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Arsenic in groundwater in the Waitaha/Canterbury region

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Abstract

Arsenic contamination in groundwater affects tens of millions of people worldwide and is regarded as a major groundwater issue in New Zealand. This study was conducted to evaluate the connection between elevated groundwater arsenic concentrations and inferred redox state of aquifers across the Canterbury region. In total, 2,428 samples from 1,172 wells were analysed for arsenic concentrations, and groundwater redox state was inferred using geochemical indicators for each well.

Most groundwater (~88% of wells; N = 1,031) had arsenic concentrations below laboratory detection limits, ~9.5% (N = 111 wells) had detectable arsenic concentrations below the New Zealand drinking-water Maximum Acceptable Value of 0.01 mg/L, and ~2.6% (N = 30 wells) had concentrations exceeding 0.01 mg/L.

Arsenic concentrations were strongly associated with reducing groundwater; 47 (~43%) of 109 wells with reducing groundwater had detectable concentrations of arsenic, including 19 wells (~17%) with arsenic greater than 0.01 mg/L. Conversely, 840 wells had water classified as oxic, and only one of those wells exceeded the 0.01 mg/L Maximum Acceptable Value for arsenic in drinking-water. Arsenic concentrations were higher in coastal areas north of Christchurch, where confined aquifers are overlain and underlain by layers of peat and low-permeability sediment.

Biogeochemical processes driving release are the same as those that cause arsenic contamination in groundwater elsewhere in the world. However, differences in regional geology and a relatively lesser availability of labile organic carbon appear to constrain the concentrations and spatial prevalence of groundwater arsenic in Canterbury compared to other arsenic-impacted regions (e.g., Southeast Asia).

Keywords

arsenic, redox, groundwater, drinking water, aquifer

Introduction

Arsenic (As) is a toxicant and carcinogen that is found in soil, minerals, and groundwater worldwide (Nordstrom, 2002; Podgorski and Berg, 2020; Smedley and Kinniburgh, 2002). Groundwater is the world's largest source of fresh water (McDonough *et al.*, 2020), and globally, consumption of naturally occurring arsenic in groundwater affects 94 million to 220 million people (Podgorski and Berg, 2020). The World Health Organization (WHO) standard concentration for arsenic in drinking-water is 0.01 mg/L (Gorchev and Ozolins, 1984), which has been adopted by New Zealand as the 'Maximum Acceptable Value' (MAV) in drinking-water (Ministry of Health, 2018).

Globally, most arsenic contamination in groundwater is associated with arsenic mobilisation due to natural processes rather than human influence (Smedley and Kinniburgh, 2002), although human activities, such as mining, timber treatment and pesticide use, have contributed to arsenic pollution, including in New Zealand (Kerr and Craw, 2021; Safa *et al.*, 2020; Robinson *et al.*, 2004). Arsenic (predominantly arsenate) is present in or on aquifer minerals, including iron and manganese oxide and hydroxide minerals, which can undergo microbially-mediated reductive dissolution when groundwater is in a reducing redox state (Borch *et al.*, 2010; Postma *et al.*, 2016). Thus, reductive dissolution of arsenic-bearing minerals is the primary trigger of arsenic release to groundwater (McMahon and Chapelle, 2008; Smedley and Kinniburgh, 2002) and is associated with elevated arsenic concentrations in Argentina (Litter *et al.*, 2019), Bangladesh (Ying *et al.*, 2017), China (Zhang *et al.*, 2020), India (Bindal and Singh, 2019), Italy (Rotiroti *et al.*, 2015), the United States (Welch *et al.*, 2000) and Vietnam (Wallis *et al.*, 2020). Although reductive dissolution of arsenic-bearing minerals is the primary driver of arsenic release, groundwater redox state can also influence the toxicity of arsenic; under reducing conditions, arsenate can be reduced to arsenite, which is more toxic (Singh *et al.*, 2011). After desorption from aquifer minerals, arsenic concentrations are dependent on hydrological factors, including dilution and flushing rates (Fendorf *et al.*, 2010; Smedley and Kinniburgh, 2002).

Arsenic is widespread in New Zealand's aquatic and terrestrial environments (Robinson *et al.*, 2004), and arsenic contamination is regarded as a major groundwater issue (Daughney and Wall, 2007). Concentrations above the drinking-water MAV have been observed in Waikato (Piper and Kim, 2006), Otago (Levy *et al.*, 2021) and Canterbury (Scott *et al.*, 2016). In Canterbury, arsenic contamination has been observed in reducing redox-state groundwater in some coastal areas (Scott *et al.*, 2016), but this study represents the first regional-scale analysis of the relationship between groundwater redox state and arsenic concentrations. To evaluate the relationship between groundwater redox state and arsenic contamination, we assessed arsenic concentration data from 1,172 wells, and used geochemical indicators to estimate groundwater redox state for each well, following the approach used by Close *et al.* (2016) and Wilson *et al.* (2020).

The Canterbury region

The Canterbury (or Waitaha) region is located on the east of Aotearoa New Zealand's South Island and is bounded by the Southern Alps to the west and the Pacific Ocean to the east (Fig. 1). Canterbury is New Zealand's largest geographic region (approximately 50,000 km^2), occupying approximately 17% of New Zealand's land area (Painter, 2018). In Canterbury, most groundwater is found in alluvial sediments (predominantly gravels) underlying the Canterbury Plains, which are one of the world's major alluvial plains (Leckie, 2003). The groundwater contained in Canterbury aquifers represents 73% of New Zealand's total groundwater by volume (Stats NZ, 2017), is the primary source of drinking-water to a population of over 600,000 (including the city of Christchurch) and provides water for 70% of New Zealand's irrigated land (Painter, 2018).

Canterbury has a temperate maritime climate (Macara, 2016). Groundwater recharge is heavily influenced by interactions between the Southern Alps and westerly winds; orographic rainfall in the Alps is a significant source of recharge for rivers and groundwater. From their sources in the Southern Alps, groundwater and braided rivers flow dominantly eastward across the Canterbury Plains before draining into the South Pacific Ocean. The Southern Alps are primarily composed of greywacke, tectonically uplifted by the collision of the Australian and Pacific plates (Browne and Naish, 2003). In some areas of the Southern Alps, arsenic concentrations are elevated in greywacke and argillite (Becker *et al.*, 2000; Horton *et al.*, 2001) and present in other minerals (e.g., calcite, quartz, and sulphides) (Horton *et al.*, 2001; Craw *et al.*, 2002). For example, in the Wilberforce valley, arsenic concentrations have been measured at 200 mg/kg (compared to a background concentration of 10 mg/kg) in some greywackes and argillites (Becker *et al.*, 2000). Weathering of the Southern Alps, followed by the erosion and eastward transport of sediment toward the coast, led to the formation of a thick assemblage of overlapping alluvial fans, which formed the Canterbury Plains (Ballance, 2017). This process has been occurring for at least the last five million years, with increased erosion and deposition during glacial periods (Ballance, 2017). As a result of this erosion and transport of arsenic-bearing bedrock material, geogenic sources of arsenic may be widespread in the alluvial gravels, with arsenic generally present in source rocks and associated sedimentary deposits. The mostly gravel aquifers of the upper plains and river valleys of Canterbury are dominated by oxic groundwater conditions (Wilson *et al.*, 2020).

In some coastal areas east of the plains there are series of confined aquifers (Fig. 1), which typically sit in glacio-fluvial gravels interbedded between aquitards formed from silts, clays, sands, and buried layers of peat extending to a depth of over 200 m (Brown *et al.*, 1988). The silts, clays, and sands were deposited in low-energy marine or estuarine environments that occurred during marine high stands during interglacial periods through the Quaternary (Browne and Naish, 2003). Groundwater is also found in some inland basins, which were formed by glacial activity and tectonic movement and partially infilled with glacio-fluvial sediments. In some parts of south Canterbury, known as the ‘downlands’, groundwater is overlain by layers of loess (of varying thickness), which were deposited during the Pleistocene (Schmidt *et al.*, 2005) (Fig. 1). In some coastal areas, particularly to the north of Christchurch and in some parts of southern Canterbury, reducing redox state conditions can be prevalent in groundwater (Close *et al.*, 2016; Wilson *et al.*, 2020).

Methods

Arsenic data analysis

Our data set includes 2,185 groundwater arsenic measurements, sampled from 1,172 wells (tested from 1 to 25 times, though most wells were only sampled once) from 1989 to 2021. The wells used in this study cover all the main aquifer types found in Canterbury (Fig. 1), and well depths ranged from 1.1 m to 433 m below ground level (mean depth of 33 m; median depth of 20 m). For wells sampled more than once, mean concentrations of arsenic were calculated for each well.

Samples were collected for various reasons, as part of long-term monitoring programmes or for specific investigations. Due to changing laboratory service providers and improving analytical technology over the course of 30+ years, analytical methods used for arsenic measurements changed through the period of sample collection. In summary,

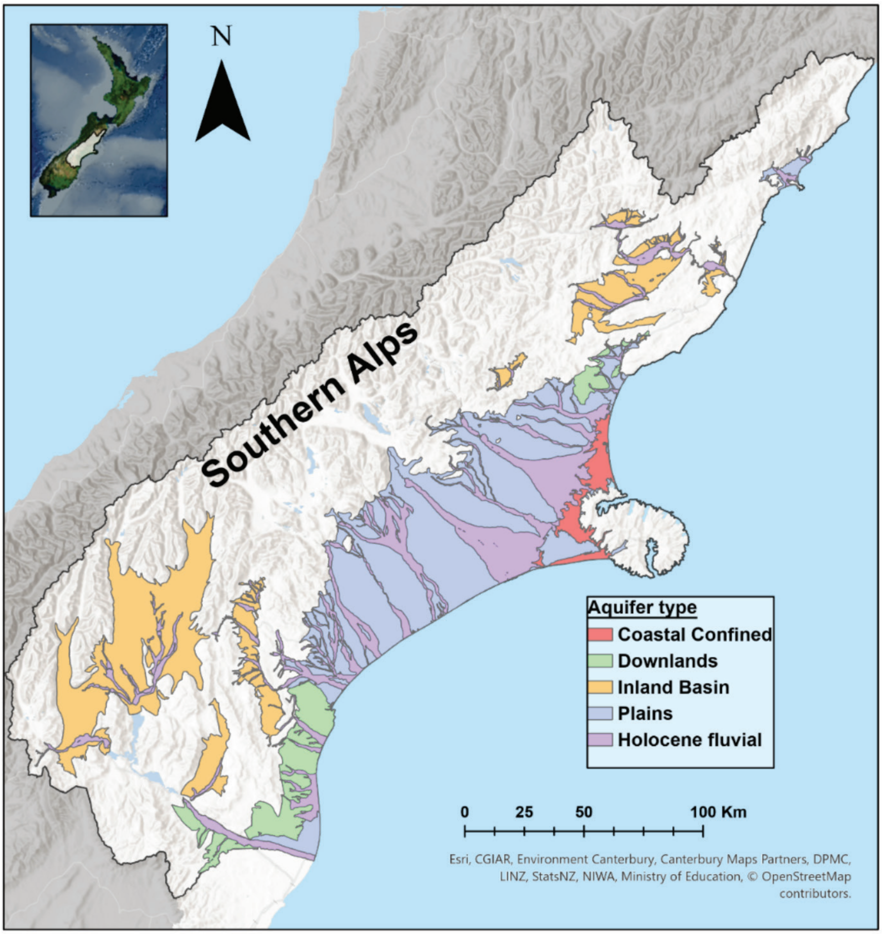

Figure 1 – Main aquifer types of Canterbury region (inset figure shows New Zealand) include coastal confined aquifers, plains aquifers dominated by gravels, downlands aquifers overlain by loess, fluvial aquifers associated with river systems, and inland basins. Broadly, groundwater flows from the Southern Alps toward the east coast, before draining into the South Pacific Ocean.

arsenic concentrations were predominantly measured by hydride generation atomic absorption spectroscopy (AAS) from 1989 to 1995; graphite furnace atomic absorption spectroscopy (GFAAS) from 1995 to 2000, and inductively coupled plasma mass spectrometry (ICPMS) from 2000 to 2021. Laboratory measurements were undertaken at IANZ accredited laboratories. Detection limits ranged from 0.0005 to 0.01 mg/L, though reported 'non-detections' in samples with detection limits of 0.01 mg/L (i.e., the drinking-water MAV) were excluded from this study.

Groundwater samples were collected by trained sampling technicians following groundwater sampling procedures based on international best practice. From 2006, sample collection followed a national protocol for state of the environment groundwater sampling (Ministry for the Environment, 2006) later replaced by the National Environmental Monitoring Standard for discrete groundwater quality sampling

(NEMS, 2019). Over time, Environment Canterbury's approach to measuring groundwater arsenic concentrations varied between measurements of dissolved arsenic and total arsenic in groundwater, depending on whether the technician filtered the samples before analysis. In New Zealand, the MAV refers to arsenic concentration (i.e., it does not distinguish between dissolved and total arsenic). Measurements of total arsenic may capture a more complete picture of the actual amount of arsenic, so we have used 'total' arsenic concentrations if available and dissolved arsenic concentrations otherwise. This study aims to assess arsenic concentrations relative to the drinking-water MAV (Ministry of Health, 2018); therefore, we have not distinguished 'dissolved' from 'total' arsenic in this study.

Redox indicators

Redox state for each well was estimated using a total of 19,687 groundwater samples. After Close *et al.* (2016) and Wilson *et al.* (2020) we broadly classified groundwater redox state into three categories: 'oxic' (or 'oxidising'), 'mixed', and 'reducing'. Redox state can be estimated by measuring concentrations of redox-sensitive parameters, such as dissolved O_2 (DO), nitrate (NO_3^-), manganese (Mn), and iron (Fe) (Close *et al.*, 2016). For example, under reducing conditions DO and NO_3^- will have low concentrations (i.e., < 1.0 mg/L for DO, < 0.5 mg/L for nitrate-N), whilst Fe and Mn might have elevated concentrations (i.e., > 0.1 mg/L for Fe; > 0.05 mg/L for Mn) due to reductive dissolution and release of iron and manganese from aquifer sediments. Following Close *et al.* (2016) groundwater was classified as 'mixed' when nitrate-N, Fe, Mn, and DO concentrations provided an inconsistent indication of redox state. Inconsistent indicators may be observed because the sample was taken from a well that samples multiple redox zones, the sample was in disequilibrium, or because of the thresholds applied to estimate redox state.

Our study used the same redox parameters as Wilson *et al.* (2020), but rather than mapping redox state, arsenic concentrations in individual wells were compared against redox state estimated from parameters in the same well. This approach enabled a direct comparison of groundwater redox state against arsenic concentrations in individual wells. We compared the distribution of the redox state classes for wells with no arsenic detections, wells with detectable arsenic concentrations, and wells with arsenic concentrations exceeding the drinking-water MAV of 0.01 mg/L for arsenic. Due to sporadic measurements of individual geochemical indicators through time, the redox estimates were based on the mean of each redox indicator measurement as the best estimate of long-term status of a given well. Therefore, redox estimates were not exclusively linked to the same samples used for arsenic measurements. One confounding factor resulting from the use of mean values over time is that temporal variations in redox state were not considered in this work.

Results

Arsenic and redox data

Of the 1,172 wells sampled for arsenic, most wells (88%) had arsenic concentrations below detection limits, 9.5% (N = 111) had detectable values below the drinking-water MAV (0.01 mg/L), and 2.6% (N = 30) had arsenic values above the drinking-water MAV (Table 1). Most wells contained oxic groundwater (N = 840; 71.7%), groundwater was mixed in 223 wells (19.0%), and reducing groundwater was observed in 109 (9.3%) wells (Table 1).

Arsenic presence and exceedances of the drinking-water MAV were strongly influenced by groundwater redox state (Table 1). In oxic groundwater, 94.9% of wells did not have detectable concentrations of arsenic and 5% of wells had arsenic detected but below

Table 1 – Exceedances of the arsenic drinking-water Maximum Acceptable Value (MAV) (0.01 mg/L), arsenic detections, and arsenic concentrations below the laboratory detection limit in relation to predicted groundwater redox state.

Arsenic concentration category	Number of wells (% of total wells)	Count of wells per redox classification (% of total wells in each redox state class)		
		Oxic	Mixed	Reducing
≥ MAV	30 (2.6%)	1 (0.1%)	10 (4.5%)	19 (17.4%)
Detected below MAV	111 (9.5%)	42 (5.0%)	41 (18.4%)	28 (25.7%)
Not detected	1031 (87.9%)	797 (94.9%)	172 (77.1%)	62 (56.9%)
Total wells:	1172	840	223	109

the MAV; only one well exceeded the arsenic drinking-water MAV (Table 1). In mixed groundwater, 4.5% of wells had arsenic concentrations above the drinking-water MAV and 18.4% of wells had detectable concentrations below the MAV. Still, in mixed groundwater, most wells (77.1%) did not have detectable concentrations of arsenic. By contrast, in reducing groundwater, 17.4% of wells had concentrations of arsenic exceeding 0.01 mg/L, whilst a further 25.7% had detectable concentrations of arsenic below the MAV. Most wells with reducing groundwater (56.9%) did not have detectable concentrations of arsenic (Table 1), but the differences between oxic and reducing groundwater with respect to arsenic concentrations were nonetheless evident.

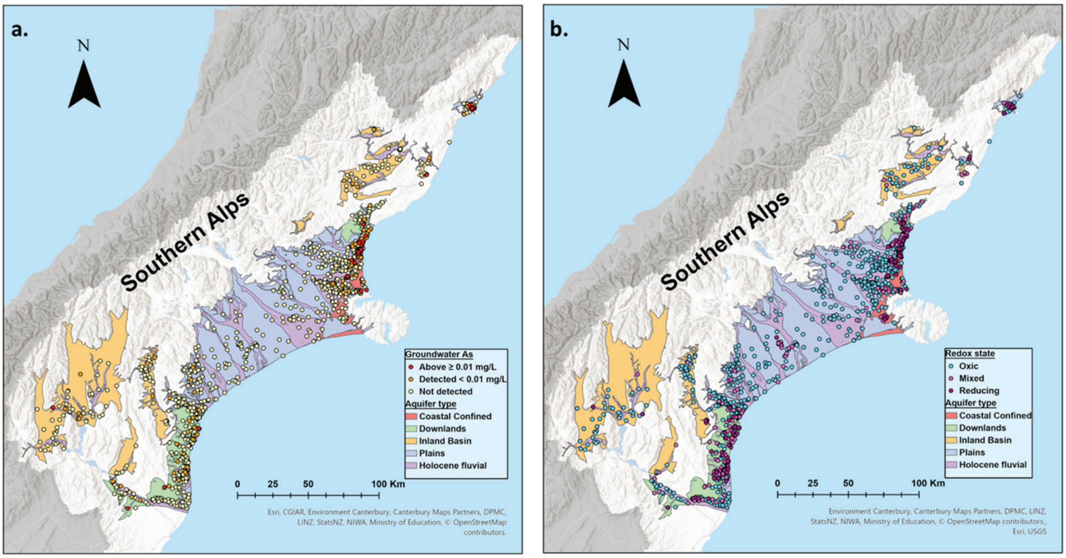

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Figure 2 – **(a)** Average groundwater arsenic concentrations in individual wells (N = 1,172) in the Canterbury region, compared to the MAV (0.01 mg/L); **(b)** Redox state per individual well in the Canterbury region. Redox state was estimated for each well using the same parameters (dissolved oxygen, nitrate, iron, and manganese) and approach as Wilson *et al.* (2020). Canterbury's main aquifer types are also shown in each map.

Arsenic and redox state across Canterbury

In the inland Canterbury Plains, the groundwater is dominated by oxic conditions (Fig. 2b), with almost no exceedances of the arsenic drinking-water MAV of 0.01 mg/L. Although a geogenic arsenic source is present, groundwater redox conditions do not enable arsenic mobilisation to occur. Similarly, in the inland basin aquifers, oxic conditions are prevalent (Fig. 2b), with arsenic concentrations generally below laboratory detection limits (Fig. 2a).

By comparison, arsenic in groundwater is more commonly found in low-lying coastal areas (Fig. 2a), which in Canterbury are typically underlain by confined aquifer systems. Measured arsenic concentrations in coastal aquifers ranged from values below detection to a maximum concentration of 0.92 mg/L (i.e., 92 times the MAV for drinking-water). In the aquifers underlying the South Canterbury downlands, reducing conditions are more common, with some exceedances of the drinking-water MAV for arsenic, though arsenic was not detected in most wells.

The spatial scale of elevated arsenic concentrations (Figs. 2a and 3) indicate that groundwater arsenic is diffusely distributed in some coastal areas of Canterbury. However, there is also spatial variability, particularly within the reducing coastal aquifers. For example, north of Christchurch there are wells where arsenic has not been detected in relative proximity (i.e., within hundreds of metres) to wells where arsenic concentrations exceeded the drinking-water MAV (Fig. 3).

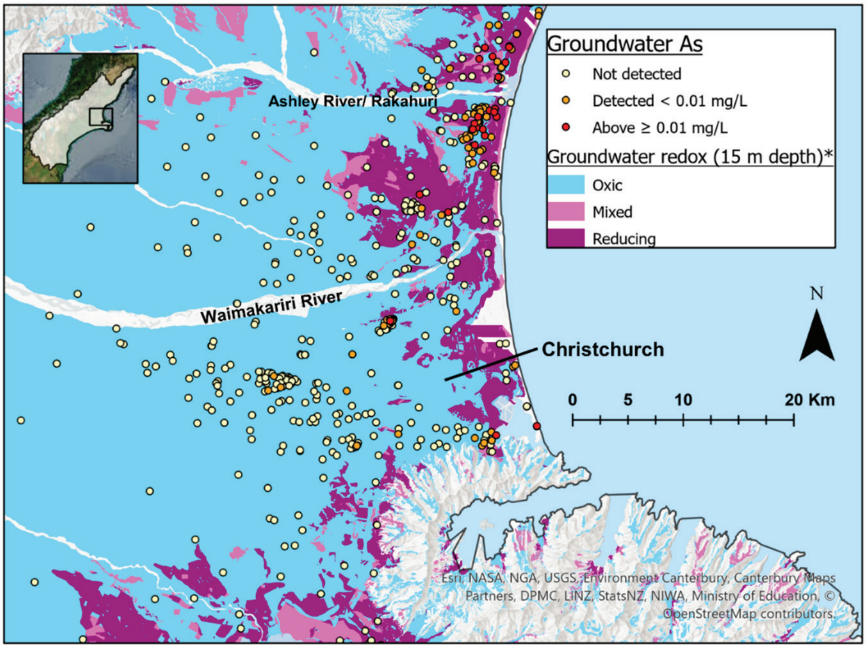

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Figure 3 – Arsenic concentrations relative to the MAV (0.01 mg/L) in an area of North Canterbury (black rectangle in inset map shows location within Canterbury). Groundwater arsenic concentrations are generally higher in reducing aquifers, whilst inland oxic aquifers have lower concentrations and fewer occurrences of arsenic. *Aquifer redox map reproduced from Wilson *et al.* (2020) using data kindly supplied by the authors.

Discussion

Relatively higher risk of arsenic contamination in coastal aquifers

Globally, reducing conditions tend to exist within geologically young aquifers in low-lying areas with low flushing rates (Smedley and Kinniburgh, 2002), such as the coastal confined aquifers of Canterbury. Elevated arsenic concentrations are very strongly associated with mixed or reducing redox state groundwater in Canterbury (Table 1), which is found primarily in the coastal confined aquifer systems and the South Canterbury downlands (Fig. 2b). In reducing groundwater systems, the drinking-water MAV for arsenic was exceeded in ~17% of wells, with a further ~26% of wells having detectable concentrations below the MAV. Further, arsenic was also present in mixed redox state groundwater, with 4.5% of wells exceeding drinking-water MAV and a further ~18% of wells having detectable arsenic concentrations below the MAV (Table 1). These data show that arsenic is a potential indicator of reducing conditions but reducing conditions do not necessarily indicate the presence of arsenic.

The prevalence of reducing conditions in coastal areas is due to the presence of in situ organic matter and confinement of aquifers by low-permeability material deposited by marine transgressions during the Quaternary (Brown and Weeber, 1992). Low-permeability material inhibits transport of oxygen from the atmosphere, recharge, and flow, potentially leading to a build-up of arsenic through time (Fendorf *et al.*, 2010). Further, layers of subsurface peat that overlie or underlie the coastal confined aquifers (Brown *et al.*, 1988) are a source of labile organic matter, which is often a critical, limiting component of reductive dissolution of arsenic-bearing minerals in groundwater (deLemos *et al.*, 2006; Fendorf *et al.*, 2010; Islam *et al.*, 2004). Organic matter release is known to fuel microbially-mediated reduction processes that release arsenic into groundwater in countries where arsenic contamination in groundwater is much more common and has been extensively studied, such as Bangladesh, Cambodia, and Vietnam (Erban *et al.*, 2013; Fendorf *et al.*, 2010; Harvey *et al.*, 2002; Stuckey *et al.*, 2016). The presence of organic matter (which drives microbial respiration) depletes dissolved oxygen in groundwater, causing groundwater to become suboxic or anoxic, which from a chemical perspective is a ‘reducing’ environment. Under reducing conditions, other favourable available electron acceptors can be used in microbial respiration, such as nitrate, manganese, iron, sulphate, and carbon dioxide, and many trace metals and metalloids, such as arsenic, chromium, and uranium (Borch *et al.*, 2010; McMahon and Chapelle, 2008). Since arsenic commonly adsorbs to the surface of iron (hydr)oxide minerals or can be found as trace contaminants within these oxides, desorption and release of arsenic can occur when reduction of iron and manganese oxides is favourable. Thus, the occurrence of arsenic release in aquifers with in situ sources of organic matter and reducing groundwater aligns with expectations based on the biogeochemical behaviour of arsenic observed elsewhere in the world.

Local-scale variability is common in arsenic-impacted groundwater (Jakobsen *et al.*, 2018; van Geen *et al.*, 2003), and our sample data also reveal complex patterns across small spatial scales in some areas of Canterbury. For example, in the reducing coastal confined aquifers north of Christchurch there are wells in which arsenic was not detected, less than one hundred metres from wells where arsenic concentrations exceeded the MAV. Although redox state influences arsenic release, variations in the source of water and the three-dimensional patterns of groundwater flow influence patterns of both redox state and arsenic contamination, which are typically complex in arsenic-impacted areas (Neumann *et al.*, 2010). For example, in some areas of the coastal confined aquifers, mixed and oxic groundwater is predicted (Wilson *et al.*, 2020), possibly due to preferential upwards leakage though aquitards, whilst seepage from the Waimakariri River (Fig. 3) supplies groundwater flow towards Christchurch (Stewart and van der Raaij, 2022), potentially diluting arsenic and supplying oxygen-rich water. Thus, in Canterbury's coastal aquifers, a combination of local-scale geochemical and hydrological variability means that arsenic-contaminated groundwater is not uniformly observed.

Oxic groundwater and low arsenic concentrations in the Canterbury Plains

In Canterbury's oxic groundwater, 95% of wells had arsenic values below detection limits, with 5% of wells having arsenic detections and one well (0.1% of oxic wells) exceeding the drinking-water MAV of 0.01 mg/L (Table 1). Most of the groundwater in the unconfined aquifers of the Canterbury Plains and inland basins is oxic (Close *et al.*, 2016; Wilson *et al.*, 2020) because the open-framework gravels that form the unconfined aquifers, and the thin soils that overlie them, allow land-surface recharge (i.e., the sum of irrigation and rainfall recharge) and transport of oxygen from the atmosphere to groundwater. Further, in some areas, recharge is dominated by seepage from the gravel-bed braided rivers, which transport oxygen-rich water from the foothills and Southern Alps. The lack of detectable concentrations of arsenic in oxic zones of the Plains (despite arsenic being present in the greywacke, rocks, and minerals of the Alps that were eroded to form them) implies that arsenic may be stored in oxic aquifer sediments, or when arsenic is released, it might be diluted to concentrations below laboratory detection limits. Further, significant parts of the Canterbury Plains are dominated by agricultural activity (Stewart and Aitchison-Earl, 2020), causing unconfined gravel aquifers to have excessive nitrate concentrations. Nitrate is a powerful oxidant (Galloway *et al.*, 2003), and the diffuse addition of anthropogenic nitrate, a more favourable electron acceptor than manganese or iron (McMahon and Chapelle, 2008), might further limit reduction of arsenic-bearing iron and manganese minerals in the aquifers of the Canterbury Plains.

In the aquifers of the Canterbury Plains, arsenic concentrations could be low because of a higher rate of sorption rather than desorption, which is influenced by redox state, although dilution could also be a factor due to high flow rates (Postma *et al.*, 2017; Sø *et al.*, 2018). For example, the much larger and fast-flowing Plains' oxic aquifers can dilute dissolved organic carbon and competing adsorbates (e.g., phosphate) whilst transporting higher concentrations (and total loads) of oxygen and nitrate, moderating arsenic release from aquifer minerals (Sø *et al.*, 2018). Thus, in aquifers on the Plains, mass loads of arsenic could be high but very difficult to spot in groundwater: rates of sorption to aquifer minerals are likely to be higher than the rate of arsenic release (owing to the oxic redox state), whilst the relatively high flow rates mean that any desorbed arsenic may be diluted to concentrations below detection limits. For example, Burbery et al. (2020) installed a denitrifying bioreactor in a fast-flowing (hydraulic conductivity of 1332 m/d) shallow unconfined gravel aquifer, in which woodchips within the bioreactor released labile organic carbon. The release of labile organic carbon drove 'pollution swapping', whereby denitrification took place under reducing conditions, but manganese, iron, and arsenic were released from aquifer minerals (Burbery *et al.*, 2022). Notably, although concentrations of arsenic reached a maximum of 0.022 mg/L (i.e., more than double the drinking-water MAV), detectable concentrations of arsenic travelled less than 60 m down-gradient before dilution or attenuation by mechanisms such as sorption (Burbery *et al.*, 2022). Thus, in Canterbury, arsenic release appears to be heavily influenced by redox state, yet on the Plains, high concentrations of geogenic arsenic in groundwater are likely only occur on local scales, where there is a source of organic carbon. In most of Canterbury, high arsenic concentrations are likely to be diluted or attenuated to concentrations below laboratory detection limits within a relatively short distance (e.g., Burbery *et al.*, 2022).

Future research

More frequent monitoring would improve understanding of arsenic behaviour in Canterbury's groundwater. For example, most wells have only been sampled once, yet regular sampling of arsenic-affected wells would allow assessment of seasonal and long-term (i.e., decadal) variability and any potential trends. Analysis of arsenic bound to aquifer sediments could shed light on mechanisms of arsenic retention and release, though these mechanisms are expected to be similar to those observed elsewhere the world. In the coastal confined aquifers, labile organic carbon is likely to be an important influence on the spatial variability observed in the coastal confined aquifers, thus measurements of dissolved organic carbon could be of value. From a monitoring perspective, the spatial variability of arsenic concentrations in some coastal areas means that it is likely to be difficult to reliably predict the concentration of arsenic in a particular well based on the results from neighbouring wells. Analysis of arsenic speciation in groundwater could also be valuable because, although the drinking-water MAV does not discriminate between arsenic species, arsenite is much more toxic than arsenate (Singh *et al.*, 2011).

Ongoing and future human-induced changes could impact arsenic contamination on local scales, even in the oxic aquifers of the Plains. Although arsenic contamination is largely of geogenic origin, there are numerous anthropogenic arsenic sources (e.g., timber treatment plants, landfills, sheep dip sites) in Canterbury, whilst human activities can also alter groundwater redox state and flow behaviour. For example, irrigation pumping and return flow can alter recharge rates, mixing, and natural flow patterns, which can influence geochemical conditions. Further, the release of organic matter (e.g., from manure spreading, constructed ponds, septic tanks, or landfill sites) can cause groundwater redox state to become reducing, whilst phosphate (released from fertiliser) can compete with arsenate for binding sites on aquifer minerals (Fendorf *et al.*, 2010; Lin et al., 2016; Smedley and Kinniburgh, 2002), though the impact of these activities on arsenic release is not well studied in Canterbury.

Conclusions

In Canterbury, arsenic in groundwater originates from greywacke and fault-fluid minerals in the Southern Alps, before being fluvially transported coastward by way of the Canterbury Plains. Region-wide, most wells (88%) had groundwater with arsenic concentrations below detection limits, even in wells with reducing redox state groundwater (56.9%). Arsenic contamination was very rare in the mostly oxic groundwater of the inland basins and the Canterbury Plains, because of dilution and oxic conditions.

Conversely, in some coastal areas, there are diffuse sources of arsenic and conditions favourable to arsenic release to groundwater. These processes contributed to exceedances of the drinking-water MAV for arsenic in 2.6% of wells sampled across the region in the period from 1989 to 2021. In reducing groundwater, which is relatively common in the coastal confined aquifers, arsenic concentrations were highly variable at relatively small spatial scales. The observed variability is likely due to a combination of the presence of arsenic-bearing iron oxides, the availability of labile organic carbon, differences in local-scale groundwater residence times, and sluggish flow rates. Thus, arsenic concentrations in Canterbury groundwater are dependent on the presence of arsenic sources, groundwater redox state, and the influence of physical hydrological factors such as mixing and dilution.

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