GEOG309 – Research for Resilient Environments and Communities: Assignment 5. Natural Arsenic in the Port Hills

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Contents

1. Executive Summary

- This project aimed to investigate findings of elevated arsenic (As) concentrations in Christchurch soils by the Environment Canterbury (ECan) contaminated land team. These findings were concluded to be of natural occurrence based on reported history of the site.
- This project looked to further determine whether these As concentrations were anomalous or more widespread, and to test the natural origin hypothesis.
- Previous literature on geogenic As in soil and water was reviewed to determine suitable locations for sampling. This knowledge was then utilised in conjunction with ECan mapping resources, and S-Maps to identify locations of interest appropriate for soil testing. An X-Ray Fluorescent Analyser (XRF) was used to efficiently identify the soil composition of the selected sites.
- After multiple sampling efforts, no significant levels of As were detected, leading us to conclude the reported findings to be 'site specific', and not of concern for the wider Port Hills area.
- This study was severely hindered by the Covid-19 pandemic and subsequent lockdowns that prevented field work from being undertaken. The XRF was limited in its ability to sample wet soil which proved problematic as we experienced consecutive days of rain prior to our available sampling days, it also only samples at a maximum depth of 10mm. The final major limitation was site access and disturbance as a result of the rapid land development of the area.
- For future research in this area considerations would need to be made in regards to the following areas: a larger sample of testing sites, ideally with less surrounding land development and construction, selection of ground and surface water for testing to understand mobility and potential exposure pathways, potentially look to investigate how urbanisation influences As in the environment, and finally, expand the scope to include Anthropogenic sources of As .

2. Introduction

This research was prompted by reports to Environment Canterbury's (Ecan) Contaminated Land division about excessive concentrations of Arsenic (As) found in soils in the Halswell area. Based on the known history of the site, it was thought that the Arsenic was not a result of any previous anthropogenic activity so was therefore determined to be of natural occurrence. The assumption that the As was geogenic broadened the scope of the project to include the Port Hills region, partly because the volcanic nature of Bank's Peninsula would explain geogenic As, but also because the specifics of the report that detail As findings is sensitive and not for publication, so a broad description of the subject area suits the required subtlety.

As is a non-threshold toxin and is considered a heavy metal of high toxicity to life (Rahman & Singh, 2019). As has been ranked 1st in the priority list of hazardous substances by the Agency of Toxic Substances and Disease Registry, (ATSDR, 2015), which ranked the list based on frequency, toxicity, and potential for human exposure. Prolonged exposure to As can result in skin lesions, cancers, pulmonary and cardiovascular disease, as well as death (WHO, 2018).

Land development has skyrocketed in recent years as the Government and industry race to solve the current housing crisis in New Zealand (Cann, 2021). The Halswell area in particular, has seen incredible levels of growth. The accelerating urban sprawl of Christchurch means that more land in the area is ripe for development, this could prove problematic if the reported findings are more common and left unchecked. This sobering scenario highlights the importance of this research.

2.1. Research Objectives

Working under the hypothesis that the detected Arsenic was of natural origin, we wanted to determine if this was an anomalous finding or whether it was more widespread. In event that we did find more Arsenic contaminated areas, we aimed to test the natural origin hypothesis.

3. Theory and Literature Review.

Our review divided the literature up into 5 subtopics: natural sources of As, anthropogenic sources of As, environmental and health impacts of As, mapping and sampling methods for As, and the history of the areas of interest to this project.

3.1. Natural Sources of Arsenic

Natural sources of arsenic are an important aspect of this investigation, as it will help us to identify possible sites of interest, within areas of Christchurch. Majority of the literature reviewed in this project is based upon research conducted outside of New Zealand, but still holds relevance to our own research.

Arsenic has a preference to coexist with sediments that form iron hydroxides and sulphide minerals (Herath et al., 2016). The weathering of sulphide minerals such as arsenopyrite (FeAsS), and forms of volcanic rock, is often a significant natural cause of the release of As into groundwater and sediments (Herath et al., 2016). There are several geochemical processes involved that cause this to occur, with the end result being a more 'mobile' species of As formed. This can occur via oxidation – reduction reactions. Under reducing conditions (anaerobic soil), As(V) is reduced to As(III), a more mobile species, resulting in the release of As (Herath et al., 2016). Anaerobic environments are often a result of high amounts of organic carbon present in the soil (due to microbial activity consuming oxygen), or if soils become permanently waterlogged (Gaw, 2016).

Another form of naturally occurring arsenic is geothermal features/volcanic activity. As present in geothermal areas generally originates from geothermal fluids, hot spring discharges, and igneous rock(such as rhyolites) (Morales-Simfors et al., 2020). Geothermal sources of arsenic can be a problem in relation to contamination of groundwater and drinking water sources, as water from geothermal features can often 'rise' or circulate into groundwater aquifers or surface waters (Bundschuh et al., 2013)

According to literature, research around arsenic levels in soils generally follows an experimental research design, with varying methods of soil sampling and analysis. This is dependent on the location, suspected source, and context of the research undertaken. For example, some may sample/test soil using a method that investigates the spatial distribution of As, relative to the source (Dittmar et al., 2007). Others may have explored the seasonal variation of As levels in soil (I.e., variation over the wet vs dry seasons. Soil testing and sampling methods outlined in literature generally included sampling by hand, soil coring, automated sampling using lysimeters, and analysis via spectroscopic techniques (such as X-ray fluorescent spectrometry).

The most significant finding of the literature sources reviewed in this topic, is that the high levels of As detected in each of the field sites were confirmed to originate from natural sources. Another common finding was that anaerobic environments tend to accelerate the mobilisation of As via reductive dissolution/geochemical processes. Arsenic can also accumulate in soils over time, as discussed by Dittmar et al., 2007. Given this information, it seemed important that we identify any areas that would be considered anaerobic, or may have been previously (e.g., drained wetlands), as they would make good 'candidate' sites for soil testing.

3.2. Anthropogenic Sources of Arsenic

Anthropogenic arsenic occurs in the environment via the use of manufactured chemicals like pesticides or through mining, damming, and smelting practices. Anthropogenic arsenic sources can contaminate soil, crops, and waterways which intern affect humans and wildlife. To better understand this process, papers by Avila-Sandoval et al (2018), Moriarty et al (2016), Cagnin et al (2017), Li et al (2016), and Rice et al (2002) were reviewed. These reports case various environments and observe the effects of arsenic from farming, mining, and timber treatment run-off.

The Rice et al (2002) study focused on arsenic timber treatment in Virginian lakes. The lake's mass of arsenic input was larger than the output causing a 70% arsenic lake-retention rate in 1998. Rice et al's study then recorded arsenic cores levels ranging from 18 to 28 µg/g. Avila-Sandoval et al (2018) and Moriarty et al (2016) observed the water and sediment contamination from local mining practices in Mexico and Canada. The reports used statistical and lab analysis to discover the high arsenic levels cause both environments to be unfit for consumption.

Cagnin et al (2017)'s study follows this concept with the investigation of the Doce River in Brazil. Damming and agriculture practices caused highly concentrated arsenic run-off into the Doce River. This contamination caused one of Brazil's greatest environmental disasters (Ferreira et al, 2020). Although there was a background arsenic concentration of 8 mg/kg approx., and post-experiment discovered elevated levels reaching 4500 mg/kg in aquatic sediments (Cagnin et al, 2017).

A study by Moriarty et al (2016) also observed arsenic levels ranging from 3.9–630 mg·kg− 1 in various Canadian lakes. The lake's arsenic bio-accessibility ranged from 7.9% to 35%. Although not likely to be consumed, contamination may have adverse environmental effects on the aquatic inhabitants. Li et al (2016) also explored the adverse arsenic effects by studying drinking wells. Li et al reported levels 620 μg/L of arsenic in a New Jersey community well.

If any of these water or sediment samples were digested there would likely be adverse health effects, as these concentrations exceed WHO's guidelines of 0.0001 mL (Machado et al, 2020). Each study recorded anthropogenic arsenic levels above the WHO guidelines. Therefore, anthropogenic arsenic sources are important factors to understand, particularly when it comes to human and environmental health.

3.3. Environmental and Health Impacts

The greatest environmental effect of Arsenic (As) is its ability to leach into groundwater and waterways, coincidently, this also has the greatest impact on human health as it acts as an exposure pathway. As contaminated groundwater is common throughout south and southeastern Asia as well as parts of South America, this presents a health crisis as groundwater is used for drinking, irrigation of crops, bathing, (WHO, 2018).

This review looked at studies that primarily focused on sampling for As in ground and surface water. Research was conducted in the following countries: Vietnam, Argentina, India, China, and Spain. All 5 studies used similar water sampling methods when sampling ground water. Some studies sampled at varying depths and included other water sources such as freshwater streams and surface run off. 3 out of the 5 studies also took soil samples from areas surrounding wells and irrigation pumps. Ahamed et al., 2006 took hair, nail, and urine samples from residents of affected villages in addition to groundwater samples

The WHO safe drinking water guideline advises that As concentrations be no higher than 10 mg L^{-1} . Concentrations in excess of the 10 mg L^{-1} guideline were found in all 5 of the reviewed studies. (Berg et al., 2001) found concentrations exceeding the guideline in 72% of the sampled wells. (Ahamed et al., 2006) found concentrations over 300 mg L^{-1} in 10% of the sample area in India.

(Tong, Guo, & Wei, 2014) found high concentrations of As in crops and soil as a result of decades of irrigation from contaminated wells and water diverted from the Yellow River.

In the case of the Argentinian study, the researchers found correlations with other parameters such as groundwater flow patterns and pH. Areas with lower hydraulic gradients corresponded with higher concentrations of As and zones of higher groundwater pH showed a clear correlation with areas of high As (Bundschuh et al., 2004).

The most useful take home from this review is from Bundschuh et al., where greater concentrations of As were found in areas of lower hydraulic gradients which affect flow patterns and transport of toxins.

Whilst all these studies focus on As concentrations in ground and surface water, the sampling methods and results were still of relevance to our project as we hypothesized that we would find high As concentrations in previously drained streams and swampland around the Halswell area as land development has intensified. This hypothesis was drawn with the help of the finding by Bundschuh et al., 2004.

3.4. Mapping and Sampling Methods

Arsenic and its compounds cannot be destroyed in the environment whether it's natural or man-made (Chung et al., 2014). This highlights the importance of knowing where arsenic is in our environment as it is a complex issue.

There are a range of mapping techniques and methods in all research fields. Mapping Arsenic is very site specific and is determined by past land use history as well as the geology of the land. Without these factors, the likelihood of finding arsenic higher than background concentrations is minimal. The two most effective ways of measuring arsenic in soil is through the use of soil samples and X-Ray Fluorescence (XRF) technology.

Taking soil samples is slow and not very efficient. Soil must be collected and prepared before it can be analyzed in a lab. This all takes place in a lab with the process occurring over multiple days. However, the result of a soil sample is a highly accurate representation of the soil contents. The XRF on the other hand is highly efficient in a field scenario. The device can be used to test soil samples quickly allowing for a range of sites to be tested in a non-destructive manner (Nakano & Tsuji, 2009). The XRF also gives a broad characterization of soils' elementary constitution in the field with minimal to no sample preparation (Tavares, Molin, Hamed Javadi, de Carvalho, & Mouazen, 2021). The downside of an XRF is that it is not as accurate as a soil sample. The device can only survey the top 1 mm of the soil and does not give a good representation of the entire soil profile. Testing with the XRF should be done to gain an idea of whether soil has elevated levels or not.

Combining both XRF and Soil collection methods proves most effective. It can improve the quality of predictive models for soil attributes (Tavares, Molin, Hamed Javadi, de Carvalho, & Mouazen, 2021). Site sampling should be conducted using the XRF to discover potential sites of elevated arsenic. Soil samples of these sites should then be conducted to fully understand whether arsenic concentrations are elevated or whether the data was just an anomaly. This allows for quick and effective sampling of multiple site locations where significant sites can be further analyzed for a more comprehensive measurement.

3.5 History

Geological processes are a driving factor to geogenic sources of Arsenic present in the environment and can be affected by multiple factors. Arsenic round the world: a review, included outlines of how naturally occurring Arsenic is formed, the outline of different processes that led to the transportation of Arsenic through soils, air, water, and other mediums. The authors covered off points that will be helpful for our project which included where elevated concentrations may be found and under what conditions will produce the highest levels.

The article by R. J. Sewell outlines that Banks Peninsula consists of Late Miocene alkalic to transitional volcanic rocks that erupted from two major composite volcanoes, Lyttleton and Akaroa. This makes up the perimeter of The Port Hills and contains the largest accumulation of volcanic rock with an area of 1200km2, (Sewell, 1988). Volcanic rock is known to be a parent material of Arsenic under the right conditions.

A Meteorological Study of the Port Hills Fire studied the effects of a significant event that occurred on the port hills in 2017. A wildfire occurred in the Port Hills and was cited as one of the country's most severe fires, (Pretorius, Sturman, Strand, Katurji, & Pearce, 2020), this has lasting effects on the geographical composition of the Port Hills.

This review focused on the geological processes that have occurred in Christchurch's history, focusing on the Banks Peninsula and The Port Hills. These are key findings to note because the geological history has shaped the landscapes we study today. The articles will aid in our understanding of sites that we have chosen and what has occurred geologically over a long period of time. It will inform us of what processes have been occurring in and around the region and for what period. They have outlined the history of volcanic activity on the Banks Peninsula which would have lasting effects on the surrounding areas, influencing Arsenic concentrations. They go on to say that high concentrations of arsenic can occur in volcanic rock types, and the Banks Peninsula located closely to the Port Hills had high volcanic activity in the past and may be a contributor to naturally elevated arsenic levels in the Port Hills. Arsenic can occur naturally, be mobile in the environment, and the levels of arsenic can vary considerably between geological regions. Notably, arsenic concentration is more dependent on the parent rock material than the soil conditions, (Mandal & Suzuki, 2002).

The Port Hills fire was an event that changed the face of the Port Hills. It is helpful to know the significant events that have occurred previously in the area that we intend to study. It gives us insight of the history of vegetation change, potential soil transport and therefore arsenic and what area that would have covered.

4. Methods

Prior to any data collection, the first stage was to identify locations for sampling/soil analysis within the Halswell and Cashmere areas of Christchurch (close proximity to the Port Hills). This was achieved through use of S-Maps which allowed the identification of soil type to determine whether they were susceptible to water logging and chemical reduction (Figure 1). Canterbury Maps Viewer was also used which provided access to data layers such as the Black Maps or drainage systems (*Figure 2*). An example of this, was the use of the digitized Black Maps layer, which meant we could identify areas that were previously wetlands/anaerobic environments.

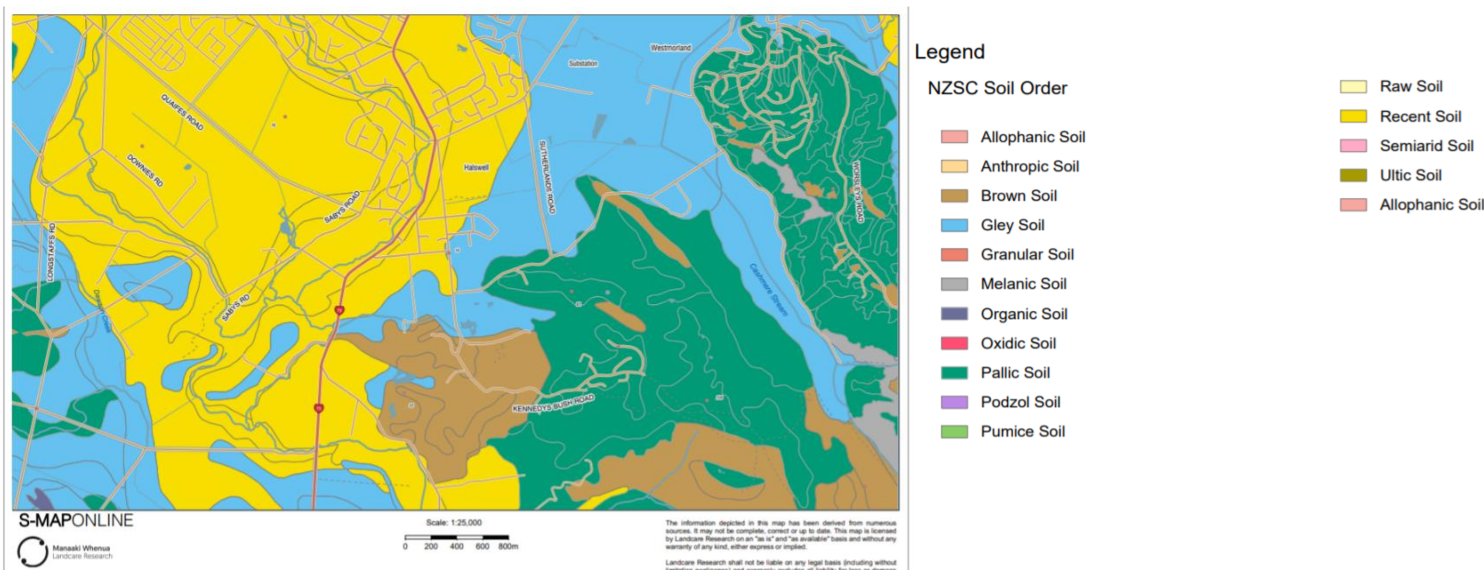

Figure 1. *Soil map and legend of the Halswell sampling area. Testing sites were identified in areas of Gley soil type – those that have been strongly affected by soil waterlogging and have been chemically reduced. Adapted from S-MapOnline. Maanaki Whenua Landcare Research., (2021).*

Figure 2. Selected testing sites using the 'Black Maps'. (Environment Canterbury Regional Council, 2021).

To investigate arsenic levels in soils, the best approach was to use an experimental research design to collect and analyse our own data. This was to involve the use of an x-ray fluorescence (XRF) analyser to detect any arsenic at shallow soil depths, followed by soil sampling and further analysis if any arsenic was detected. An XRF operates by irradiating a targeted area of soil with x-rays, exciting the material within the soil. Each chemical element then produces a specific amount of energy, released in the form of fluorescent x-rays, which are detected by the analyser (ThermoFisher Scientific, 2020).

This method of analysis delivers immediate results and is non-destructive, which made it well suited to our research approach - given its convenience and our restricted time schedule for the project.

Figure 3*. Soil testing at site 'one' with an XRF.*

At each testing site, approximately 4-5 sets of readings were taken at randomly selected spots within the site. The selection of the testing 'spots'– which is more of a random sampling approach, as opposed to one that is systematic or stratified, and this was also dependent on the nature of the terrain i.e., the extent of human influence. For example, Site 'One' (*see Figure 4*) consisted of a man-made wetland area, with a pile of soil excavated from one of the ponds on an adjacent section of land. The testing spots for this site were on and around the soil pile, which, given the negative results, was deemed too disturbed. The soil around the base of nearby trees was then tested with the thinking that it was less likely for there to have been any disturbance.

Figure 4. Site 'One' soil testing location.

Additionally, it was necessary to have a control site, to compare against the rest of our testing sites. This needed to be a location that was likely to be unaffected by factors or processes that may lead to elevated levels of arsenic, such as those discussed above (*see Section 3*). It was therefore decided that the Halswell Quarry area would be a good candidate for a control site *(see Figure 5)*, as the likely parent material (if the arsenic was to be geogenic) was easily accessible to test. In addition, the quarry site was located above the high-water table of the areas we had been testing, meaning it would not have previously been a wetland or swamp environment.

Figure 5. Control site at Halswell Quarry.

5. Results

The data, summarised below, was extracted from the XRF directly and collated on an excel spreadsheet.

Table 1. Background concentration of As in relation to the selected testing sites. (Environment Canterbury Regional Council, 2021).

Testing Site	**Background Concentration of As (ppm)**
1	11.5
2	8.7
3	8.7
4	4.6
5	4.6

Table 2. 'Day One' testing results, where LOD = 'Limit of Detection' (16 ppm).

Site	**Reading**	**As (ppm)**
1	#1	<LOD
1	#2	<LOD
1	#3	<LOD
1	#4	<LOD
1	#5	<LOD
2	#6	<LOD
2	#7	<LOD
2	#8	3975
2	#9	<LOD
2	#10	<LOD

Table 3. 'Day Two' testing results, where LOD = 'Limit of Detection' (16 ppm).

Site	**Reading**	**As (ppm)**
3	#1	<LOD
3	#2	8568
3	#3	92
3	#4	<LOD
3	#5	<LOD
4	#6	<LOD
4	#7	<LOD
4	#8	<LOD
4	#9	<LOD
4	#10	<LOD
4	#11	<LOD
5	#12	<LOD
5	#13	7565
5	#14	<LOD
5	#15	10
5	#16	<LOD
5	#17	<LOD

6. Discussion

The XRF was the only sampling technique used. The XRF was able to produce samples within just a few minutes and therefore was optimal for short field-testing days when visiting multiple sites and was a great tool to us because of its versatility, (Johnson, Hooper, & Conrey, 1999). However, the XRF only gives a very small estimate of the overall sites, testing only a few centimetres below the soil. Conditions also varied between sites and days, and because of the nature of the XRF, it requires dry and bare soils. In some of the sites we visited the soils had been dampened by rain the previous day, leading to inconsistencies between sites and samples. If time permitted using another method of sampling would eliminate some variables and differing site conditions as a factor for results.

No significant sources of arsenic were found in any of our sites, and this may be due to multiple factors. Some of which being, the disturbance from anthropogenic activities, limited scope of the site and no sources of geogenic arsenic present. Of the sites we visited using reference from the black maps, very few had been unaltered by human activities. The sites varied from construction sites, parks and wetlands and housing areas. From our initial scoping to visiting the site they differed extremely from what we had expected. We were unable to access some sites and when we tested in the highly disturbed sites, any geogenic arsenic that may have occurred could have been transported elsewhere. The only significant contamination of arsenic came directly from Chromated Copper Arsenate (CCA) treated timber posts that we used to see if we could get a reading from anything and the soil directly beneath it where it had leached from the post, and therefore was known to be of anthropogenic origin. The only other result came from the last site at 10ppm which was greater than the background concentration, however, when testing a patch of soil 30cm away there was no arsenic detected. This indicates that when, if any, arsenic is detected that it is likely to be an anomaly and very site specific.

Despite not finding any significant sources of arsenic through our testing, the results are still significant. Arsenic is a dangerous carcinogenic substance, as mentioned in section 2, that when exposed to causes serious health and environmental issues, (Bali & Sidhu, 2021). Arsenic can also be taken up by crops and other plants, (Bali & Sidhu, 2021), which may be on properties and provide a direct exposure pathway.

The remediation of soils with arsenic contamination comes at a high financial cost, (Jang, Hwang, Choi, & Park, 2005). Not only could it be present in soil, if conditions were correct, arsenic has the potential to become mobile and travel into waterways and groundwater. This has the potential to contaminate valuable sources of drinking water and contaminant lakes, rivers, and streams which act as another exposure pathway to humans and other organisms. Because we did not find any significant results other than from CCA treated timber, we were unable to search for the origin of the reported arsenic.

7. Limitations in our research.

7.1 Covid – 19

During this project, our field research was restricted due to Covid-19. Lockdown levels 3 and 4 lasted for over a month, under these restrictions group work and soil sampling was not possible. This also meant we could not meet and discuss ideas in person, meetings were restricted to zoom/online. When our group was able to sample in level 2 there were still health restrictions in place. Social distancing, masks, and individual transportation to sites were required, which added an extra layer of complexity to our method. Additionally, our group were not able to go into Environment Canterbury Regional Council until Alert Level 1, meaning we were unable to meet our community partners face to face - unless in the field.

7.2 XRF Analysis

The XRF equipment also had limitations; it can only analyse small areas at shallow depths. This means that the results recorded may not be a completely accurate representation of the sites investigated. The XRF also cannot be used under wet or damp conditions. This meant that the project fieldwork was highly weather dependent, and the already limited time available for testing was even smaller. The XRF also had a detection limit of 16 ppm, which was later lowered to 8ppm. This meant that any As present at lower concentrations than this would not have been detected.

7.3 Site Selection

The sites available to be tested were limited to areas with low/no land development. New Zealand is currently in a housing crisis and undergoing rapid urbanisation, thus, when our group went to sample sites, it was found that many of them had been built on. This drastically shrunk the sampling pool. Out of the sites that had not been built, some also had restricted access due to land ownership (i.e. private property or construction sites). There was also a potential risk of anthropogenic activity neighbouring some of the sites, likely disrupting the soil and giving less accurate results.

8. Conclusion

This project found no significant levels of arsenic from any of the chosen sites. The abnormal/elevated levels detected can be related to anthropogenic activity, as testing occurred on and around CCA treated timber for these values. The parent material tested also showed no sign of high arsenic concentrations. Therefore, from our research we conclude that the urbanised Port Hills areas do not have any high levels of natural arsenic. However, anthropogenic activity throughout Christchurch has previously caused elevated levels of human-induced arsenic in soils. This field needs more research but is known to produce higher elevations of arsenic at a localised scale. We recommend residents get their property tested especially if there are known land use activities that may have led to increased concentrations. Groundwater should also be monitored and tested if residents are using private groundwater wells.

9. Future Research

To improve future research projects, we suggest the following ideas. Firstly, a more comprehensive testing procedure should be included. This would involve more testing locations to account for different sources and forms of arsenic as well as conducting more tests at each site. Soil samples should also be taken to gain more accurate results, as well as a second method of sampling. Groundwater contamination is a major global public-health issue (Bundschuh et al., 2013) and was an area our project did not look at. Testing of groundwater systems would be beneficial to gain a better understanding of arsenic distribution. A major issue this project found was the influence of human activity, in relation to the disturbance of soil through urbanisation/land development. It may be of interest to research this disturbance further, and how it influences arsenic levels. This should involve the testing of soil and organic matter displaced to waste sites but also testing where wood has been dumped or burnt as this can influence high levels through CCA wood.

10. Acknowledgements

We would like to thank Sally Gaw for all her help and guidance while supervising this project. We appreciate all the feedback and collaboration she offered, especially during the Covid-19 lockdown. We would also like to acknowledge and thank our Environment Canterbury partners Michael Massey and Hannah Mirabueno for their ideas and enthusiasm around this community project.

11. References

Ahamed, S., Kumar Sengupta, M., Mukherjee, A., Amir Hossain, M., Das, B., Nayak, B., Chakraborti, D. (2006). Arsenic groundwater contamination and its health effects in the state of Uttar Pradesh (UP) in upper and middle Ganga plain, India: A severe danger. *Science of The Total Environment, 370*(2), 310-322. doi:https://doi.org/10.1016/j.scitotenv.2006.06.015

ATSDR. (2015). Priority list of hazardous substances. Retrieved from https://www.atsdr.cdc.gov/spl/index.html#modalIdString_myTable2015

Avila-Sandoval, C., Júnez-Ferreira, H., González-Trinidad, J., Bautista-Capetillo, C., Pacheco- Guerrero, A., & Olmos-Trujillo, E. (2018). Spatio-temporal analysis of natural and anthropogenic arsenic sources in groundwater flow systems. International Journal of Environmental Research and Public Health, 15(11), 2374. https://doi.org/10.3390/ijerph15112374

Bali, A. S., & Sidhu, G. P. S. (2021). Arsenic acquisition, toxicity and tolerance in plants - From physiology to remediation: A review. *Chemosphere, 283*, 131050. doi:https://doi.org/10.1016/j.chemosphere.2021.131050

Berg, M., Tran, H. C., Nguyen, T. C., Pham, H. V., Schertenleib, R., & Giger, W. (2001). Arsenic Contamination of Groundwater and Drinking Water in Vietnam: A Human Health Threat. *Environmental science & technology, 35*(13), 2621-2626. doi:10.1021/es010027y

Bundschuh, J., Farias, B., Martin, R., Storniolo, A., Bhattacharya, P., Cortes, J., Albouy, R. (2004). Groundwater arsenic in the Chaco-Pampean Plain, Argentina: case study from Robles County, Santiago del Estero Province. *Applied Geochemistry, 19*(2), 231-243. doi:https://doi.org/10.1016/j.apgeochem.2003.09.009

Bundschuh, J., Maity, J. P., Nath, B., Baba, A., Gunduz, O., Kulp, T. R., Jean, J.-S., Kar, S., Yang, H.-J., Tseng, Y.-J., Bhattacharya, P., & Chen, C.-Y. (2013). Naturally occurring arsenic in terrestrial geothermal systems of western Anatolia, Turkey: Potential role in contamination of freshwater resources. *Journal of hazardous materials, 262*, 951-959. https://doi.org/10.1016/j.jhazmat.2013.01.039

Cagnin, R. C., Quaresma, V. S., Chaillou, G., Franco, T., & Bastos, A. C. (2017). Arsenic enrichment in sediment on the eastern continental shelf of brazil. The Science of the Total Environment, 607-608, 304- 316. https://doi.org/10.1016/j.scitotenv.2017.06.162

Cann, G. (2021). Housing crisis: Why are Kiwis so hell-bent on owning their own home? *Stuff.co.nz*. Retrieved from https://www.stuff.co.nz/life-style/homed/housing-affordability/300363549/housing-crisis-why-are-kiwis-so-hellbent-on-owning-their-own-home

Chung, J.-Y., Yu, S.-D. and Hong, Y.-S. (2014). Environmental Source of Arsenic Exposure. *Journal of Preventive Medicine & Public Health, 47,* 253-256.

Dittmar, J., Voegelin, A., Roberts, L. C., Hug, S. J., Saha, G. C., Ali, M. A., Badruzzaman, A. B. M., & Kretzschmar, R. (2007). Spatial Distribution and Temporal Variability of Arsenic in Irrigated Rice

Fields in Bangladesh. 2. Paddy Soil. *Environmental science & technology, 41*(17), 5967-5972. https://doi.org/10.1021/es0702972

Environment Canterbury Regional Council. (2021). *Canterbury Maps Viewer.* Retrieved from https://mapviewer.canterburymaps.govt.nz/

Ferreira, F. F., Freitas, M. B. D., Szinwelski, N., Vicente, N., Medeiros, L. C. C., Schaefer, Ernesto, C., Reynaud, G., Dergam, J. A., & Sperber, C. F. (2020). Impacts of the Samarco tailing dam collapse on metals and arsenic concentration in freshwater fish muscle from Doce river, southeastern Brazil. Integrated Environmental Assessment and Management, 16(5), 622-630. https://doi.org/10.1002/ieam.4289

Gaw, S. (2016). *Statement of Evidence of Dr Sally Gaw.*

Herath, I., Vithanage, M., Bundschuh, J., Maity, J. P., & Bhattacharya, P. (2016). Natural Arsenic in Global Groundwaters: Distribution and Geochemical Triggers for Mobilization. *Current pollution reports, 2*(1), 68-89. https://doi.org/10.1007/s40726-016-0028-2

Jang, M., Hwang, J. S., Choi, S. I., & Park, J. K. (2005). Remediation of arsenic-contaminated soils and washing effluents. *Chemosphere, 60*(3), 344 354. doi:https://doi.org/10.1016/j.chemosphere.2004.12.018

Johnson, D., Hooper, P., & Conrey, R. (1999). XRF Analysis of Rocks and Minerals for Major and Trace Elements on a Single Low Dilution Li-tetraborate Fused Bead. Advances in X-Ray Analysis, 41.

Li, Y., Ye, F., Wang, A., Wang, D., Yang, B., Zheng, Q., Sun, G., & Gao, X. (2016). Chronic arsenic poisoning probably caused by arsenic-based pesticides: Findings from an investigation study of a household. International Journal of Environmental Research and Public Health, 13(1), 133. https://doi.org/10.3390/ijerph13010133

Machado, I., Falchi, L., Bühl, V., & Mañay, N. (2020). Arsenic levels in groundwater and its correlation with relevant inorganic parameters in uruguay: A medical geology perspective. The Science of the Total Environment, 721, 137787- 137787. https://doi.org/10.1016/j.scitotenv.2020.137787

Mandal, B. K., & Suzuki, K. T. (2002). Arsenic round the world: a review. Talanta, 58(1), 201-235. doi:https://doi.org/10.1016/S0039-9140(02)00268-0

Morales-Simfors, N., Bundschuh, J., Herath, I., Inguaggiato, C., Caselli, A. T., Tapia, J., Choquehuayta, F. E. A., Armienta, M. A., Ormachea, M., Joseph, E., & López, D. L. (2020). Arsenic in Latin America: A critical overview on the geochemistry of arsenic originating from geothermal features and volcanic emissions for solving its environmental consequences. *The Science of the total environment, 716*, 135564-135564. https://doi.org/10.1016/j.scitotenv.2019.135564

Moriarty, M. M., Lai, V. W., Koch, I., Cui, L., Combs, C., Krupp, E. M., Feldmann, J., Cullen, W. R., Reimer, K. J., & Argonne National Lab. (ANL), Argonne, IL (United States). Advanced Photon Source (APS). (2016;). Speciation and toxicity of arsenic in mining- affected lake sediments in the Quinsam watershed, British Columbia. The Science of the Total Environment, 466-467(467); 01, 2014), 90- 99. https://doi.org/10.1016/j.scitotenv.2013.07.005

Nakano, K., & Tsuji, K. (2009). Nondestructive elemental depth profiling of Japanese lacquerware 'Tamamushi-nuri' by confocal 3D-XRF analysis in comparison with micro GE-XRF. X-ray spectrometry, 38(5), 446-450. doi:10.1002/xrs.1163

Pretorius, I., Sturman, A., Strand, T., Katurji, M., & Pearce, G. (2020). A Meteorological Study of the Port Hills Fire, Christchurch, New Zealand. Journal of Applied Meteorology and Climatology, 59(2), 263-280. doi:10.1175/JAMC-D-19-0223.1

Rahman, Z., & Singh, V. P. (2019). The relative impact of toxic heavy metals (THMs) (arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: an overview. *Environmental monitoring and assessment, 191*(7), 1-21. doi:10.1007/s10661-019-7528-7

Rice, K. C., Conko, K. M., & Hornberger, G. M. (2002). Anthropogenic sources of arsenic and copper to sediments in a suburban lake, northern Virginia. Environmental Science & Technology, 36(23), 4962-4967. https://doi.org/10.1021/es025727x

Sewell, R. J. (1988). Late Miocene volcanic stratigraphy of central Banks Peninsula, Canterbury, New Zealand. New Zealand Journal of Geology and Geophysics, 31(1), 41-64. doi:10.1080/00288306.1988.10417809

Tavares, T. R., Molin, J. P., Hamed Javadi, S., de Carvalho, H. W. P., & Mouazen, A. M. (2021). Combined use of vis-nir and xrf sensors for tropical soil fertility analysis: Assessing different data fusion approaches. Sensors (Basel, Switzerland), 21(1), 1-23. doi:10.3390/s21010148

Thermo Fisher Scientific. (2020). *What is XRF (X-ray Fluorescence) and How Does it Work?* Retrieved 20/9 from https://www.thermofisher.com/blog/ask-a-scientist/what-is-xrf-x-ray-fluorescence-and-how-does-it-work/

Tong, J., Guo, H., & Wei, C. (2014). Arsenic contamination of the soil–wheat system irrigated with high arsenic groundwater in the Hetao Basin, Inner Mongolia, China. *Science of The Total Environment, 496*, 479-487. doi:https://doi.org/10.1016/j.scitotenv.2014.07.073

WHO. (2018). Arsenic. Retrieved from https://www.who.int/news-room/fact-sheets/detail/arsenic