



Ministry for the
Environment
Manatū Mō Te Taiao

Sustainable Management Fund

Client Report 2001/05

Section 2 of 4

Executive summary
Recommendations
Pressure indicators
Results

CONFIDENTIAL

**Determination of non-point
source chemical
groundwater quality
indicators for
New Zealand aquifers**

**M R Rosen
S G Cameron
R R Reeves**

April 2001

Determination of non-point source chemical groundwater quality indicators for New Zealand aquifers

Prepared for

MINISTRY FOR THE ENVIRONMENT

**M R Rosen
S G Cameron
R R Reeves**

CONFIDENTIAL

**Client Report 2001/05
Job Number 53053C.10**

April 2001

COMMERCIAL IN CONFIDENCE: This report has been prepared by the Institute of Geological & Nuclear Sciences Limited exclusively for and under contract to the Ministry for the Environment. Unless otherwise agreed in writing, all liability of the Institute to any party other than the Ministry for the Environment in respect of the report is expressly excluded.

COPYRIGHT: This work is copyright. The copying, adaptation, or issuing of this work to the public on a non-profit basis is welcomed. No other use of this work is permitted without the prior consent of the copyright holder(s).

CONTENTS

	Page
List of Figures	iii
List of Tables	iii
EXECUTIVE SUMMARY	vi
RECOMMENDATIONS	vi
1.0 INTRODUCTION	1
1.1 What is an indicator?.....	2
1.2 Need for groundwater indicators.....	3
2.0 INTERNATIONAL CONTEXT	4
3.0 NEW ZEALAND CONTEXT	7
4.0 CHEMICAL PARAMETERS CONSIDERED	8
5.0 METHODS	10
5.1 Relationship between groundwater chemistry, land use and aquifer geology.....	12
5.1.1 Summary of geological information	12
5.1.2 Summary of land use information.....	13
5.1.3 Summary of hydrogeological information	15
5.2 Statistical analysis	16
5.2.1 Principal component analysis.....	21
5.3 Descriptive analysis	23
6.0 PRESSURE INDICATORS	23
6.1 Timing of monitoring as a function of groundwater age	25
7.0 RESULTS	26
7.1 Aquifer geology.....	26
7.2 Land use	29

	Page
7.3	Principal component analysis..... 35
7.3.1	Temporal PCA analysis..... 40
7.4	Metals as indicators..... 40
7.5	Pesticides as indicators..... 46
7.5.1	Well selection..... 49
7.5.2	Sampling and analyses 49
7.5.3	GC-MS 50
7.5.4	ELISA test kits 50
7.5.5	Results..... 51
8.0	DISCUSSION 58
8.1	Nitrogen as an indicator 58
8.2	Indicators based on statistics..... 65
8.3	Indicators based on descriptive analysis of data 68
8.4	Primary indicators 69
8.5	Secondary indicators 70
8.6	Gaps and ways to enhance the indicator network 71
9.0	DEVELOPMENT OF INDICATORS WORLD WIDE WEB PAGE 73
10.0	CONCLUSIONS 74
11.0	ACKNOWLEDGEMENTS 77
12.0	REFERENCES 77

LIST OF FIGURES

	Page
Figure 1.1 Map of New Zealand showing NGMP well sites.....	9
Figure 5.1 Flow diagram of methodology of statistical analysis	20
Figure 5.2 Bivariate scatter of data.....	22
Figure 7.1 Box and whisker plots of aquifer lithology categories with mean concentration higher than database mean that are significant at the 95% confidence level.....	30
Figure 7.2 Box and whisker plots of aquifer lithology categories with mean concentration higher than database mean but the differences in mean values are not significant at the 95% confidence level	31
Figure 7.3 Box and whisker plots of land use categories with mean concentration higher than database mean that are significant at the 95% confidence level	36
Figure 7.4 Box and whisker plots of land use categories with mean concentration higher than database mean but the differences in mean values are not significant at the 95% confidence level.....	37
Figure 7.5 Principal component loadings	39
Figure 7.6 (a) Plot of principal component weights for a well in Gisborne, (b) Plot of the dominant component 1 elements over time.....	41
Figure 7.7 Arsenic concentrations plotted against chloride for those wells that contained As concentrations above the detection limit of the method.....	44
Figure 7.8 Copper concentrations plotted against lead.....	47
Figure 7.9 Sampling sites for the GC-MS pesticide testing	56
Figure 7.10 (a) Pesticide detections using the GC-MS technique, (b) Pesticide detections using the high sensitivity atrazine test kits.....	57
Figure 8.1 Changes in chemical composition over time depending on land use in a shallow unconfined aquifer in the Tasman District.....	61
Figure 8.2 Ammonium concentrations over time of a well in Taranaki compared to the nitrate concentrations for the same well.....	62
Figure 8.3 Plots of component weights for a well in the Bay of Plenty and a well in Canterbury	64

	Page
Figure 8.4 Plot of nitrate and sulphate concentrations over time for a well in the Bay of Plenty	64
Figure 8.5 Plot showing changes in sodium, chloride and bromide concentrations with time over a five year period for Pupu Springs, Tasman District.....	67
Figure 8.6 Plot of nitrate and chloride concentrations in groundwater down-gradient of a land treatment facility.....	67

LIST OF TABLES

Table 2.1 Recommended chemical indicators of environmental change in groundwater systems	6
Table 4.1 Chemical parameters used to assess indicators in groundwater	11
Table 5.1 Summary of aquifer geology information	12
Table 5.2 Summary of land use information	14
Table 5.3 Summary of land use information dates	15
Table 5.4. Summary of aquifer condition.....	16
Table 5.5 Mean chemical concentration for all wells.....	17
Table 6.1 Pressure indicators for non-point source groundwater quality	24
Table 7.1 Mean concentrations of chemical parameters for specified aquifer lithology.....	27
Table 7.2 P-value statistics for aquifer lithology.....	28
Table 7.3 Mean concentrations of chemical parameters for specified land use	32
Table 7.4 P-value statistics for land use data.....	33
Table 7.5 GC-MS results compared to atrazine test kits and HS atrazine test kit results for the same groundwater samples.....	52
Table 7.6 Compounds that show cross reactivity to both normal and high sensitivity atrazine test kits and their least detectable dose	54
Table 8.1 Proposed primary indicators listed against the probable causes of contamination	70

Table 8.2 Proposed secondary indicators listed against the probable causes of contamination 70

LIST OF APPENDICES

Appendix 1. Land use categories at NGMP wells 84

Appendix 2. Aquifer lithology categories at NGMP wells..... 88

Appendix 3. Principal component analysis loading results 90

Appendix 4. Plots of component weights for temporal data from 12 wells 91

EXECUTIVE SUMMARY

The New Zealand Ministry for the Environment commissioned the Institute of Geological & Nuclear Sciences Ltd. to develop indicators of groundwater quality through a grant from the Sustainable Management Fund. The development of groundwater indicators is part of the overall Environmental Performance Indicators programme administered by the Ministry for the Environment. This report summarises the testing and selection of groundwater quality indicators for non-point source (diffuse) chemical contamination of groundwater using the "pressure-state-response" framework. "Pressure" indicators were chosen qualitatively based on the most important national pressures effecting groundwater quality. The "state" indicators that were chosen are based on statistical principal component analysis of chemical data taken from the National Groundwater Monitoring Programme. In addition, descriptive evaluation of "state" indicators was included for those parameters where significant temporal data were not available (pesticides and metals). Land use information and geological knowledge of the aquifers included in the survey were used to test the significance of the "state" indicators chosen.

Eight primary "pressure" and "state" indicators and five secondary "state" indicators have been chosen to assess changes in groundwater quality with time. The recommendation section of this report lists the indicators chosen. The indicators selected will be valuable in assessing changes in groundwater quality from non-point source contamination caused by fertiliser applications, impacts of human and animal wastes applied to land, leaching of animal wastes from pastoral farming, pesticide application, contaminants from sheep dips, and corrosion of metals from urban settings. "Response" indicators were not evaluated in this study. It will be beneficial for the regional authorities and the Ministry for the Environment to evaluate and choose "response" indicators based on the "pressure" and "state" indicators developed in this report.

RECOMMENDATIONS

The recommendation of this report is that the following non-point source "pressure" and "state" indicators for groundwater quality be implemented:

Pressure Indicators

1. Percentage change of each land use in an aquifer area (both recharge areas and confined areas)
2. Measurement of stocking rates on pastoral land uses
3. Amount and type of fertiliser applied to land (e.g. NPK or urea) or produced and imported
4. Amount of triazine pesticides applied to land (or produced and imported)
5. Number of well with appropriate wellhead protection per unit area
6. Number of sites with contaminated soils detected
7. Percent change in chemical indicators of recharge water quality from streams, lakes and rivers
8. Abstraction volume of groundwater per aquifer

"State" Indicators**Major ions:**

Primary indicators	Potassium, sulphate, chloride
Secondary indicators	Alkalinity, sodium, bromide, magnesium (in Tasman district)

Nutrients:

Primary indicators	Nitrogen as total nitrogen, or nitrate and/or ammonium depending on aquifer conditions and expected contaminants.
--------------------	---

Metals:

Primary indicators	Total arsenic and total lead (total dissolved arsenic and lead may also be used)
Secondary indicators	Total copper (total dissolved copper may also be used)

Pesticides:

Primary indicator	Atrazine: High sensitivity atrazine test kits with detection limits of at least 0.015 mg m ⁻³ have been shown to be a cost effective method of testing for atrazine.
-------------------	---

These "state" indicators should be used in the following context related to the "pressure" indicators:

Pressure indicator	Related state indicator
Percentage change of each land use in an aquifer area (both recharge areas and confined areas)	Percent average change in indicator chemical (nitrogen, chloride, sulphate) concentrations relating to land use in an aquifer
Measurement of stocking rates on pastoral land uses	Percent average increase in indicator chemical (nitrogen, chloride, sulphate) concentrations relating to stocking numbers in an aquifer
Amount and type of fertiliser applied to land (e.g. NPK or urea) or produced and imported	Percent average change in indicator chemical (nitrogen, potassium, chloride, sulphate, magnesium) concentrations relating to fertiliser use in an aquifer
Amount of triazine pesticides applied to land (or produced and imported)	Percent detection of atrazine in wells, percent change in copper concentrations relating to a given land use.
Number of well with appropriate wellhead protection per unit area	Percent average change in indicator chemical (nitrogen, potassium, chloride, sulphate, magnesium) concentrations. (<i>microbiological indicators may be more appropriate for this state indicator</i>).
Number of sites with contaminated soils detected	Number of detections of arsenic and lead in groundwater
Percent change in chemical indicators of recharge water quality from streams, lakes and rivers	Percent average change in indicator chemical (nitrogen, potassium, sodium, chloride, sulphate, magnesium) concentrations in wells in the recharge area of an aquifer
Abstraction volume of groundwater per aquifer	Percent average change in indicator chemical (nitrogen, potassium, sodium, chloride, bromide, sulphate, magnesium) concentrations per land use in an aquifer

This list of both the "pressure" and "state" indicators is intended to cover as many major issues for non-point source groundwater contamination as possible. It is not intended that all of these possible indicators be monitored in all areas of the country. Two major constraints will be the data and resources available in each region to monitor some of the "pressure" indicators. However, to insure that a national indicator programme for groundwater contamination is useful, some common "pressure" and "state" indicators should be chosen that are monitored throughout the country.

Details of how and when these indicators should be applied are detailed in this report.

6.0 PRESSURE INDICATORS

For any particular issue, the ability to quantitative measure the cause of the issue is the means to establish "pressure" indicators. For example, measurement of land use change or amounts of water extracted are pressures that "state" indicators need to address to be effective. Pressure indicators of changes to non-point source groundwater quality will in a broad sense be mainly related to land use change or intensification of land use activities. However, quantitative measures of water abstraction and wellhead protection may also relate to groundwater quality issues and need to be addressed.

On a national basis, pressure indicators include measurements of stocking numbers, land use changes, fertiliser application rates or fertiliser production and importing, pesticide use or purchases, identification of wells that need better wellhead protection, and groundwater abstraction volumes. In order to make such a system work all regional councils and unitary authorities would need to collect the same sorts of information and maintain the data on databases that can be easily transferred to a national database. This means good quality control procedures need to be put in place and a database-handling framework needs to be developed that includes the handling of meta-data and data transfer.

Table 6.1 lists possible "pressure" indicators and related "state" indicators that can be used to evaluate the "pressure" indicators. The "state" indicators are developed in Section 7. "Response" indicators are not included in the table because it was felt that they should be developed either under national policy guidance through the Ministry for the Environment or regionally by regional authorities.

Table 6.1 Pressure indicators for non-point source groundwater quality

Pressure indicator	Related state indicator (see Section 7)
Percentage change of each land use in an aquifer area (both recharge areas and confined areas)	Percent average change in indicator chemical (nitrogen, chloride, sulphate) concentrations relating to land use in an aquifer
Measurement of stocking rates on pastoral land uses	Percent average increase in indicator chemical (nitrogen, chloride, sulphate) concentrations relating to stocking numbers in an aquifer
Amount and type of fertiliser applied to land (e.g. NPK or urea) or produced and imported	Percent average change in indicator chemical (nitrogen, potassium, chloride, sulphate, magnesium) concentrations relating to fertiliser use in an aquifer
Amount of triazine pesticides applied to land (or produced and imported)	Percent detection of atrazine in wells, percent change in copper concentrations relating to a given land use.
Number of well with appropriate wellhead protection per unit area	Percent average change in indicator chemical (nitrogen, potassium, chloride, sulphate, magnesium) concentrations. (<i>microbiological indicators may be more appropriate for this state indicator</i>).
Number of sites with contaminated soils detected	Number of detections of arsenic and lead in groundwater
Percent change in chemical indicators of recharge water quality from streams, lakes and rivers	Percent average change in indicator chemical (nitrogen, potassium, sodium, chloride, sulphate, magnesium) concentrations in wells in the recharge area of an aquifer
Abstraction volume of groundwater per aquifer	Percent average change in indicator chemical (nitrogen, potassium, sodium, chloride, bromide, sulphate, magnesium) concentrations per land use in an aquifer

Eight "pressure" indicators have been chosen that reflect the most important pressures on groundwater quality in New Zealand. The first four indicators relate to different aspects of agricultural land use in New Zealand, although urbanisation is also included in the first indicator. The next two indicators relate mostly to past land uses and how to evaluate the mistakes made in the past. The seventh indicator documents the pressures from land uses that

impact surface water that is then recharged to groundwater. For this indicator to be effective changes in "state" chemical indicators need to be monitored both in the surface water bodies and in the groundwater near the recharge area. The last indicator may also be used as a water quantity indicator, but over abstraction can change groundwater flow directions and could cause water quality problems related to salt water intrusion or mixing with polluted surface or groundwater. Measurement of some of the pressure indicators may be best conducted in the recharge areas of aquifers, however, land uses above confined aquifers may also effect groundwater quality if there is poor wellhead protection or if the confining layer does not permit a perfect seal. For these reasons we suggest that it is important to measure these parameters throughout the land area above the aquifer.

The list of both the "pressure" and "state" indicators in Table 6.1 is intended to cover as many major issues for non-point source groundwater contamination as possible. It is not intended that all of these possible indicators be monitored in all areas of the country. Two major constraints will be the data and resources available in each region to monitor some of these "pressure" indicators. However, to insure that a national indicator programme for groundwater contamination is useful, some common "pressure" and "state" indicators should be chosen that are monitored throughout the country.

6.1 Timing of monitoring as a function of groundwater age

An aspect of both the "pressure" and "state" indicators that is not addressed in this report directly is the timing of monitoring as a function of groundwater flow rates. Obviously, when groundwater flow is fast changes in water quality will be quicker than in areas where groundwater flow is slow. However, providing data on groundwater flow for the entire country is beyond the scope of this report and needs to be considered on a regional or aquifer basis by each regional authority. Therefore only a general recommendation on the frequency of monitoring is made in this report.

The National Groundwater Monitoring Programme monitors aquifers from a wide variety of aquifers of differing ages. Rosen (1999) suggested that monitoring on a quarterly basis is the minimum amount of sampling that should be considered. The reason for this is that any longer frequency will take too long to detect any statistically significant changes. For

example, if monitoring occurs on a yearly basis, it will take between 4 to 6 years to obtain enough data to indicate a trend. This may mean that solving the problem that is creating the increase may be more difficult or impossible to solve after such a long period of time. Even in aquifers with groundwater that is tens to hundreds of years old it will be useful to monitor on a quarterly basis particularly if poor wellhead protection is an issue in the basin. Therefore, it is recommended that "state" indicators be monitored on at least a quarterly basis.

"Pressure" indicators should be monitored on a yearly or biennial basis. This is because changes in the pressure indicators such as land use, fertiliser application, stocking rates etc can only be efficiently collated, at best, on a yearly basis.

7.0 RESULTS

The results of the statistical analyses were separated into two categories; aquifer lithology and land use. These categories were compared to the chemical analyses for wells that fall into each category. Sections 7.1, 7.2 and 7.3 detail the main results from these comparisons. The remaining sections present the results of the descriptive analyses.

7.1 Aquifer geology

Mean chemical concentrations for aquifer lithology categories were compared to the mean chemical concentrations for the database (see Section 5.0 for methodology). Seven aquifer lithology categories (sandstone, siltstone, limestone, shell, volcanic sediment, basalt, and silt) had mean concentrations of a particular chemical variable above the mean concentration of the database (Table 7.1). For example, the mean calcium concentration for wells drawing groundwater from sandstone or limestone aquifers, or aquifers containing shell material were 46.16, 47.98, and 34.66 mg/l, respectively. The mean calcium concentration for the database was 25.84 mg/l. The statistical significance of the difference between the mean concentrations of a particular chemical parameter for a given aquifer lithology and the mean concentration for the rest of the database were established using p-value statistics (Table 7.2). Mean concentrations of chemical parameters that were statistically significantly higher at the 95% confidence level than the mean database concentrations for particular aquifer lithology categories are:

- Calcium: in limestone aquifers or aquifers containing shell material
- Alkalinity: in sandstone, or aquifers containing silt or shell material
- Potassium: in aquifers containing shell material or volcanic sediment
- Nitrate-nitrogen: in basalt aquifers
- Ammonium: in aquifers containing shell material
- Magnesium: in aquifers containing shell material
- Chloride: in aquifers containing shell material
- Sodium: in siltstone aquifers, or aquifers containing shell material
- Silica: in aquifers containing volcanic sediment
- Bromide: in aquifers containing shell material

Table 7.1 Mean concentrations of chemical parameters for specified aquifer lithology. Highlighted cells are statistically significant at the 95% confidence level.

	Average database concentration	Sandstone	Siltstone	Limestone	Shell	Volcanic sediment	Basalt	Silt
Calcium	25.84	46.16		47.98	34.66			
Alkalinity	117.90	262.55	262.55	165.31	301			428.08
Sulphate	11.38			16.39				
Potassium	2.76				7.44	6.05	3.56	
Nitrate-nitrogen	2.58					4.18	9.32	
Ammonia	0.32				1.35			
Phosphate	0.05						0.07	
Magnesium	7.78	9.95			14.04			
Manganese	0.19							0.22
Iron	0.54		1					
Chloride	28.48				72.93			
Sodium	28.48	52.54	67.05		54.35			
Silica	28.87					65.52		
Bromide	0.11				0.11			

Table 7.2. P-value statistics for aquifer lithology. Highlighted cells are statistically significant at the 95% confidence level

	Siltstone	Sandstone	Limestone	Shell	Silt	Volcanic sediment	Basalt	Silt
Calcium		0.4226	0.02821	0.0007068				
Alkalinity	0.08597	0.002941	0.1477	0.001				0.03695
Sulphate			0.3009					
Potassium				0.0101		0.004207	0.519	
Nitrate						0.4138	0.02167	
Ammonia				0.003569				
Phosphate							0.1068	
Magnesium		0.3604		0.02008				
Manganese					0.1001			
Iron	0.149							
Chloride				0.008298				
Sodium	0.01318	0.1182		0.01053				
Silica						0.00001494		
Bromide				0.04324				

Figure 7.1 shows log format box and whisker plots of the aquifer lithology categories that have mean concentrations higher than the database mean and are statistically significant at the 95 % confidence level. The aquifer lithology is displayed below the x-axis. The number of wells in each category is given at the bottom of the plots. Ten chemical parameters have mean concentrations for a particular aquifer lithology category that are greater than the database mean concentrations but the differences are not statistically significant at the 95% confidence level. These are:

- Calcium: in sandstone aquifers
- Alkalinity: in siltstone or limestone aquifers
- Sulphate: in limestone aquifers
- Potassium: in basalt aquifers
- Nitrate-nitrogen: in aquifers containing volcanic sediment
- Phosphate: in basalt aquifers
- Magnesium: in sandstone aquifers
- Manganese: in aquifers containing silt material
- Iron: in siltstone aquifers
- Sodium: in sandstone aquifers

7.2 Land use

Mean chemical concentrations for land use categories were compared to the mean chemical concentrations for the database. Twelve land use categories (drystock, cattle, sheep, deer, dairy, cropping, horticulture, orcharding, lifestyle blocks, urban, golf course, and native bush) had mean concentrations of a particular chemical parameter above the mean concentration of the database (Table 7.3). For example, the mean potassium concentration for wells with cattle farming occurring within 10 m and 200 m is 3.97 mg/l. The mean potassium concentration for the database is 2.76 mg/l.

The statistical significance of the difference between mean concentrations of a particular chemical parameter for a given land use and the mean concentration for the database were established using p-value statistics (Table 7.4). Mean concentrations of chemical parameters that were statistically significantly higher at the 95% confidence level than the mean database concentrations for particular land use categories are:

- Alkalinity: in groundwater from confined aquifers wells where dairy farming occurs in the recharge area of the aquifer; or in unconfined aquifers wells where dairy farming occurs within 200 m of wells.
- Sulphate: in groundwater from unconfined aquifer wells where orchards occur within 200m
- Potassium: in groundwater from unconfined aquifer wells where cattle farming occurs within 10 m or 200m.
- Nitrate-nitrogen: in groundwater from confined aquifers wells where horticulture occurs in the aquifer recharge area.
- Phosphate: in groundwater from unconfined aquifer wells within 10 m or 200 m of urban areas.
- Magnesium: in groundwater from unconfined aquifers wells where the land use is dominated by horticulture; or in confined aquifers wells where horticulture occurs in the aquifer recharge area.
- Manganese: in groundwater from confined aquifer wells where sheep farming occurs in the aquifer recharge area.

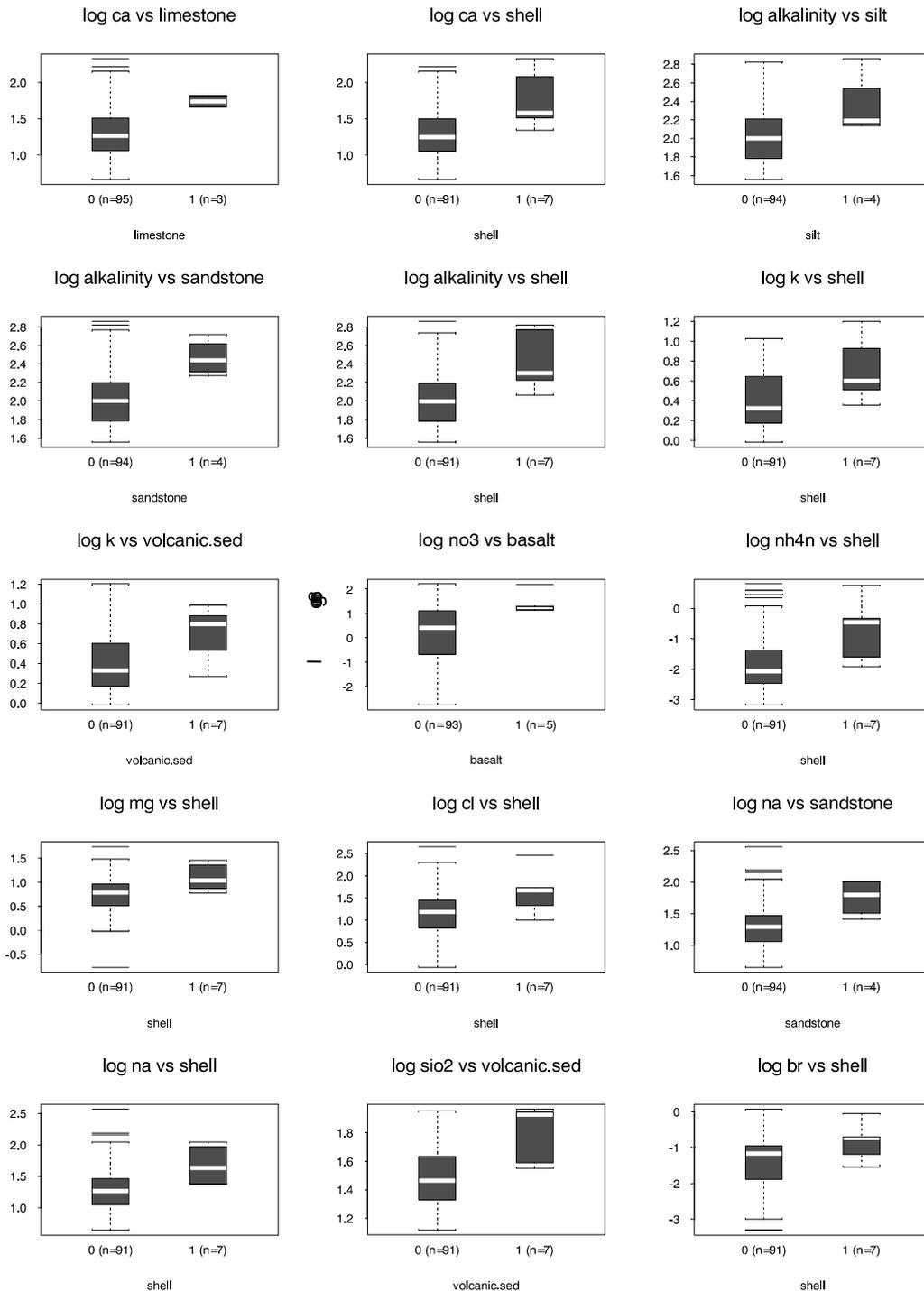


Figure 7.1 Box and whisker plots of aquifer lithology with mean concentration higher than database mean that are significant at the 95% confidence level. The light strip is the median, the upper and lower limit of the shaded box is the first standard deviation, the horizontal line connected by a dashed line to the shaded box are the upper and lower quartiles. The whiskers extend to the extreme of the data as long as that extreme is no more than 1.5 times the interquartile range beyond the end of the box. Isolated horizontal lines are outliers.

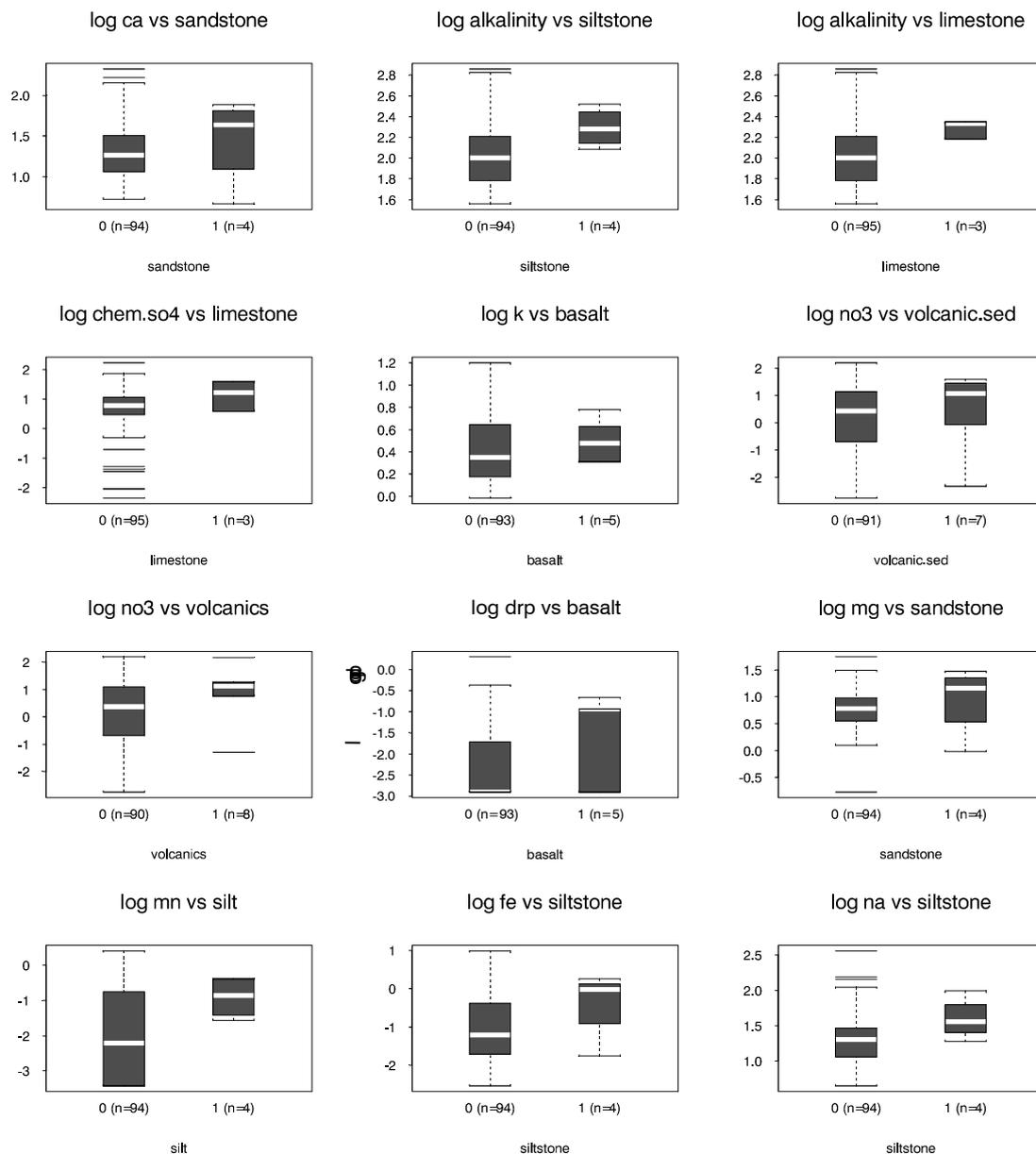


Figure 7.2 Box and whisker plots of aquifer lithology categories with mean concentration higher than database mean but the differences in mean values are not significant at the 95% confidence level. The light strip is the median, the upper and lower limit of the shaded box is the first standard deviation, the horizontal line connected by a dashed line to the shaded box are the upper and lower quartiles. The whiskers extend to the extreme of the data as long as that extreme is no more than 1.5 times the interquartile range beyond the end of the box. Isolated horizontal lines are outliers.

Table 7.3. Mean concentrations of chemical parameters for specified land use

	Average database concentration	Drystock	Cattle	Sheep	Deer	Dairy	Cropping	Horticulture	Orchard	Lifestyle block	Urban	Golf course	Native bush
Calcium	25.84		Recharge = 32.08						Recharge = 30.22				
Alkalinity	117.90		General = 144.16										
			10 m = 144.16										
			200 m = 144.16										
		Recharge = 128.54	Recharge = 157.96			Recharge = 150.71							
Sulphate	11.38								200 m = 16.17	200 m = 17.12			
Potassium	2.76		General = 3.97										
			10 m = 3.97										
			200 m = 3.97										
			Recharge = 5.49										
Nitrate-nitrogen	2.58							Recharge = 4.66					
Ammonia	0.32												
Phosphate			General = 0.06		General = 0.06						General = 0.24		
	0.05		10 m = 0.06								10 m = 0.06		
			200 m = 0.06								200 m = 0.07	200 m = 0.06	
		Recharge = 0.06											
Magnesium	7.78							General = 9.95	Recharge = 11.11				
Manganese	0.19		Recharge = 0.22	Recharge = 0.25		Recharge = 0.48							
Iron	0.54		Recharge = 0.59	Recharge = 0.137									
Chloride	28.48												200 m = 198.6
Sodium	27.86					Recharge = 35.82							200 m = 151.92
Silica	28.87		Recharge = 48.23										
			200 m = 53.62										
Bromide	0.11						10 m = 0.19	General = 0.13					
Fluoride	0.16	200 m = 0.33											
Lead	0.00012								Recharge = 0.00065		General = 0.0006		

Table 7.4. P-value statistics for land use data

	Drystock	Cattle	Sheep	Deer	Dairy	Cropping	Horticulture	Orchard	Lifestyle block	Urban	Golf course	Native bush
Calcium		Recharge = 0.2812						Recharge = 0.1933				
Alkalinity	Recharge = 0.2556	General = 0.2074	Recharge = 0.4099									
		10 m = 0.2074		Recharge = 0.03089								
		Recharge = 0.4175										
Sulphate							200 m = 0.0231	200 m = 0.3707				
Potassium		General = 0.04746						Recharge = 0.6297		200 m = 0.5423	200 m = 0.7041	
		10 m = 0.04746										
		200 m = 0.04746										
		Recharge = 0.1691										
Nitrate						Recharge = 0.03305						
Phosphate				General = 0.8631						General = 0.0438	200 m = 0.2475	
									10 m = 0.007114			
									200 m = 0.05699			
Magnesium							General = 0.03841	Recharge = 0.2272				
Manganese		Recharge = 0.2272	Recharge = 0.07864		Recharge = 0.1313							
Iron		Recharge = 0.3754	Recharge = 0.5669		Recharge = 0.339							
Chloride												200 m = 0.0005948
Sodium					Recharge = 0.02723							200 m = 0.0008748
Silica		200 m = 0.3023										
		Recharge = 0.2157			200 = 0.6557							
Bromide						10 m = 0.01934	General = 0.5842					
Fluoride	200 m = 0.01958											
Lead								Recharge = 0.4465		General = 0.3649		

The differences in mean concentrations are not significant because the aquifer lithology mean concentration values are within the upper quartile of the database mean concentration, or the number of wells with the aquifer lithology category is low (Figure 7.2).

- Chloride: in groundwater from unconfined aquifers wells where native bush occurs within 200 m.
- Sodium: in groundwater from confined aquifer wells where dairy farming occurs in the aquifer recharge area; or in groundwater from unconfined aquifer wells where native bush occurs within 200 m.
- Bromide: in groundwater from unconfined aquifer wells where crop farming occurs within 10 m.
- Fluoride: in groundwater from unconfined aquifer wells where drystock farming occurs within 200 m.

Figure 7.3 shows log-format box and whisker plots of the land use categories that have mean concentrations higher than the database mean and are statistically significant at the 95 % confidence level. The land use category is displayed below the x-axis of the plots.

Twelve chemical parameters have mean concentrations for a particular land use category that are greater than the database mean concentrations but the differences are not statistically significant at the 95% confidence level. These are:

- Calcium: in groundwater from confined aquifers wells where cattle farming or orchards occur within the aquifer recharge area.
- Alkalinity: in groundwater from unconfined aquifers wells where with cattle farming occurs within 10 m; or in groundwater from confined aquifer wells where cattle, drystock, sheep, or dairy farming occurs within the aquifer recharge area.
- Sulphate: in groundwater from unconfined aquifer wells where lifestyle blocks within 200 m.
- Potassium: in groundwater from confined aquifer wells with cattle farming or orchards occur in the aquifer recharge area; or in groundwater from unconfined aquifers where within 200 m of a golf course or urban area.

- Phosphate: in groundwater from unconfined aquifer wells within 200 m of a golf course; or in aquifers where deer farming is the dominant land use.
- Magnesium: in groundwater from confined aquifer wells where orchards occur in the aquifer recharge area.
- Manganese: in groundwater from confined aquifer wells where cattle and dairy farming occurs in the aquifer recharge area.
- Iron: in groundwater from confined aquifer wells where dairy, cattle or sheep farming occurs in the aquifer recharge area.
- Silica: in groundwater from confined aquifer wells where cattle farming occurs in the aquifer recharge area; or in unconfined aquifer wells where cattle or dairy farming occurs within 200 m.
- Bromide: in groundwater from aquifers where horticulture is the dominant land use.
- Lead: in groundwater from confined aquifer wells where orchards occur within the aquifer recharge area; or in wells in urban areas.

The differences in mean concentrations are not significant because the land use mean concentration values are within one standard deviation of the database mean concentration, or the number of wells with the land use category is low (Figure 7.4).

7.3 Principal component analysis

The principal component loadings for the groundwater composition are presented in Appendix 3 and in graphical form in Figure 7.5. The results show that the first and second principal components are made up of sodium, alkalinity, potassium, chloride, calcium, bromide, nitrate-nitrogen, copper, magnesium, and sulphate. This suggests that these chemical parameters may be useful indicators of groundwater quality because they constitute the majority of the variance in the chemical data scatter. However, it does not take into consideration whether these chemical variables are actually meaningful groundwater quality indicators or what they indicate. The indicators suggested using PCA are discussed in terms of their hydrogeological and land use contexts in Section 8.2.

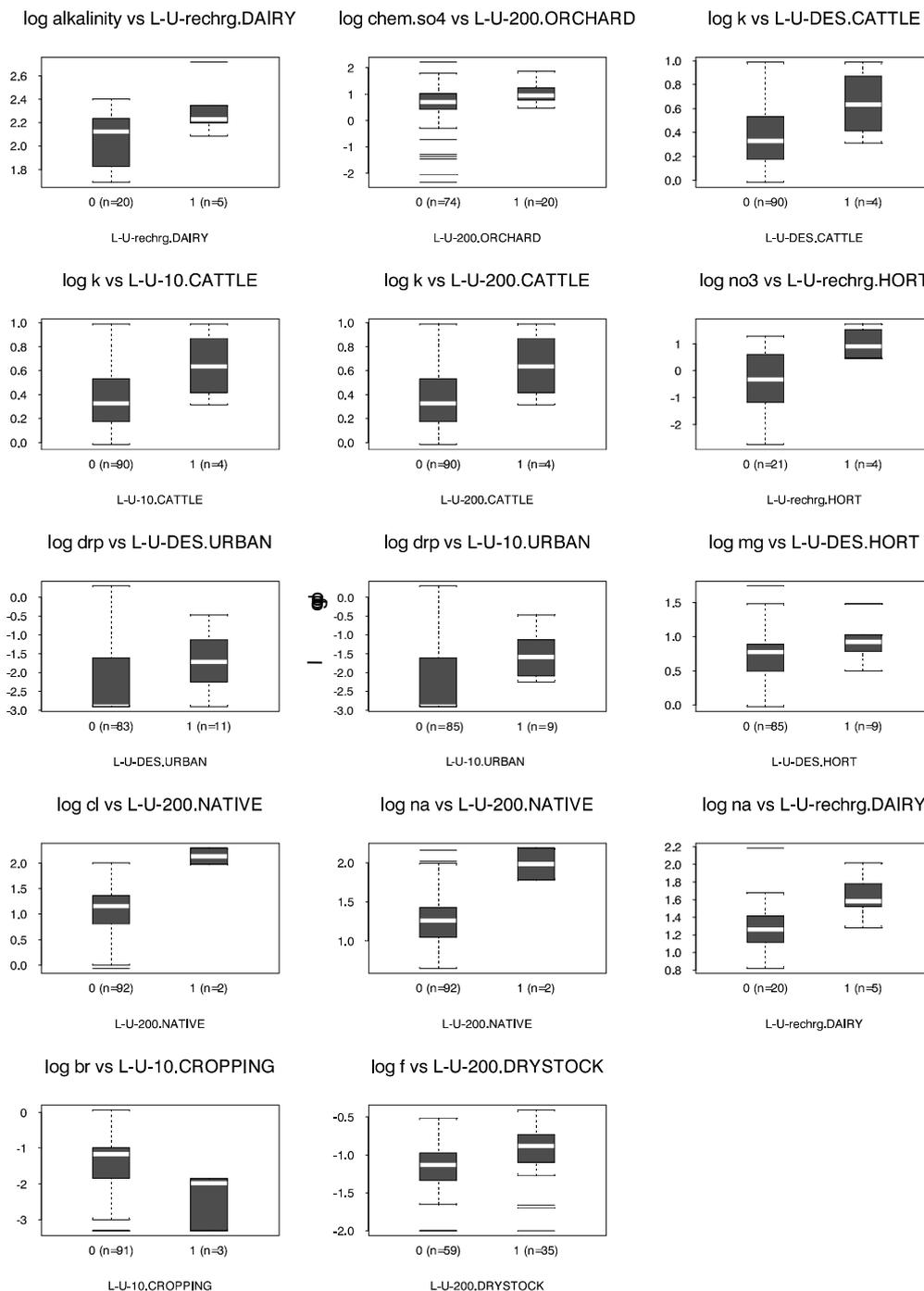


Figure 7.3 Box and whisker plots of land use categories with mean concentration higher than database mean that are significant at the 95% confidence level. The light strip is the median, the upper and lower limit of the shaded box is the first standard deviation, the horizontal line connected by a dashed line to the shaded box are the upper and lower quartiles. The whiskers extend to the extreme of the data as long as that extreme is no more than 1.5 times the interquartile range beyond the end of the box. Isolated horizontal lines are outliers.

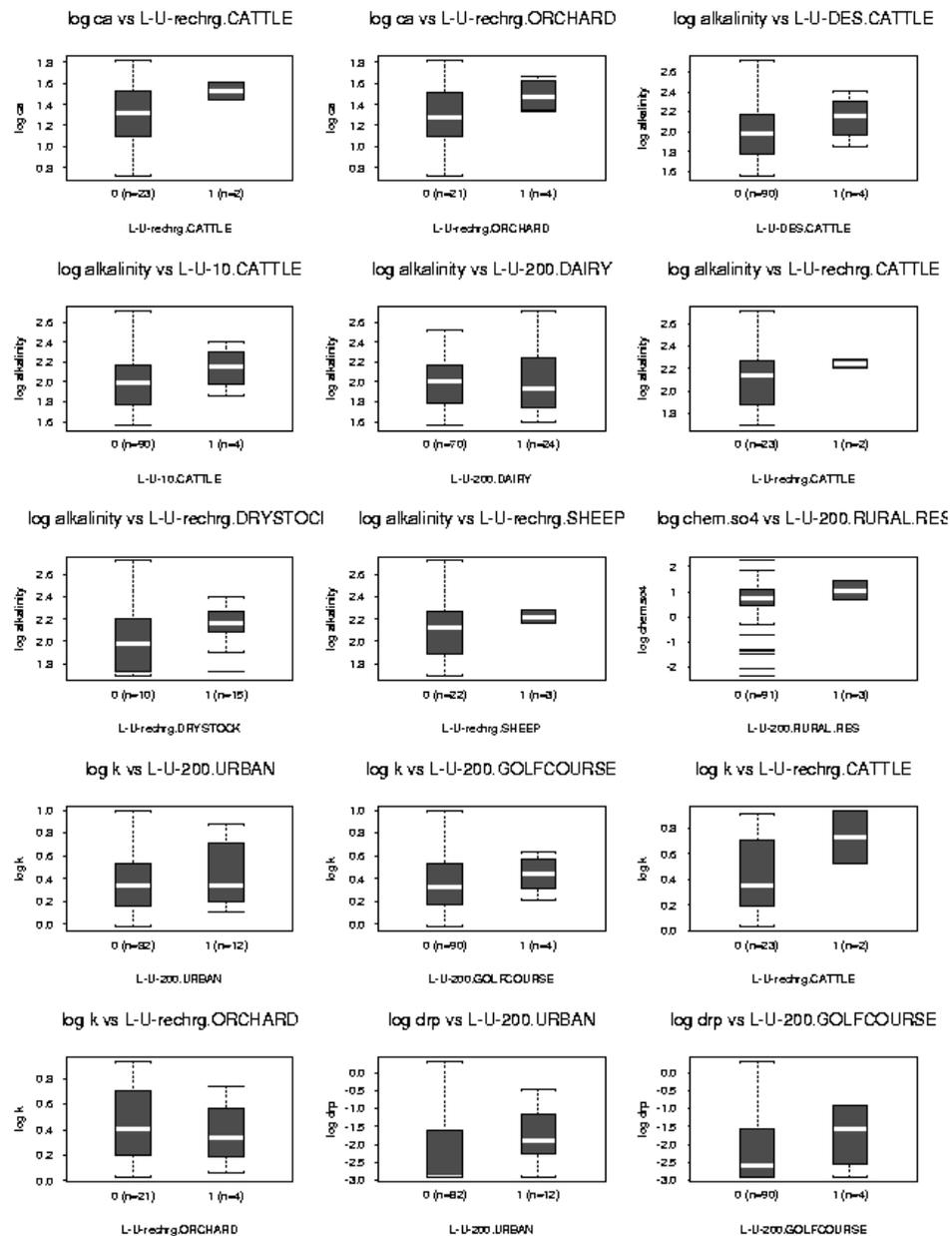


Figure 7.4 Box and whisker plots of land use categories with mean concentration higher than database mean but the differences in mean values are not significant at the 95% confidence level. The light strip is the median, the upper and lower limit of the shaded box is the first standard deviation, the horizontal line connected by a dashed line to the shaded box are the upper and lower quartiles. The whiskers extend to the extreme of the data as long as that extreme is no more than 1.5 times the interquartile range beyond the end of the box. Isolated horizontal lines are outliers.

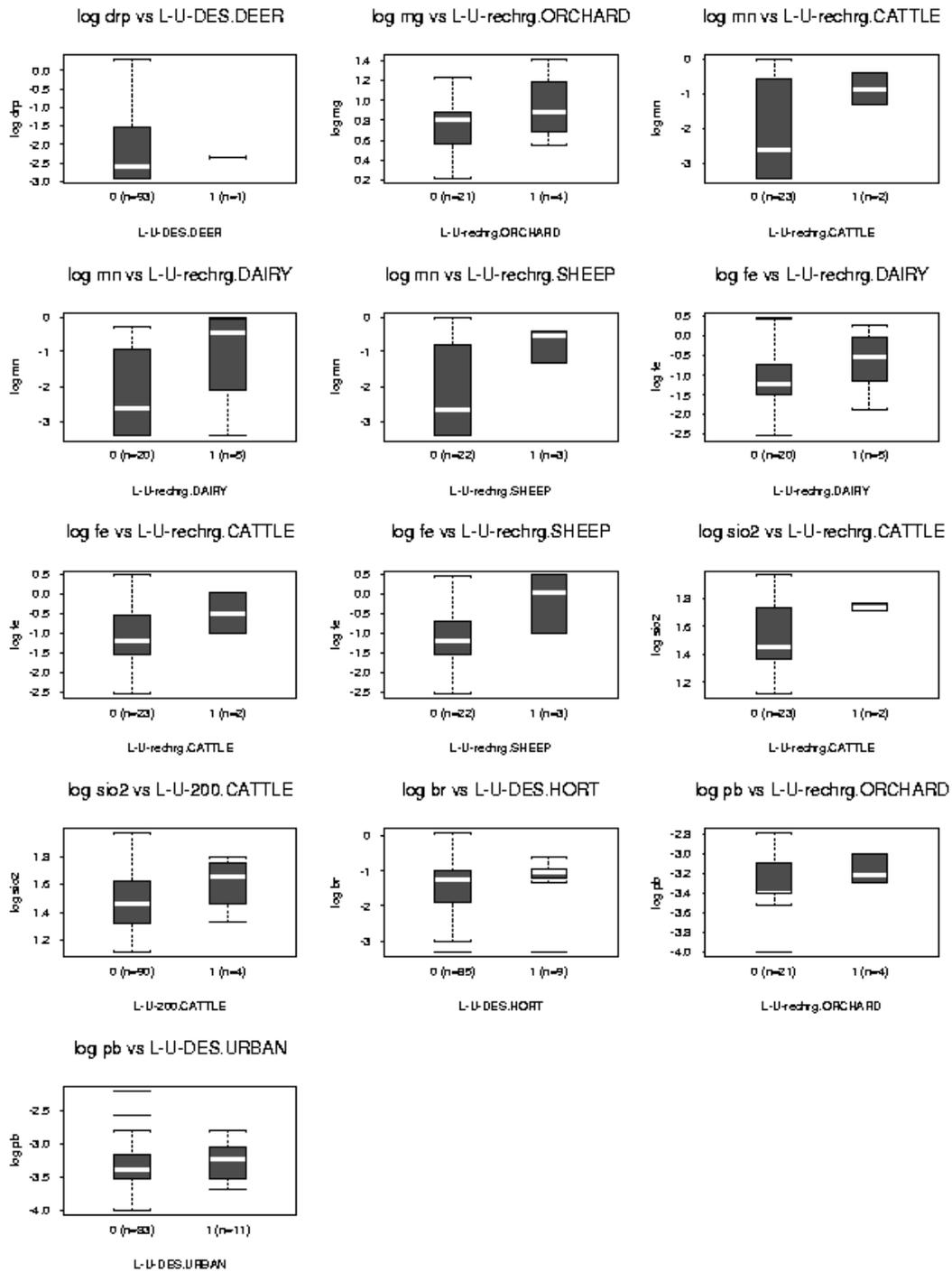


Figure 7.4 continued Box and whisker plots of land use categories with mean concentration higher than database mean but the differences in mean values are not significant at the 95% confidence level.

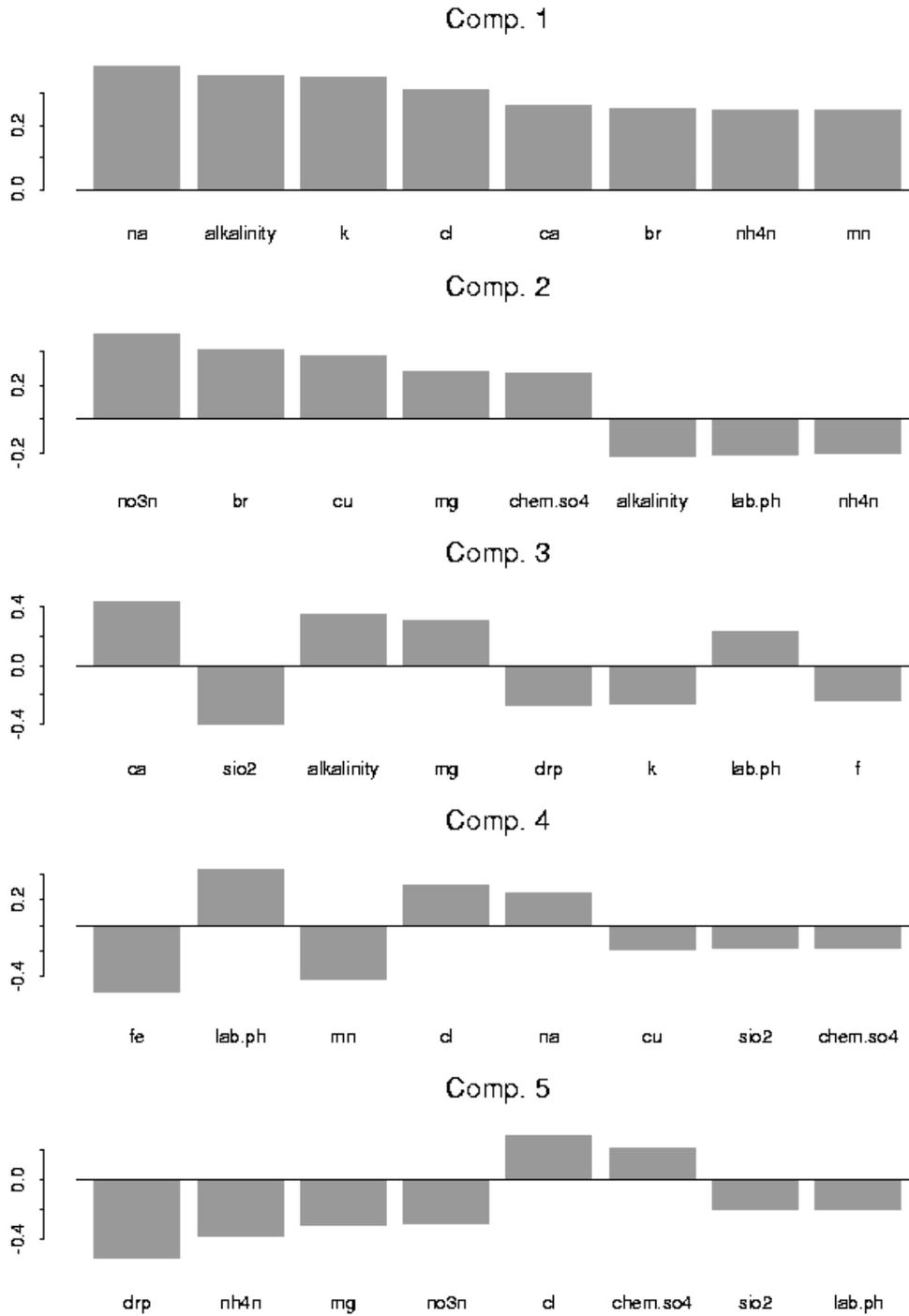


Figure 7.5 Principal component loadings.

7.3.1 Temporal PCA analysis

The temporal PCA analysis was conducted on wells from the Waikato, Canterbury, Gisborne, Hawkes, Bay, Bay of Plenty, and Tasman District. Plots of the component weights of the first two principal components are presented in Appendix 4, although some of the more important graphs are illustrated in the text. In eight of the twelve wells analysed, nitrate plotted as being significant only in component 2, whereas most of the other species explained much of the first component. More detail about this aspect of the PCA for nitrate is discussed in Section 8.1. Sulphate was also significant in 5 of the wells as component 2. Component 1 usually contained a cluster of five or six parameters that showed similar patterns for certain elements such as Ca, Na, Mg, and K (Figure 7.6a). However, these variations did not always produce trends that could be used to determine if water quality was improving or declining (Figure 7.6b). In general, the temporal analysis using PCA indicated that the important indicators determined using the mean chemical data (i.e. nitrate, sulphate, chloride, and potassium) explained much of the temporal variation as well, although some interpretation is necessary to determine the most important components.

7.4 Heavy metals as indicators

Although heavy metals were included in the statistical analysis of NGMP wells, there was only one round of metals testing. This indicated that a qualitative approach should also be used to assess the metal data. This section reviews the metal data in a qualitative way and briefly reviews the mobility of metals in groundwater described in Rosen (in press). The mobility of heavy metals in the unsaturated zone above the water table has been studied extensively by many authors (Alloway, 1990). However, the fate of heavy metals below the water table has not been studied to the same extent because some soil studies indicated that many heavy metals are retained in the soil and do not pass into the groundwater easily. In addition, determining the fate of heavy metals in both the unsaturated and saturated zones is complex and requires a thorough knowledge of the aquifer conditions expected before predictions of their mobility can be made (Allen et al., 1993). However, because the mobility of heavy metals is dependent on a wide range of common, and often competing, environmental factors (including pH, Eh, and competition from other elements for adsorptive sites) it is important to stress the interdependence of the mobility of each element on these environmental factors.

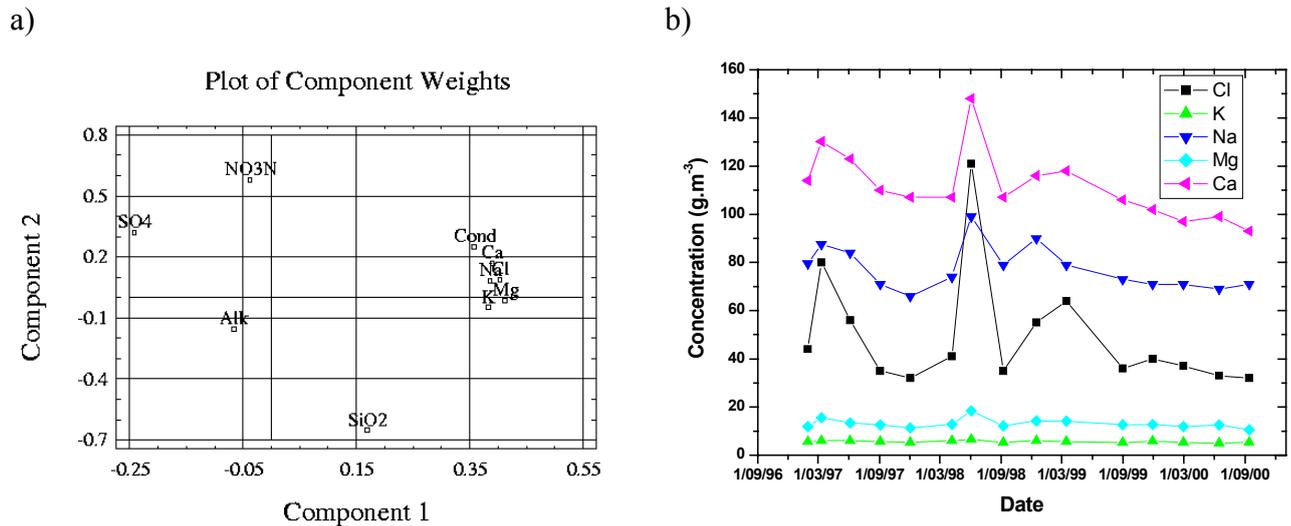


Figure 7.6 a) Plot of principal component weights for a well in Gisborne. Cl, K, Na, Mg, Ca and the electrical conductivity of the sample dominate component 1 (highest numbers on the x-axis). b) Plot of the dominant component 1 elements Cl, K, Na, Mg and Ca over time. Although variation is consistent in most of these elements, the variations do not readily show a distinct trend in water quality for the well.

There are a number of conditions that affect the mobility or retention of heavy metal species in the environment in general, and in groundwater specifically. Tanji and Valoppi (1989) outlined the possible biotic and abiotic processes that affect the reactivity and mobility of trace elements. They stated that the speciation and reactivity of the trace element, and mobility and transport processes influence the presence or accumulation of trace elements in groundwater. The rate and extent of these reactions are influenced by many environmental conditions that are in most cases specific to an individual site. Furthermore, the mobile forms of the trace elements are subjected to many competing reactions. Because of the complexity of this situation, there are few generalisations that can be made about the reactivity and mobility of heavy metals in groundwater. For example, cationic trace species, such as copper, tend to be strongly retained by earth materials due to ion exchange, sorption, and mineral solubility, but anionic species (e.g. CrO₄ and AsO₄) are more mobile (Tanji and Valoppi, 1989).

Although generalisations about the mobility of heavy metals may be limited, there are a few basic processes that seem to control many of the metal species present in groundwater. The most important processes are: 1) ion exchange and adsorption onto mineral surfaces, 2)

oxidation state of the groundwater, 3) pH, and 4) formation of organic ligands. For example, both cationic and anionic trace species that form complexes with organic and inorganic ligands have greater mobilities than those that do not. Reaction rates involving metals tend to increase with increasing temperature, and the solubility of minerals containing cationic metals increases as pH decreases, while that of anionic minerals increases with increasing pH.

The application of equilibrium concepts to metal migration in groundwater is appropriate if the residence time of groundwaters exceeds the rates of reaction (Langmuir and Mahony, 1985). For most important reactions Langmuir and Mahony (1985) suggested that the reaction rates vary from a fraction of a second (hydration, acid-base complexation, adsorption and desorption), minutes to hours (oxidation-reduction, gas solution and exsolution), weeks (precipitation and dissolution), months (polymerisation and hydrolysis, isotopic exchange) and years (mineral crystallisation). Because the residence times of groundwaters range from a few days to thousands of years in deep or slow moving aquifer, chemical reactivity in most groundwater systems may be described by equilibrium concepts. An excellent review of all the processes listed above and can be found in Tanji and Valoppi (1989).

Because of the great capacity of most heavy metals to be adsorbed onto oxides and clays in soils, it is generally considered that heavy metals are immobilised in the soil zone and do not contribute greatly to groundwater contamination. However, preferential flow paths in an aquifer cause increased transport of metals than would be predicted from uniform-flow contaminant transport models (Pang and Close, 1999). In addition, there are many competing reactions taking place in the soil zone and in the aquifer that may mobilise heavy metals. In particular the redox and pH conditions in the aquifer, and the association of heavy metals with organic substances and colloids (Pang and Close, 1999), may create an environment conducive to heavy metal transport. For example, a study of an agricultural site in the Netherlands indicated that high concentrations of nitrate in manure applications gave rise to a series of chemical reactions in the soil matrix that released heavy metals (including As) to the shallow groundwater (van Beek et al., 1989).

In February to April 1998, samples of groundwater were collected from all NGMP wells in 13 regions of the country for total dissolved heavy metals (copper, chromium, arsenic, and lead). No samples were collected from Southland and West Coast because they were not part of the

NGMP at the time. Samples were analysed by inductively coupled plasma mass spectroscopy to obtain low levels of detection. Samples were collected in special acid washed bottles, but were collected during the normal NGMP Autumn sample collection by regional council staff. Samples were field filtered and acidified with ultra pure nitric acid on-site, so that results represent total dissolved metals and not total metal concentrations. Blind duplicates were collected at some sites, but no special sampling techniques were introduced, so atmospheric or handling contamination may have occurred in some samples. However, the sampling gives an overall picture of metal concentrations in the NGMP and provides the first national coverage of metals in New Zealand (Rosen, 1998).

Eighty-seven samples were analysed for As, Cr, Cu, and Pb and detection limits for each element were As: 1 mg m^{-3} , Cu: 0.5 mg m^{-3} , Cr: 0.5 mg m^{-3} , Pb: 0.1 mg m^{-3} . As was detected in 23% (n=20) of the samples, Cu in 89% (n=77), Cr in 17% (n=15), and Pb in 93%(n=81) of the samples. Median values for As and Cr are equal to the detection limit of the method, indicating that these elements are rare in the groundwater that was sampled. However, of the 20 samples that had detectable As, 8 were from the Bay of Plenty (4) and Gisborne (4) out of 12 bores from which groundwater was sampled. Concentrations of As were low between 12 and 1 mg m^{-3} (Figure 6.7), but because As was found in such a large percentage of samples compared to other areas, it suggests that the correlation is real. The highest concentration of As recorded was from Canterbury at 54 mg m^{-3} , and 3 other wells had As concentrations above the New Zealand drinking water standard of 10 mg m^{-3} (Figure 7.7) only one of which (Bay of Plenty) was located near geothermal activity. Because the concentration in groundwater from the Canterbury well was high compared to all the other wells where groundwater was sampled, groundwater from the well was sampled again by Environment Canterbury to ensure the result was not anomalous. They again found high concentrations of As in the groundwater. This led to a relatively intensive study by Environment Canterbury to try to detect the reason for the high As concentrations. The investigations revealed that the soil near the well was also contaminated with As and groundwater from other wells in the area were also contaminated (Hayward and Smith, 2000). It was determined that the source of the As was from an old sheep foot trough site (used for controlling foot rot in sheep) located just up-gradient of the well, although other potential As sources may also exist in the area. Even though the aquifer is confined, and the foot trough has not been used in over 50 years, the persistence of As in the soil and the potential for it to leach into the groundwater is high.

Arsenic bearing chemicals were used extensively in sheep and cattle dips for the control of parasites in the first half of the twentieth century (Hadfield and Smith, 1999), and many thousands of these sites still exist throughout the country. In addition, later preparations for dipping sheep in the mid-twentieth century also included organochlorine compounds (such as dieldrin, hexachlorocyclohexane, DDT, DDE, aldrin, and endrin), which are environmentally persistent. Dipping sites were often located adjacent to water supplies. Hadfield and Smith (1999) estimated that the Waikato region alone contains over 10,000 sheep dip sites. Given the number of sites and the persistence of As in soil and groundwater, it is likely that future investigations like the one in Canterbury will turn up further contamination.

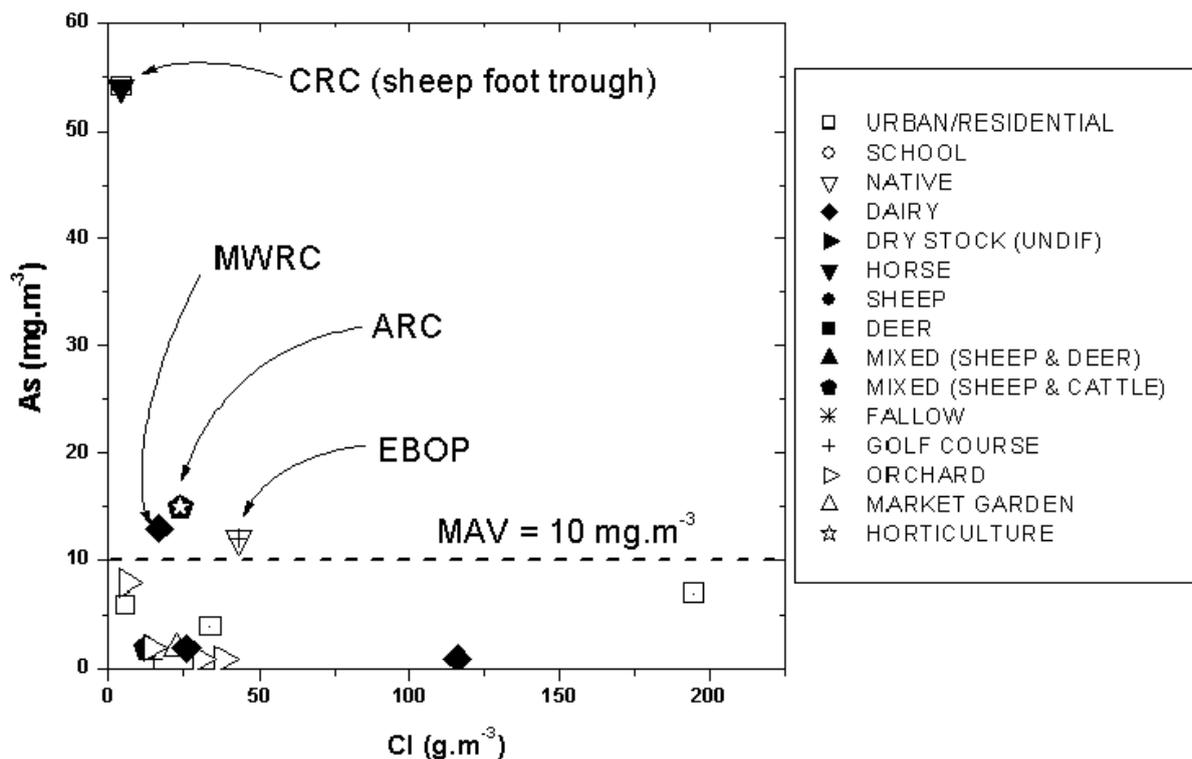


Figure 7.7 Arsenic concentrations plotted against chloride for those wells that contained As concentrations above the detection limit of the method. CRC = Canterbury Regional Council (now Environment Canterbury), ARC = Auckland Regional Council, MWRC = Manawatu-Wanganui Regional Council (now Horizons.mw), and EBOP = Environment Bay of Plenty (from Rosen, in press).

Heavy metals are routinely measured in the Bay of Plenty groundwater monitoring network (Hodges, 1994; 1995). Four of the five sites monitored for the NGMP were analysed for heavy metals under the Environment Bay of Plenty (EBOP) survey. The results of the 1995 EBOP survey indicated that two of the wells had higher arsenic concentrations at that time, than those found in the NGMP survey. However, it is not clear in the report whether the results are for total metal concentrations (which include sediment in the sample) or for total dissolved metals (filtered samples). The concentrations found by EBOP were above the MAV for arsenic (Hodges, 1995). Results from the Bay of Plenty samples and samples collected as part of a survey of arsenic in New Zealand drinking water supplies indicate that areas where natural geothermal activity is common may also have high (greater than the NZ MAV) arsenic concentrations (Davies et al., 1994). In addition, Davies et al. (1994) also found high concentrations (3-4 mg m⁻³) of arsenic in Napier City wells but their investigation could not determine the cause of these high concentrations.

The MAV for As was lowered from 50 mg m⁻³ to 10 mg m⁻³ in 1994 (Davies et al., 1994). This lower value was calculated from data on lifetime risk of incidence of skin cancer. However, there is increasing evidence that there are links between the incidence of internal cancers and arsenic concentrations in water supplies at lower concentrations (Davies et al., 1994). For these reasons the US EPA is proposing to lower the arsenic MAV to 5 mg m⁻³ (Andres, 2000). If New Zealand were to follow this example, many water supplies on the North Island would be above this MAV. For these reasons, it is recommended that As be included as an indicator of geothermal or other natural contamination and as an indicator of possible contamination due to agricultural or industrial activities.

The highest recorded concentration of Cr in the groundwater was 6 mg m⁻³. Most samples were below 1 mg m⁻³, and no trends can be ascertained from this data. Cr concentrations are unlikely to be a good indicator for groundwater quality due to its generally low concentration in New Zealand groundwater. Although the number of wells with detectable Pb was high, the concentrations were low, (most <1 mg m⁻³, high of 6 mg m⁻³). Because clean sampling techniques were not used, it is possible that the lead detected was from atmospheric or other contamination during the sampling process. However, if further clean sampling could be conducted, this issue could be resolved. Lead may be a good indicator of urban or industrial pollution and because of this should be considered as a tentative indicator until further testing

can be done. Copper was detected in all regions at low levels (Figure 7.8). The maximum concentration was 31 mg m^{-3} in the Manawatu-Wanganui region. The average concentration is 3 mg m^{-3} and the median is 1 mg m^{-3} . High concentrations seem to be more prevalent in rural areas than in urban areas (which were often below detection), suggesting that agrichemicals may influence Cu concentrations or that there is wider rural use of pipework and fittings that include copper. However, further work needs to be done to substantiate this apparent relationship. Because copper is relatively insoluble in soil solutions, Cu is not recommended as a primary indicator at this time. No other relationship to land uses could be determined from the data.

7.4.1 Heavy metal sampling techniques

Details of techniques used for heavy metal sampling, including clean sampling, are described in Rosen et al. (1999). The main concern about sampling for heavy metals is whether to sample for total metals (no field filtering) or for total dissolved metals (including filtering in the field). The NGMP samples discussed above included field filtering, but many councils and consultants do not filter in the field. There are pros and cons to both methods and neither method will necessarily give more accurate results. From a drinking water standard point of view it is the total amount of metals that are ingested that can pose a risk to human populations, therefore monitoring of total metals may be more appropriate in this context. However, this means that metals that are bound to sediment or piping materials will also be included in the analysis and the result may be more representative of the plumbing system than the conditions in the aquifer. Although total dissolved metal analyses should be undertaken and can be useful in comparison to total metal concentrations, we recommend that total metals be routinely analysed as the indicator because of human health considerations.

7.5 Pesticides as indicators

The results presented in this section have been published in two papers by Rosen et al. (2000) and Close and Rosen (in press). This section is a summary of Rosen et al (2000). However, the interested reader should consult both of these papers for more detail.

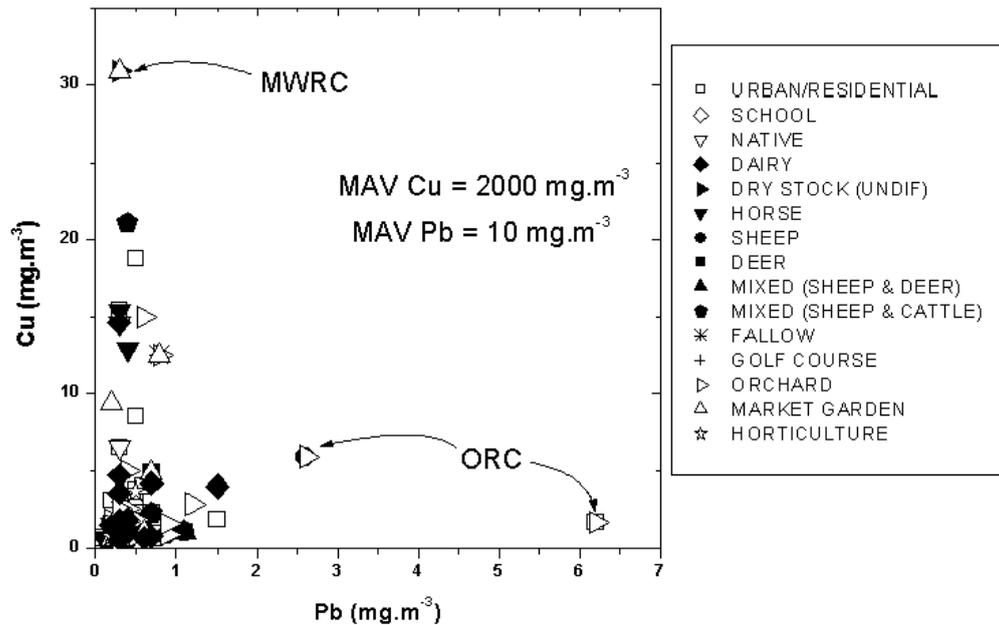


Figure 7.8 Copper concentrations plotted against lead. Note that all samples of both elements are below the New Zealand MAV. ORC = Otago Regional Council (from Rosen, in press).

Holland and Rahman (1999) have recently surveyed pesticide usage in New Zealand. They found that total pesticide use (excluding mineral oil) grew from about 3300 tonnes of active ingredient (ai) per annum in 1983 to a peak of about 3700 tonnes ai per annum in 1994 and then declined to the 1998 total of 3300 tonnes. Herbicides continue to dominate pesticide use (68%), followed by fungicides (24%) and insecticides (8%).

Previous national and regional groundwater surveys have shown the presence of low levels of pesticides in some groundwater systems, particularly those shallow unconfined systems that are vulnerable to pollution. The first national survey of pesticides in groundwater took place in 1990 (Close, 1993a,b). A second survey was conducted in 1994 (Close, 1996). Seven different pesticides were detected in the 1990 survey, mostly at concentrations $< 1 \text{ mg m}^{-3}$. However, one well had 37 mg m^{-3} of atrazine, which was significantly higher than allowed by the drinking water guidelines current at that time.

The second national survey in 1994 aimed to provide a more even geographic distribution of wells than the first survey, with sampling taking place in most regions throughout New Zealand. There were no wells with pesticides present in groundwater above the Maximum Acceptable Value (MAV) for drinking water (Ministry of Health, 1995) in the second survey. Pesticides were detected in groundwater from 16 out of the 118 wells sampled (13.6%), with most (78%) levels below 1 mg m^{-3} . Ten different pesticides were detected, with the triazine group being the most frequently found.

A third national pesticide survey was conducted in the summer of 1998/1999 to provide a national overview of pesticides in New Zealand's groundwater systems, to examine changes with time from earlier surveys, and to examine factors linked with pesticide contamination. This survey was conducted as part of this Sustainable Management Fund project and as part of the National Groundwater Monitoring Programme (NGMP). This third survey was conducted in a similar manner to the second survey. However, as part of this survey, two enzyme-linked immunosorbent assay (ELISA) test kits were evaluated for their usefulness in providing an indication of pesticide contamination in New Zealand. The reason for testing the ELISA kits is that analysing for a full spectrum of pesticides using standard gas chromatography-mass spectroscopy (GC-MS) techniques is costly (approximately \$300 NZ per sample), but ELISA test kits commonly cost less than \$20 NZ per sample (excluding labour costs). However, the ELISA test kits are specific to one pesticide, or group of pesticides, so that multiple tests would be needed on each sample if the pesticide in the sample is unknown. If a particular test kit could be utilised that would provide a reliable indication of whether pesticides were present in the sample, or not, then significant savings in monitoring costs could be achieved.

This section presents the results of testing the "normal" and high sensitivity atrazine test kit against GC-MS analysis of groundwater samples collected as part of the third national survey. Atrazine was chosen to test because triazine-group pesticides have been detected in many of the wells sampled in previous surveys (Close, 1993b, 1996). However, the atrazine test kit has cross reactivity with at least 11 other pesticides. Atrazine and related triazines are widely used in New Zealand as a herbicide, and a high sensitivity kit is available that allows detection down to 0.015 mg m^{-3} .

7.5.1 Well selection

Wells were selected to give a good overlap with wells in the NGMP (see Rosen, 1997; 1999 for details). This enabled the NGMP chemical composition data to assist interpretation of the pesticide results. About 50% of the wells sampled where groundwater was sampled for pesticide analysis were in the NGMP. Other selection criteria were the importance of each aquifer to the region, the application rate of pesticides in the area, and the vulnerability of the aquifer to contamination. Shallower, unconfined aquifers would be expected to be more at risk than deeper aquifers. Information was requested at each site for well location, water level, depth of the well screen, the type of aquifer and the general land use in the area. A balance was sought between selecting wells that were most vulnerable to contamination (screened near the water table), and wells that reflected the general usage of the aquifer. Sixty-eight percent of the selected wells were from unconfined aquifers. The location of the sampled wells is given in Figure 7.9.

All the regional councils and unitary authorities with groundwater management responsibility participated in the survey. In law all regional and unitary authorities have responsibility for groundwater management. You need to rephrase this to recognise that one chose not to be involved. The level of involvement and number of wells from which groundwater was sampled in each region depended on the usage of pesticides in the region, the importance of groundwater resources to the region, and whether the council had recently carried out regional monitoring of pesticides. A total of 98 groundwater samples were taken from 95 wells (Table 6.5) and analysed by GC-MS. Three blind duplicate samples were also taken. A total of 93 groundwater samples were analysed by the "normal" atrazine test kit and 29 samples were analysed using the high sensitivity atrazine test kits.

7.5.2 Sampling and analyses

Water levels were recorded where possible and the wells were flushed before sampling. The groundwater temperature was recorded for most wells. If the wells were part of the NGMP then samples of groundwater from each of them were also collected for major chemical component analysis.

7.5.3 GC-MS

Samples were collected in three 1-liter solvent-washed glass sample bottles containing sodium thiosulphate preservative. These were sent to ESR for pesticide analysis. The samples were analysed for acid herbicides and semi-volatile organic compounds (SVOC) using gas chromatography with mass spectrometry detector (GC-MS). The acid herbicide analysis involved solid phase extraction and derivatisation of the extract with diazomethane followed by GC-MS measurement. The SVOC analysis involved extraction with dichloromethane and analysis by GC-MS. The detection limits for this survey were significantly lower than the limits for the earlier national surveys by a factor of between 5 and 10 for the SVOC and were generally between 0.01 and 0.02 mg m⁻³ for SVOC, and were 0.1 mg m⁻³ for acid herbicides. Non target compounds were identified by a mass spectral library search and, where possible, quantified against an authentic standard. Two triazine metabolites, desethyl atrazine (DEA) and deisopropyl atrazine (DIA), were also analysed as part of the SVOC scan. Three samples were taken in the field as blind duplicates with dummy well identification, and analysed to give a quality control check.

The two triazine metabolites were included as pesticides in the reporting of the number of pesticide detections and in the subsequent data analysis. Both DEA and DIA are phytotoxic, with DEA being almost as phytotoxic as atrazine, and DIA being five times less phytotoxic than atrazine (Kaufman and Kearney, 1970). These two metabolites are structurally and toxicologically similar to atrazine, and are treated as pesticides in this study.

7.5.4 ELISA test kits

One 40 ml solvent-washed glass vial per well was collected for ELISA analysis and sent to The Institute of Geological & Nuclear Sciences Ltd., Wairakei Research Centre, for analysis. Samples were kept chilled below 4°C until analysed. The samples were analysed following the directions accompanying the Ohmicron RaPID Assays test kits. The groundwater sample to be tested was added, along with an enzyme conjugate, to a disposable test tube, followed by paramagnetic particles with antibodies specific to triazines attached. Both the atrazine, which may be in the sample, and the enzyme labeled atrazine (the enzyme conjugate) compete for antibody binding sites on the magnetic particles. After an incubation period of 15 minutes at room temperature, a magnetic field was applied to hold the paramagnetic particles (with the atrazine) in the tube and allow the unbound reagents to be decanted. The particles were then

washed with a washing solution after decanting. The presence of atrazine was detected by adding the enzyme substrate (hydrogen peroxide) and the chromogen (3,3',5,5'-tetramethylbenzidine). The enzyme-labeled atrazine analog bound to the atrazine antibody catalyses the conversion of the substrate/chromogen mixture to a coloured product. The reaction was stopped after a 20 minute incubation period and stabilised by the addition of acid. The colour developed is inversely proportional to the concentration of atrazine in the sample. The coloured sample was then quantitatively analysed at 450 nm wavelength on a Perkin Elmer Lambda 6 UV/VIS spectrophotometer. The washing solution was used as a blank during the analysis. The high sensitivity (HS) atrazine test kit followed a similar procedure to the "normal" atrazine test kit outlined above, except that after the enzyme conjugate was added the solution was incubated for 30 minutes at room temperature. Standards are provided with the test kits so that calibration curves can be achieved for both test kits. All analyses were done in duplicate to indicate the precision/repeatability of the analysis. There were insufficient HS atrazine test kits available to analyse all samples collected, so samples in which pesticides were detected using the GC-MS above the detection limit (0.015 mg m^{-3}) were chosen for analysis (Table 7.5). Eight additional samples from which no pesticides had been detected were chosen at random to assess the possibility of false positive results. No atrazine or cross reactivity products were detected in these samples.