



The Concentration of Arsenic (and other trace elements) in Watercress in Christchurch

Waterways

Summer Scholarship Report

WCFM Report 2013-004

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TITLE: The Concentration of Arsenic (and other trace elements) in
Watercress in Christchurch Waterways

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Executive Summary

This report investigates the concentration of arsenic (and other trace elements) in watercress (*Rorippa nasturtium-aquaticum*) growing in small, spring-fed lowland streams and drains of the Christchurch region. Watercress is an aquatic perennial herb that grows in drains and lowland streams and such aquatic plants can act as hyper-accumulators of arsenic. Sampling site location has been based on previous reports of elevated arsenic in local groundwater, and focussed on four sites; Woodend/Tuahiwi, Te Waihora/Lake Ellesmere, Lyttleton and the University of Canterbury Campus. Sediments and water samples were also collected at these sites.

Trace metal concentrations were measured from 5 waterways at Tuahiwi, 5 at Te Waihora, 1 at Ferrymead and 1 at the University of Canterbury campus. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine trace metal concentrations in watercress, sediments and water. Analysis of the watercress revealed low arsenic concentrations at all sites (maximum of 0.4 mg/kg_{dry weight}). Low concentrations of arsenic were also found in the sediment and waters of the lowland streams studied, despite the fact that high As levels have been previously been noted in the groundwaters that feed these streams near Tuahiwi and in coastal Christchurch areas. The limited scope of this sampling, and/or the timing of this study (summer) may be contributing to this result.

However, the concentrations of some of the other trace elements were observed to be high in watercress at sites close to urban activities; specifically at the UC campus and at the Ferrymead site. Zinc concentrations in watercress collected from most sites exceeded food safety guidelines, and in the two urban waterways, lead also significantly exceeded these guidelines. There are multiple sources of lead and zinc in an urban environment, so this result is not unexpected. However, the relatively low consumption rate of watercress in a daily diet means that this source is unlikely to make a major contribution in the total daily dietary intake of these metals.

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Section 1 Introduction

1.1 Mahinga Kai and Watercress

Historically the gathering and eating wild kai (food) has been a very important part of Maori customs and traditions, and continues to be so.¹ However, in certain New Zealand locations, declining water quality poses a threat to the cultural and historical approach of mahinga kai (freshwater food) gathering. Affected species include koura (freshwater crayfish), kakahi (freshwater mussels), tuna (long fin eel), watercress and introduced rainbow trout.² The concentrations of trace elements detected in these kai depend on the geology, geography and land use of the region they are collected from. To evaluate the risk involved with harvesting wild kai, trace element concentrations must be determined and compared with food safety guidelines, taking into account rates of consumption.²

The quantity of watercress consumed by the Maori population throughout New Zealand is above the recommended level of 1.0 meal per month.² The consumption rate is of concern as watercress is an aquatic/semi aquatic macrophyte which can accumulate arsenic at concentrations 100-50,000 times that of other plants growing in the same conditions.² This phenomenon is called hyperaccumulation which occurs due to a hypertolerance of arsenic. Iron oxide that resides in the surfaces of watercress leaves, stems and roots facilitates the arsenic absorption.¹ Limits placed on arsenic by Food Standards Australia New Zealand (FSANZ) requires that no more than 1mg/kg _{dry weight} be present in edible vegetation.³ Raised concentrations of arsenic in watercress have potential implications for human health as arsenic is a suspected carcinogen particularly increasing the risk of bladder, liver and lung cancer.⁴

1.2 Potential Sources of Arsenic and other Trace Elements

Raised concentrations of arsenic (As) in soils and waters within New Zealand can be traced to both natural and anthropogenic sources. Volcanic rock, arsenic-based pesticides and copper-chromium-arsenic (CCA) treated timber are well recognized sources of arsenic.⁵

Two processes can result in the release of As from volcanic rock into groundwater: geothermal heating and decay of organic sediment layers. In geothermal active locations, high concentrations of As are recorded as heated water dissolves As from surrounding volcanic rock, as in the Taupo Volcanic Zone of New Zealand.⁴

Canterbury is not a geothermally active area but there are coastal areas in Canterbury where aquifer sediment consists of marine and swampy deposits. Groundwater in coastal swampy sediments can have low concentrations of oxygen, as bacteria consume oxygen in

the breakdown of organic matter, and these conditions result in the release of arsenic, iron and manganese into the groundwater.^{6,12} There are also over 50,000 sites within Canterbury where arsenic-based pesticides have been used in sheep dips.^{5,7} Groundwater that has been tested near these sites shows elevated concentrations of arsenic, ranging from 0.15-2.42 mg/L and usually decreasing within 15-25 meters from the site.⁷ Finally, CCA-treated timber is used throughout New Zealand, and can lead to raised concentrations of As near waste wood storage, landfill and timber treatment sites. Timber treatment effluent is considered to be the major source of As contamination and can lead to groundwater contamination⁵.

Trace elements other than arsenic, that are also considered toxic, include Mn, Tl, Fe, Cr, Co, Ni, Cu, Zn, Cd and Pb.⁸ Natural sources of these trace metals in Canterbury can be attributed to the anoxic release of metals in coastal aquifers and to the weathering of the Port Hills volcanic terrain, as occurs along the northern flank of Te Waihora, where the volcanic rocks contain high concentrations of Cr, Cu, Ni and Zn.^{6,9}

Anthropogenic sources of trace metals in rural Canterbury include phosphate-based fertilisers and pesticides which can leach Cd, Ni, Mn, Cu, As, Zn and Pb into the environment. In urban settings, stormwater runoff can carry elevated trace elements into local streams, depending on the commercial, residential and industrial land use proportions of the urban catchments.¹⁰ In Christchurch, studies have shown worn tyre and vehicle brakes deposit high concentrations of Zn, Cu and Pb onto impervious surfaces.¹¹ Other contaminants found in urban runoff include Al, Co, Cd, Ni, Tl, V, Cu, Cr, As, Pb, Zn, Mn, and Fe.¹⁰

1.3 Canterbury Geology and Hydrology

The basement rocks of North Canterbury, formed over 2.5 million years ago, are covered by sediments consisting of sandstone, greensands, mudstone, claystone, limestone, conglomerate and gravel including a few layers of volcanic layers of basalts.⁶ The shallower sediments in north Canterbury have formed within the last 1.8 million years and consist of gravel, sand, silt and clay layers deposited by the erosion of the southern alps and other natural processes.⁶ The Waimakariri River is largely responsible for the deposition of the shallower sediments during interglacial periods. The deposited alluvial sediment layers host a groundwater system consisting of confined and unconfined aquifers, with unconfined aquifers feeding lowland springs and streams near the coast. Estuarine, marine and swamp deposits exist near the coast, and contain higher concentrations of organic material than in the glacial/alluvial deposits.¹²

The Te Waihora catchment covers an area of 276,000 hectares of the Southern Alps, Canterbury Plains and Banks Peninsula. The lake initially formed around 8000 years ago, and

now sources two thirds of its water from artesian spring fed streams and one third from Selwyn and Banks Peninsula surface water.¹³

1.4 Purpose of this Research

The aim of this research was to determine whether watercress growing in the lowland springs, streams and drains of the Christchurch region contained elevated levels of arsenic.

The focus was principally on spring-fed lowland streams in areas where As is known to be elevated in the local groundwater; Woodend/Tuahiwi and the coastal zone of Christchurch city at Ferrymead, as well as in areas where no groundwater As has been reported, in the streams feeding Te Waihora/Lake Ellesmere and in the Christchurch CBD at the UC campus.

Section 2 Methodology

2.1 Sampling and sample preparation

Water, sediment and watercress samples were collected from 5 sites within the Tuahiwi/Woodend area in December 2012 (see Table 2.1 and Figure 2.1.1). The samples were collected from lowland streams where watercress is commonly collected by local iwi, as identified by a local resident, Professor Te Maire Tau from the UC Ngai Tahu Research Centre. In January 2013 additional samples were taken from 5 sites in the Te Waihora/Lake Ellesmere area (see Table 2.1 and Figure 2.1.2), 1 site from the University of Canterbury (see Figure 2.1.3), and 1 site from Ferrymead (Figure 2.1.4).

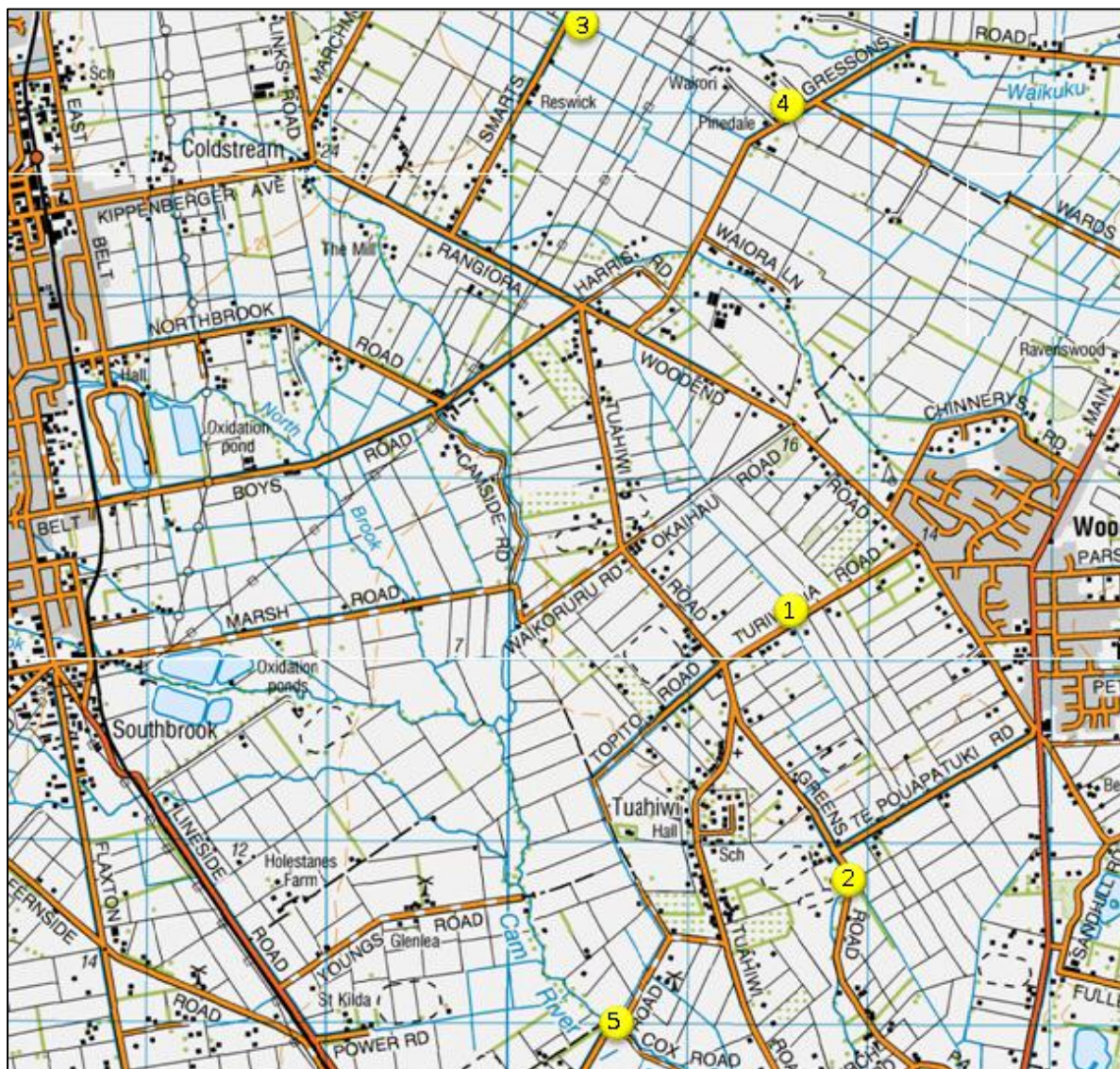


Figure 2.1.1 Sample site locations at Tuahiwi/Woodend¹⁴

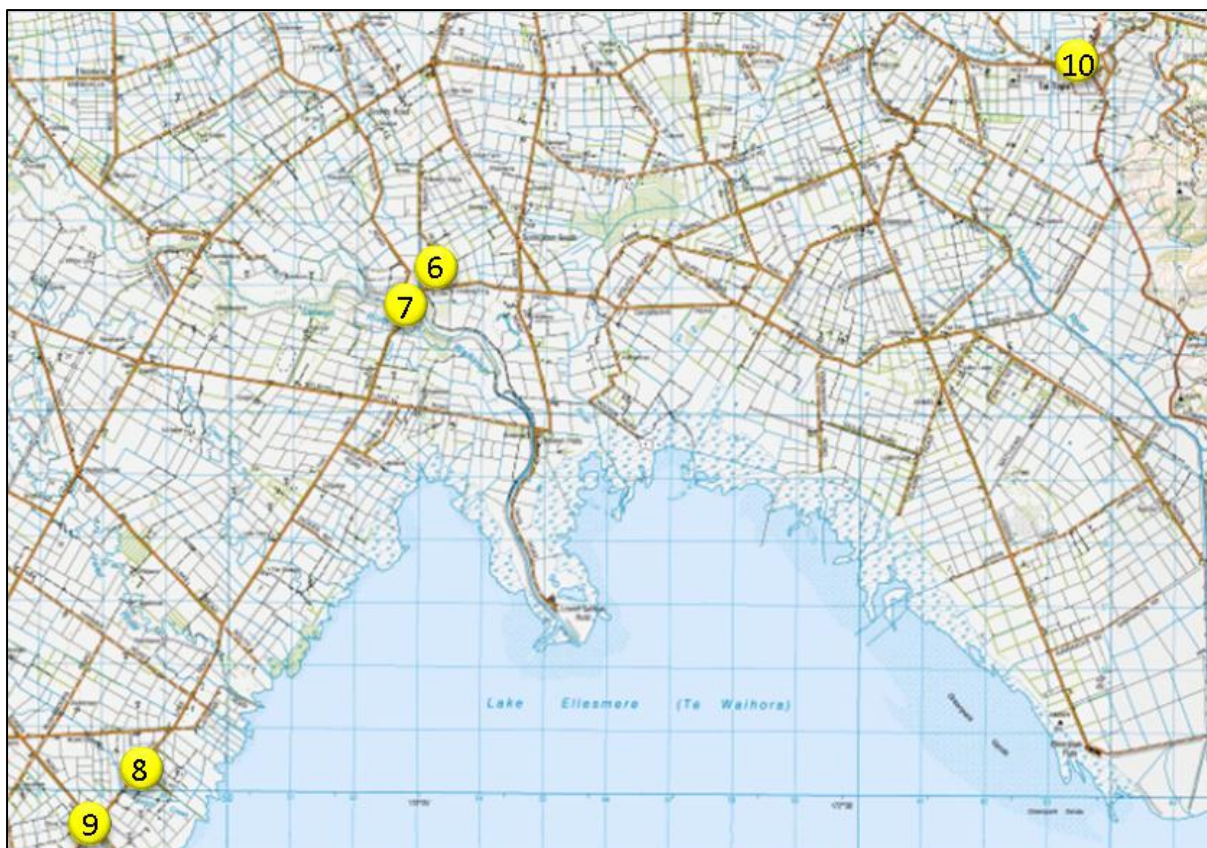


Figure 2.1.2 Sample site locations on tributaries of Te Waihora/Lake Ellesmere¹⁴

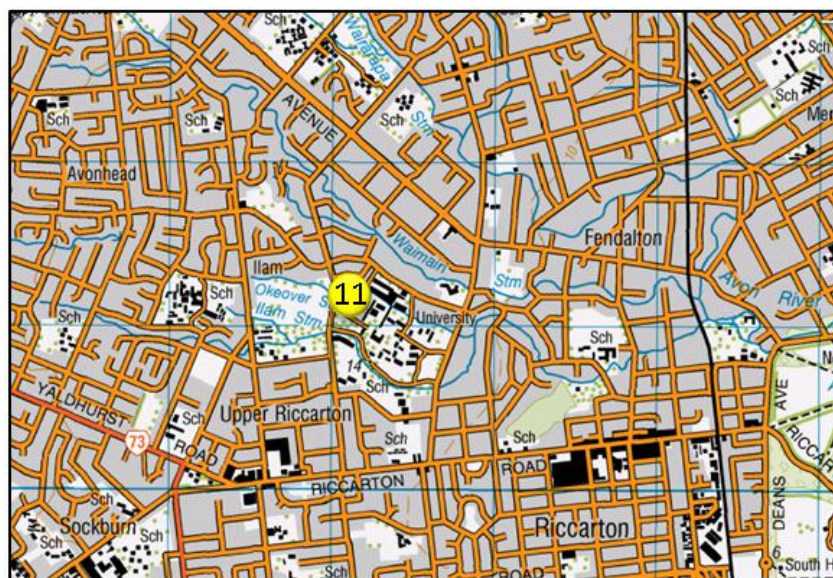


Figure 2.1.3 Sample site location on Okeover Stream at the University of Canterbury campus¹⁴

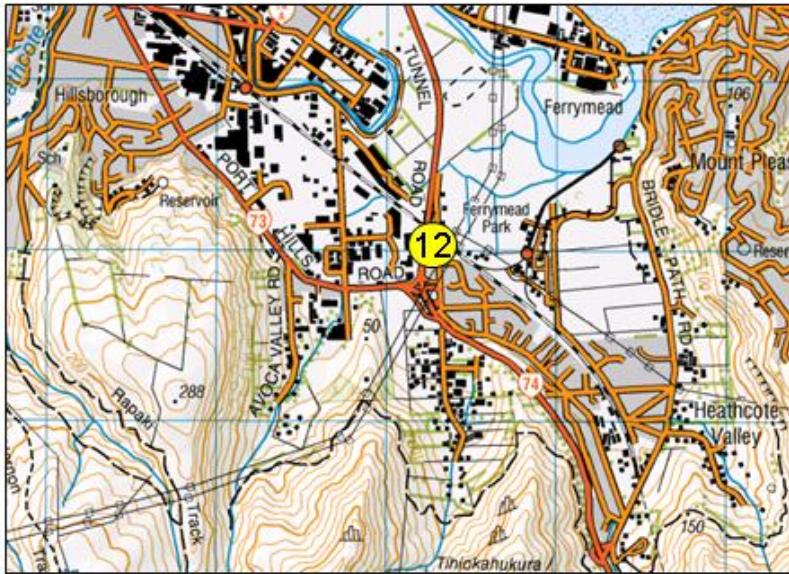


Figure 2.1.4 Sample site location on a tributary of the Heathcote River, at Ferrymead¹⁴

Table 2.1 – Sampling site details

Site	Location
<i>Tuahiwi</i>	
1	Turiwhaia Rd, Tuahiwi
2	Cnr Greens and Te Pouapatuki Rd, Tuahiwi
3	Smarts Rd, Tuahiwi
4	Gressons Rd, Tuahiwi
5	Bramleys Rd, Tuahiwi
<i>Te Waihora</i>	
6	Cnr Pannets Rd and Days Rd
7	Cnr The Lake Rd and Goulds Rd
8	Cnr The Lake Rd and Colletts Rd
9	Cnr The Lake Rd and Drain Rd
10	Tai Tapu Rd in Tai Tapu
Other sites	
11	University campus, on Okeover walkway near community garden
12	Tunnel Rd, Ferrymead

Watercress samples were collected from the lowland streams using scissors and were stored in ziplock plastic bags (Figure 2.1.5 & 2.1.6). Sediments were collected using a grab sampler and sediment containers. To avoid cross contamination, each container was stored in a sealable bag. Water samples were collected using an acid washed container and were stored in 50mL vials. At each site the container was rinsed 3 times to avoid cross

contamination. All samples were placed in an insulated container with ice packs to keep them cool.

The sediments and watercress were then placed in individual acid washed trays and dried for three to five days, with watercress dried at 50°C and sediments at 70°C. The watercress was crushed in a grinder until it reached a powder form. The sediments were double bagged and disaggregated using a metal rolling pin. Sediment particles were then separated using 2mm nylon sieves, and the <2mm fraction analysed for trace elements.



Figure 2.1.5. Watercress growing in a lowland stream at Tuahiwi.



Figure 2.1.6. Sampling emergent watercress at Tuahiwi.

2.2 Sample Analysis

2.2.1 Watercress digestion

For each sample 0.2g of watercress was weighed into 50mL acid washed digestion tubes. 5mL of concentrated HNO₃ was added to each tube. The samples were digested at 85°C for an hour and left to cool. Each sample was then made up to 20mL with milli-Q water and gently stirred. The samples required filtration using 0.20µm hydrophilic filters and 20mL syringes. The samples were then diluted 5 times by adding 4mL of 2% HNO₃ to 1mL of each sample. The samples were thoroughly mixed and then analysed by ICP-MS. The data is presented in both dry weight and fresh weight concentrations. The fresh weight concentrations were calculated using the pre-dried and post-dried weights.

2.2.2 Sediment digestion

For sediment samples the EPA Method 200.8 method was followed. 1g of each sample was measured into 50 mL acid washed polycarbonate digestion tubes. 4mL of HNO₃ (1+1) and 10mL of HCl (1+4) were added to each tube. The samples were digested at 85°C for half an hour and left to cool. One day later they were made up to 20mL with milli-Q water and gently stirred. The samples were then diluted 21 times by adding 10mL of 2% HNO₃ to 0.5mL of each sample. The samples were thoroughly mixed and then analysed using ICP-MS.

2.2.3 Water

For dissolved trace elements, water samples were filtered on the same day they were collected using 0.45µm (sites 1-5) and 0.2 µm (sites 6-12) filters and 20mL syringes. New filters were used for each sample and first rinsed with the sample to avoid contamination. All water samples (unfiltered and filtered) then had 50µL of concentrated HNO₃ added to preserve the sample, for analysis using ICP-MS.

2.3 Quality Control

All reagents used in the analysis were of high analytical grade and appropriate measures were taken to reduce potential contamination. To check sampling and analytical method rigour, a number of quality control methods have been employed. During watercress digestion and analysis, a blank was digested with each batch as well as two certified reference material samples (Tomato Leaves Reference Material #15739). Recoveries for the standard reference material were 88% and 113% in the two batches, with those for other

trace elements ranging from 58.9% to 110.5%, as shown in Table 2.4.1. With every 10 samples, a duplicate digestion was undertaken, and with every 20 samples, a triplicate digestion was undertaken and used for spike recovery. The average difference between duplicates was 6.4% for the stems and 6.25% for leaves.

For water analysis, two trip blanks (deionised water transferred into containers in the field) were collected, and a duplicate analysis was undertaken on every 5th sample. The average difference between duplicates was 14.0% for dissolved concentrations and for total concentrations was 16.1%. A triplicate analysis, with one replicate used for spike recovery, was undertaken for every 12 samples.

For sediment digestions a blank was digested in each batch, and a standard reference sediment material (Marine Sediment Reference Material #2702) was also digested. Every 10 samples, a duplicate digestion was undertaken, and every 20 samples, a triplicate digestion was used for spike recovery. The average difference between duplicates was 14.2%. Recoveries for the standard reference material ranged from 53.0% to 84.8% as shown in Table 2.4.1. The digestion method used detects only surface-bound elements in the sediment and not those included in the mineral matrices. This method therefore indicates the amount of readily available trace elements.

Table 2.4.1 Percentage recoveries of As and other trace elements from the standard reference materials; Tomato Leaves #1573, and Marine Sediment #2702.

Element	Tomato Leaves		Marine Sediment
	Batch 1 (Tuahiwi)	Batch 2 (Te Waihora)	
As	88.4	113.7	73.4
Fe	58.9	73.7	-
Co	62.4	75.2	-
Ni	60.7	72.0	53.0
Cu	88.2	103.1	70.4
Zn	83.3	110.5	70.7
Cd	85.19	96.7	69.8
Mn	–	–	74.0
Pb	–	–	84.8

Section 3 Results

3.1 General Waterway Health

Parameters that reflect the general water health of each sample site is shown in Table 3.1.1. Temperatures recorded ranged from 14.2-17.0°C; within normal temperature ranges for New Zealand lowland rivers sustaining aquatic life. The pH results ranged from 6.56 to 8.02, within the ANZECC (2000) recommended range of 6.5-9.0 for aquatic life protection.¹⁵ Conductivities were typical of lowland streams of the Christchurch and Selwyn regions, and all below the ANZECC (2000) guideline for salinity of 1000mg/L (equivalent to a conductivity of approx. 1500 µS/cm).¹⁵

Dissolved oxygen (DO) was relatively low in two of the tributaries of Te Waihora, but no anoxic waters were observed. ANZECC (2000) recommend that DO concentrations remain above 80%-90% saturation (6mg/L) for the protection of aquatic eco-systems.¹⁵ Only the two tributaries fell below this guideline.

Table 3.1.1 General water health parameters from the sampling sites at Tuahiwi and Te Waihora. “nm” denotes not measured.

Site	pH	Conductivity (µS/cm)	DO (mg/L)	Temp (°C)
<i>Tuahiwi</i>				
1	7.49	155.6	6.95	17.0
2	8.02	168.6	9.70	nm
3	6.80	110.5	5.47	14.2
4	7.19	128.3	7.54	15.8
5	7.74	128.5	9.58	16.7
<i>Te Waihora</i>				
6	7.03	258	3.94	15.9
7	6.93	349	6.75	14.3
8	6.56	550	4.12	15.3
9	6.79	287	7.55	16.8
10	7.11	214	7.71	18.1

3.2 Arsenic

The results for As concentrations in watercress stems and leaf samples are shown, together with As in the sediment and water, in Table 3.2.1. None of the sites showed elevated As in

the watercress, water or in the sediment. In both stem and leaf samples the levels of As were below the New Zealand Food Standard Guidelines for dry weight As content. Sediment and water As concentrations were also below the ANZECC recommended guidelines for aquatic life protection.¹⁵

Table 3.2.1 Concentrations of trace elements (mgkg⁻¹ unless noted) in watercress stem and leaf samples, sediment and water collected from Tuahiwi, Te Waihora, Ferrymead and University of Canterbury campus sites (refer Table 2.1). Concentrations for watercress are given as dry weight (dw) and fresh weight (fw). The sediment fraction analysed was <2mm, and the water As concentration was for both total (unfiltered) and dissolved (filtered) As. FSANZ (2013)³ and ANZECC (2000)¹⁵ guidelines for aquatic life protection in sediment and waters are also shown.

Site	Leaf As		Stem As		Sediment As	Total As	Dissolved As
	dw	fw	dw	fw		µg.L ⁻¹	µg.L ⁻¹
1	0.1	0.01	0.1	<0.01	5.2	1.6	0.9
2	0.4	0.04	0.2	0.01	3.7	0.7	1.3
3	0.1	0.01	0.1	<0.01	1.4	0.6	0.1
4	<0.1	<0.01	<0.1	<0.01	2.1	0.6	0.3
5	0.1	0.01	0.1	<0.01	1.6	1.7	0.3
6	0.2	0.01	0.1	<0.01	1.8	1.4	0.3
7	0.1	<0.01	0.1	<0.01	3.7	1.9	2.3
8	0.1	<0.01	<0.1	<0.01	0.7	1.4	0.4
9	0.1	<0.01	0.1	<0.01	0.8	1.5	0.9
10	0.1	<0.01	0.1	<0.01	2.2	1.6	0.5
11	0.2	0.01	0.1	<0.01	7.0	0.3	0.2
12	0.2	0.01	0.3	0.01	0.7	2.1	n/a
<i>min</i>	0.1	<0.01	<0.1	<0.01	0.7	0.3	0.1
<i>max</i>	0.4	0.04	0.3	0.01	7.0	2.1	2.3
<i>med</i>	0.1	0.01	0.1	<0.01	2.1	1.45	0.4
FSANZ	1.0		1.0				
ANZECC					20	13	

3.3 Other Trace Elements

Watercress trace element concentrations for watercress stem and leaf samples (see Table 3.2.1) had the highest concentrations for Fe, Mn and Zn. The lowest concentrations were found for Co, Ni, Cd, and Pb, while those for Cu were intermediate.

FSANZ Food Safety standards³ are set for Cu, Zn, Cd and Pb. There are no current food safety standards for Mn, Fe and Ni. The watercress significantly exceeded Zn and Pb standards in leafs and stems at the urban stream sites; the UC Campus Okeover Stream site 11, and at Ferrymead site 12, and at site 7 (a tributary of Te Waihora), where stem Cd levels were also too high. In the watercress leaves, Zn and Pb standards were marginally exceeded in a number of the Tuahiwi sites also.

Table 3.2.1 Summary of trace element concentrations (mgkg⁻¹ dry weight) stem and leaf samples from watercress collected from Tuahiwi, Te Waihora, Ferrymead and the University of Canterbury campus (refer Table 2.1 for location and Appendix Table A1 for raw data). FSANZ³ limits are given for comparison.

	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Stems								
min	12.5	45	0.1	0.2	0.8	18.7	<0.1	0.1
max	276.8	273	0.6	0.6	8.2	238	0.3	0.6
med	55.9	97	0.2	0.2	3.4	35.6	0.1	0.1
Leaves								
min	25.5	56	0.2	0.3	1.2	23.5	<0.1	0.1
max	609.5	676	1.1	1.1	14.9	238	0.3	2.3
med	145.4	163	0.3	0.6	5.8	55.2	0.1	0.2
FSANZ					30	40	0.1	0.1

Table 3.2.2 Concentrations of total and dissolved trace elements (µgL⁻¹) in water samples collected from Tuahiwi, Te Waihora, Ferrymead and University of Canterbury campus, and ANZECC guidelines for 95% aquatic life protection.¹⁵ Raw data is given in Table A2 in the Appendix.

	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Total								
min	1.4	20	0.1	0.1	0.3	0.1	<0.1	0.1
max	290	760	3.0	12.4	6	21.5	<0.1	1.6
median	39.1	160	0.3	0.25	0.5	0.75	<0.1	0.25
Dissolved								
min	1.1	10	0.1	0.1	0.2	0.5	<0.1	0.1
max	113	430	0.4	0.6	2.9	17.4	<0.1	0.8
median	28.9	110	0.2	0.2	0.4	1.9	<0.1	0.3
ANZECC	1900			11	1.4	8.0	0.2	3.4

In the waters, only sites 11 & 12 showed significant elevation of trace element concentrations; with high concentrations of Cu & Zn at site 11, and of Cu, Zn, Ni and Co at site 12 (Table 3.2.2). None of the other metals were significantly elevated at these sites. At site 11 & 12, total Cu and Zn concentrations significantly exceeded ANZECC-recommended guidelines for 95% aquatic life protection. Cu and Zn are common urban contaminants and their elevation in these streams reflects the urban nature of these catchments.

Trace element concentrations in sediments were reflective of the elements found to be elevated in the watercress, with high concentrations of Pb and Cd, as well as Cu and Zn, at sites 11 & 12. ANZECC (2000) Interim Sediment Quality Guidelines (ISQG)¹⁵ for the protection of aquatic life in freshwater sediments, for Pb and Zn were exceeded at these sites, and for also for Cu at site 11. The concentrations of all trace elements were again reflecting the largely urban nature of these catchments, with multiple sources of these metals

Table 3.3.1 Summary of trace element concentration of in sediment samples collected from Tuahiwi, Te Waihora, Ferrymead and the University of Canterbury campus site (raw data for individual sites given in Appendix Table A3). ANZECC ISQG values are given for comparison.

	Mn	Ni	Cu	Zn	Cd	Pb
min	128.3	7.1	4.2	28.6	<0.1	7.1
max	852.0	14.7	76.0	487.3	1.0	76.8
median	175.9	8.8	10.4	73.5	0.1	14.9
mean	429.9	9.8	17.0	123.8	0.2	23.2
ANZECC	-	21	65	200	1.5	50

Section 4 Discussion

There was very little evidence of any As enrichment in water, sediments or the watercress growing at the sites sampled, despite the fact that high As levels have been noted in the groundwaters near Tuahiwi and in coastal Christchurch areas. This is likely to be due to the limited scope of this sampling, and possibly also to the fact that sampling was undertaken in summer when lowland stream flows are low and groundwater input may be limited by drawdown of the water table.

However, the concentrations of some of the other trace elements were observed to be high in watercress at sites close to urban activities; specifically at the UC campus and at the Ferrymead site. Zn concentrations in watercress collected from most sites exceeded recommended FSANZ Food Safety guidelines, and at urban sites 11 & 12, Pb also significantly exceeded these guidelines. Cd concentrations exceeded the guidelines only at site 7, near Te Waihora.

Using a maximum estimate of typical daily watercress consumption, of 33 gms/day², we were able to calculate the maximum trace metal concentrations likely to be consumed per person per day. This is shown in Table 4.1, for the consumption of watercress leaves of median and maximum freshweight trace element concentrations (refer Table A1).

Table 4.1. Total trace metal consumption via watercress leaves, in mg/person/day, as calculated from fresh weight leaf concentrations (refer Appendix Table A1). The JECFA¹⁶ recommended intake for these metals in mg/day is also shown, for a 70 kg female - 82kg male range.

	Med	Max	JECFA
Fe	0.36	1.72	56-66
Cu	0.011	0.041	35-41
Zn	0.13	0.41	70-82
As	0.0003	0.0013	0.21 – 0.25
Cd	0.0003	0.0007	1.8-2.1
Pb	0.0003	0.0026	Alara*

*As low as reasonably achievable.

The standards used to determine acceptable levels of intake are based on the Joint FAO/WHO Expert Committee on Food Additives (JECFA)¹⁶. These values are also shown in Table 4.1, recalculated to apply to a 70kg female or 82 kg male body weight.

It is clear that consumption of these trace elements via watercress is most unlikely to exceed JECFA recommended tolerable intakes. However, it should be noted that there are many potential sources of these trace elements in a standard diet, as confirmed in the New Zealand's total diet survey¹⁷ which is run every 5-6 years and testing 123 foods for many constituents, including the trace elements studied here.

Section 5 Conclusions

The results of this study show that the concentrations of As in the water, sediments and watercress in waterways sampled at Tuahiwi, Te Waihora, Ferrymead and the University of Canterbury were within acceptable limits for the protection of aquatic life and the consumption of watercress as a food item.

However, at the urban sites (UC campus and Ferrymead) the watercress had relatively high concentrations of zinc and lead, as did the sediments and waters at these sites. Watercress collected from these sites exceeded recommended food safety guidelines for Zn and Pb. However, given likely consumption rates, such watercress is unlikely to provide a major source of these metals in a standard diet.

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Appendix 1

Table A1. Raw analytical data for trace elements other than As, in mg.kg⁻¹ dry weight (dw) and fresh weight (fw), in; a) watercress stems and b) watercress leaves .

a)

Site	Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	dw	fw	dw	fw	dw	fw	dw	fw	dw	fw	dw	fw	dw	fw	dw	fw
1	58	2.08	85	3	0.1	<0.01	0.5	<0.01	8.2	0.29	34	1.22	<0.1	<0.01	0.1	<0.01
2	276.8	9.93	178	6	0.2	0.01	0.2	0.01	6.1	0.22	36.6	1.31	<0.1	<0.01	0.1	0.01
3	12.5	0.45	72	3	0.1	<0.01	0.2	<0.01	2.5	0.09	18.7	0.67	0.1	0.01	0.1	<0.01
4	20.2	0.72	45	2	0.1	<0.01	0.2	<0.01	3.2	0.11	27.1	0.97	0.1	<0.01	0.1	<0.01
5	37.2	1.34	137	5	0.2	0.01	0.3	0.01	3.4	0.12	84.8	3.04	<0.1	<0.01	0.2	0.01
6	101.8	3.65	273	10	0.6	0.02	0.2	0.01	0.8	0.03	22.1	0.79	<0.1	<0.01	0.1	<0.01
7	76.6	2.75	129	5	0.3	0.01	0.3	0.01	5.0	0.18	114.7	4.11	0.3	0.01	0.2	0.01
8	53.8	1.93	78	3	0.1	<0.01	0.2	0.01	3.3	0.12	24.7	0.88	0.1	<0.01	0.1	<0.01
9	175.4	6.29	90	3	0.5	0.02	0.6	0.02	5.3	0.19	47.9	1.72	<0.1	<0.01	0.1	<0.01
10	43.2	1.55	52	2	0.1	<0.01	0.2	0.01	2.6	0.09	34.5	1.24	0.1	<0.01	0.1	<0.01
11	13.6	0.49	105	4	0.2	0.01	0.2	0.01	6.5	0.23	86.3	3.09	<0.1	<0.01	0.6	0.02
12	226.2	8.11	137	5	0.2	0.01	0.2	0.01	3.4	0.12	238.8	8.57	0.1	<0.01	0.5	0.02

b)

Site	Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	dw	fw	dw	fw	dw	fw	dw	fw	dw	fw	dw	fw	dw	fw	dw	fw
1	162.6	14.97	303	27	0.3	0.03	0.9	0.03	13.4	1.23	45.9	4.23	0.1	0.01	0.3	0.02
2	609.5	56.10	56	52	0.4	0.04	0.6	0.04	8.4	0.77	58.4	5.37	<0.1	<0.01	0.2	0.03
3	25.5	2.35	164	15	0.2	0.02	0.6	0.02	4.4	0.4	23.5	2.16	0.2	0.02	0.1	0.01
4	46.4	4.27	98	9	0.2	0.02	0.6	0.02	5.5	0.51	43.9	4.04	0.1	0.01	0.1	0.01
5	86.4	7.96	235	21	0.5	0.04	0.5	0.04	6.3	0.58	134.7	12.4	0.1	0.01	0.2	0.02
6	243.5	8.73	676	24	1.1	0.04	0.3	0.01	1.2	0.04	30.2	1.08	<0.1	<0.01	0.3	0.01
7	76.6	2.75	129	5	0.3	0.01	0.3	0.01	5.0	0.18	114.7	4.11	0.3	0.01	0.2	0.01
8	128.8	4.62	154	6	0.3	0.01	0.7	0.02	6.1	0.22	40.6	1.46	0.1	<0.01	0.2	0.01
9	307.5	11.03	225	8	0.8	0.03	1.1	0.04	8.3	0.30	63.6	2.28	<0.1	<0.01	0.2	0.01
10	162.1	5.81	163	6	0.4	0.01	0.7	0.03	5.2	0.19	52.0	1.87	0.1	<0.01	0.2	0.01
11	35.8	1.28	361	13	0.5	0.02	0.7	0.02	14.9	0.53	130.9	4.70	<0.1	<0.01	2.3	0.08
12	218.0	7.82	132	5	0.2	0.01	0.3	0.01	3.4	0.12	238.5	8.56	0.1	<0.01	0.5	0.02

Table A2 Concentrations of total (T) and dissolved (D) trace elements ($\mu\text{g.L}^{-1}$) in water samples collected at watercress sampling sites. n/a is not analysed.

Site	Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	T	D	T	D	T	D	T	D	T	D	T	D	T	D	T	D
1	61.5	28.9	600	290	<0.1	<0.1	0.4	0.3	1.2	0.4	1	3.8	<0.1	<0.1	1.6	0.8
2	86.7	60.4	760	410	<0.1	<0.1	0.4	0.4	0.5	0.4	1.5	1.3	<0.1	<0.1	1	0.7
3	1.4	1.1	20	10	<0.1	<0.1	0.1	0.2	0.3	0.3	0.1	0.5	<0.1	<0.1	0.2	0.3
4	4.3	3.8	100	40	<0.1	<0.1	0.2	0.2	0.4	0.4	0.3	0.6	<0.1	<0.1	0.3	0.3
5	9.8	7.9	130	50	<0.1	<0.1	0.2	0.2	0.4	0.3	0.4	3.3	<0.1	<0.1	1.2	0.7
6	108.3	81.4	210	140	0.3	0.2	0.2	0.1	0.4	0.2	0.5	2.1	<0.1	<0.1	0.1	0.1
7	35	33.4	510	430	0.2	0.2	0.7	0.6	1.8	0.8	2.5	1.6	<0.1	<0.1	0.3	0.3
8	94.1	113	250	110	0.3	0.4	0.3	0.4	0.5	0.6	0.4	2.3	<0.1	<0.1	0.1	<0.1
9	43.1	41.9	130	110	0.3	0.3	0.5	0.5	1.6	1.6	1	1.9	<0.1	<0.1	0.1	0.1
10	19.6	19.8	120	70	0.1	0.1	0.2	0.2	0.3	0.4	0.5	1.9	<0.1	<0.1	0.1	0.1
11	5.5	2.9	190	10	0.5	0.2	0.2	0.1	6	2.9	21.5	17.4	<0.1	<0.1	1.2	0.1
12	290	n/a	30	n/a	3	n/a	12.4	n/a	2.9	n/a	13.5	n/a	<0.1	n/a	0.2	n/a

Table A3. Concentration of trace elements (mg.kg^{-1}) in <2mm fraction of sediment samples collected from Tuahiwi, Te Waihora, Lyttleton and the University of Canterbury campus.

Site	Mn	Ni	Cu	Zn	Cd	Pb
1	157.0	14.7	12.3	86.6	0.1	17.0
2	569.0	11.9	10.4	104.7	0.1	14.9
3	194.2	8.8	4.2	28.6	<0.1	7.1
4	175.3	12.2	12.2	71.7	0.1	18.3
5	157.5	8.5	5.4	73.5	0.1	10.1
6	170.3	8.7	5.6	39.3	0.0	14.4
7	852.0	7.5	15.2	122.3	0.4	18.9
8	155.1	9.2	6.1	43.4	0.1	9.6
9	175.9	8.4	4.2	44.2	<0.1	8.2
11	128.3	7.1	76.0	260.5	0.2	59.5
12	577.7	10.6	35.3	487.3	1.0	76.8