

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Pollution of the Aquatic Biosphere by Arsenic and other Elements in the Taupo Volcanic Zone

A thesis presented
in partial fulfilment of the requirements
for the degree of
Master of Science in Biology
at
Massey University

Brett Harvey Robinson

1994

MASSEY UNIVERSITY



1095010577

Abstract

An introduction to the Taupo Volcanic Zone and probable sources of polluting elements entering the aquatic environment is followed by a description of collection and treatment of samples used in this study.

The construction of a hydride generation apparatus for use with an atomic absorption spectrophotometer for the determination of arsenic and other hydride forming elements is described. Flame emission, flame atomic absorption and inductively coupled plasma emission spectroscopy (I.C.P.-E.S.) were used for the determination of other elements.

Determinations of arsenic and other elements were made on some geothermal waters of the area. It was found that these waters contribute large (relative to background levels) amounts of arsenic, boron and alkali metals to the aquatic environment. Some terrestrial vegetation surrounding hot pools at Lake Rotokawa and the Champagne Pool at Waiotapu was found to have high arsenic concentrations.

Arsenic determinations made on the waters of the Waikato River and some lakes of the Taupo Volcanic Zone revealed that water from the Waikato River between Lake Aratiatia and Whakamaru as well as Lakes Rotokawa, Rotomahana and Rotoehu was above the World Health Organisation limit for arsenic in drinking water ($0.05 \mu\text{g}/\text{mL}$) at the time of sampling.

Arsenic accumulates in the sediments of the Waikato River and Lakes of the Taupo Volcanic Zone. The levels were variable, but characteristically around $100 \mu\text{g}/\text{g}$.

Trout taken from the Waikato River and some lakes in the Taupo Volcanic Zone, had flesh arsenic concentrations of the same order of magnitude as the water from which they were taken. Trout from Lakes Rotorua, Rotoiti and Rotomahana contained average flesh mercury concentrations above the World Health Organisations limit for mercury in foodstuffs ($0.5 \mu\text{g}/\text{g}$). There were positive correlations between weight, length and flesh mercury concentration.

Freshwater mussels from Lakes Rotorua and Tarawera had arsenic concentrations above the World Health Organisations limit for arsenic in foodstuffs (2 µg/g). Shellfish taken from the mouth of the Waikato river and from Raglan were below the World Health Organisation's limit for arsenic and mercury.

Aquatic macrophytes from the Waikato River had arsenic concentrations many times greater than the water from which they were taken. Some samples of *Ceratophyllum demersum* had arsenic concentrations above 1000 µg/g dry weight.

Water cress from the Waikato River at Broadlands and Orakei Korako contained on average 400 µg/g and 30 µg/g arsenic respectively. An experiment was conducted on the uptake of arsenic by water cress. It was found that water cress does accumulate arsenic if placed in an arsenic solution.

Acknowledgments

I would like to express thanks to my supervisors, Prof RR Brooks, Dr HA Outred and Prof J Kirkman, for their advice, assistance and encouragement throughout the period of this work.

I am greatly indebted to the New Zealand Department of Health for a grant towards operational costs.

Thanks are also due to DJ Stack and the staff at the Eastern Region Fish and Game Council, Rotorua for the collection of trout from the Waikato River and nearby streams.

Julie Hanna, Tania Reihana, and Craig Simpson are also thanked for their assistance and advice on the location and collection of samples.

I acknowledge the receipt of a MURF scholarship for operational expenses.

Table of Contents

Abstract.....	2
Acknowledgments	3
List of Figures.....	6
List of Tables	7
Chapter 1: General Introduction and Methods.....	11
1.1 Introduction	11
1.2 Sample Collection and Treatment	15
1.3 Elemental Analysis.....	17
1.4 Development of a Hydride Generation Apparatus for Accurate Arsenic Determinations	18
1.41 Introduction	18
1.42 The Instrument.....	19
1.43 Method of Use of the Instrument.....	23
1.44 Performance of the Instrument	25
1.5 Treatment of Data	28
Chapter 2: Arsenic and other Elements in some Geothermal Areas of the Taupo Volcanic Zone.	29
2.1 Introduction	29
2.11 Tokaanu Hot Springs.....	31
2.12 Wairakei Hydrothermal System.....	32
2.13 Rotokawa Geothermal Field.....	35
2.14 Waiotapu.....	37
2.15 General Comment	37
2.2 Methods	39
2.3 Results	40
2.4 Discussion	49
Chapter 3: Arsenic in the Environment.....	53
Chapter 4: Pollution of the Natural Lakes in the Taupo Volcanic Zone by Arsenic and other Elements.....	56
4.1 Introduction	56
4.2 Methods	58
4.3 Results	59
4.4 Discussion	73
Chapter 5: Pollution of the Waikato River system by Arsenic and other Elements.....	81
5.1 Introduction	81
5.2 Methods	87
5.3 Results	87
5.4 Discussion	102
Chapter 6: The Uptake of Arsenic by Water Cress	112
6.1 Introduction	112
6.2 Methods	113
6.3 Results	114
6.4 Discussion	118
Chapter 7: Concluding summary	120
References	122

List of Figures

1. The Taupo Volcanic Zone.....	13
2. Schematic diagram of the hydride generation apparatus.....	21
3. Standard deviation of peak height (4 readings) vs flow rate of NaBH_4	24
4. Peak height vs [As].....	26
5. Peak height vs [Hg].....	27
6. Two simple models for the origin of heat and chemicals in geothermal waters.....	30
7. [Li] vs [Rb] in some thermal waters of the T.V.Z.	42
8. [Mg] vs [Rb] in some thermal waters of the T.V.Z.	43
9. [Mg] vs [Li] in some thermal waters of the T.V.Z.	44
10. [Mg] vs [K] in some thermal waters of the T.V.Z.....	45
11. Local cycle of arsenic in a stratified lake.....	55
12. [As] vs [Li] in the waters of some lakes in the T.V.Z.....	61
13. [As] vs [Na] in the waters of some lakes in the T.V.Z.....	62
14. [As] vs [K] in the waters of some lakes in the T.V.Z.	63
15. [Li] vs [K] in the waters of some lakes in the T.V.Z.	64
16. [Mg] vs [Na] in the waters of some lakes in the T.V.Z.....	65
17. Water [As] vs Sediment [As] for some lakes in the T.V.Z.....	66
18. Body weight vs flesh [Hg] for trout in Lake Rotorua.....	71
19. Body weight vs flesh [Hg] for trout in Lake Rotomahana.....	72
20. Map of the Waikato River.....	84
21. Water [As] vs distance downstream for water in the Waikato River (November 1993).....	90

22. Water [As] vs distance downstream for water in the Waikato River (February 1994).....	91
23. [As] vs [Li] along the length of the Waikato River.....	92
24. [As] vs [Na] along the length of the Waikato River	93
25. [As] (D.W.) vs distance downstream for <i>Ceratophyllum</i> in the Waikato River.....	98
26. [As] (D.W.) vs distance downstream for <i>Egeria</i> in the Waikato River	99
27. Bathing solution [As] vs time for plant 'A'	116
28. Bathing solution [As] vs time for plant 'B'.....	117

List of Tables

1. Flame types, lamp currents and wavelengths used for some analyses.....	17
2. Conventions used by Brookes <i>et al</i> (1966)	28
3. Data reported from hot spring water in the Tokaanu thermal area by Mahon and Klyen (1968).....	32
4. Data calculated by Ellis and Wilson (1960) of elemental output from the Wairakei hydrothermal system.....	33
5. Data calculated by Axtmann (1975) of elemental discharge into the Waikato from the Wairakei borefield.....	33
6. Chemical Analysis of Wairakei discharge water by Rothbaum and Middendorf (1987).....	34
7. Analysis of discharge precipitates from Rotokawa thermal area by Weissberg (1969).....	36
8. Concentrations ($\mu\text{g/mL}$) of some elements in hydrothermal waters in the Taupo Volcanic Zone.....	40
9. Concentrations ($\mu\text{g/mL}$) of some elements in water from West Hold, Ohaaki power station	41
10. Concentration ($\mu\text{g/mL}$) of some elements from the cooling tower of Ohaaki power station	45
11. Correlation data (r) for arsenic, magnesium and the alkali metals in some geothermal waters in the Taupo Volcanic Zone	46
12. Concentrations ($\mu\text{g/mL}$) of some elements in the water from the Tokaanu stream.....	47
13. Arsenic concentrations ($\mu\text{g/g}$ dry weight) in some plants around a hot pool at Lake Rotokawa.....	48
14. Arsenic concentrations ($\mu\text{g/g}$ dry weight) in some plants around the Champagne pool at Waiotapu	48
15. The chemical composition ($\mu\text{g/mL}$) of hypothetical 'pure' geothermal water	51
16. Concentrations ($\mu\text{g/mL}$) of some elements in waters taken from lakes in the Taupo Volcanic Zone.....	59

17. Correlation data (<i>r</i>) for arsenic, magnesium and the alkali metals in water and sediments of the lakes in the Taupo Volcanic Zone	60
18. Concentration ($\mu\text{g/mL}$) of arsenic in sediments from some lakes in the Taupo Volcanic Zone.....	66
19. Levels of arsenic ($\mu\text{g/g}$ fresh weight) in the flesh of trout from Lakes Tarawera and Okataina	67
20. Levels of mercury in flesh and livers of trout from some lakes in the Taupo Volcanic Zone.....	68
21. T -Tests (values of P) for differences in trout flesh mercury concentrations for trout from different natural lakes in the Taupo Volcanic Zone.....	69
22. Correlation data (<i>r</i>) for trout in lakes of Taupo Volcanic Zone	70
23. Mercury and arsenic concentrations ($\mu\text{g/g}$) of the soft portions of some fresh water mussels from Lakes Rotorua and Tarawera	73
24. Calculations using lithium, rubidium, and arsenic, of amount of the geothermal water entering some lakes in the Taupo Volcanic Zone as a percentage of total water entering the lake	75
25. Maximum allowable daily consumption of trout flesh by adult humans to keep within an acceptable daily intake of 30 μg of mercury.	78
26. Estimates of the arsenic inputs into the Waikato River from geothermal areas by Reay (1973).....	82
27. Average arsenic concentrations ($\mu\text{g/g D.W.}$) of some aquatic macrophytes from the Waikato River as reported by Reay (1971).....	85
28. Table of correlations (<i>r</i>) of distance down stream and the concentrations of some elements in water samples from the Waikato River.....	88
29. Concentration ($\mu\text{g/mL}$) of arsenic, magnesium and the alkali metals in water samples from the Waikato River	89
30. Concentrations ($\mu\text{g/mL}$) of some elements in water from the Waikato River at Broadlands.....	94
31. Concentrations ($\mu\text{g/g}$) of some elements in sediments from selected locations along the Waikato River.....	95
32. Arsenic and mercury concentrations ($\mu\text{g/g}$) in trout taken from the Waikato River and nearby streams.....	96

33. Table of correlations (r) of arsenic, mercury, length of fish and head width for trout taken from the Waikato River	96
34. T -Tests (values of P) for differences in mercury concentrations in brown and rainbow trout from different locations in the Waikato River	97
35. Concentrations ($\mu\text{g/g D.W.}$) of arsenic, antimony, zinc and copper in some aquatic macrophytes from the Waikato River	97
36. Average arsenic concentrations ($\mu\text{g/g}$) of some organisms in / near the Waikato River.....	100
37. Concentrations ($\mu\text{g/g}$) of arsenic and mercury in mullet, and shellfish from the mouth of the Waikato River and an estuary near Raglan	101
38. Plant weights, and arsenic concentrations of plants ($\mu\text{g/g}$) and solutions ($\mu\text{g/mL}$) in experiment	115