenic analyses were collected in plastic 250 mL nitric acid preserved bottles. All such samples were cooled with ice to <4 °C and sent to Hills Laboratories for analysis. Detection limits and analytical methods used are listed in **Table 3**.

A total of 302 groundwater samples were collected and analysed for either total arsenic or acid soluble arsenic. Most samples were collected during 2002 (104 samples) or 2004 (158 samples). Other sampling dates and number of samples collected were during 1992 (1), 1995 (24), 1999 (1), 2003 (4) and 2005 (10).[5]

2.2.2 Sampling for speciation determination

Determination of the redox state of dissolved arsenic in water is important for interpreting its toxicity, mobility, and geochemical transformations in the environment. Proper filtration and preservation of a water sample is essential for stabilizing the As(III/V) ratio prior to analysis (McCleskey et al., 2004). Filtering the sample removes

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[5] The exact sampling dates and times are recorded in Environment Waikato spreadsheet 934634.

most of the colloidal material and micro-organisms that can affect the dissolved As(III/V) ratio (Gihring et al., 2001; Wilkie and Hering, 1998). The preservation of the water samples by acidification prevents oxidation and precipitation of iron and manganese hydroxides that can coprecipitate or absorb arsenic (Wilkie and Hering, 1998). The oxidation of As(III) in conjunction with the photoreduction of Fe(III) can occur unless light is excluded. The exclusion of light prevents photochemical reactions that can affect the arsenic redox distribution (Hug et al., 2001; Emett and Khoe, 2001).
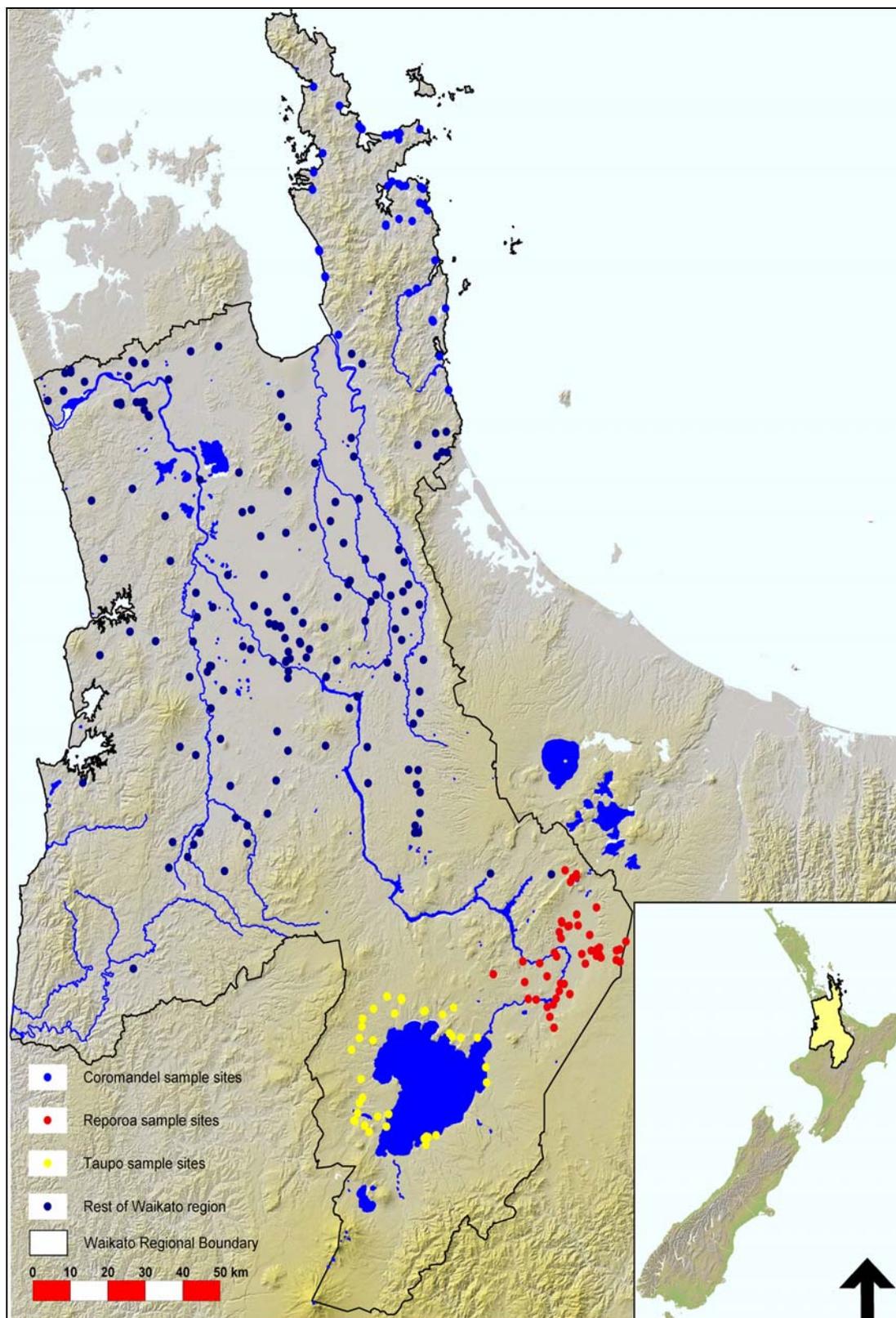
Figure 2   Groundwater sampling locations

Second-round groundwater samples for arsenic species determination were collected from 21 bores where total and/or acid soluble arsenic concentrations in the groundwater were initially found to exceed the New Zealand drinking water standards PMAV of 10 parts per billion (ppb).[6] Eight of these samples were collected from bores in Reporoa, seven from the Taupo area, and three each from the Coromandel and Hamilton Basin areas. All samples for arsenic speciation determination were collected during 2004.

Groundwater samples collected for analysis of arsenic(III) were field-filtered using 0.45-µm filters into plastic 100 mL sulphuric acid preserved bottles, whereas those collected for analysis of arsenic(V) were collected in plastic 250 mL nitric acid preserved bottles. Arsenic speciation samples were then placed in a dark chilli-bin to exclude sunlight and cooled with ice to <4°C and transported to the laboratory for analysis.

2.2.3 Analysis

The samples of groundwater were analysed at a commercial laboratory (Hill Laboratories, Hamilton, accredited by *International Accreditation New Zealand*, IANZ, formerly TELARC). The analytical methods used and their detection limits and methods are listed in **Table 3**. A total of 302 groundwater samples were analysed for total or acid soluble arsenic, and 21 samples were also tested for the arsenic species.

The Environment Waikato data set for non-speciated arsenic represents two slightly different sample preparation techniques. Differences are in the laboratory approach for determining 'acid-soluble' elements compared with 'total' elements. In the former case, the mildly acid-preserved sample is filtered[7] before being digested with more acid, and then diluted for analysis. In the latter case, the digestion acid is added before filtration, while suspended particulates are still present in solution. A total element determination therefore gives the sum of the element that was associated with any suspended particulates added to that which was present in the dissolved phase. By contrast, results of an 'acid soluble' element determination are less likely to reflect a contribution from suspended particulates.[8]

In the case of arsenic in Waikato groundwater, some samples were analysed by both techniques. It was found that where a sample was analysed by both approaches, the two measurements were usually within analytical error of each other. An extremely high correlation between total arsenic and acid soluble arsenic (R=0.996, N=19, p<0.0001) and slope of 0.996 (indistinguishable from 1.0) implies that very little arsenic is carried in suspended particulates.[9] For this reason it was felt appropriate to merge the two data sets.

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[6] Although a total of 30 groundwater samples exceeded the PMAV in total, nine of these in the Reporoa area were associated with an additional data set relating to new test bores, that was outside the framework of the Regional Sampling programme. Groundwater from these bores was not tested for arsenic species.

[7] Filtration is at 0.45 µm, a threshold used as an operational cut-off to represent the 'dissolved' fraction.

[8] Sizeable variations between the two types of determination often occur for aluminium, where a 'total' aluminium determination will include the contribution from suspended sediments (often aluminosilicate minerals) being carried in the water, as well as truly dissolved aluminium.

[9] Or if it is, the size range of these forms is less than the standard operational filtration size (0.45 µm).

Table 3   Groundwater chemical determinands, methods and detection limits.

Determinand	Method Used	Detection Limit
Sample filtration for general testing	Sample filtration through 0.45μm membrane filter.	N/A
Acid soluble extraction	Nitric acid extraction (pH1.65-1.85, 18hr) US EPA 200.1	N/A
Total (nitric acid) digest	Boiling nitric acid digestion.	N/A
Total (nitric) acid digest for low level metals	Boiling nitric acid digestion. APHA 3030 E 20th ed. 1998	N/A
pH	pH meter APHA 4500-H+ B 20th ed. 1998	0.1 pH units
Electrical Conductivity (EC)	Conductivity meter, 25°C APHA 2510 B 20th ed. 1998	0.1 mS/m
Electrical Conductivity (EC)	Conductivity meter, 25°C APHA 2510 B 20th ed. 1998	1 μS/cm
Approx Total Dissolved Salts	Calculation: from Electical Conductivity	2 $g.m^{-3}$
Alkalinity	Titration to pH 4.5 APHA 2320 B (Modified for alk <20) 20th ed. 1998	1 $g.m^{-3}$ as $CaCO_3$
Free carbon dioxide	Calculation: from alkalinity and pH, valid where TDS is not >500 mg/L and alkalinity is almost entirely due to hydroxides, carbonates or bicarbonates. APHA 4500-CO2 D 20th ed. 1998	1 $g.m^{-3}$
Calcium	Boiling nitric acid digestion. ICP-OES	0.02 $g.m^{-3}$
Magnesium	Boiling nitric acid digestion. ICP-OES	0.005 $g.m^{-3}$
Total Hardness	Calculation: from Ca and Mg APHA 2340 B 20th ed. 1998	1 $g.m^{-3}$ as $CaCO_3$
Sodium	Boiling nitric acid digestion. ICP-OES	0.5 $g.m^{-3}$
Potassium	Boiling nitric acid digestion. ICP-OES	0.1 $g.m^{-3}$
Total Ammonium-N	Phenol/hypochlorite colorimetry. Flow injection analyser. (NH4-N = NH4+-N + NH3-N) APHA 4500-NH3 H 20th ed. 1998	0.01 $g.m^{-3}$
Nitrate-N	Filtered sample. Ion Chromatography. APHA 4110 B 20th ed. 1998	0.05 $g.m^{-3}$
Chloride	Filtered sample. Ion Chromatography. APHA 4110 B 20th ed. 1998	0.5 $g.m^{-3}$
Sulphate	Filtered sample. Ion Chromatography. APHA 4110 B 20th ed. 1998	0.5 $g.m^{-3}$
Boron	Boiling nitric acid digestion. ICP-OES	0.005 $g.m^{-3}$
Total Iron	Boiling nitric acid digestion. ICP-OES	0.01 $g.m^{-3}$
Total Manganese	Boiling nitric acid digestion. ICP-OES	0.005$g.m^{-3}$
Acid Soluble Arsenic	Dilute nitric acid extraction. ICP-MS. APHA 3125 B 20th ed. 1998	0.001 $g.m^{-3}$
Total Arsenic	Nitric acid digestion. ICP-MS. APHA 3125 B 20th ed. 1998	0.001 $g.m^{-3}$
Arsenic (III)	Citrate buffer (pH 5)/Sodium borohydride, Hydride Generation Atomic Fluorescence Aggett & Aspell, Analyst (101) 341-347 1976	0.001 $g.m^{-3}$
Arsenic (V)	Calculation: Total As - As(III)	0.001 $g.m^{-3}$
Total Copper	Boiling nitric acid digestion. ICP-OES	0.005 $g.m^{-3}$
Total Zinc	Boiling nitric acid digestion. ICP-OES	0.005 $g.m^{-3}$

3   Results and discussion

3.1   Regional summary statistics

Full results for total and acid soluble arsenic in the 302 groundwater samples analysed are provided in **Appendix 1**.[10]   Summary statistics for arsenic in groundwater of the Waikato region are provided in **Table 4**.   Data is also provided for the sub-regional sampling areas identified as the Reporoa basin, Taupo area, Coromandel Peninsula, and the Waikato region excluding the three former areas.

In interpreting these statistics it should be noted that:

- Arsenic results were reported by the analytical laboratory in units of g/m^3 (= mg/L or parts-per-million), but for ease of tabulation and discussion are presented here in units of µg/L (= mg/m^3 or parts-per-billion).[11] The usual detection limit for arsenic in freshwater by ICP-MS is 1 µg/L (0.001 g/m^3) (**Table 3**). For purposes of deriving summary statistics, non-detected results were taken as being equal to half the detection limit (*i.e.* 0.5 µg/L).

- Arithmetic means are reported in **Table 4**, but it should be noted that all datasets show a strong positive skew, which causes arithmetic means to be positively biased. Better measures of the central tendency are represented by the median and geometric means. The 95% confidence error around the geometric mean represents a best estimate of where the geometric mean of an underlying area is likely to fall, based on the samples tested from that population.

The summary data for arsenic in groundwater (**Table 4**) reveals the following features:

1. Medians (and geometric means) of the sample set are relatively low, and below half-PMAV (5 µg/L) for all areas, implying that the true medians (or geometric means) of the underlying populations are also likely to fall below this threshold. At first glance this may appear reassuring. However, the greatest potential health risks lie at the upper end of the distribution rather than with the median.

2. At the upper end, a significant proportion of drinking water standard non-compliances do occur. Over the Waikato region as a whole, about one in five samples (18.5%) exceeded half-PMAV, and one in ten (9.9%) exceeded the PMAV.

3. However, most of these non-compliances are caused by groundwater samples sourced from only three sub-regional areas – the Reporoa basin, the nearby North-Eastern Taupo area, and the Coromandel Peninsula. When these areas (N = 147 samples) are removed, the exceedance rate in the rest of the Waikato region samples (N = 155) is relatively modest. In the rest of the Waikato region, one in ten groundwater samples (10%) exceeded half-PMAV, but only one in thirty-three (3%) exceeded the PMAV.

4. Confirming the importance of the three sub-regional areas, comparison of confidence intervals shows that the Reporoa basin (N=51), the North-Eastern Taupo area (N=50), and the Coromandel Peninsula (N=46) shows that each have statistically more arsenic in their groundwater than the rest of the Waikato region (N=155), which constitutes a comparably sized dataset.

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[10]   Complete analytical results for arsenic and the other determinands over the 302 samples analysed are archived in spreadsheet form in Environment Waikato document 934634.

[11]   To convert from g/m^3 to µg/L, multiply the former by 1000.

Table 4   Summary statistics for arsenic in Waikato groundwater.

Statistic	Waikato region overall	Waikato region excluding Reporoa, Taupo and the Coromandel Peninsula	Reporoa basin	North Eastern Taupo area	Coromandel Peninsula
Number of samples (N)	302	155	51	50	46
Arithmetic mean (µg/L)	13.1	6.8	47.5	5.5	4.8
Standard deviation (µg/L)	72.6	71.3	119.9	11.6	9.9
Standard error (µg/L)	4.2	5.7	16.8	1.6	1.5
95% error on arithmetic mean (µg/L)	8.2	11.3	33.7	3.3	3.0
Skewness	8.9	12.3	3.2	5.4	4.3
Median (µg/L)	0.5	0.5	2.0	2.8	2.0
Geometric mean (µg/L)	1.3	0.7	4.2	2.5	1.8
95% error on geometric mean (µg/L)	± 0.2	± 0.1	± 2.8	± 0.8	± 0.7
95% confidence interval (µg/L)	[1.1 – 1.6]	[0.6 – 0.8]	[1.4 – 7.0]	[1.7 – 3.4]	[1.1 – 2.5]
Minimum (µg/L)	0.5	0.5	0.5	0.5	0.5
Maximum (µg/L)	888.5	888.5	556.5	79.5	61.0
Range (µg/L)	888.0	888.0	556.0	79.0	60.5
Midrange (µg/L))	444.5	444.5	278.5	40.0	30.8
Number equal or exceeding half-PMAV	56	10	21	14	11
Number equal or exceeding PMAV	30	3	17	6	4
Percent equal or exceeding half-PMAV	18.5	6.5	41.2	28.0	23.9
Percent equal or exceeding PMAV	9.9	1.9	33.3	12.0	8.7

5.   The highest raw PMAV non-compliance rate is seen for groundwater samples sourced from the Reporoa basin. In this area, two-fifths (41.2%) of samples exceeded half-PMAV, and one-third (33%) still exceeded the PMAV. Assuming the sampling was representative of the Reporoa area (and this appears to be the case), these results imply that anyone developing a new groundwater bore in the Reporoa basin would have a one-in-three chance of drawing water that exceeds the drinking water PMAV.

6.   In the Coromandel Peninsula, the elevated arsenic concentrations were predominantly found at old mine adits around the Kuaotunu area.

In the New Zealand Drinking Water Standards (2005), a concept of 'allowable exceedances' is included for use with a given water supply, whereby a certain number of non-compliances may be tolerated on probability grounds. For example, with 300 samples (as for the overall data set), and for 95% confidence that the PMAV is exceeded for no more than 2% of the time, only two exceedances would be tolerated. For 50 samples (as for the sub-regional areas), no exceedances would be permitted. In this dataset, there were 60 exceedances, far more than would be tolerable if it happened that groundwater of the Waikato region were treated as one large rural water supply.

Maps showing the major areas of arsenic elevation in Waikato groundwater are provided in **Figure 3**. Contours are derived in relation to both the drinking water PMAV (10 µg/L), and half this value (5 µg/L).

3.2   School supplies

Ninety school water supply bores were tested for a range determinands, of which arsenic was one. Most of the school water supply bores were sampled during 2002 and 2003, and a handful were re-sampled at later dates (with one being re-sampled again in 2006). Of the 90 schools, arsenic was:

- Present at 10 µg/L or above in 4 water supplies (4.4% of samples);
- Present at 5 µg/L or above (half the drinking water standard) in 11 supplies (12.2%);
- Below 5 µg/L in 79 supplies (88%);
- Not detected (below 0.5 µg/L) in 65 supplies (72%).

Where found in the initial round of sampling, non-compliances with the PMAV were modest rather than extreme. There was no particular geographic pattern for the four schools where PMAVs for arsenic were exceeded: of these, two were in Thames Coromandel district, one in Rotorua, and one in Matamata-Piako.

Analytical results were forwarded to all schools. For those where arsenic was present at half-PMAV or above in the groundwater samples collected, the school was informed about this and the associated health implications. It is understood that treatment options or use of alternative groundwater supplies have been investigated by a number of schools. In the case of the highest exceedance, re-sampling was undertaken, and the situation was further investigated by the school concerned in collaboration with the District Health Board and Ministry of Education.
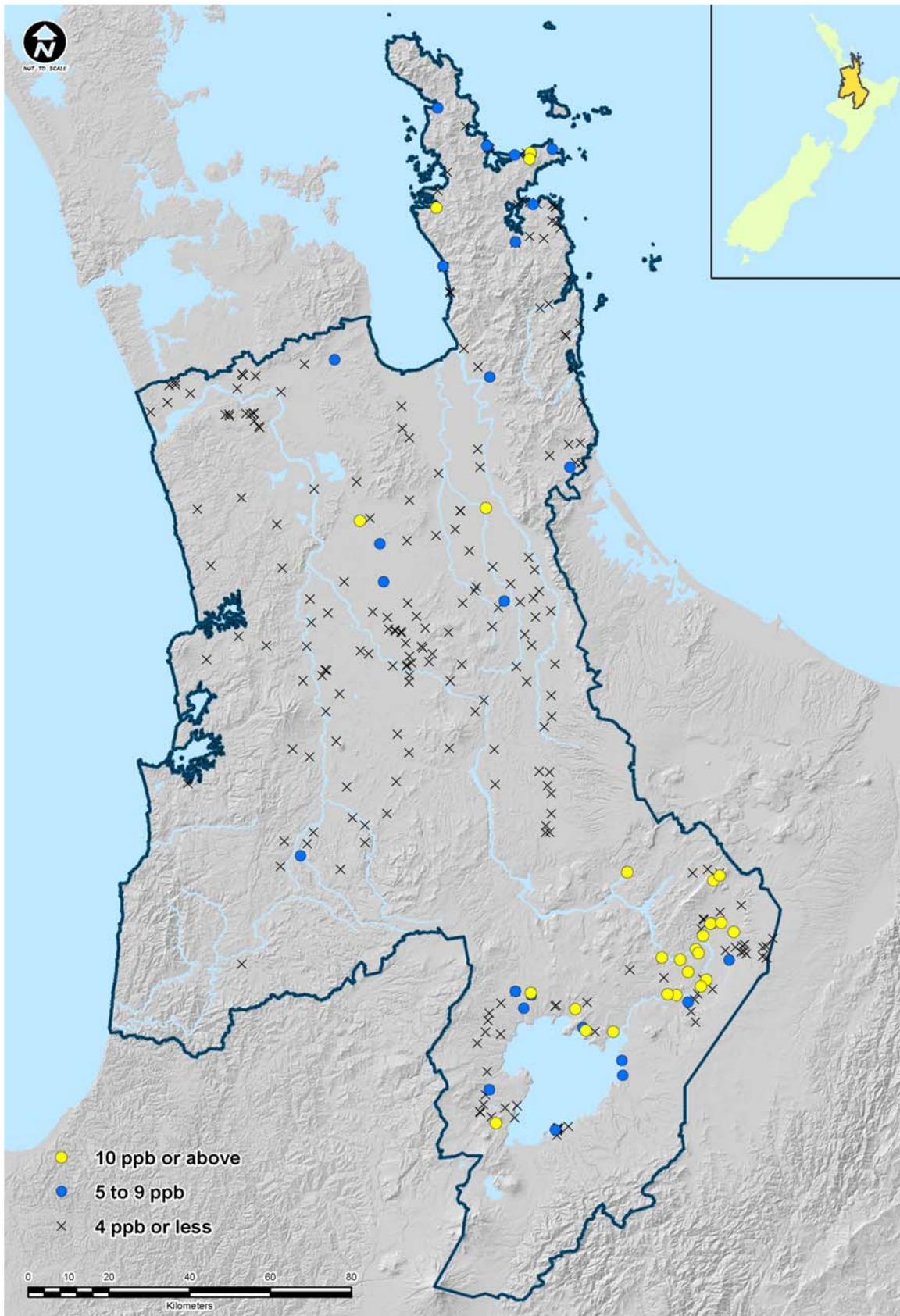
Figure 3   Concentrations of arsenic in Waikato groundwater samples.

3.3   Temporal variability

Within the total dataset, groundwater at a total of 28 locations was tested for either acid soluble arsenic on at least two separate occasions (21 sample pairs), or total arsenic on at least two separate occasions (7 sample pairs). Time elapsed between sampling dates for the acid soluble pairs varied from 8 months to 154 months, with a median and mode of about 24 months. Sample results for sites sampled twice are listed in **Appendix 2**.

Assessing differences in arsenic concentrations in groundwater between the first and second sampling dates is subject to the following constraints:

- An analysis based on ratios of results only would fail at low arsenic concentrations (below 5 µg/L), because at these levels such an approach would not account for normal variation attributable to analytical error.[12]   To allow for this, in this assessment, the magnitude of analytical and sampling error is taken as being four times the detection limit (1 µg/L) or 4 µg/L.

- At the other end of the range, at high arsenic concentrations, the marginal significance of a 4 µg/L absolute variation is minimal.[13]

For the purpose of this assessment, a more-than-minor difference is therefore taken as where two results from the same site show a variation in arsenic concentrations of more than 4 µg/L which **also** corresponds to more than 20% relative difference in sample results. The first condition accounts for the effect of real analytical and sampling error at low arsenic concentrations, whereas the second allows for the relative insignificance of such variation at high arsenic concentrations.

Analysis of the data in this way shows that 17 of the 28 sites where groundwater was sampled twice (about 60%) showed no substantial difference in arsenic concentrations between the first and second sampling (**Appendix 2**).   However, 11 of the 28 sites where groundwater was sampled twice (about 40%) showed a more-than-minor change, either up or down. There is therefore clear evidence that whereas arsenic concentrations in Waikato groundwaters remain stable in about 60% of cases, in about 40% of cases they may vary substantially with time. Where more-than-minor changes were observed, arsenic concentrations varied by a median factor of 4, with a range from 1.4 to 81 times.[14]

These observations are consistent with literature reports of seasonal variation in arsenic in shallow groundwater. In a 12 month study of Washington groundwater in 26 wells, Frost et al. (1993) reported that arsenic concentrations for individual wells varied from 1 to 19-fold over time.

In the Waikato region, such variation is likely to be linked to changes in subsurface redox conditions causing the release of arsenic from iron oxides and/or generation of arsenite (As(III)), as outlined in **Sections 1.2** and **3.4**. Groundwater flow is also likely to exert a significant influence. In Southern Bangladesh, reductive dissolution of iron oxides has been identified as the most significant release mechanism, but groundwater flow and time also both exert strong influences on arsenic concentrations in the groundwater (Burgess et al*.,* 2000). In keeping with this, Rodriguez et al. (2004) reported that arsenic concentrations in groundwater of the Zimapan Valley Mexico correlate with local geology and rainfall (which influences groundwater volume and flow).

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[12]   For example, one site showed 2 µg/L on the first sampling occasion and 5 µg/L on the second: this is a real difference of 3 µg/L but a relative percentage difference of 150%.
[13]   For example, one site showed 647 µg/L arsenic on the first occasion and 542 µg/L on the second: this is a real difference of 105 µg/L but a relative percentage difference of only 16%.
[14]   Arithmetic average factor 15, geometric mean factor 5.7.

Of particular interest, however, is that in about half of the cases where a change in arsenic concentration was observed (6 of 11 cases), the variation was sufficient to cause the 10 µg/L drinking water PMAV to be exceeded in one sample but not the other. Overall, this effect was evident in about 20% of all sites sampled twice.[15]   This suggests that in about 10% of cases (half of 20%), a single point-in-time measurement of arsenic in groundwater that shows compliance with the drinking water PMAV may be misleading. This finding is also consistent with overseas work – in their Washington study, Frost et al. (1993) noted that of groundwater from 26 wells sampled:

"4 out of the 8 wells with As levels close to the maximum contamination level (MCL) ... would have been considered safe on the basis of a single sample, but would have exceeded the MCL at another time of the year."

Due to the possibility of variation in arsenic concentrations in a given bore, it is recommended that groundwater from new drinking water bores developed in the Waikato region should be tested four times for the first year, once during each quarter, to ensure the results are representative.

3.4   Reasons why arsenic becomes elevated in Waikato groundwater

3.4.1   General

Analysis for arsenic in groundwater samples has highlighted that certain locations in the Waikato region are more susceptible to arsenic concentrations that may exceed the maximum acceptable values for drinking water. The main areas that have been identified as high risk zones for possible arsenic contamination in groundwater are Reporoa, North-Eastern Taupo, and specific locations within the Coromandel Peninsula (**Section 3.1**). In general terms this pattern is consistent with expectations, in that all three areas are subject to geothermal activity, and the Coromandel Peninsula also contains areas of natural sulphide mineralisation and is covered with the remnants of gold mining by old mine shafts and adits. Arsenic concentrations in groundwater appear to be related to several natural factors such as geothermal influence, geological weathering and water-rock interaction.

Geothermal heating and sulphide mineralisation might often represent two dominant primary sources of elevated subsurface arsenic in the Waikato region, but the exact arsenic concentrations reached in groundwater at a given bore appear to be determined by a range of secondary factors superimposed over these primary sources. Secondary factors might include (among other factors) retention and release on subsurface iron oxides, microbially mediated or abiotic changes in arsenic speciation, and groundwater volume and flow, and time (**Section 1.2**, Burgess et al*.,* 2000). In addition, in some areas, arsenic may be elevated in groundwater despite the apparent absence of a geothermal or sulphide mineral primary source.

Relationships between arsenic and other groundwater parameters that are evident in the Waikato data set are examined in detail in this section.

3.4.2   Possible relationships with water-type

The Piper diagram is one of several graphical techniques that can be used for classification of water class (Güler et al*.,* 2002). Input parameters are simply four major cations (sodium, potassium, calcium and magnesium) and three major anions (chloride, sulphate and bicarbonate/carbonate). In this work, a Piper diagram for all data coded by geographical area (Reporoa, Coromandel, Taupo and Rest of Region) was derived from all data using the *AquaChem* computer package (Waterloo Hydrogeologic, Inc.). Results are shown in **Figure 4**.

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[15]   In other cases, sample results were either both well above the PMAV or well below it (**Appendix 2**).
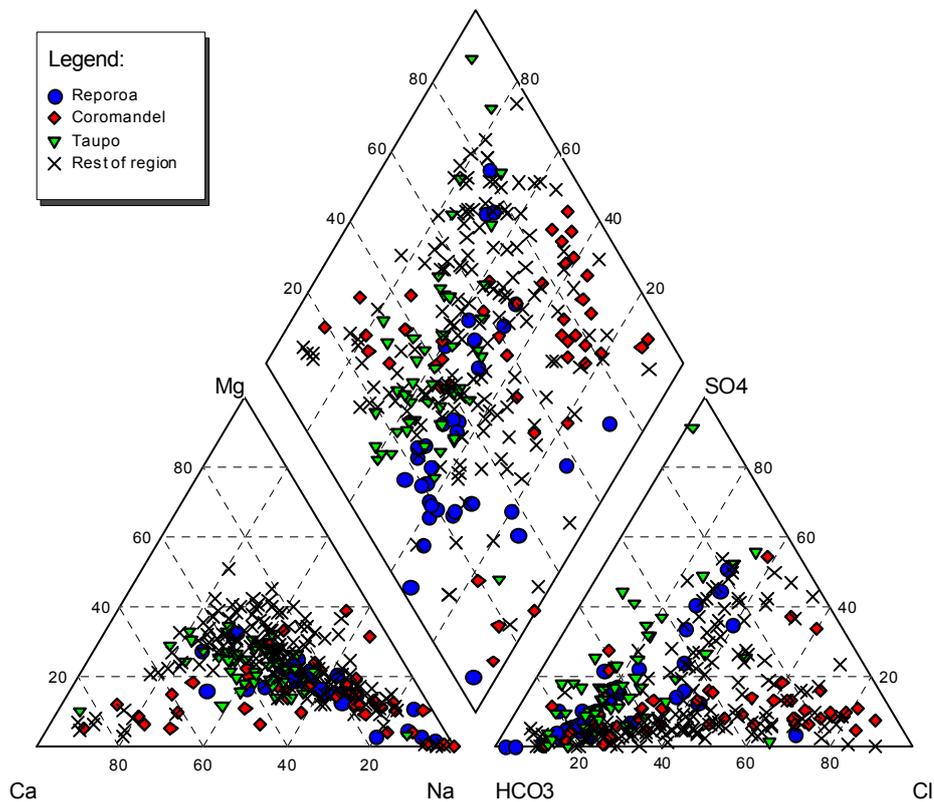
Figure 4   Piper plot of Waikato region arsenic dataset.

Piper diagrams display relative concentrations of the selected major cations and anions for a given sample in two separate trilinear plots (**Figure 4**: cations bottom left, and anions bottom right). The two points for each sample are then projected to form a single point in the central diamond, that represents the overall water type for a given sample in general terms. Waters represented by points toward the bottom of the central diamond are **alkali carbonate** in nature, whereas those at the top are **permanently hard**. Those on the diamond's right hand quadrant are regarded as **saline**, and those on the left as **temporarily hard** (Hounslow, 1995). In this dataset, the geothermal nature of some samples needs to be borne in mind. A term such as saline (higher sodium+potassium and sulphate+chloride) may indicate a saltwater influence, but might equally result from geothermal activity.

The three areas that stand out as having higher concentrations of arsenic in groundwater were Taupo, Reporoa and parts of the Coromandel Peninsula (**Section 3.1**). From the Piper diagram (**Figure 4**), groupings for different sub-regional areas are not particularly distinct, but in general terms it can be seen that:

- The majority of samples from Taupo group into a cluster that might be characterised as 'moderate' temporary hardness, characterised by marginally higher calcium+magnesium and bicarbonate than other waters.

- A significant portion (but not all) of the Reporoa waters tend more toward the alkali carbonate class (higher sodium+potassium and bicarbonate); although other samples are quite central (denoting no one dominating ion). A handful of Taupo and Reporoa samples are more toward the permanently hard category (higher calcium+magnesium, accompanied by higher sulphate+chloride).

- Coromandel water samples mainly spread from left to right across the centre of the diamond, from temporarily hard to saline (higher sodium+potassium and sulphate+chloride).

However, none of these nominal groupings in itself is sufficient to explain higher arsenic observed in the three sub-regional areas than in the rest of the region. As can be seen from **Figure 4**, samples from the rest of the region show a fairly even spread of results across the Piper diagram's central diamond.

When only groundwater samples from the sites that exceed the drinking water PMAV for arsenic are graphed (**Figure 5**), no distinct grouping emerges, except that such waters tend **not to** be either temporarily or permanently hard.
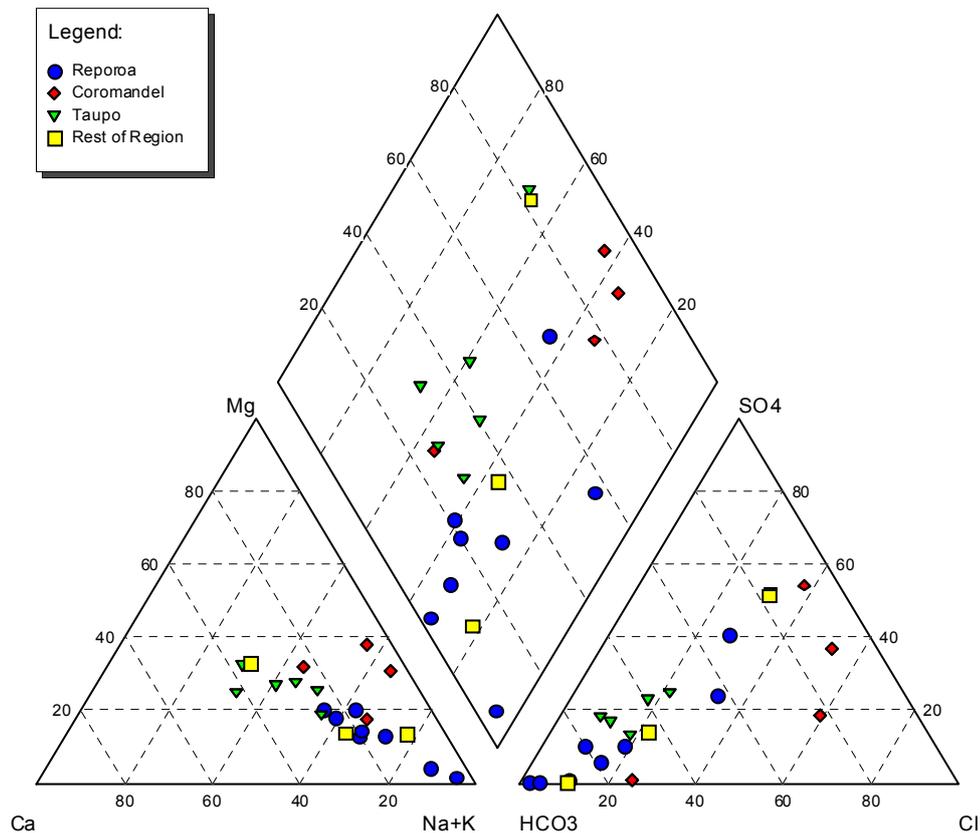
Figure 5   **Piper plot of sites where arsenic concentrations above the PMAV.**

A more detailed breakdown of water type for all PMAV exceedances is also provided in **Appendix 3**.

Within the Reporoa subset of this data, an alkali carbonate cluster is evident. A reasonable subset of Reporoa waters were (approximately) alkali carbonate in nature (**Figure 4**), but those that were not tended not to show a drinking water PMAV exceedance for arsenic (**Figure 5**). However, several 'rest of region' samples in this water class showed no PMAV exceedance (**Figure 4**), suggesting that this water class characteristic should not be interpreted as being causative of higher arsenic in groundwater.

Lack of specific clustering for samples collected from across the Waikato region is not particularly surprising. Over smaller areas, the major constituents of groundwater may well fall into defined groups. For example, in their review of arsenic in Marlborough's Rarangi Shallow Aquifer, Wilson and Davidson (2005) report that most samples group as part of a Ca-HCO$_3$ (temporarily hard) cluster. However, even where they do exist, such groupings of internally consistent major chemical parameters are not necessarily 'causative' of higher arsenic.

Overall, the Piper diagram analyses are equivocal in a number of ways, but do show that proportionately fewer PMAV exceedances were in waters characterised as either temporarily hard or permanently hard. Water with more calcium+magnesium and either carbonate+bicarbonate or sulphate+chloride appears less likely to be associated with a drinking water PMAV exceedance for arsenic (in contrast with the Marlborough aquifer results of Wilson and Davidson (2005)). However, the significance of these apparent associations is open to question. Pearson's correlation analysis of the log-normalised data for the Waikato region as a whole does not show the presence of an inverse relationship between these variables and arsenic concentrations in groundwater. In the full data set, average arsenic in groundwater is almost completely uncorrelated with total hardness (R = 0.018, N = 286 pairs), calcium (R = 0.012, N = 285), magnesium (R = 0.000, N = 285), chloride (R = –0.083, N = 286), sulphate (R = 0.002, N = 285) and free carbon dioxide (R = –0.109, N = 260).

3.4.3 Correlations

Güler et al. (2002) suggest that use of conventional graphical methods to group samples is not efficient and can produce biased results, partly through subjectivity of the interpretation. For data in this investigation, multivariate statistical techniques may offer a better means of systematically identifying associations between variables. Where identified, such associations still do not necessarily denote an underlying cause-and-effect relationship, but in combination with other mechanistic and circumstantial evidence, can often be used to identify probable causative factors.

In this work, a Pearson's correlation analysis was carried out on both the full data set, and data sets for each sub-regional area of interest. Prior to derivation of the correlation matrix, variables were log-normalised to correct for skew of the sample distribution. 'Highly' (p<0.001) and 'very' (p<0.01) significant correlations between variables in each of these data sets are listed in **Table 6**.[16]

A number of scatter-plots that yielded 'very' (p<0.01) significant correlations were not particularly convincing by visual inspection, suggesting that even with log-normalisation, residual skew in some variables may have been sufficient to suggest associations not reflective of most of the data, through the influence of a handful of pairs. However, the 'highly' (p<0.001) significant correlations showed better evidence of trends being spread throughout datasets. The focus of this discussion will therefore be mainly on the 'highly' (p<0.001) significant correlations.[17]

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[16] Due to differing numbers of samples (variation in N) between variables, a correlation matrix is not presented here, because direct comparison of R-values may be misleading. Instead the approach has been to determine probabilities (p-values) from correlation coefficients (R-values) with reference to the number of sample pairs in each case. The original correlation matrices are available in Environment Waikato spreadsheet 934634. For the total data set, the number of pairs were as follows: N = 286: alkalinity, chloride, conductivity, iron, hardness, manganese, pH, and zinc; N = 285: boron, calcium, potassium, magnesium, sodium, ammoniacal-nitrogen, nitrate-nitrogen, and sulphate; N = 261: total dissolved solids; N = 260: copper, free CO_2; N = 174: water temperature; N = 135: lithium; N = 109: groundwater depth.

[17] Designation of a correlation as highly significant should not be taken to imply that a given variable might account for most of the variation seen in arsenic concentrations, but that an apparent relationship exists, the existence of which is highly unlikely to be caused by chance alone.

Table 5 **Probability values for 'highly significant' (p<0.001) and 'very significant' (p<0.01) correlations between arsenic and other variables.** Where an entry is left blank, the correlation (if any) did not reach a significance level of at least $p < 0.01$.

	Arsenic				
	Total Dataset	**Reporoa**	**Taupo**	**Coromandel**	**Rest of region**
Alkalinity	<0.01	<0.001			
Boron					
Calcium					
Chloride					
Conductivity					
Copper					
Iron	<0.001	<0.001			<0.001
Free CO_2					
Groundwater Depth					
Hardness					
Potassium					
Lithium	<0.001	<0.001			<0.001
Magnesium			<0.01 (but caused by one outlier)		
Manganese	<0.001	<0.001			<0.001
Sodium	<0.01	<0.01	<0.001 (but caused by one outlier)		
Ammonium-nitrogen	<0.001	<0.001			
Nitrate-Nitrogen	<0.001 (negative slope)		<0.001 (but caused by one outlier)		
pH	<0.01	<0.001			
Sulphate					
Total Dissolved Solids					
Water temperature	<0.01 (negative slope)				
Zinc					

Highly correlated variables in the total arsenic dataset show a number of interesting features. These are as follows:

1. Concentrations of arsenic in groundwater samples show highly ($p < 0.001$) significant positive correlations with concentrations of iron, manganese, and ammonium-nitrogen, and a highly significant negative correlation with nitrate-nitrogen.

   - This group of results is mechanistically consistent with reducing conditions in the subsuface being a key factor behind arsenic release to groundwater. Under reducing conditions, some nitrate nitrogen (NO_3^-) converts to the ammonium form (NH_4^+), and in addition amorphous iron and manganese oxides begin to dissolve.

   - Behaviour of these variables in relation to that of arsenic therefore suggests that reducing conditions are associated with higher arsenic in groundwater. In terms of mechanism, the association of arsenic with iron in Waikato soils (**Figure 1**) suggests that a portion of release of arsenic to groundwater is caused by reductive dissolution of the iron oxide phases.

- Under reducing conditions, manganese oxides tend to dissolve more readily than iron oxides and may also contribute some arsenic to groundwater.[18]

2. Concentrations of arsenic in groundwater samples show a highly ($p<0.001$) significant positive correlation to concentrations of lithium.

- Lithium is often regarded as a tracer for geothermally-influenced water. However, in this data set, two other indicators of geothermal influence are not correlated with either lithium or arsenic. These are conductivity and chloride.

- Lithium shows the same pattern as arsenic for variables associated with reductive dissolution of metal oxides. Lithium concentrations show a high ($p<0.001$) positive correlation with iron, manganese, and ammonium nitrogen, and a high negative correlation with nitrate nitrogen.

- The data set for lithium was smaller than that for arsenic (N=135 for lithium samples compared with 302 samples for arsenic). However, samples tested for lithium were collected from throughout the Waikato region, not only from the significant geothermal areas.

- Inter-correlations and sampling considerations might therefore suggest that like arsenic, elevated lithium in Waikato groundwater may originate from two dominant sources: direct geothermal influence, and reductive dissolution of metal oxides. As with arsenic, this suggests a role of metal oxides in the subsurface retention and release of lithium.

Highly significant correlations between arsenic and iron, manganese and lithium are also evident in both the Reporoa area subset (N=51 samples tested for arsenic), and the Waikato region excluding Reporoa, Taupo and the Coromandel Peninsula (N=155 samples tested for arsenic). Persistence of the lithium-arsenic correlation in this wider Waikato area (N=83 pairs) along with presence of the lithium-iron and lithium-manganese correlations, again suggests that reductive dissolution of iron oxides may be a significant source of groundwater lithium in non-geothermal areas of the Waikato region. The idea that reductive dissolution of iron oxides might also be a source of groundwater lithium may not have been identified previously.

No robust correlations better than $p<0.01$ were evident between arsenic and the other groundwater variables in either the Taupo (N=50) or Coromandel (N=46) area subsets. A possible reason for this may be that more than one dominant source is responsible for the higher concentrations of arsenic in groundwater in each of these areas. For example, if elevated arsenic in the Coromandel bores is sometimes caused by dissolution of sulphide minerals, sometimes by geothermal heating, and sometimes by reductive dissolution of iron oxides, then an arsenic-iron correlation attributable to the third mechanism would be unlikely to show up against statistical noise introduced by the other two mechanisms. In Taupo, lack of any firm correlations might suggest that both direct geothermal influences and reductive dissolution processes may contribute to elevated arsenic in groundwater in equal measure, with neither showing up as the dominant signal.

In terms of drinking water compliance, the exact sources of arsenic are less important than the fact arsenic is elevated in a given location (**Table 4**, **Figure 3**). However, inter-element correlations suggest that two significant sources of elevated arsenic (and lithium) in Waikato groundwater are reductive dissolution of metal oxides, and (perhaps more indirectly) geothermal heating.

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[18] However, manganese oxides are present at lower concentrations than iron oxides, and in Waikato surface soils, tend to correlate most strongly with trace cations (Environment Waikato spreadsheet 927529). It is likely that manganese oxides carry a net negative surface charge at typical pH values of Waikato surface soils, but different conditions may prevail in the subsurface.

3.4.4 Linear regression

In order to gauge the magnitude of total variation of arsenic in groundwater that might be attributable to either reductive dissolution of metal oxides or geothermal processes, linear regression was carried out, with arsenic treated as the dependent variable. Either of the variables iron and manganese might be taken to represent reductive dissolution processes. Ammonium-nitrogen and nitrate nitrogen are also linked to reducing conditions, and it might be suggested that the most complete picture of the influence of reductive dissolution would involve grouping all four variables.   By contrast, the variable lithium might represent both reductive dissolution and geothermal influences. Results are provided in **Appendix 4**. Results of the linear regression should only be viewed as approximate and indicative, because there is some question over how well the grouped variables really represent a given condition.

- **Reductive dissolution:** linear regression suggests that reductive dissolution represented by iron, manganese, nitrate and ammonium, if causative, might account for about 20% of the variation seen in the total arsenic dataset.

- **Geothermal influence:** Variation 'explained' by lithium is the highest of any variable, at 35%. However, if it is assumed that 20% of this is the reductive dissolution component, geothermal influences alone might be taken to account for an additional 15% of the arsenic variation within the total dataset.

Variation over the total dataset referred to in discussion of the linear regression analysis is the site-to-site variation. This type of variation will occur for both geothermal and reductive dissolution causes, but only the latter is expected to show significant intra-site variability over time. At a given site, geothermal release is expected to yield a less variable arsenic signal than metal oxide retention-release (as for example seen in the Wairakei Geothermal Power Station discharge).

In **Section 3.3**, it was noted that significant variation in concentrations of arsenic in groundwater had occurred at about 40% of all sites that were sampled twice. The finding from linear regression that reductive dissolution might account for about 19% of the total dataset's variation may suggest that this mechanism is likely to make a significant contribution to temporal variations that are observed in arsenic concentrations in groundwater.

3.4.5 Summary

Graphical and statistical approaches (**Sections 3.4.2**, **3.4.3** and **3.4.4**) were used to identify the probable factors that can combine to cause an increase in arsenic concentrations in Waikato groundwater.   In combination with observational data relating to changes in arsenic over time (**Section 3.3**), analysis of the data suggests at least two mechanisms are likely to be responsible for higher concentrations of arsenic in groundwater where these are observed.   These are the direct influence of geothermal sources, and the reductive dissolution of subsurface iron and manganese oxides. Short and medium term changes in concentrations of arsenic in groundwater with time are most likely to come about through the second mechanism.

Identification of these probable general mechanisms leading to higher concentrations of arsenic in Waikato groundwater does not preclude the presence of other sources in specific cases. Other causes are likely to exist, but not show up as consistent signals over the full data due to the low number of sites. For example, the most likely source of arsenic to some water supplies in the Coromandel Peninsula is release from sulphide minerals. This may be facilitated by presence of old mine workings in some areas, including flooded mine adits. Clear identification of release mechanisms in area-specific sources of this type would require a more detailed site-specific investigation for each instance.

3.5 Arsenic speciation in cases where arsenic concentrations in groundwater are high

As noted in **Section 2.2.2**, 21 samples were collected for speciation analysis in cases where the original groundwater analyses showed an exceedance of the drinking water PMAV (10 µg/L). Results for these samples are presented in **Table 6**.

Table 6   **Total arsenic, arsenite and arsenate in the 21 samples for which arsenic speciation was measured.** Total arsenic and As(III) are measured directly, and As(V) is estimated as the difference between the two. Results for each sub-regional area have been ranked from lowest to highest in terms of total arsenic.

Sub-regional Area	As total (µg/L)	As(III) (µg/L)	As(V) (µg/L)	Percent As(III)(%)[a]
Reporoa (N=8)[b]	1	<1	<1	<50
	5	3	2	60
	14	<1	14	<7
	18	<1	18	<5
	20	4	17	19
	22	2	19	10
	239	210	33	86
	571	580	1	>99.8
Taupo (N=7)	6	<1	6	<14
	11	<1	11	<8
	12	<1	12	<8
	13	6	6	50
	19	<1	19	<5
	40	<1	36	<3
	78	<1	78	<1
Coromandel (N=3)	18	<1	18	<5
	21	22	<1	96
	23	<1	23	<4
Hamilton Basin (N=3)	8	<1	8	<11
	11	9	2	82
	1210	<1	1210	<0.08

a.   Calculated as the ratio As(III) / (As(III)+As(V)), multiplied by 100.
b.   Percent arsenite (As(III)) for the first result for Reporoa is considered to be unreliable because the detected values were at the method detection limit. This was a case where the total arsenic content had decreased by the time of the second sampling (**Section 3.2**).

In **Section 1.2.1** it was noted that conversion of **arsenate** (As(V) or AsO_4^{3-}) to **arsenite** (As(III) or AsO_2^-) is significant in terms of potential exposure and risk to people drinking such groundwater, because the latter is usually more mobile in the subsurface than the former (Bose and Sharma, 2002), due to differing adsorption characteristics (Dixit and Hering, 2003). The toxicity of arsenite is also estimated to be between 25-50 times greater than that of arsenate (Xu et al., 2003).

Samples sizes in this work are too limited to make any firm inferences about differences between sub-regional areas, because no strong or consistent patterns emerge (**Table 6**). Considered as a whole, results for the 20 samples where arsenic was reliably detected reveal the following features.

- The less mobile and toxic arsenate form dominates in 70% of cases (14/20 samples), but;

- Substantial conversion to the more mobile and toxic form arsenite had occurred in 30% of cases (6/20 samples);

- In the three cases showing very high arsenic (239, 571 and 1210 µg/L total arsenic) there is no consistent pattern. One of these three was entirely arsenate, another entirely arsenite, and the third 86% arsenite and 14% arsenate. Total arsenic is therefore unreliable as a means of guessing likely speciation.

In the cases of the 21 arsenic speciation sites, the redox status of the sampled groundwater was estimated using the *AquaChem* computer package (Waterloo Hydrogeologic, Inc.) which provides an algorithm to estimate **pe** (electron activity) from redox-dependent couples. In this case the nitrate/ammonium couple was used to estimate pe. Results for each of the sites were plotted on a pe-pH diagram which describes the equilibrium (thermodynamic) stability fields or various forms of arsenic in a simple aqueous system, and this is presented in **Figure 6**.

On a pe-pH diagram (**Figure 6**), all the sampled sites fall into a reasonably tight grouping. All samples showed a positive redox potential at point of sampling, conditions under which the arsenate form is expected to dominate once equilibrium has been reached.

The relative ratios of arsenite to arsenate expected at equilibrium for a given pe and pH value[19] can also be directly estimated using the following equation (Daus et al., 2000):

$$[As(III)]/[As(V)] = 10^{(2 \times (14.5 - 2pH - pe))}$$

Equilibrium arsenite/arsenate ratios for the 21 samples calculated using this equation ranged from 10^{-11} to 10^{-14}.

The pe-pH diagram (**Figure 6**), and direct estimates of equilibrium ratios, both therefore imply that if equilibrium has been reached in these samples, the arsenic should be present entirely as arsenate. However, by contrast, the observations (**Table 6**) demonstrate that 30% of samples were dominated by arsenite, the reduced form of arsenic. Of the 21 samples, eight showed more than 20% arsenite, seven more than 50% arsenite, four more than 80% arsenite, and two were essentially entirely arsenite. The average ratio of arsenite to total arsenic for the eight samples showing significant arsenite was 0.68. At the average pH of the same water samples, reaching this ratio by abiotic means[20] implies that at some point the water has experienced a pe value of about 0.8, which corresponds to an E_h of 0.046 V (46 mV).[21]

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[19] And in the absence of selective removal of one form from solution to an adsorptive phase.
[20] Microbial transformation pathways may exist which could facilitate the conversion to arsenite under less anoxic conditions.
[21] The relationship between pe and E_h is pe = (F/(2.303RT)) x Eh, where Eh is in Volts, F = 96500 C/mol, R = 8.31447 J, and T is temperature in Kelvin.
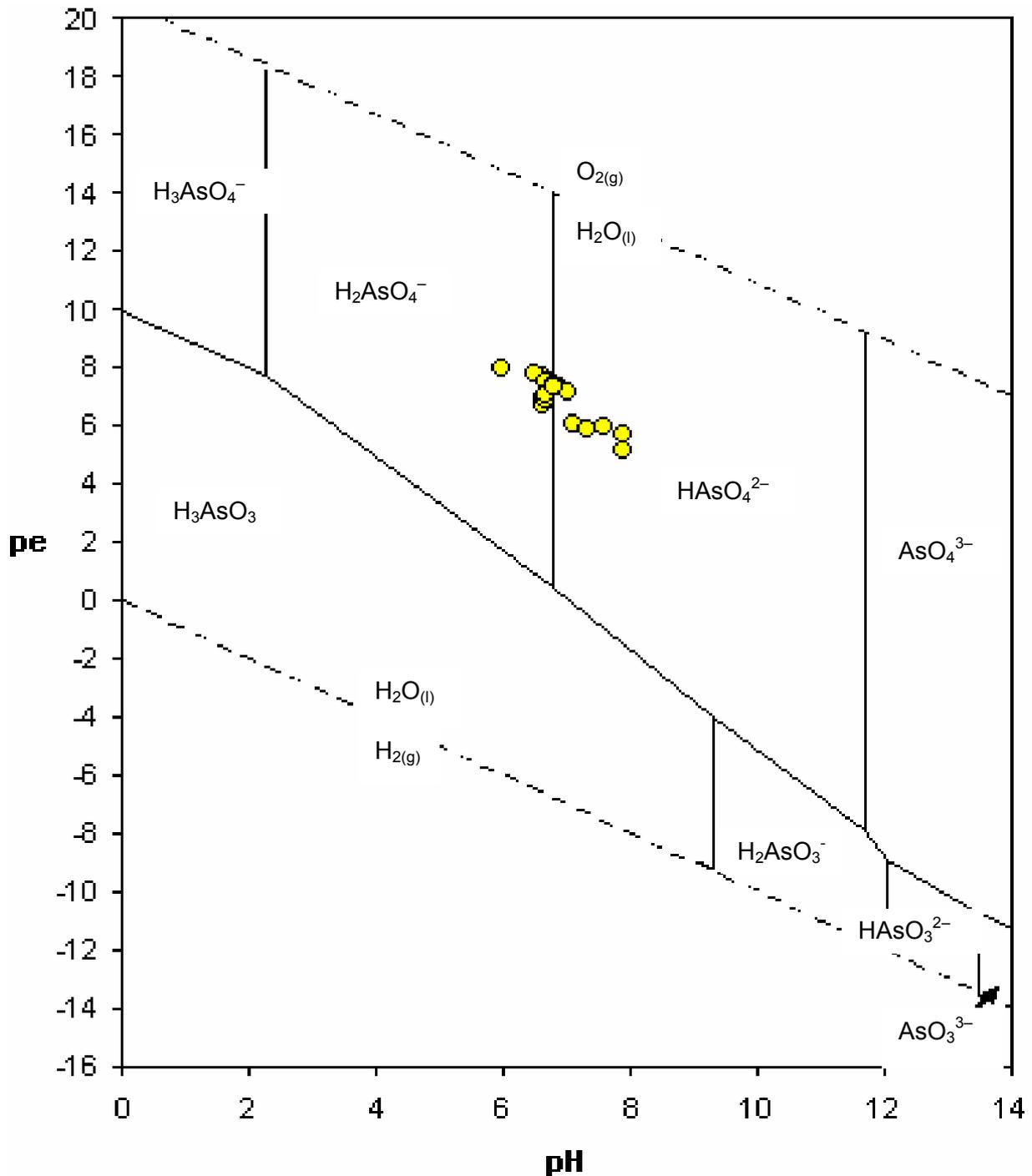
Figure 6   **pe-pH diagram for arsenic speciation sites.**

Together, this set of results suggest that:

- At the point arsenic is mobilised by reductive dissolution, a reasonable proportion is converted to arsenite. If this were not the case, this form would not be observed to dominate 30% of samples (**Table 6**).

- As this water mixes with more oxygenated water, gradual conversion of mobilised arsenic back to the arsenate form will begin to occur, because this is the more stable equilibrium form under the pe-pH conditions of the groundwater as collected (**Figure 6**).

- However, such conversion is not an instant process, but takes time. In chemical terms, such a reaction is referred to as kinetically limited.[22] Oxidation of arsenite to arsenate can be rapid in the presence of suitable oxidants such as dissolved ferric ions, but has been described as often being very slow at neutral pH values (Daus et al., 2000). Kinetic limitations to this oxidation are also evident in Waikato River water, where up to 50% arsenite has been observed at Hamilton during the summer months (McLaren and Kim, 1995), despite being produced by reductive release from anoxic lake sediments many kilometres upstream.

This process is speculative, but would provide a reason why elevated arsenic is entirely arsenite at some groundwater bores but entirely arsenate at others (**Table 6**). In theory, water that has spent longer travelling through a subsurface oxygenated zone should contain proportionately more arsenic in the arsenate form. This possibility also suggests techniques for reducing the total toxicity of arsenic-containing water, which in reality is as dependent on the speciation of arsenic as the total concentration. Leaving water to stand, bubbling with air, or boiling the water, should facilitate the conversion of arsenite to arsenate. Boiling may be reasonably efficient, because (following the Arrhenius equation) most reaction rates approximately double for every 10 °C rise in temperature.

For correlation analysis on the speciation samples, variables were grouped in to the following categories: arsenic variables, representatives of adsorptive phases, indicators of redox status,[23] major cations, minor cations, anions and possible geothermal source indicators, and bulk solution properties. To correct for positive skew, all variables except pH and pe were log-normalised prior to derivation of the correlation matrix.

Table 7   Probability values for 'highly significant' ($p<0.001$) and 'very significant' ($p<0.01$) correlations between arsenite and other variables.

Nominal category	Variable	Correlation with arsenite (As(III))	Correlation with the arsenite ratio
Adsorptive phases	Fe		
	Mn	$p<0.01$	
Redox indicators	NH$_4$	$p<0.001$	$p<0.001$
	NO$_3$	$p<0.01$ (negative slope)	$p<0.01$ (negative slope)
	E$_h$, pe	$p<0.001$ (negative slope)	$p<0.01$ (negative slope)
Major cations	Na	$p<0.01$	
	K		
	Mg		
	Ca		
Minor cations	Cu		
	Zn		
Anions & geothermal indicators	SO$_4$	$p<0.01$	$p<0.01$
	B		
	Cl		
	CO$_2$		
Bulk solution properties	Total dissolved solids		
	Conductivity		
	pH	$p<0.001$	
	Hardness		
	Alkalinity	$p<0.001$	$p<0.001$

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[22]   Kinetic factors, which determine rate of a reaction, are distinct from thermodynamic factors, which determine the long-term endpoint.

[23]   Indicators of redox status were ammonium, nitrate, and Eh and pe. These are all in fact inter-related because Eh and pe were estimated from the other variables using the computer package *AquaChem,* Waterloo Hydrogeologic, Inc.
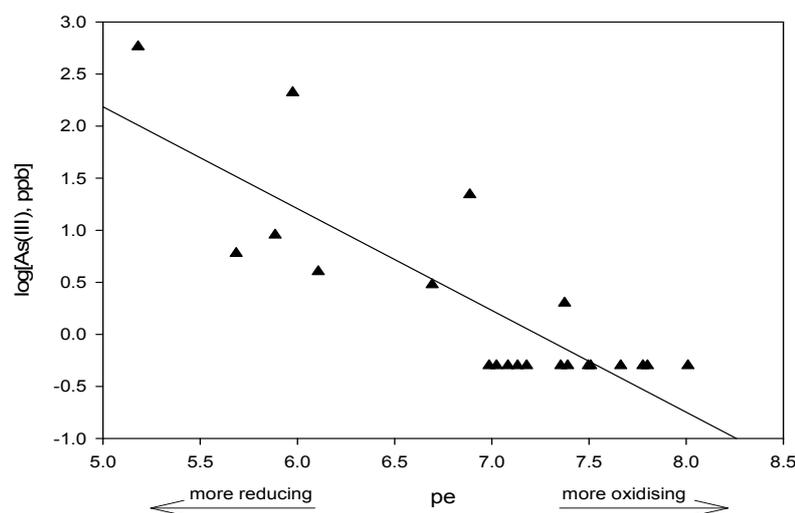
Figure 7 **Relationship between concentrations of arsenite (As(III)) and redox condition for the arsenic speciation sites.** Redox condition is estimated based on the nitrate/ammonium couple.

All samples were evidently in oxygenated (oxic) groundwaters when sampled (indicated by the nitrate/ammonium couple, **Figure 6**). This implies that at equilibrium the arsenate form should prevail. However, a correlative ($p<0.001$) relationship exists linking the absolute concentration of arsenic (III) with solution E_h and pe. Higher total concentrations of arsenite are present when conditions are more reducing.

Correlative relationships also exist between arsenite and pH, alkalinity and sulphate (**Table 7**). The last of these is probably indicative of sulphate reduction, which itself implies that conditions that favour the greatest release of arsenite are the most strongly reducing. This is because the reaction sequence resulting from progressive reduction in a closed system follows the order oxidation of organic matter > denitrification > manganese reduction > ammonification > iron reduction > sulphate reduction with pyrite precipitation (Drever 1997 cited in Wilson & Davidson, 2005). Arsenic precipitation is largely dependant on redox potential and pH. The co-precipitation of arsenic with sulphides and iron oxides is a significant removal mechanism for arsenic in aqueous environments (Bodek et al*.,* 1988), and it is also quite possible that some of the arsenite present in these samples was released from sulphide minerals as well as from metal oxides.

Interpreting other relationships is more difficult due to the limited size of the data set for the speciation samples and will not be attempted. In this small data set, no relationships better than $p<0.01$ exist between dissolved iron and total arsenic, arsenate, or arsenite; whereas over the full data set, the relationship between arsenic and iron is highly ($p<0.001$) significant. In general, the main robust finding from the correlation analysis is that concentrations and relative proportions of the more toxic and mobile form of arsenic (arsenite) increase as groundwater conditions become more reducing, which is in accord with expectations.

4 Potential effects of resource use on arsenic in groundwater

4.1 General

Although most arsenic in groundwater is expected to be natural arsenic, there are means by which resource use could have an influence on arsenic concentrations in groundwater. The most significant would be where a land use causes a change in the chemistry governing arsenic release from hydrated iron oxides.

4.2 Dissolved organic matter

As noted above, arsenic release can come about through iron oxides being reduced (receiving electrons). This is facilitated by presence of a reducing agent – which is something that can be oxidised (donate electrons).

Under oxic conditions, the tendency for electron donation is low. For a water table close to the ground surface, conditions are typically oxic because dissolved oxygen in groundwater remains in equilibrium with atmospheric oxygen. As conditions become more anoxic, electron donation tendency increases. Consumption of oxygen by microbial activity shifts the equilibrium toward the anoxic. As a water table moves downward, the supply of atmospheric oxygen also becomes restricted. Dissolved oxygen in aquifer recharge water is attributed to contributions from surface sources, such as seepage from river beds.

The extent of oxygen depletion is often contingent upon the presence of dissolved organic matter (DOM), which acts as a substrate for microbial activity, and an electron donor. The former results in lower dissolved oxygen or reducing conditions, whereas the latter means that DOM can directly act as a reducing agent (Islam and Von Bernuth, 2005). These are mechanistically inter-related, but both together facilitate the reductive dissolution of iron oxides.

A reasonable proportion of DOM is represented by comparatively low molecular weight compounds classified as fulvic acids. In addition to potentially facilitating dissolution of arsenic-bearing minerals, fulvic acid complexes of arsenic are relatively stable in the aqueous phase. This means that once released to solution, subsurface transport of the desorbed arsenic may be enhanced to some extent by the formation of these types of complexes (Mukhopadhyay and Sanyal, 2004).

Fertilisation and cultivation of soil results in higher soil productivity, increasing the partial pressure of carbon dioxide (Jones et al., 2003) (increasing acidity) and levels of DOM. Land use influences both the production rate and isotopic composition of DOM (Kalbitz et al., 2000). DOM can therefore be a significant component entering groundwater in agricultural areas. It is also an important aspect of soil fertility, acting as a substrate for microbial activity, and a primary source of mineralizable nitrogen, sulphur, and phosphorus. According to Haynes (2005), leaching of DOM greatly influences the nutrient and organic matter content, and pH, of groundwater.

However, water utilisation and increased rates of aquifer recharge can also result in more oxygenation of groundwater, by drawing through surface waters at a faster rate than previously (Hadfield, 2005).

Overall, there appear to be at least three means by which aspects of resource use **might** eventually work to cause release of more arsenic to groundwater through enhancing the reductive dissolution of iron oxides. None of these have been quantified, but potential mechanisms are:

1. Soil cultivation and fertilisation itself resulting in higher concentrations of dissolved organic matter (DOM) working its way through groundwater systems and causing a net depletion of oxygen;

2. Irrigation of dairy effluent on to land. This has the potential to mediate enhanced arsenic release over the longer term through the supply of additional DOM.[24]

3. Cases where abstraction of water has resulted in the groundwater table dropping, and this has in turn been sufficient to cause a change in redox conditions. (This may often make the water more oxic, but there may also be causes where a drop in the groundwater table causes a greater contribution from less oxygenated waters.)

It is unclear how significant any anthropogenically enhanced arsenic release, would be, and over what timescale this might be expected to occur. The impact of some of these mechanisms might only be felt in the medium to longer term, as DOM works its way through groundwater systems, and released arsenic makes its way gradually out.

Tentative support for a link between agricultural land use and arsenic concentrations in groundwater does exist in the literature. Ayotte et al. (1999) report that in New England coastal basins arsenic in groundwater correlates with land-use data, with significantly higher concentrations being found in agricultural areas than in undeveloped areas.[25] Links between arsenic release and land use pattern were also reported by Chatterjee et al. (2003).

In the Bengal basin, arsenic is being released by both the reduction of arsenic-bearing hydrated iron oxides, and the oxidation of arsenic-enriched organic sediments, with each mechanism feeding the other. Excessive extraction of groundwater and enhanced recharge rate in shallow aquifers also increases the mixing of iron oxides with organic degradation fragments, further increasing arsenic release (Kamra et al., 2002; Acharyya and Shah, 2004).

Due to the potential for such links to exist between agricultural land use and arsenic release, ongoing monitoring of arsenic in regional groundwater is recommended, so that any upward trends can be identified.

4.3 Dissolved anions

Dissolved phosphate ($PO_4^{3-}{}_{aq}$) and silicate ($SiO_4^{4-}{}_{aq}$) can also decrease retention (Sharma et al., 2003) and increase the desorption and release of arsenic bound to both iron oxides and insoluble organic matter.[31] This is likely to be primarily by anion exchange, and is more effective for phosphate than silicate because arsenate and phosphate are isostructural, and can more effectively compete with each-other for the same surface adsorption sites.

In some parts of the Waikato region, most notably Taupo, dissolved phosphate and silicate in groundwater are often naturally elevated. Anthropogenic phosphate is also added in the primary form of phosphate fertilisers and recycled form as excreta from grazing animals. The total amount of superphosphate added to New Zealand surface soils is estimated at about 2 million tonnes per year (Fert Research, 2004), of which about 17% is deposited to soils of the Waikato region (Statistics New Zealand, 2004).

Two New Zealand reviews have recently been published relating to phosphate runoff in New Zealand agriculture (Gillingham and Thorrold, 2000; Hart et al., 2004). Most phosphate added to soils is retained in surface soil horizons (Loganathan and Hedley,

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[24] Effluent irrigation is also a supply of additional microbial populations, but these tend to be filtered out in the soil as the groundwater moves

[25] This result is regarded as tentative due to confounding by the types of bedrock underlying different land uses in New England, where agricultural land is predominantly on one type of bedrock.

1997), but a certain proportion can leach (directly or indirectly) to groundwater. In the most recent review, Hart et al. (2004) have explored how physicochemical characteristics of different forms of phosphate fertilizer relate to solubility, runoff and leaching.

Nitrate (NO_3^-) can also compete for arsenate surface exchange sites, but is less effective than phosphate at causing arsenic release (Mukhopadhyay and Sanyal, 2004). However, leaching of nitrate is to groundwater is usually more significant than leaching of phosphate, and nitrate levels in Waikato groundwater are trending upwards as the delayed effects of agricultural practices are gradually transmitted through subsurface groundwater systems. Stream waters in undeveloped catchments of Lake Taupo typically contain about 0.1–0.2 mg/L nitrate (Vant and Smith, 2002), a figure in keeping with the 0.15 mg/L estimate for natural groundwater nitrate in the Lakes Rotorua and Okareka areas (Morgenstern et al., 2004). Concentrations of nitrate in Rotorua Lakes groundwater are currently about 2.7 mg/L, about 18 times higher than their natural baseline value, and still climbing.

Although nitrate and arsenate are only weakly competitive, equilibrium mass balance implies that significant arsenate desorption may start to occur through competition with nitrate, once nitrate concentrations increase sufficiently. In the natural condition, the concentration of groundwater nitrate was about 50 times higher than that of arsenate. A groundwater nitrate level of 1.5 mg/L is about 500 times higher.

On the other hand, Senn and Hemond (2002) have shown that in anoxic lake sediments, nitrate acts to cause less arsenic release, by favouring the oxidation of iron. This research raises a question about the possible interactions between agriculturally-derived dissolved organic matter (DOM) and nitrate. Although DOM should work to facilitate iron oxide reduction and arsenic release, in anoxic zones, dissolved nitrate may be partly compensating by working in the opposite direction. However, the high ($p<0.001$) positive correlation between the dissolved reduced form of nitrogen (ammonium nitrogen, NH_4^+) and arsenic in Waikato groundwater, accompanied by the high negative correlation between nitrate and arsenic (**Table 5**) suggests that groundwater nitrate levels are presently insufficient to prevent arsenic release from occurring. Instead, these correlations suggest that (over a significant part of the total data set) low dissolved oxygen is driving the reduction of both nitrogen and iron oxides.

5   Findings

5.1   Occurrence of high arsenic in Waikato groundwater

The main findings of this work are outlined below.

1. Over the Waikato region as a whole, about 10% of groundwater samples exceeded the drinking water standard for arsenic, and about 20% exceeded half this value (**Section 3.1**).   Most of these non-compliances occur in samples sourced from three sub-regional areas that show statistically higher concentrations of arsenic in groundwater than the rest of the Waikato region. These are the Reporoa Basin, the North Eastern Taupo area, and the Coromandel Peninsula. Excluding these areas, only 2% of samples exceeded the drinking water standard (**Section 3.1**). Drinking water standard exceedance rates in each sub-regional area were as follows (**Table 8**):

Table 8:   **Percentages of groundwater samples exceeding 10 µg/L (the drinking water standard) and 5 µg/L (half this value) within each area.**

Area	Percent exceeding PMAV	Percent exceeding half PMAV
Reporoa Basin	33%	41%
North Eastern Taupo	12%	28%
Coromandel Peninsula	9%	24%
Rest of Waikato	2%	7%
Overall Waikato average	10%	19%

2. The highest raw PMAV non-compliance rate is seen for samples sourced from the Reporoa basin where 33% of samples exceeded the drinking water standard (**Section 3.1**).

3. Maps showing the location of sampling sites with elevated arsenic were derived (**Figure 3**).

4. About 40% of sites where groundwater was sampled on two occasions show more-than-minor change in arsenic concentrations over time, either up or down. This is likely to be linked to groundwater chemistry. In about 10% of cases, a single point-in-time measurement of arsenic in groundwater that shows compliance with the drinking water standard may be misleading (**Section 3.3**).

5.2   Reasons why arsenic becomes elevated in Waikato groundwater

Results of graphical and statistical analyses suggest at least two mechanisms are responsible for elevated arsenic where it is observed. These are:

1. The direct influence of geothermal sources, which might be responsible for at least 15% of the total variation of arsenic concentrations in groundwater, and;

2. The reductive dissolution of subsurface iron and manganese oxides, which might explain at least 20% of the total variation.

Short and medium term changes in concentrations of arsenic in groundwater with time are most likely to come about through the second mechanism. Identification of these

probable general mechanisms leading to elevated arsenic in Waikato groundwater does not preclude the presence of other sources and mechanisms in specific cases, and the co-occurrence of sources.

5.3   Arsenic speciation

Analysis of chemical speciation of arsenic in groundwater samples that exceeded the drinking water standard showed that in cases where arsenic is elevated, the arsenite (As(III)) form is a significant component of total arsenic in about 30% of cases. This is of potential health relevance because the toxicity of arsenite is estimated to be between 25-50 times greater than that of the arsenate (As(V)) form that usually dominates.   The drinking water standard makes no distinction between arsenic species, although it is understood that epidemiological data upon which it is based may implicitly take an 'average' species ratio into account because it represents real exposure data.

Inter-correlations in the data set indicate that total concentrations of arsenite increase as the groundwater becomes more anoxic, which is as expected.

However a pe-pH analysis suggests that at the point of sampling, most groundwater should contain sufficient oxygen to favour the oxidised arsenate form. The fact that 30% of samples contain the reduced arsenite form suggests that this is produced by reduction, but conversion back to arsenate once the water becomes sufficiently oxic is a kinetically limited process. This has parallels to the persistence of arsenite that is formed in the Waikato River surface water system during the summer months.

5.4   Potential influence of resource use

Certain aspects of resource use have the potential to increase the release of natural arsenic to groundwater and drinking supplies sourced from this, but such links have not been explicitly demonstrated. The most significant of these in Waikato soils are expected to be factors leading to enhanced reduction of subsurface iron oxides (**Section 3**). Other factors include water use and competitive adsorption by leached phosphate or nitrate.

Land-use factors that might potentially lead to increased arsenic in groundwater may include:

- Fertilisation and cultivation of agricultural soils leading to higher concentrations of dissolved organic matter (DOM) in the subsurface;
- Irrigation of farm effluent on to land, also leading to higher concentrations of DOM;
- Agricultural sources of phosphate and nitrogen, leaching to groundwater, causing competitive desorption of natural arsenic;
- Use of shallow groundwater to an extent that results in enhanced recharge of shallow aquifers, drawing through dissolved organic matter and other species such as phosphate and nitrogen.

However, none of these factors have been explicitly quantified.

6 Recommendations

6.1 Individual water supply bores, human exposure and risk

The potential for elevated arsenic in groundwater is not an issue with which many water users are aware, but this work has now delineated areas of the Waikato region that are susceptible to this problem. The following recommendations are suggested as appropriate means of mitigating risks associated with elevated arsenic concentrations in groundwater:

Risk communication and hazard management:

1. It is recommended that an information package be developed, to advise bore owners of potential risks associated with arsenic in small drinking water supplies sourced from groundwater and how these can be managed. Information should include identification of the high-risk areas, an outline of potential health issues, recommendations for assessing arsenic in drinking water (including the need to allow for temporal variation), and a broad outline of treatment options. Relevant agencies: Environment Waikato and the Waikato District Health Board.

Standard analytical suite for groundwater testing:

2. It is recommended that a request be forwarded to commercial analytical laboratories to consider adding arsenic to the standard suite of determinands that are routinely assessed as part of groundwater testing, along with a copy of this report. Relevant agencies: Environment Waikato and commercial analytical laboratories.

Bores with high arsenite:

3. It would be useful for detailed research be undertaken on water from wells that produce mainly arsenite, to determine such aspects as factors leading to production of arsenite, temporal variation in total concentrations and speciation, risks to people drinking such water, and factors that most efficiently facilitate the conversion to arsenate. Relevant agencies: such work might be best carried out by a University or Crown Research Institute.

6.2 Regional trends and speciation

4. Ongoing monitoring of arsenic in regional groundwater is recommended as the best means of identifying the existence of any long term trends that might be linked to human activities, such as irrigation of farm effluent on to land, or draw-down of groundwater. Relevant agency: Environment Waikato.

5. An ongoing programme to measure arsenic speciation in supplies that exceed the drinking water standard would also be of benefit. For example, international work into mechanisms of arsenic toxicity may eventually lead to separate standards for total arsenic and arsenite in drinking water supplies, and ongoing monitoring of arsenite would be beneficial in this regard.   Relevant agency: Environment Waikato.

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Appendix 1. Arsenic concentrations in groundwater ranked from highest to lowest (µg/L, parts-per-billion). Non detected (nd) denotes a sample result less than 0.1 µg/L. (For source data see Environment Waikato document 934634.)

Waikato Region overall					Taupo area		Reporoa basin		Waikato Region excluding Reporoa, Taupo and the Coromandel Peninsula		Coromandel Peninsula	
888.5	10.5	5.0	2.5	2.0	79.5	3.0	556.5	9.0	888.5	2.0	61.0	3.0
556.5	10.5	5.0	2.5	2.0	22.5	3.0	505.0	8.0	10.5	1.8	23.0	3.0
505.0	10.0	5.0	2.5	1.8	19.0	3.0	389.0	7.0	10.5	1.5	22.0	2.0
389.0	10.0	5.0	2.0	1.8	12.5	3.0	233.5	5.0	8.0	1.3	17.5	2.0
233.5	9.0	4.0	2.0	1.5	11.5	2.5	141.0	4.0	7.5	1.3	9.0	2.0
141.0	9.0	4.0	2.0	1.5	10.0	2.5	111.0	4.0	7.5	1.0	8.0	2.0
111.0	8.5	4.0	2.0	1.3	8.5	2.0	103.0	3.0	7.0	1.0	7.0	2.0
103.0	8.0	4.0	2.0	1.3	7.5	2.0	100.0	3.0	6.0	1.0	7.0	2.0
100.0	8.0	4.0	2.0	1.0	7.0	2.0	86.0	2.0	6.0	1.0	6.0	2.0
86.0	8.0	4.0	2.0	1.0	7.0	2.0	23.0	2.0	5.0	1.0	6.0	2.0
79.5	7.5	4.0	2.0	1.0	6.0	2.0	22.0	2.0	4.0	0.8	6.0	2.0
61.0	7.5	3.5	2.0	1.0	6.0	2.0	19.5	2.0	3.0	0.8	4.0	1.0
23.0	7.5	3.5	2.0	1.0	5.0	2.0	18.0	2.0	2.5	0.8	4.0	1.0
23.0	7.0	3.0	2.0	1.0	5.0	1.8	16.0	1.0	2.0	0.8	3.5	Plus 19 nd
22.5	7.0	3.0	2.0	1.0	4.0	1.5	12.5	1.0	2.0	Plus 125 nd		
22.0	7.0	3.0	2.0	1.0	4.0	1.0	12.0	1.0	2.0			
22.0	7.0	3.0	2.0	1.0	3.5	1.0	10.0	Plus 18 nd				
19.5	7.0	3.0	2.0	1.0	3.0	1.0						
19.0	7.0	3.0	2.0	1.0	3.0	1.0						
18.0	6.0	3.0	2.0	1.0	3.0	Plus 10 nd						
17.5	6.0	3.0	2.0	1.0	3.0							
16.0	6.0	3.0	2.0	1.0								
12.5	6.0	3.0	2.0	0.8								
12.5	6.0	3.0	2.0	0.8								
12.0	6.0	3.0	2.0	0.8								
11.5	6.0	3.0	2.0	0.8								
				Plus 172 nd								

Appendix 2. Acid soluble and total arsenic concentrations in groundwater where the same site was sampled on two different occasions. (For source data see Environment Waikato document 934634.)

Acid soluble arsenic, µg/L		Absolute and relative differences		Both conditions met
Sampling date 1	Sampling date 2	Absolute difference (µg/L)	Percentage difference (%)	(>4 µg/L and >20%)
12	13	1	8	
10	10	0	0	
7	9	2	29	
1	81	80	8000	YES
22	23	1	5	
12	12	0	0	
21	22	1	5	
14	3	11	79	YES
22	22	0	0	
29	17	12	41	YES
219	228	9	4	
21	18	3	14	
58	19	39	67	YES
19	8	11	58	YES
11	11	0	0	
647	542	105	16	
12	1	11	92	YES
14	567	553	3950	YES
2	5	3	150	
1	1	0	0	
19	19	0	0	
Total arsenic, µg/L				
Sampling date 1	Sampling date 2			
11	10	1	9	
78	40	38	49	YES
13	13	0	0	
12	12	0	0	
40	10	30	75	YES
6	48	42	700	YES
19	27	8	42	YES

Appendix 3. Water types for groundwater with arsenic concentrations above the PMAV.

Water type by arsenic exceedance	Number of bores	Water Type by region	Number of bores
Na-Ca-Mg-HCO$_3$	3	**Reporoa**	
Na-HCO$_3$	3	Na-HCO$_3$	2
Na-Mg-Ca-HCO$_3$	2	Na-Ca-HCO$_3$	1
Ca-Mg-Na-SO$_4$-Cl	1	Na-Ca-Mg-HCO$_3$	1
Ca-Mg-Na-SO$_4$-NO$_3$	1	Na-Ca-Mg-SO$_4$-HCO$_3$	1
Fe-Ca-Mg-Na-HCO$_3$	1	Na-Fe-HCO$_3$	1
Fe-Na-Mg-HCO$_3$	1	Na-HCO$_3$-Cl	1
Na-Ca-HCO$_3$	1	Na-Mg-HCO$_3$	1
Na-Ca-Mg-SO$_4$-HCO$_3$	1	**Taupo**	
Na-Cl-HCO$_3$	1	Na-Ca-Mg-HCO$_3$	2
Na-Fe-Ca-HCO$_3$	1	Na-Mg-Ca-HCO$_3$	2
Na-Fe-HCO$_3$	1	Ca-Mg-Na-SO$_4$-NO$_3$	1
Na-HCO$_3$-Cl	1	Fe-Ca-Mg-Na-HCO$_3$	1
Na-Mg-Cl-SO$_4$	1	**Coromandel**	
Na-Mg-HCO$_3$	1	Fe-Na-Mg-HCO$_3$	1
Na-Mg-SO$_4$-Cl	1	Na-Cl-HCO$_3$	1
		Na-Mg-Cl-SO$_4$	1
		Na-Mg-SO$_4$-Cl	1
		Rest of Region	
		Ca-Mg-Na-SO$_4$-Cl	1
		Na-Fe-Ca-HCO$_3$	1
		Na-HCO$_3$	1

Appendix 4. Percent of arsenic variation over the total dataset that is 'explained' by other variables in linear regressions.

Reductive dissolution linked variables	Percent of arsenic variation 'explained'
Fe	12.2
Mn	16.9
Fe+Mn	17.4
NH_4	10.6
NO_3	4.4
Fe+Mn+NH_4+NO_3	19.1
Geothermal and reductive dissolution linked variables	
Li	35.1
Other variables	
Na	3.1
pH	3
Alkalinity	2.5
Conductivity	0.6
B	0.6
Ca	-0.3
Cl	0.3
K	-0.2
Mg	-0.4
SO_4	-0.4
TDS	0.1
Other combinations	
Fe+Mn+NH_4+NO_3+Na+pH	20.2
Li+Fe+Mn+NH_4+NO_3+Na+pH	43.2