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Groundwater quality monitoring 2012-13

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Prepared by:
John Hadfield

For:
Waikato Regional Council
PO Box 4010
HAMILTON EAST

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Peer reviewed by:
Jonathan Caldwell Date February 2014

Approved for release by:
Tony Petch Date March 2014

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Executive Summary

This report documents the routine groundwater quality monitoring undertaken by the Waikato Regional Council, primarily for the period 2012/2013. Reporting includes summary statistics from a regional network of 111 wells sampled annually, a community network of 81 wells sampled every two years and subset of 30 regional wells sampled quarterly. The regional network is designed to represent the range of groundwater characteristics across the region rather than investigate the impacts from specific point source discharges.

Results indicate clear evidence of substantial land-use impacts on groundwater quality. The most common anthropogenic contaminant is nitrate. Nitrate exceeded the maximum acceptable value (MAV) for drinking at 15.3% of the regional network wells. A further 17.2% are over half the MAV concentration and another 40.5% of wells have concentrations above normal background (< 1 g m^{-3}). Many of the remaining 27% have anaerobic conditions where nitrate cannot occur or may have water of an age older than farming influence. Nitrate most commonly exceeds the drinking water standards in the Pukekohe, Hamilton Basin and southern Hauraki Plains areas. Arsenic and manganese are natural determinands each exceeding the drinking water guidelines in about 5% of wells each.

Although there is similarly clear evidence of land-use impacts in the community network, only one of these supplies exceeded the MAV for nitrate (and is not used for potable supply). About 11% are above half the MAV for nitrate, while about half the wells have nitrate concentrations of 1 mg l^{-1} or less. A greater portion of community network wells have anaerobic groundwater (about 14% compared to 3.6% for regional networks). Manganese and arsenic are the determinands which most commonly exceed their MAVs in the community network (7.4% and 3.84% exceedances respectively). The community wells are sampled before any treatment which may be undertaken to meet MAVs for potable supply.

Quarterly monitoring of a subset of 30 regional wells commenced predominantly in 1995. Nitrate concentration trend analyses from these records shows that 30% are increasing while 40% are decreasing.

Pesticide and microbial occurrences are also monitored four yearly at selected regional and community wells. Pesticides were not detected at 77.5% of the 40 regional sites used and 95% of the selected community wells. There was one exceedance in each of the networks, both being for the organochlorine dieldrin. Other pesticides detected were predominantly from the relatively mobile and persistent triazine group (all below half MAV concentration).

Micro-organism occurrence in groundwater is the highest priority quality concern from a health perspective. *E. coli* analysis of samples from 61 regional and 21 community wells was undertaken. These included 14 wide diameter wells (one being for a community supply), which are more likely to be contaminated as they are shallow and more difficult to seal. *E-coli* were detected in 57% of the wide diameter wells and about 3% of narrow diameter wells.

1 Introduction

1.1 Background

The groundwater quality monitoring programme gathers information to enable effective management of this resource which is a council responsibility under the Resource Management Act. It provides a snapshot of groundwater quality in the Waikato region as well as indicating spatial and temporal trends. The groundwater quality is compared with standards and guidelines to assess its suitability for use. The monitoring data can be used to examine factors which influence the observed quality (essentially land-use). In the long-term, the monitoring information enables an evaluation of the effectiveness of management of this resource. This dataset is of increasing value. It is important to continue gathering comprehensive and reliable data to enable informed management of our groundwater resources in the future.

The primary objective of this report is to document the groundwater quality monitoring undertaken in the period from autumn 2012 to the summer of 2012/2013. It includes annual monitoring of regional and community networks (described in sections 2 to 4) and quarterly sampling at a lesser number of sites focused on nitrate and pesticide occurrence. There are other datasets related to specific investigations, such as the Lake Taupo catchment and Coromandel coastal aquifer studies, which are not included in this report.

This data report is the second in this format since the implementation of the Regional Groundwater Monitoring Programme. Routine monitoring of groundwater began in 1995 with a relatively smaller number of sites (~30). A larger regional network of 108 wells was established in 1996 and was monitored for two years on a six monthly basis. In 2002 this network was increased to 112 and in 2004 110 of these wells were monitored annually. Approximately this number has been maintained since, although some sites have changed by necessity.

A subset of about 30 of the regional network wells has been monitored quarterly. The quarterly and annual sampling of the ‘Regional’ network is represented in Appendix 1. This shows that for various, predominantly logistic, reasons not all wells have the same length of record.

A ‘Community’, network described in section 2 was established in 2000 (Hadfield and Nicole, 2000). This comprised a total of 90 school supplies which is sampled two yearly. Other community supply information was collated from available external district supply data in 2000. A total of 89 schools were sampled in 2002/3 and 88 in 2004. A total of 80 or more school monitoring wells has been maintained in the network since. Again data records vary in length due to school closures and logistic reasons.

An electronic copy of this report can be obtained from the Waikato Regional Council website: www.waikatoregion.govt.nz/publications.

1.2 Report content

This report provides information on the routine annual monitoring of groundwater quality at regional and community sites across the Waikato region. Summary information is also provided for quarterly monitoring of about 30 sites to investigate nitrogen trends and four sites for pesticide occurrence. The annual plan performance target for regional groundwater quality monitoring is 110 regional sites and 80 community (school) sites.

The principal objectives of this report are to document the monitoring networks and present summary statistics. Recent (2012/13) regional and community network results are compared with drinking water standards and guidelines. Trends in nitrate and pesticide occurrence at selected sites are also presented.

1.3 Water quality guidelines and standards

The drinking-water standards apply to water that is designed to be used for human consumption, food preparation, utensil washing, oral hygiene or personal hygiene. They are intended to protect public health and be appropriate for large community, as well as privately owned, drinking-water supplies.

The standards alone are not sufficient to protect against health risks from contaminated drinking-water. They define, based on current knowledge, chemical concentrations that constitute no significant health risk to a person (weighing 70 kg) who consumes two litres of that water a day over their lifetime (assumed to be 70 years). A degree of uncertainty over the magnitude of the risk always exists. Although the standards are set with respect to health risk, aesthetic guidelines are also provided. This is because the public generally assesses the quality of water on aesthetic perceptions. The use of multiple barriers to protect against supply contamination decreases risk and the reliance on supply treatment (MoH, 2005). Notably this includes source water protection.

Table 1 lists the maximum acceptable values for inorganic determinands of health significance from the Ministry of Health Drinking-water Standards for New Zealand (MoH, 2005). Datasheets for the determinands that have been found to exceed these standards are included in Appendix V. Table 2 lists guideline values for aesthetic determinands, which have nuisance rather than health significance. Again datasheets are included in Appendix V for determinands that have been found to exceed these standards.

The following abbreviations are used in Tables 1 and 2.

ATO	Concentrations of the substance at or below the health-based guideline value that may affect the water's appearance, taste or odour.
DBP	Disinfection by-product. Any difficulty meeting a DBP MAV must never be a reason to compromise adequate disinfection. Trihalomethanes and haloacids are DBPs. Some DBPs may also have other sources.
NTU	Nephelometric turbidity unit.
PMAV	Provisional MAV (because it is provisional in the WHO Guidelines (GDWQ) or the WHO has no guideline value but the DWSNZ has retained a MAV or developed its own).
TCU	True colour unit. The colour after the sample has been filtered.
WHO	World Health Organization.

Table 1: Maximum acceptable values (MAVs) in mg/L for inorganic determinands of health significance (reproduced from Ministry of Health, 2005)

Name	MAV	Remarks
Antimony	0.02	
Arsenic	0.01	For excess lifetime skin cancer risk of 6 x 10^{-4}. PMAV, because of analytical difficulties
Barium	0.7	
Beryllium[1]	0.004	PMAV
Boron[2]	1.4	
Bromate	0.01	For excess lifetime cancer risk of 7 x 10^{-5}. PMAV
Cadmium	0.004	
Chlorate	0.8	PMAV. Disinfection must never be compromised. DBP (chlorine dioxide)
Chlorine	5	Free available chlorine expressed in mg/L as Cl_2. ATO. Disinfection must never be compromised
Chlorite	0.8	Expressed in mg/L as ClO_2. PMAV. Disinfection must never be compromised. DBP (chlorine dioxide)
Chromium	0.05	PMAV. Total. Limited information on health effects
Copper	2	ATO
Cyanide	0.08	Total cyanides
Cyanogen chloride	0.08	Expressed in mg/L as CN. Total. DBP (chloramination)
Fluoride[3]	1.5	
Lead	0.01	
Lithium[1]	1	PMAV
Manganese	0.4	ATO
Mercury	0.002	Total
Molybdenum	0.07	
Monochloramine	3	DBP (chlorination)
Nickel	0.02	PMAV
Nitrate, short term[4]	50	Expressed in mg/L as NO_3. The sum of the ratio of the concentrations of nitrate and nitrite to each of their respective MAVs should not exceed one
Nitrite, long term	0.2	Expressed in mg/L as NO_2. PMAV (long term)
Nitrite, short term[14]	3	Expressed in mg/L as NO_2. The sum of the ratio of the concentrations of nitrate and nitrite to each of their respective MAVs should not exceed one
Selenium	0.01	
Silver	0.1	PMAV
Uranium	0.02	PMAV

Notes: Where WHO Guideline values are based on 60 kg bodyweight, the DWSNZ uses 70 kg bodyweight. See the datasheets for calculations (WHO 2004).

1 MAV retained despite no WHO guideline value.

2 WHO guideline PMAV is 0.5 mg/L.

3 For oral health reasons the Ministry of Health recommends that the fluoride content for drinking-water in New Zealand be in the range of 0.7–1.0 mg/L. This is *not* a MAV.

4 Now short term only. The short-term exposure MAVs for nitrate and nitrite have been established to protect against methaemoglobinaemia in bottle-fed infants.

Table 2: **Guideline values (GV) for aesthetic determinands** (reproduced from Ministry of Health, 2005)

Determinand	**GV**	Units	**Comments**
aluminium	0.10	mg/L	Above this, complaints may arise due to depositions or discoloration.
ammonia	1.5 0.3	mg/L	Odour threshold in alkaline conditions. For control of chloramine formation in chlorinated water.
calcium			See hardness.
chloride	250	mg/L	Taste, corrosion.
chlorine	0.6–1.0	mg/L	Taste and odour threshold (MAV 5 mg/L)
2-chlorophenol	0.0001 0.01	mg/L	Taste threshold. Odour threshold.
colour	10	TCU	Appearance.
copper	1	mg/L	Staining of laundry and sanitary ware (PMAV 2 mg/L)
1,2-dichlorobenzene	0.001 0.002	mg/L	Taste threshold. Odour threshold (MAV 1.0 mg/L)
1,4-dichlorobenzene	0.0003 0.006	mg/L	Odour threshold. Taste threshold (MAV 0.4 mg/L)
2,4-dichlorophenol	0.0003 0.04	mg/L	Taste threshold. Odour threshold.
ethylbenzene	0.002 0.08	mg/L	Odour threshold. Taste threshold (MAV 0.3 mg/L)
hardness (total) (Ca + Mg) as $CaCO_3$	200 100–300	mg/L	High hardness causes scale deposition, scum formation. Low hardness (<100) may be more corrosive. Taste threshold.
hydrogen sulphide	0.05	mg/L	Taste and odour threshold.
iron	0.2	mg/L	Staining of laundry and sanitary ware.
magnesium			See hardness.
manganese	0.04 0.10	mg/L	Staining of laundry. Taste threshold (MAV 0.4 mg/L)
monochlorobenzene	0.01	mg/L	Taste and odour threshold (MAV 0.3 mg/L)
odour (threshold odour number)	3		Odour should be acceptable.
pH	7.0–8.5		Should be between 7.0 and 8.0. Most waters with a low pH have a high plumbosolvency. Waters with a high pH: have a soapy taste and feel. Preferably pH <8 for effective disinfection with chlorine.
sodium	200	mg/L	Taste threshold.
styrene	0.004	mg/L	Odour threshold (MAV 0.03 mg/L)
sulphate	250	mg/L	Taste threshold.

Determinand	GV	Units	Comments
taste			Should be acceptable to most consumers.
temperature			Should be acceptable to most consumers, preferably cool.
Toluene	0.03 0.04	mg/L	Odour. Taste threshold (MAV 0.8 mg/L)
total dissolved solids	1000	mg/L	Taste may become unacceptable from 600–1200 mg/L.
trichlorobenzenes (total)	see below		(MAV 0.03 mg/L)
1,2,3-trichlorobenzene	0.01	mg/L	Odour threshold.
1,2,4-trichlorobenzene	0.005	mg/L	Odour threshold.
1,3,5-trichlorobenzene	0.05	mg/L	Odour threshold.
2,4,6-trichlorophenol	0.002 0.3	mg/L	Taste threshold. Odour threshold (MAV 0.2 mg/L)
Turbidity	2.5	NTU	Appearance. For effective terminal disinfection, median turbidity <1 NTU, single sample <5 NTU.
Xylene	0.02	mg/L	Odour threshold (MAV 0.6 mg/L)
Zinc	1.5	mg/L	Taste threshold. May affect appearance from 3 mg/L.

2 Groundwater quality monitoring networks

2.1 Monitoring well network design

The regional groundwater quality network is designed to represent the range of groundwater characteristics across the region. It is not designed to investigate the impacts on quality of specific point source discharges. Figure 1 shows the network is widely distributed spatially.

Groundwater systems are three dimensional and substantial changes in groundwater quality can occur with depth. Groundwater may therefore be monitored at the same location at various depths. Figure 1 shows the distribution of sampling wells in the monitoring network. This regional network was selected to represent predominantly vulnerable aquifers with relatively young groundwater primarily in aerobic condition. Wells with significant iron concentrations are under-represented in this network. There are few wells representing ‘ambient’ conditions apart from where older groundwater may have been sampled. Water quality records are not long enough to show very long-term trends which often occur in groundwater. Monitoring well construction and other details are provided in Appendix II.

There are very few dedicated sampling wells and therefore monitoring is dependent on access to available, predominantly privately owned wells. As a consequence there have been changes to access over time resulting in monitoring records of variable length (Appendix I). There are two changes in the regional monitoring network since the previous report. Well 65-8 has been replaced by well 72-5510 and well 71-26 has been replaced by well 72-2138. Both are due to wells ‘collapsing’.

Given that, where possible, water supply wells are drilled to avoid poor quality water and lesser permeable formation; such situations are expected to be under-represented in the network. Apart from spatial distribution, an important criterion is that wells are properly documented to inform interpretation. This is with regard primarily to both well construction and geology. Some early exceptions are progressively being rectified.

An initial smaller groundwater monitoring network was focused on nitrate occurrence and excluded wells with iron-rich or anaerobic groundwater. About 30 of these wells have been retained as part of the regional network but are monitored quarterly (denoted with N for 'Nitrate' sub-network) in Table 3.

Wells monitored in 2012-2013 are summarised in Table 4 and their locations are illustrated in Figure 1. A total of 111 wells were sampled including 10 wells (designated by *) which are monitored as part of the National Groundwater Quality Programme (NGMP). These are sampled by Waikato Regional Council for analysis by the Institute of Geological and Nuclear Sciences. Wells samples which are also analysed four yearly to produce pesticide and microbial environmental indicators are shown with a (P) and (M) respectively. These are environmental indicators derived from both regional and community groundwater networks, which can be found on the www.waikatoregion.govt.nz website.

A community monitoring network was introduced in 2000 for three principal reasons, which are firstly, to provide a network of school supplies that would be of particular interest to the community, secondly to provide an objectively determined network and finally to provide a stable network with dependable access. This last aspect has not been as dependable as initially thought given changes to rural schools. Also as these supplies require potable water, they tend to be shut down once exceedances occur, thereby skewing the results slightly towards higher quality.

The community monitoring network is monitored every two years (due to cost and logistic constraints) and the current network of 81 schools is illustrated in Figures 1. The following changes have been made to the community network since the previous report: wells 60-314 (Puriri Valley) and 64-881 (Mangateparu) are no longer available or included and 65-142 (Maihihi), 72-749 (Otewa) and 71-63 (Aria) have been added. Three further schools have now been renumbered 64-500 (Manuwaru) to 72-5981, 64-994 (Ngarua) to 72-2137 and 69-2073 (Ngati Haua) to 72-2047 (new well).

The relatively low frequency of groundwater monitoring reflects the low velocities and slow changes seen in groundwater quality. Deeper groundwater may be quite old with substantial lags being evident between land-use change and groundwater quality impacts. The low frequency of groundwater monitoring does however extend the period required to gather sufficient records for statistical analysis.

There are four wells monitored quarterly for pesticide occurrence. These are wells where a range of pesticides have been detected and for which ongoing monitoring has been undertaken to enable more detailed analysis and modelling (Hadfield and Smith, 1995, Technical Report 2011/14). They are a subset of the regional monitoring network.

There are site sheets for each monitoring well documenting the location with finder diagrams, photos of the wells and pumping equipment. They also describe the sampling procedure and list any safety and health concerns and requirements. A characteristic of monitoring non-dedicated wells is that logistics frequently change and site sheets must be continually updated. Examples of site sheets for both the regional and community networks are included in Appendix IV.

Site information for the regional monitoring network is included in Table 4. This includes well and screen depths. Aquifer characteristics and land-use are also described. These are subsequently summarised as part of factor analysis.

Table 3: Regional groundwater monitoring network (wells grouped by district)

(N = quarterly nitrate monitoring; M = microbial indicator, P = pesticide indicator and * =National Groundwater Monitoring Programme)

Map No.	Well	Map Reference	Indicator
Coromandel			
1	60-12	T11:549-811	P,N,*
2	60-124	T11:514-810	
3	60-167	T12:633-487	M
4	60-190	T11:608-805	M
5	63-269	T12:674-315	M
6	60-316	T12:346-583	M
7	60-345	T12:590-559	M
8	60-348	T11:639-630	P,M
9	72-3559	T10:536-937	
10	60-407	T10:442-950	M
11	60-480	T11:331-653	M
12	72-2691	T12:658-388	
Franklin			
13	61-113	R12:832-388	P, N
14	61-126	R13:607-298	M,N
15	61-135	R12:667-367	P,M
16	61-143	R13:853-287	P,M
17	61-208	R12:668-365	N
18	61-221	R13:872-253	N
19	61-230	R13:885-276	
20	61-245	R13:800-287	P
21	61-258	R12:821-351	N, *
22	61-280	R13:845-287	P,N
23	61-54	R12:834385	P,M
24	61-59	R13:791-285	P,M,N
25	61-702	R13:874-256	
26	61-85	R12:652-359	P,M, *
27	61-93	R13:861-289	P,M, *
Hauraki			
28	63-201	T13:656-166	P,M
29	63-240	T13:592-183	
30	63-328	T13:668-215	
31	63-43	S13:229251	
32	63-57	T13:414204	P,M,N
33	63-74	S12:229-300	
34	63-78	T13:670-165	M
35	72-1223	T13:639-211	
Matamata-Piako			
36	64-108	T14:465-802	M,N
37	64-111	T14:413-846	
38	64-117	T14:565-844	N
39	64-12	T14:496-863	P,M,N
40	64-120	T15:510-655	P,N,*
41	64-20	T14:531-738	P,M

Map No.	Well	Map Reference	Indicator
42	64-43	T14:546-712	M,N
43	64-46	T14:557-780	N
44	64-50	T14:595-797	P,M,N
45	64-511	T14:544-741	*
46	64-7	T14:449-908	P,M
47	64-70	T14:557-901	M,N
48	64-831	T14:519-818	P
49	64_720	T13:372-045	*
Otorohonga			
50	65-4	S15:999-433	
51	65-6	S16:091-358	M
52	72-5510	S16:135-261	P,M
Rotorua			
53	66-58	U17:048-996	M
54	66-6	U16:943-152	P,M,N
55	66-92	U17:017-019	
56	66-93	U17:017-019	P
57	66-96	U17:053-958	
South Waikato			
58	67-11	T15:535-620	N
59	67-15	T15:580-510	P,M,N
60	72-4500	T16:593-246	M
61	67-4	T16:582-244	P
62	67-404	T16:596-292	M
63	67-483	T16:582-244	
64	67-55	T16:591-395	M
65	67-573	T16:568-398	M
66	67-83	T16:598-345	
Taupo			
67	68-301	T17:656-804	M
68	68-317	T17:605-811	M
69	68-320	U18:749-747	P,M
70	72-3696	U18:771-678	P,M
71	68-912	U18:830-764	M
72	68-964	T18:506-533	*
73	72-1008	T17:526-844	P
74	72-1011	T18:674-758	
75	72-1069	T18:440-775	
76	72-1072	T18:442-602	
77	72-1081	T18:422-545	P
78	72-1082	T18:429-565	
79	72-1087	T18:442602	
80	72-1089	T18:440-775	
81	72-356	T17:685-821	
82	72-392	T17:609-813	M
83	72-431	T17:528-806	
Waikato			
84	69-163	S14:156-795	P,M
85	69-1709	S14:228-743	M, *

Map No.	Well	Map Reference	Indicator
86	69-173	S14:151-871	M,N
87	69-19	S14:193-751	P,M
88	69-248	S14:192-779	P,M
89	69-295	S14:238-717	P,M
90	69-365	S13:123-022	P,M,N
91	69-374	S14:211-746	P,M
92	69-62	S14:227-742	
93	69-81	S14:982-739	M,N
94	69-97	S14:242-816	P,M
95	62-5	S14:145-689	P,M
Waipa			
96	70-1134	S15:037-649	N, *
97	70-21	S15:238-661	M,N
98	70-22	S15:238-660	P,M,N
99	70-31	S15:295-668	M
100	70-44	S15:244-635	N
101	70-47	T15:303-689	P,M,N
102	70-50	S15:251-665	M
103	70-56	S15:204-660	P,N
104	70-65	S15:030-635	P,M,N
105	70-74	S15:040-546	P,M,N
106	70-76	T15:430-574	N
Waitomo			
107	71-1	S16:140-235	
108	72-2138	S16:992-213	M
109	71-3	S16:936-223	
110	71-4	S16:925-156	
111	71-5	S16:977-185	M

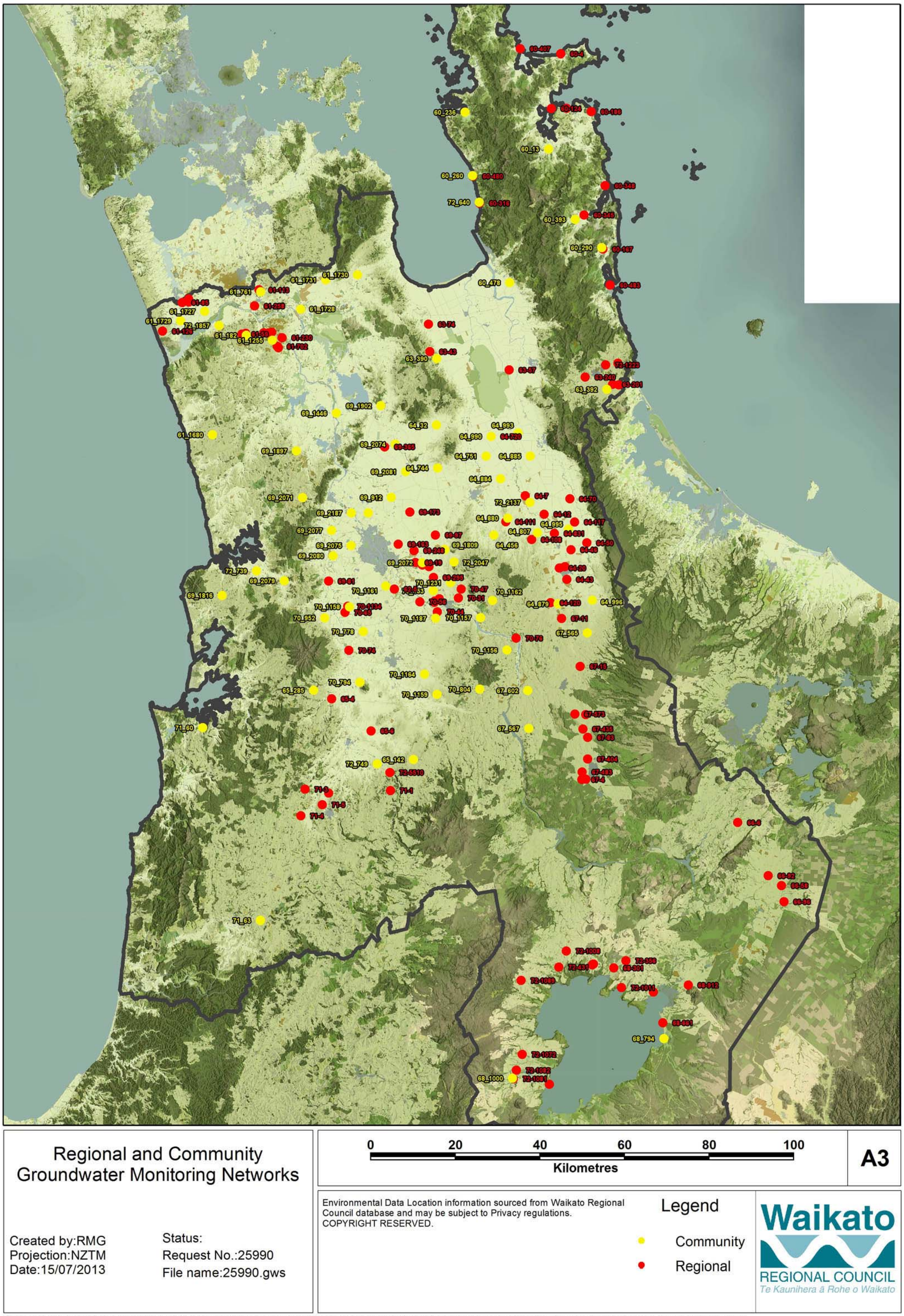


Figure 1: **Groundwater monitoring well networks**

Table 4: Regional groundwater monitoring network site information (from doc 1430954)

Well	Easting	Northing	Well Depth	Screen Top	Screen bottom	Lithology	Confinement	Land Use	Land Cover
62-5	2714570	6368910	6.2			Sand	Unconfined	Horticultural	High Producing Exotic Grassland
61-258	2682075	6435057	35	24.8	35	Basalt	Unknown	Agriculture	High Producing Exotic Grassland
60-4	2753610	6493800	4.1	0	4.1	Sand	Unconfined	Urban	High Producing Exotic Grassland
67-11	2753600	6362000	18.5	15.5	18.5	Pumice	Unknown	Dairy	High Producing Exotic Grassland
67-4	2758240	6324390	15			Ignimbrite	Unconfined	Dairy	High Producing Exotic Grassland
67-55	2759190	6339530	127			Ignimbrite	Confined	Agriculture	High Producing Exotic Grassland
70-74	2703970	6354600	6.71	3.66	6.71	Sand	Unconfined	Urban	Built-up Area
66-58	2804800	6299600	38	32.5	38	Ignimbrite	Unconfined	Dairy	High Producing Exotic Grassland
61-126	2660600	6429200	6.09			Sand	Unconfined	Dairy	High Producing Exotic Grassland
67-83	2759640	6334200	80			Ignimbrite	Unknown	Dairy	High Producing Exotic Grassland
70-21	2724000	6366100	6.41			Sand	Unconfined	Horticultural	High Producing Exotic Grassland
70-22	2723900	6365800	6.42			Sand	Unconfined	Horticultural	High Producing Exotic Grassland
60-124	2751370	6481020	6	3	6	Sand	Unconfined	Urban	Manuka and or Kanuka
70-31	2729500	6366800	4.82			Sand	Unconfined	Dairy	High Producing Exotic Grassland
60-12	2754978	6481067	9	2	6	Sand	Unconfined	Urban	High Producing Exotic Grassland
69-173	2718200	6386900	6	4	6	Pumice	Unconfined	Dairy	High Producing Exotic Grassland
61-59	2679100	6428500	26.6	19.5	26.6	Basalt	Confined	Urban	High Producing Exotic Grassland
63-57	2741465	6420005	5	3	5	Sand	Unconfined	Agriculture	High Producing Exotic Grassland
70-47	2730200	6368900	4.5	2.5	4.5	Sand	Unconfined	Dairy	High Producing Exotic Grassland
68-912	2783000	6276400				Ignimbrite	Unknown	Urban	High Producing Exotic Grassland
69-97	2724200	6381500	4.71			Sand	Unconfined	Horticultural	High Producing Exotic Grassland
61-93	2686100	6428900	26	19	26	Basalt	Unconfined	Forestry	Short-rotation Cropland
69-163	2715510	6379400	4	3.5	4	Sand	Unconfined	Urban	High Producing Exotic Grassland
64-20	2753090	6373770	9	5.2	8	Sand	Unconfined	Horticultural	High Producing Exotic Grassland
60-316	2734620	6458960	7	1	7	Gravel	Unconfined	Urban	Built-up Area
61-85	2665200	6435900	35	19.56	35	Basalt	Confined	Horticultural	High Producing Exotic Grassland
68-320	2774909	6274792	62	46	62	Ignimbrite	Unknown	Dairy	Indigenous Forest
60-186	2760688	6480260	76	24.4	76	Ignimbrite	Confined	Park/Reserve	High Producing Exotic Grassland
67-15	2757900	6350800	20			Pumice	Unconfined	Agriculture	High Producing Exotic Grassland
67-573	2756640	6339680	90			Ignimbrite	Confined	Dairy	High Producing Exotic Grassland
72-356	2768500	6282100	42	37	42	Ignimbrite	Confined	Urban	Other Exotic Forest

Well	Easting	Northing	Well Depth	Screen Top	Screen bottom	Lithology	Confinement	Land Use	Land Cover
61-113	2683137	6438799	13	10	13	Basalt	Unconfined	Horticultural	Short-rotation Cropland
70-44	2724630	6363600				Sand	Unknown	Dairy	High Producing Exotic Grassland
72-1223	2763970	6421150	92.5	19.1	92.5	Ignimbrite	Confined	Urban	Orchard and Other Perennial Crops
67-483	2758330	6326150				Ignimbrite	Confined	Dairy	High Producing Exotic Grassland
71-4	2692700	6316000	90		90	Limestone	Unknown	Dairy	Pine Forest - Open Canopy
72-5510	2713500	6326100	9.5	7.5	9.5	Ignimbrite	Unconfined	Dairy	High Producing Exotic Grassland
60-345	2758990	6456140	27	13	27	Ignimbrite	Unconfined	Dairy	High Producing Exotic Grassland
61-135	2666700	6436700	51.82	19.56	51.82	Basalt	Unconfined	Dairy	Short-rotation Cropland
72-1081	2742200	6254584	4.6	0.45	4.6	Sand	Unconfined	Urban	High Producing Exotic Grassland
68-964	2750601	6253247	5	2	5	Sand	Unknown	Agriculture	Built-up Area
72-431	2752822	6280632	48	45.7	48	Ignimbrite	Confined	Agriculture	High Producing Exotic Grassland
61-143	2685320	6428740	34	12	34	Basalt	Confined	Horticultural	Short-rotation Cropland
70-56	2720510	6365940	4.5			Sand	Unconfined	Dairy	High Producing Exotic Grassland
68-317	2760584	6281129	104	71	104	Ignimbrite	Unknown	Agriculture	High Producing Exotic Grassland
60-407	2744200	6495000	5			Sand	Unconfined	Urban	High Producing Exotic Grassland
63-328	2766800	6421500	49	19.5	49	Ignimbrite	Confined	Agriculture	High Producing Exotic Grassland
60-167	2763340	6448160	19.5	16.7	19.5	Sand	Semi-confined	Urban	High Producing Exotic Grassland
64-43	2754800	6371100	21.6	18.6	21.6	Sand	Unconfined	Urban	Urban Parkland/ Open Space
69-365	2712400	6402120	6	2.5	6	Pumice	Unconfined	Horticultural	High Producing Exotic Grassland
63-43	2722961	6424320	73	26	73	Greywacke	Confined	Agriculture	High Producing Exotic Grassland
64-12	2749570	6386340	11.5	9.5	11.5	Sand	Unconfined	Dairy	High Producing Exotic Grassland
61-702	2687400	6425600	44.5	21.46	44.5	Basalt	Unknown	Horticultural	High Producing Exotic Grassland
63-74	2722650	6430710	50.8	26.2	50.8	Greywacke	Confined	Dairy	High Producing Exotic Grassland
69-1709	2722530	6374470	5	2.5	5	Gravel	Unconfined	Dairy	High Producing Exotic Grassland
65-6	2709100	6335800	13	9.5	13	Ignimbrite	Unconfined	Dairy	High Producing Exotic Grassland
64-831	2751950	6381850	9	3	9	Pumice	Unconfined	Dairy	High Producing Exotic Grassland
64-50	2759510	6379630	16.1	14.3	16.1	Pumice	Unknown	Dairy	High Producing Exotic Grassland
61-221	2687600	6425300	44.5	20	44.5	Basalt	Unconfined	Agriculture	Orchard and Other Perennial Crops
71-1	2713600	6321900	10	4	10	Sand	Confined	Agriculture	High Producing Exotic Grassland
71-2138	2699200	6321300	49		49	Limestone	Confined	Agriculture	High Producing Exotic Grassland
63-240	2759200	6418300	91.5	58.5	91.5	Ignimbrite	Confined	Horticultural	High Producing Exotic Grassland

Well	Easting	Northing	Well Depth	Screen Top	Screen bottom	Lithology	Confinement	Land Use	Land Cover
67-38	2759240	6324460	25			Ignimbrite	Unconfined	Dairy	High Producing Exotic Grassland
69-248	2719200	6377900	2.75			Pumice	Unconfined	Horticultural	High Producing Exotic Grassland
69-62	2722693	6374153	9.15			Sand	Unconfined	Agriculture	High Producing Exotic Grassland
67-404	2759600	6329170	9			Ignimbrite	Unconfined	Dairy	High Producing Exotic Grassland
63-78	2767000	6416500	24	13	24	Ignimbrite	Confined	Dairy	High Producing Exotic Grassland
72-1089	2744056	6277506	36.2			Ignimbrite	Confined	Agriculture	Built-up Area
72-1069	2744056	6277506	11.7	2.7	11.7	Ignimbrite	Unconfined	Agriculture	Built-up Area
60-483	2765030	6439770	8.95	6		Sand	Unconfined	Urban	Built-up Area
72-392	2760908	6281338	93			Ignimbrite	Unconfined	Agriculture	High Producing Exotic Grassland
69-81	2699220	6370780	2.25			Unknown	Unknown	Dairy	High Producing Exotic Grassland
68-301	2765617	6280398	53.6	49	53.6	Ignimbrite	Confined	Dairy	High Producing Exotic Grassland
72-1072	2744279	6260255	21	14.5	20.5	Ignimbrite	Confined	Agriculture	Other Exotic Forest
72-1087	2744279	6260225	6.6	0.6	6.6	Ignimbrite	Unconfined	Agriculture	Other Exotic Forest
69-19	2719500	6375100	3.95			Pumice	Unconfined	Dairy	Orchard and Other Perennial Crops
70-1134	2703700	6364900	10.6	4	6	Sand	Unconfined	Horticultural	High Producing Exotic Grassland
65-4	2699900	6343300	33.6			Pumice	Unconfined	Urban	High Producing Exotic Grassland
66-92	2801700	6301890	48.5	17.2	19.16	Gravel	Unconfined	Dairy	High Producing Exotic Grassland
66-93	2801700	6301890	8	2	8	Gravel	Unknown	Urban	High Producing Exotic Grassland
71-3	2693700	6322200	26		26	Limestone	Confined	Forestry	High Producing Exotic Grassland
68-661	2777100	6267600	6	3	6	Gravel	Unconfined	Park/Reserve	Lake and Pond
66-6	2794600	6314300	38	32	38	Pumice	Unconfined	Dairy	High Producing Exotic Grassland
64-70	2755530	6389900	11.8	9.1	11.8	Pumice	Unconfined	Dairy	High Producing Exotic Grassland
61-230	2688500	6427650	43	18.3	43	Basalt	Unconfined	Horticultural	Short-rotation Cropland
61-208	2666750	6436030	18.3			Basalt	Unknown	Horticultural	High Producing Exotic Grassland
70-50	2725075	6366593	7.3			Sand	Unconfined	Urban	High Producing Exotic Grassland
61-245	2680000	6428700	14.5	8.5	14.5	Basalt	Unconfined	Horticultural	Built-up Area
64-720	2737200	6404500	6	2.8	6	Pumice	Unknown	Agriculture	High Producing Exotic Grassland
71-5	2697700	6318600	81.6		81.6	Limestone	Confined	Dairy	High Producing Exotic Grassland
60-348	2763890	6462970	13.5	6.5	13.5	Sand	Unconfined	Park/Reserve	Built-up Area
64-511	2754400	6374100	21.5	18.5	21.5	Pumice	Unknown	Dairy	Built-up Area
70-76	2742990	6357390	30			Ignimbrite	Unknown	Dairy	High Producing Exotic Grassland
69-295	2723700	6371600	6.35			Pumice	Unconfined	Horticultural	High Producing Exotic Grassland

Well	Easting	Northing	Well Depth	Screen Top	Screen bottom	Lithology	Confinement	Land Use	Land Cover
67-435	2758498	6336196	60			Ignimbrite	Unconfined	Dairy	High Producing Exotic Grassland
64-108	2746600	6380400	23	18.5	22.5	Sand	Confined	Horticultural	High Producing Exotic Grassland
64-46	2755780	6378030	12.1			Sand	Unknown	Urban	High Producing Exotic Grassland
70-65	2703030	6363450	4.3			Unknown	Unknown	Dairy	High Producing Exotic Grassland
64-7	2745180	6390620	7.92	4.26	7.92	Pumice	Unconfined	Dairy	High Producing Exotic Grassland
64-111	2740580	6384580	83	58.3	83	Ignimbrite	Confined	Dairy	High Producing Exotic Grassland
69-374	2721100	6374500	2.93			Sand	Unconfined	Horticultural	Short-rotation Cropland
72-1008	2754600	6284400	8	2	8	Ignimbrite	Unconfined	Agriculture	High Producing Exotic Grassland
72-1082	2742928	6256557	7.98	1.99	7.98	Ignimbrite	Unconfined	Agriculture	Pine Forest - Closed Canopy
63-201	2765600	6416600	48	26	48	Ignimbrite	Unknown	Horticultural	High Producing Exotic Grassland
64-117	2756660	6384490	16	8	16	Sand	Unconfined	Dairy	High Producing Exotic Grassland
61-54	2683457	6438482	19.8	14.32	19.8	Basalt	Unknown	Agriculture	Short-rotation Cropland
66-96	2805346	6295825	116	104	116	Pumice	Unconfined	Urban	High Producing Exotic Grassland
72-1011	2767461	6275810	5.88	2.3	5.88	Ignimbrite	Unconfined	Agriculture	Lake and Pond
61-280	2684200	6428800	23.2	15.5	23.2	Basalt	Confined	Forestry	Indigenous Forest
64-120	2750980	6365660	22.2	6	22.2	Sand	Unconfined	Dairy	Short-rotation Cropland
60-480	2733090	6465270	7.7			Gravel	Unconfined	Urban	High Producing Exotic Grassland

2.2 Sample collection

Sample collection is generally consistent with the national protocol for state of environment groundwater sampling (doc 1464180) produced for the Ministry for the Environment in 2006 (MfE, 2006). The principal exception is that pH is measured in the laboratory rather than the field. Waikato Regional Council does not maintain field pH instruments because more dependable results were found from when samples were promptly returned to the laboratory for rapid analysis. Another departure is that field measurement of dissolved oxygen is not always undertaken due to modifying influences such as in-situ pumps.

Sampling protocols include pre-planning, calibration of field equipment, and selection of appropriate sampling containers. At each site the water level is measured and the purge volume calculated. This is generally three annular volumes. Temperature and conductivity are monitored in a flow cell to ensure stability within 0.2 ^{o}C and 3% respectively before sampling. Filtering is undertaken in the lab with some exceptions such as sampling for the NGMP. Quality control measures undertaken are also in accordance with Waikato Regional Council's ISO 9001:2000 standards. These include procedures for the collection, transport and storage of samples, and methods for data verification and quality assurance to ensure the consistency of data across the programme.

After sampling, bottles are kept cooled to below 4^{o}C but are not frozen. Samples are delivered to the laboratory within 48 hours and generally 24 hours. Chain-of-custody sheets are provided and the suite of analyses checked on delivery to the laboratory. Samples are analysed at an IANZ registered laboratory. Back-up samples are held for two months until results have been verified by routine quality assurance procedures. All data from field measurements and laboratory analyses are stored in Waikato Regional Council's water quality archiving database (HYDSTRA).

A groundwater sampling protocol summary designed to be taken into the field is included in Appendix 3.

2.3 Water quality determinands

The monitoring networks reported here have been analysed for a large number of determinands but there has been a base suite developed. Samples were analysed at Hill Laboratories (Hamilton) for what is described as 'routine' parameters comprising: pH; conductivity; total dissolved solids; alkalinity; carbon dioxide; calcium; magnesium; hardness; sodium; potassium; chloride, sulphate, boron, total iron, manganese, copper and zinc. In addition ammonium, and dissolved iron and manganese have been analysed as part of the 'base' suite.

Dissolved arsenic, cadmium, and fluoride analyses, which were undertaken in 2010 were not included in 2012/13. Cadmium and fluoride were all well below the drinking water guidelines and therefore not continued (doc 1911495). Arsenic continues to be measured as total rather than dissolved (which would be cost additional). Antimony and silica were added to analyses in 2012. The former was a one-off check and the latter to confirm results as an approximate water age surrogate.

Environment Waikato (now Waikato Regional Council) promoted the use of the following 'base' suite of groundwater quality laboratory determinands to aid in national reporting (Table 5). These were adopted by the Groundwater Forum in May 2006 to provide consistency between Regional Councils.

Table 5: Base suite of chemical determinands

Parameter	Detection Limit[1]	Justification
pH (7.0-8.5)	0.1 pH Units	Important for interpretation, other parameter estimation and aesthetic compliance
Electrical Conductivity	1 µS/cm	Important for ion balance check and other parameter estimation
Alkalinity	1 $g.m^{-3}$ as $CaCO_3$	Important for interpretation and other parameter estimation
Calcium	0.02 $g.m^{-3}$	Major ion, interpretation (e.g. Piper plot) and ion balance[2]
Magnesium	0.005 $g.m^{-3}$	Major ion, interpretation (e.g. Piper plot) and ion balance
Sodium (200)	0.5 $g.m^{-3}$	Major ion, interpretation (e.g. Piper plot) and ion balance
Potassium	0.1 $g.m^{-3}$	Major ion, interpretation (e.g. Piper plot) and ion balance
Nitrate-N [11.3]	0.02 $g.m^{-3}$	Important nutrient management, health concern and ion balance
Chloride (250)	0.5 $g.m^{-3}$	Major ion, interpretation, saltwater intrusion
Sulphate (250)	0.2 $g.m^{-3}$	Major ion, interpretation (e.g. Piper plot) and ion balance
Total Ammoniacal-N (1.5)	0.01 $g.m^{-3}$	Nutrient management, redox/Eh estimation from nitrate/ammonium couple, (DIN), check, aesthetic
Dissolved Iron (0.2)	0.02 $g.m^{-3}$	Redox indicator, (cf total iron) indicates sample quality, aesthetic, treatment consideration
Dissolved Manganese	0.005 $g.m^{-3}$	Health concern, redox indicator (cf total Mn sample quality)

Note: Values given in square brackets are maximum acceptable values for drinking water (MoH, 2005). Rounded brackets provide maximum acceptable aesthetic values.

[1] Guideline only with bolded entries being more critical

[2] Anion/Cation balance to check data quality

Table 6: Determinands derived by calculation (from Table 5)

Calculated parameter	Justification (no cost)
Total Dissolved Salts (1000)	May be calculated from electrical conductivity
Free carbon dioxide	Calculated from alkalinity and pH
Bicarbonate	Calculated from alkalinity and pH
Carbonate	Calculated from alkalinity and pH
Total Hardness (200)	Aesthetic, practical treatment indicator, calculated from Ca and Mg

As well as the inorganic chemical determinands listed, analyses have been undertaken for a large suite of pesticides at selected locations (four wells on a quarterly basis) in the period reported. Detection limits and methods for all analyses are listed in Appendix 2.

Specification sheets listing analyses details for nitrate, pesticide and microbial indicators are available in docs 634883, 875033 and 936338.

2.4 Quality control

Quality control measures are carried out in accordance with Waikato Regional Council's ISO 9001:2000 standards. These include procedures for the collection, transport and storage of samples. Data verification and quality assurance methods are also invoked to ensure data consistency. Samples are sent to an IANZ registered laboratory for analysis. Back-up samples are held for two months until results have been verified by routine quality assurance procedures.

All the data from field measurements and laboratory analysis are stored in Waikato Regional Council's water quality archiving database (Wiski). For subsequent data analysis purposes, non-detect results are assumed to be half the value of the corresponding limit of detection.

2.5 Reports

Groundwater quality indicators for nitrate, pesticides and micro-organisms are reported on WRC's website www.waikatoregion.govt.nz. There are also numerous relevant sub-regional and issue related groundwater quality reports, including:

- Groundwater chemistry of the Mangaonua-Mangaone catchments (Marshall, 1986)
- Groundwater chemistry of the Northern Waikato District (Ringham et al., 1990)
- Groundwater resources of the Tokoroa region (Bird, 1987).
- Groundwater chemistry of the Piako catchment (Hadfield, 1993);
- Pesticide contamination of groundwater in the Waikato Region (Hadfield and Smith,1999)
- Community groundwater supply protection (Hadfield and Nicole, 2000)
- Hydrogeology of Lake Taupo Catchment – Phase 1 (Hadfield et al., 2001)
- Hauraki groundwater quality trends 1992-2002 (Hadfield, 2003)
- Water resources of the Reporoa Basin (Piper, 2005).

Waikato Regional Council's State of the Environment Report briefly characterises groundwater resources in the region (Environment Waikato, 1999). The state and trends of groundwater quality are also reported nationally by the Institute of Geological and Nuclear Sciences (2007). Previous groundwater quality monitoring for 2010/11 is reported in Council's document 1911495.

3 Monitoring Results

3.1 Regional network results and summary statistics

Results of water quality analyses for the regional network are listed in Table 7. Summary statistics are also presented in Table 8. Non-detect results are given the half detection value for analysis purposes. There are 111 samples for all determinands except for arsenic and antimony which have 106 and silica which has 105.

There is very clear evidence of substantial land-use impacts on groundwater quality. The most common anthropogenic contaminant is nitrate. For simplicity, ambient nitrate-N concentrations in aerobic (or oxic) conditions may be considered to be less than 1 g m^{-3}. Further arbitrary categories are listed below:

Ambient	< 1 g m^{-3}
Influenced	>1 g m^{-3} and < 5.65 g m^{-3} (half MAV)
Impacted	>5.65 g m^{-3} and < 11.3 g m^{-3} (MAV)
Excessive	>11.3 g m^{-3}

About 27% of the regional network wells have nitrate at 'ambient' concentrations. Many of these are due to the existence of anaerobic conditions. About 40.5% of wells are land-use' influenced and about 17.2% are 'impacted. Nitrate exceeded the drinking water standards at 17 wells (15.3%).

Nitrate-N results are illustrated spatially in Figures 2 and 3. Figure 2 shows regional monitoring network nitrate concentrations relative to drinking water guidelines. The concentrations are compared spatially to estimated nitrogen leaching through soils in

Figure 3. It is evident that measured incidences of nitrate exceeding the drinking water standards are most common in the Pukekohe, Hamilton Basin and southern Hauraki Plains areas.

In the Hauraki Plains there is a general trend of decreasing nitrate concentration northward with progressively low-lying, finer and peaty sediments. It is associated with a change from recharge to discharge flow regimes and more reducing groundwater conditions (i.e. lower redox). Nitrate concentrations are generally highest in shallow, vulnerable aquifers and are lowest in very deep or iron-rich waters.

Table 7: **Regional groundwater quality network monitoring results (concentrations in g m^{-3}, conductivity in mS m^{-1}, (D) indicates dissolved rather than total concentrations).**

Well Number	Date	Alkalinity	As	B	Ca	Cl	Cond.	Cu	Fe (D)	Fe	Free CO_2	Hardness
Coromandel												
60-12	18/12/2012	59	0.0037	0.023	23	5.7	14.1	< .00053	< .02	< .021	< 1	62
60-124	18/12/2012	220	0.0016	0.026	99	15.5	53.8	0.005	< .02	0.116	10	270
60-167	18/12/2012	76	0.0035	0.0142	< .053	16.3	19.6	< .00053	< .02	< .021	7	< 1
60-190	18/12/2012	26	0.0015	0.023	5.4	42	20.5	0.00085	< .02	< .021	33	26
63-269	19/12/2012	14	< .0011	0.0182	3.1	37	17.6	0.0024	< .02	0.056	7	21
60-316	17/12/2012	123	< .0011	0.032	32	39	39.0	0.00171	< .02	0.061	33	121
60-345	18/12/2012	20	< .0011	0.0117	3.1	17.2	11.5	< .00053	< .02	< .021	35	15.1
60-348	18/12/2012	26	< .0011	0.0152	6.6	16.2	12.4	0.0032	< .02	< .021	25	28
72-3559	17/12/2012	55	0.0013	0.029	19.4	33	24.2	0.00081	< .02	0.23	39	65
60-407	17/12/2012	13	< .0011	0.022	4.0	22	11.9	0.0038	< .02	0.48	6	21
60-480	17/12/2012	210	0.0022	0.56	46	36	66.8	0.00191	< .02	0.044	35	191
72-2691	18/12/2012	12	0.0137	0.030	54	370	124.6	0.0027	7.3	12.9	16	280
Franklin												
61-113	2/12/2012	4	< .0011	0.0159	7.0	21	17.0	0.00056	< .02	0.38	53	33
61-126	2/12/2012	32	< .0011	0.029	19.1	61	37.1	< .00053	< .02	0.147	18	98
61-135	10/12/2012	26	< .0011	0.0189	8.3	25	26.3	< .00053	< .02	< .021	19	60
61-143	10/12/2012	10	< .0011	0.014	14.6	27	35.5	0.0023	< .02	0.051	21	98
61-208	2/12/2012	50	< .0011	0.042	11.9	62	41.7	0.0057	< .02	0.31	41	83
61-221	2/12/2012	31	< .0011	0.0131	7.3	18.7	17.3	< .00053	< .02	< .021	18	45
61-230	10/12/2012	15	< .0011	0.012	4.9	17.7	15.4	0.0014	< .02	0.077	22	34
61-245	10/12/2012	3	< .0011	0.026	3.2	35	15.4	0.0007	< .02	0.046	70	19.6
61-258	2/12/2012	70	< .0011	0.0142	12.5	21	23.1	< .00053	< .02	< .021	10	73
61-280	10/12/2012	19	< .0011	0.0164	7.3	21	22.2	< .00053	< .02	< .021	29	58
61-54	10/12/2012	9	< .0011	0.0173	2.5	16.3	16.2	0.003	< .02	0.16	11	31
61-59	2/12/2012	11	< .0011	0.028	2.6	16.9	12.2	0.0025	< .02	< .021	18	18.3
61-702	10/12/2012	35	< .0011	0.0121	7.2	18.5	17.0	0.00196	< .02	0.068	22	46
61-85	2/12/2012	26	< .0011	0.020	8.3	32	25.0	< .00053	< .02	0.037	26	55
61-93	2/12/2012	35	< .0011	0.0171	28	82	52.2	0.002	< .02	0.167	27	171

Well Number	Date	Alkalinity	As	B	Ca	Cl	Cond.	Cu	Fe (D)	Fe	Free CO_2	Hardness
Hauraki												
63-201	12/12/2012	32	0.0013	0.0096	5.0	11.5	10.9	0.0068	4.3	5.2	25	20
63-240	12/12/2012	64	< .0011	0.012	13.2	12.2	16.4	0.0021	< .02	0.065	3	54
63-328	12/12/2012	43	< .0011	0.0143	7.7	11.8	12.4	< .00053	< .02	< .021	4	34
63-43	12/12/2012	11	< .0011	0.0161	2.0	26	20.5	< .00053	< .02	0.128	26	17
63-57	18/12/2012	32	< .0011	0.017	11.9	23	26.3	0.00061	0.26	0.59	10	72
63-74	12/12/2012	111	0.0013	0.0113	23	22	28.6	0.0021	< .02	1.03	22	95
63-78	12/12/2012	8	< .0011	0.0123	2.0	17.9	9.2	0.00197	< .02	2.1	23	10.1
72-1223	18/12/2012	36	< .0011	0.0149	4.3	11.5	11.3	< .00053	0.3	3.2	28	18
Matamata-Piako												
64-108	30/11/2012	14	< .0011	0.0182	14.7	23	30.0	< .00053	< .02	< .021	32	68
64-111	17/12/2012	105	< .0011	1.02	10.0	16.9	24.7	< .00053	0.28	0.38	8	38
64-117	28/09/2012	33	0.110	0.079	24	27	41.5	< .00053	<0.02	< .021	17	107
64-12	14/12/2012	20	0.0029	0.010	15.3	34	29.9	0.00152	0.22	0.81	26	75
64-120	4/12/2012	33	< .0011	0.0118	7.7	5.8	12.5	< .00053	< .02	0.15	22	30
64-20	28/11/2012	26	< .0011	0.0197	14.1	23	23.6	0.00127	< .02	0.031	36	65
64-43	30/11/2012	26	< .0011	0.024	11.8	18.7	21.7	0.00068	< .02	< .021	18	55
64-46	18/12/2012	23	< .0011	0.031	16.1	23	25.1	< .00053	< .02	< .021	18	73
64-50	6/12/2012	25	< .0011	0.0112	15.1	28	24.7	< .00053	< .02	0.111	22	64
64-511	4/12/2012	30	0.0014	0.071	6.4	7.7	13.7	0.0009	< .02	< .021	16	29
64-7	14/12/2012	24	< .0011	0.030	23	29	37.1	< .00053	< .02	< .021	25	112
64-70	6/12/2012	24	< .0011	0.0135	6.6	25	17.4	0.00105	< .02	< .021	24	32
64-831	20/12/2012	38	0.0018	0.0149	7.5	2.7	11.2	0.0024	< .02	1.87	11	32
64-720	4/12/2012	16	< .0011	0.016	47	132	73.0	0.0084	1.08	1.83	29	189
Otorohanga												
65-4	5/12/2012	17	< .0011	0.0089	12.2	38	27.4	0.021	< .02	0.47	13	58
65-6	5/12/2012	26	< .0011	0.0115	3.7	12	11.0	0.00142	< .02	0.039	7	17.3
72-5510	5/12/2012	22	< .0011	0.0114	6.7	7.5	9.5	0.00054	< .02	0.059	7	28
Rotorua												
66-58	7/12/2012	22	0.0124	0.0082	1.9	2.5	5.2	< .00053	< .02	< .021	3	9.5
66-6	7/12/2012	26	< .0011	0.0171	10.0	25	25.1	0.00072	< .02	0.035	32	41

Well Number	Date	Alkalinity	As	B	Ca	Cl	Cond.	Cu	Fe (D)	Fe	Free CO_2	Hardness
66-92	7/12/2012	210	0.64	0.22	3.5	4.7	40.5	< .00053	0.64	0.68	7	12.6
66-93	7/12/2012	36	0.0055	0.025	8.5	10	17.6	< .00053	0.35	0.39	28	28
66-96	7/12/2012	25	< .0011	0.0075	3.0	3.6	6.6	< .00053	0.25	2.5	3	12.9
South Waikato												
67-11	30/11/2012	27	< .0011	0.032	18.8	9.6	21.9	< .00053	< .02	< .021	27	67
67-15	7/12/2012	23	< .0011	0.0132	5.9	13.1	14.3	0.0007	< .02	< .021	14	26
72-4500	13/12/2012	36	< .0011	0.0098	9.0	10.3	14.9	0.00098	< .02	0.024	17	36
67-4	13/12/2012	47	< .0011	0.0145	10.6	13.1	17.8	< .00053	< .02	< .021	19	43
67-404	13/12/2012	26	< .0011	0.026	13.6	15.2	21.4	< .00053	< .02	< .021	31	54
67-483	13/12/2012	71	< .0011	0.0109	9.0	13.8	18.9	< .00053	0.18	0.31	41	36
67-55	13/12/2012	16	< .0011	0.0097	1.6	4.7	5.5	< .00053	< .02	< .021	7	7.8
67-573	13/12/2012	19	< .0011	0.0084	5.0	11	11.0	< .00053	< .02	0.022	17	23
67-83	13/12/2012	26	< .0011	0.016	8.6	11.9	14.5	< .00053	< .02	< .021	19	36
Taupo												
68-301	7/12/2012	32	0.0116	0.008	5.4	4	11.9	< .00053	< .02	0.024	4.7	26
68-317	7/12/2012	27	0.0039	0.0075	7.3	8.4	15	< .00053	< .02	< .021	5.5	31
68-320	20/12/2012	18	0.005	0.0141	25	19.1	36.6	0.0042	0.02	0.57	3.5	111
72_3696	19/12/2012	41	0.0099	0.018	6.7	4.1	12.8	0.00113	< .02	< .021	9	28
68-912	19/12/2012	37	0.004	0.0107	9.9	9.7	17.3	< .00053	< .02	< .021	21	38
68-964	19/12/2012	29	0.0023	0.028	4.8	4.4	7.7	0.0013	0.04	0.087	14	23
72-1008	23/01/2013	20		0.015	7.8	4.9	10.2	0.025		8.4	5	37
72-1011	7/12/2012	36	0.0084	0.0086	5.4	5.3	12.5	< .00053	< .02	< .021	12.3	24
72-1069	5/06/2013	39		0.057	3.5	2	13.5	0.0073	< .02	2.7	22	14.3
72-1072	22/01/2013	40		0.0059	5.7	3.4	8.7	0.0078		2.7	2.8	23
72-1081	19/12/2012	30	< .0011	< .0053	4.1	4.5	8.3	< .00053	3.4	7.5	23	15.1
72-1082	19/12/2012	22	< .0011	0.0073	4.3	4.6	7.4	< .00053	< .02	0.027	8	16.3
72-1087	22/01/2013	21		< .0053	4	3	7.3	< .00053		< .021	3.5	14.5
72-1089	5/06/2013	47		0.067	11.1	3.7	17.3	0.00131	< .02	0.22	21	46
72-356	7/12/2012	29	0.0017	0.0111	4.9	4.1	10.1	0.00075	0.05	0.154	4.5	21
72-392	7/12/2012	27	0.0025	0.0058	8.3	7.7	16.4	0.003	< .02	0.29	7.6	36
72-431	7/12/2012	27	0.0052	0.0076	4.9	4.1	8.9	< .00053	< .02	< .021	9.8	22

Well Number	Date	Alkalinity	As	B	Ca	Cl	Cond.	Cu	Fe (D)	Fe	Free CO$_2$	Hardness
Waikato												
69-163	17/12/2012	42	0.0018	0.044	47	31	46.2	0.0053	0.12	3.8	38	165
69-1709	4/12/2012	50	< .0011	0.022	12.1	11.1	18.5	0.0026	< .02	< .021	17	51
69-173	30/11/2012	14	< .0011	0.049	14.0	19.6	23.9	0.00103	< .02	0.28	40	52
69-19	14/12/2012	35	< .0011	0.080	19.7	15.2	23.6	0.0042	< .02	1.73	30	78
69-248	6/12/2012	26	< .0011	0.023	9.6	8.2	14.0	0.00141	< .02	0.3	19	38
69-295	6/12/2012	60	< .0011	0.026	8.5	9	27.6	0.0111	0.03	0.89	34	37
69-365	30/11/2012	35	0.0062	0.026	17.0	19.3	27.9	0.0023	< .02	1.01	27	81
69-374	30/11/2012	29	< .0011	0.185	24	22	29.2	0.0035	< .02	0.087	20	99
69-62	18/12/2012	28	< .0011	0.153	9.6	5.1	15.8	< .00053	< .02	< .021	12	52
69-81	14/12/2012	19	< .0011	0.0191	5.0	10.8	13.5	0.0088	< .02	0.23	61	24
69-97	17/12/2012	24	< .0011	0.0147	9.1	12.8	16.7	0.0054	< .02	< .021	21	41
62-5	17/12/2012	28	< .0011	0.040	13.3	18.3	22.7	0.0027	< .02	< .021	19	66
Waipa												
70-1134	4/12/2012	33	< .0011	0.0111	9.5	12.5	15.0	< .00053	< .02	0.067	27	49
70-21	20/12/2012	86	0.006	0.0142	35	1.6	22.5	0.0081	< .02	3.3	14	98
70-22	18/12/2012	42	< .0011	0.032	17.8	9.2	23.9	0.0026	< .02	< .021	44	76
70-31	30/11/2012	21	< .0011	0.030	12.9	15.3	20.3	< .00053	< .02	< .021	17	50
70-44	28/11/2012	55	0.0027	0.049	17.2	13.6	27.2	0.123	< .02	3.8	27	77
70-47	28/11/2012	25	< .0011	0.0175	21	14.6	21.9	0.0014	< .02	0.104	21	76
70-50	17/12/2012	50	0.0013	0.040	28	21	35.6	0.02	< .02	0.94	28	103
70-56	28/11/2012	35	< .0011	0.022	21	14.8	28.0	< .00053	< .02	0.031	20	93
70-65	4/12/2012	17	< .0011	0.0112	6.8	12.9	15.6	0.00158	< .02	0.083	28	34
70-74	4/12/2012	20	< .0011	0.020	5.6	8.1	10.9	0.0074	< .02	< .021	16	24
70-76	28/11/2012	23	< .0011	0.0099	5.5	14.3	13.9	< .00053	< .02	< .021	20	26
Waitomo												
71-1	5/12/2012	16	< .0011	0.0117	4.9	9.5	10.4	0.0039	< .02	0.029	5	24
72-2138	5/12/2012	155	< .0011	0.0135	59	8.5	33.0	0.0028	< .02	0.06	4	160
71-3	5/12/2012	190	< .0011	0.0178	77.0	8.5	40.1	0.0019	< .02	0.8	18	200
71-4	5/12/2012	168	0.0086	0.0174	84	8.8	35.6	0.026	< .02	30	5	240
71-5	5/12/2012	112	0.0074	0.020	44	8.8	27.8	< .00053	< .02	< .021	2	125

Well Number	Date	K	Mg	Mn (D)	Mn	Na	NH_4	NO_3	pH	Sb	Si (D)	Si	SO_4	TDS	Temp.	Zn
Coromandel																
60-12	18/12/2012	1.38	1.04	0.004	0.0047	4.5	0.016	0.44	8.1	0.00024	4.4	9.4	1.9	94	16.8	< .0011
60-124	18/12/2012	3	4.6	0.0007	0.0073	13.7	< .01	4.5	7.6	< .00021	8.6	18.4	27	360	17.0	0.24
60-167	18/12/2012	1.97	< .021	0.0006	0.00069	45	< .01	< .05	7.4	< .00021	34	73	2	131	18.2	< .0011
60-190	18/12/2012	8.8	3	< .0005	< .00053	24	< .01	0.05	6.2	< .00021	47	101	5.6	137	19.2	0.026
63-269	19/12/2012	2.4	3.2	0.0013	0.00104	24	< .01	2.1	6.6	< .00021	15.2	33	6.6	118	18.4	0.0025
60-316	17/12/2012	1.37	9.8	0.0065	0.0067	37	< .01	0.27	6.9	< .00021	26	56	16.9	260	17.2	0.0071
60-345	18/12/2012	3.9	1.81	0.0053	0.0053	14.4	< .01	1.72	6.0	< .00021	22	47	3	77	17.3	0.0042
60-348	18/12/2012	1.42	2.8	0.0009	0.00092	12.7	< .01	0.62	6.3	< .00021	7.7	16.4	7.7	83	19.2	0.0017
72-3559	17/12/2012	1.08	3.9	0.029	0.035	26	0.019	0.26	6.4	< .00021	7.5	16	12	162	17.6	0.0016
60-407	17/12/2012	1.39	2.7	0.0064	0.0159	14	< .01	1.48	6.6	< .00021	5	10.6	5.2	80	17.3	0.0113
60-480	17/12/2012	4.3	18.3	0.032	0.033	79	0.011	0.57	7.1	< .00021	15.5	33	85	450	17.8	0.0099
72-2691	18/12/2012	22	34	0.76	0.78	108	0.3	0.05	6.2	< .00021	40	86	0.7	830	19.4	0.194
Franklin																
61-113	2/12/2012	0.36	3.8	0.062	0.079	17.4	< .01	8.8	5.2	< .00021	7.6	16.2	6.4	114	16.1	0.0144
61-126	2/12/2012	3.3	12.2	0.023	0.021	31	< .01	4.1	6.6	< .00021	11.5	25	36	250	15.4	0.0034
61-135	10/12/2012	1.36	9.5	< .0005	< .00053	26	< .01	15.9	6.4	< .00021	15.7	34	2.2	176	16.2	0.072
61-143	10/12/2012	1.96	14.9	0.0043	0.0047	23	< .01	31	6.0	< .00021	8.7	18.6	1.2	240	15.4	0.03
61-208	2/12/2012	1.06	12.9	0.0039	0.0044	46	< .01	12.5	6.4	< .00021	25	53	9.8	280	16.5	0.084
61-221	2/12/2012	1.2	6.6	< .0005	< .00053	15	< .01	5.7	6.6	< .00021	15.1	32	2	116	16.1	0.0078
61-230	10/12/2012	1.24	5.3	0.0017	0.00179	14.5	< .01	8	6.1	< .00021	9.5	20	1.3	103	15.7	0.0108
61-245	10/12/2012	1.87	2.8	0.146	0.151	18.1	< .01	0.35	5.0	< .00021	4.6	9.9	9.6	103	15.7	0.0062
61-258	2/12/2012	1.99	10.1	< .0005	< .00053	16.4	< .01	2.6	7.2	< .00021	24	51	2.5	155	15.3	0.0039
61-280	10/12/2012	1.14	9.6	0.0028	0.0024	18.9	< .01	13.6	6.1	< .00021	9.8	21	1.4	149	16.6	0.0087
61-54	10/12/2012	0.9	6.1	0.0032	0.0033	17	< .01	10.6	6.2	< .00021	7.7	16.4	1.1	108	16.0	0.0145
61-59	2/12/2012	1.14	2.9	0.0048	0.0046	15.4	< .01	4.5	6.1	< .00021	6.7	14.4	2.8	82	15.4	0.0097
61-702	10/12/2012	1.09	6.8	0.0009	0.00066	13.6	< .01	5	6.5	< .00021	16.5	35	1.6	114	15.0	0.0064
61-85	2/12/2012	1.46	8.4	0.0008	0.00093	25	< .01	10.7	6.3	< .00021	14.5	31	3	168	16.4	0.144
61-93	2/12/2012	2.6	25	< .0005	0.00061	27	< .01	22	6.4	< .00021	16.1	34	1.6	350	15.5	0.0031

Well Number	Date	K	Mg	Mn (D)	Mn	Na	NH_4	NO_3	pH	Sb	Si (D)	Si	SO_4	TDS	Temp.	Zn
Hauraki																
63-201	12/12/2012	1.96	1.82	1.13	1.13	10.8	0.12	< .05	6.4	< .00021	19.3	41	0.8	73	15.2	1.45
63-240	12/12/2012	2.6	5.1	0.0007	0.00104	12.2	< .01	0.22	7.6	< .00021	24	52	1.9	110	17.4	0.39
63-328	12/12/2012	2.4	3.5	< .0005	< .00053	11	< .01	0.1	7.3	< .00021	28	60	2.7	83	17.0	0.065
63-43	12/12/2012	4.6	2.9	0.0039	0.004	32	< .01	10.9	5.9	< .00021	19.5	42	2.1	137	16.0	0.082
63-57	18/12/2012	7.4	10.2	0.0109	0.0118	18.3	0.019	7.5	6.8	< .00021	30	65	30	176	16.1	0.0056
63-74	12/12/2012	3.7	8.9	0.023	0.028	22	< .01	0.06	7.0	< .00021	28	60	7.8	192	18.4	0.0183
63-78	12/12/2012	2.1	1.2	0.0019	0.0156	11.7	< .01	1.82	5.8	< .00021	11.1	24	1.9	62	15.2	0.0086
72-1223	18/12/2012	3.7	1.8	0.082	0.09	12.4	0.016	0.08	6.4	< .00021	40	86	1.7	76	17.1	3.7
Matamata-Piako																
64-108	30/11/2012	10.1	7.7	0.0015	0.00136	22	< .01	21	5.9	< .00021	40	85	7.8	200	16.2	0.0071
64-111	17/12/2012	2.9	3.1	0.32	0.34	44	< .01	0.07	7.4	< .00021	21	45	0.6	165	18.6	1.11
64-117	28/09/2012	38	11.5	0.12	0.00119	16.1	< .01	17.9	6.6	< .00021			52	280	15.6	0.0127
64-12	14/12/2012	7.4	9.1	0.0095	0.0096	22	0.33	7.3	6.2	0.00036	34	73	37	200	15.9	0.0042
64-120	4/12/2012	4.4	2.7	< .0005	0.01	10.5	< .01	2.4	6.5	< .00021	33	70	7.6	84	16.1	0.0036
64-20	28/11/2012	6.3	7.2	0.0071	0.007	14.3	< .01	3.1	6.2	< .00021	33	72	33	158	15.8	0.003
64-43	30/11/2012	6.9	6.3	< .0005	< .00053	15.3	< .01	8.5	6.5	< .00021	35	76	12.4	145	16.0	0.0012
64-46	18/12/2012	7	7.9	0.0008	0.00063	15.5	< .01	4.6	6.4	< .00021	36	76	38	168	15.8	0.0027
64-50	6/12/2012	7.1	6.3	< .0005	0.00089	14.8	< .01	6.1	6.4	< .00021	36	77	26	165	16.0	0.0131
64-511	4/12/2012	5.1	3.2	< .0005	< .00053	11.8	< .01	3.8	6.6	< .00021	36	78	6.9	92	16.4	0.0015
64-7	14/12/2012	13.4	13.5	< .0005	< .00053	19.6	< .01	18.5	6.3	< .00021	35	75	42	250	16.1	0.0058
64-70	6/12/2012	4.1	3.7	3.9	3.4	14.2	< .01	0.7	6.3	< .00021	45	96	16.5	116	16.7	0.0104
64-831	20/12/2012	3.3	3.3	0.001	0.035	8.6	< .01	2.6	6.8	< .00021	23	49	9.4	75	16.4	0.0169
64-720	4/12/2012	18.6	17.6	0.21	0.198	49	0.191	22	6.0	< .00021	32	68	40	490	15.0	0.194
Otorohanga																
65-4	5/12/2012	7.4	6.6	0.0096	0.0105	24	< .01	14	6.4	< .0042	21	45	1	184	15.6	3.9
65-6	5/12/2012	5.1	1.97	0.0011	0.00077	12.3	< .01	2.3	6.9	< .0042	39	85	1.4	74	17.0	0.0058
72-5510	5/12/2012	1.79	2.6	0.0023	0.0028	7	< .01	0.78	6.8	< .0042	11.1	24	9.3	64	14.0	0.0022
Rotorua																
66-58	7/12/2012	1.38	1.16	< .0005	< .00053	6.9	< .01	0.16	7.2	< .00021	37	79	1.2	35	12.4	< .0011
66-6	7/12/2012	12	3.8	0.043	0.044	23	< .01	8.5	6.2	< .00021	38	82	17.2	168	14.2	0.0117
66-92	7/12/2012	1.75	0.93	0.185	0.167	98	1.43	< .05	7.8	< .00021	36	77	< .5	270	21.4	0.0014

Well Number	Date	K	Mg	Mn (D)	Mn	Na	NH_4	NO_3	pH	Sb	Si (D)	Si	SO_4	TDS	Temp.	Zn
66-93	7/12/2012	9	1.66	0.28	0.25	19.5	0.017	4.7	6.4	0.00074	42	91	13.6	118	16.0	0.0033
66-96	7/12/2012	2.7	1.31	0.0155	0.0192	7.7	< .01	0.37	7.3	< .00021	25	54	1.9	44	12.8	< .0011
South Waikato																
67-11	30/11/2012	7	4.9	< .0005	< .00053	10	< .01	9.8	6.3	< .00021	18.8	40	21	147	15.0	0.069
67-15	7/12/2012	8.2	2.7	< .0005	< .00053	12.1	< .01	3.8	6.5	< .00021	41	87	7.5	96	15.3	0.0089
72-4500	13/12/2012	3.6	3.3	< .0005	< .00053	14	< .01	2.9	6.6	< .00021	16.7	36	7.4	100	13.3	0.0033
67-4	13/12/2012	3.6	4.1	< .0005	0.001	18.7	< .01	3.3	6.7	< .00021	18.5	40	6.1	120	13.0	0.0028
67-404	13/12/2012	7.3	4.9	0.0007	0.00083	13.3	< .01	12.2	6.2	< .00021	17	36	7.2	143	14.0	0.0027
67-483	13/12/2012	4	3.3	0.183	0.193	27	< .01	< .05	6.5	< .00021	19.6	42	3.2	126	12.7	0.0107
67-55	13/12/2012	3.2	0.92	< .0005	< .00053	6.4	< .01	0.76	6.6	< .00021	37	80	0.5	37	14.2	< .0011
67-573	13/12/2012	4.2	2.5	0.0006	0.00078	10.7	< .01	4.1	6.3	< .00021	38	82	< .5	74	13.9	< .0011
67-83	13/12/2012	3.6	3.5	< .0005	< .00053	12.2	< .01	5	6.4	< .00021	21	46	4.3	97	13.9	0.003
Taupo																
68-301	7/12/2012	1.58	3	< .0005	0.00089	12.8	< .01	3	7.1	0.00024	33	71	9.3	80	12	0.004
68-317	7/12/2012	3.3	3	< .0005	< .00053	15.2	< .01	4.8	7	0.00027	35	75	12.9	101	13.2	0.0117
68-320	20/12/2012	3.4	12.1	0.0173	0.0194	23	0.013	28	7	0.00087	28	61	47	250	18.2	0.0182
72_3696	19/12/2012	0.67	2.6	< .0005	< .00053	15.4	< .01	3.8	7.0	< .00021	31	65	8.7	86	15.5	0.0033
68-912	19/12/2012	3.4	3.3	< .0005	< .00053	16.8	< .01	4	6.6	< .00021	41	88	20	116	17.6	0.0011
68-964	19/12/2012	2.6	2.6	0.0026	0.0025	5.9	< .01	0.36	6.6	0.00022	22	48	3.3	51	13.5	0.0135
72-1008	23/01/2013	6.2	4.2		0.25	5.8	< .01	3.6	6.9				7	68	16.2	0.069
72-1011	7/12/2012	1.7	2.6	< .0005	< .00053	15.8	< .01	2.9	6.8	< .00021	34	74	7.2	84	12.5	< .0011
72-1069	5/06/2013	32	1.35	0.0011	0.027	3.5	0.012	0.23	6.6				14.6	91	13	0.023
72-1072	22/01/2013	2.2	2.1		0.7	9	0.127	0.06	7.5				< .5	58	12.7	0.0043
72-1081	19/12/2012	3.4	1.17	0.27	0.31	7.6	< .01	0.06	6.4	< .00021	19.6	42	0.6	56	12.3	0.0029
72-1082	19/12/2012	3.4	1.35	0.0009	0.00146	6.6	< .01	1.68	6.7	0.00029	24	52	2.8	49	13.2	0.0016
72-1087	22/01/2013	3.2	1.1		0.00154	6.7	< .01	1.63	7.1				3.7	49	13.1	< .0011
72-1089	5/06/2013	5	4.4	0.0007	0.00134	13.9	< .01	4	6.7				13.8	116	13.5	0.0153
72-356	7/12/2012	2.3	2.1	0.0017	0.00185	10.9	< .01	2.1	7.1	< .00021	39	84	6.4	68	12.4	0.021
72-392	7/12/2012	2.7	3.7	0.0029	0.0031	14.9	< .01	5.2	6.8	< .00021	34	72	19.1	110	11.5	0.45
72-431	7/12/2012	1.63	2.3	< .0005	< .00053	8.6	< .01	1.82	6.7	< .00021	38	81	4.2	60	13.6	< .0011
Waikato																
69-163	17/12/2012	15.7	11.6	0.089	0.129	11.1	0.012	19.5	6.3	< .00021	17.2	37	72	310	15.5	0.115

Well Number	Date	K	Mg	Mn (D)	Mn	Na	NH_4	NO_3	pH	Sb	Si (D)	Si	SO_4	TDS	Temp.	Zn
69-1709	4/12/2012	4.1	5	< .0005	< .00053	14.9	< .01	2.5	6.8	< .00021	14.1	30	11.7	124	15.2	0.0022
69-173	30/11/2012	22	4.2	0.039	0.039	8.7	< .01	6	5.8	< .00021	16.3	35	37	160	14.7	0.045
69-19	14/12/2012	5.2	6.9	0.0029	0.101	10.7	< .01	12.4	6.4	< .00021	15.2	33	12.8	158	15.8	0.0143
69-248	6/12/2012	3.6	3.5	0.0009	0.0076	9.4	< .01	1.7	6.4	< .00021	26	56	20	94	15.4	0.0085
69-295	6/12/2012	11.4	3.9	0.0015	0.033	37	< .01	4.3	6.6	< .00021	18.4	39	42	185	14.9	0.025
69-365	30/11/2012	12.2	9.4	0.051	0.051	14.3	0.014	6	6.4	< .00021	22	47	41	187	15.4	0.0135
69-374	30/11/2012	3.9	9.6	0.0008	0.00186	12	< .01	11.5	6.5	< .00021	22	47	31	196	15.4	0.0122
69-62	18/12/2012	2.8	6.9	0.0006	0.00089	9.3	< .01	5.9	6.7	< .00021	20	43	13.5	106	15.8	0.0043
69-81	14/12/2012	7.3	2.9	0.0023	0.0085	11.9	< .01	2.2	5.8	< .00021	25	53	17.8	90	17.3	0.0103
69-97	17/12/2012	4.3	4.5	0.0005	< .00053	12.5	< .01	3.2	6.4	< .00021	27	58	23	112	15.6	0.0167
62-5	17/12/2012	7.1	7.9	0.0006	< .00053	13.1	< .01	12	6.5	< .00021	21	45	12.3	152	15.5	0.0047
Waipa																
70-1134	4/12/2012	2.9	6.3	0.0038	0.0062	8.4	< .01	2.9	6.4	< .00021	13.5	29	8.2	100	15.3	0.0019
70-21	20/12/2012	4.8	2.8	0.124	0.154	7.3	0.26	2.5	7.1	0.0004	16.9	36	19.8	151	16.6	0.033
70-22	18/12/2012	9.7	7.8	0.0007	0.00095	11.7	< .01	6.1	6.3	< .00021	27	58	34	160	15.8	0.063
70-31	30/11/2012	10.8	4.4	0.0074	0.0117	10.8	0.29	7.9	6.4	< .00021	18	39	17.7	136	15.5	0.0019
70-44	28/11/2012	6.6	8.3	0.0027	0.0085	18.7	0.027	9.1	6.6	< .00021	36	76	18.7	182	15.3	1.16
70-47	28/11/2012	6.4	5.8	0.0012	0.003	8.2	< .01	2.6	6.4	< .00021	13.1	28	41	147	15.6	0.0088
70-50	17/12/2012	20	8.1	0.0015	0.0115	15.5	< .01	18.6	6.6	< .00021	25	54	26	240	17.4	0.0163
70-56	28/11/2012	5	10	< .0005	< .00053	12.6	< .01	7.7	6.6	< .00021	25	53	43	188	15.4	0.0016
70-65	4/12/2012	4.2	4.3	0.005	0.0133	13	< .01	0.92	6.1	< .00021	27	57	28	104	14.9	0.039
70-74	4/12/2012	2.3	2.3	< .0005	< .00053	9.6	< .01	3.6	6.4	< .00021	12.9	28	4.6	73	15.6	0.02
70-76	28/11/2012	5	3	< .0005	< .00053	12.3	< .01	4.5	6.4	< .00021	38	81	2.9	93	16.0	0.0033
Waitomo																
71-1	5/12/2012	1.75	3	0.0065	0.012	9.3	< .01	4.4	6.8	< .0042	9.2	19.8	2.9	69	14.8	0.025
72-2138	5/12/2012	1.66	2.8	< .0005	< .00053	8.6	< .01	0.8	7.9	< .0042	10.9	23	4.7	220	14.9	0.0163
71-3	5/12/2012	1.19	2.3	0.0007	0.00106	8.1	< .01	0.93	7.3	< .0042	7.9	16.9	7.5	270	15.0	0.0023
71-4	5/12/2012	3.8	6.3	< .0005	0.86	6	< .01	2.6	7.8	< .0042	4.9	10.4	3.3	240	14.9	0.3
71-5	5/12/2012	2.2	3.5	< .0005	< .00053	10.1	0.01	0.06	8.0	< .0042	16.1	34	18.8	186	14.6	< .0011

Table 8: General groundwater quality statistics for the regional well network (concentrations in g m^{-3}, conductivity in mS m^{-1}, (D) indicates dissolved rather than total concentrations).

Determinand	Mean	Median	Min	Max	St Dev	Skew	non-detect
Alkalinity	42	28	3	220	42	2.79	0
As	0.0094	0.00055	0.00055	0.6400	0.0628	9.86	75
B	0.0390	0.0170	0.0026	1.0200	0.1112	7.38	2
Ca	14.6	9.0	0.03	99.0	16.6	2.87	1
Cl	20.9	14.3	1.6	370	37.4	7.78	0
Cond.	22.3	17.6	5.2	124.6	15.6	3.29	0
Cu	0.0037	0.00098	0.00026	0.12300	0.01231	8.58	44
Fe (D)	0.19	0.0	0.0	7.3	0.9	6.45	93
Fe	0.973	0.060	0.010	30.000	3.314	6.85	40
Free CO_2	20	19	1	70	13	1.03	1
Hardness	59.6	41	1	280	54	2.12	1
K	5.33	3.6	0.4	38.0	5.9	3.12	0
Mg	5.6	3.8	0.0	34.0	4.9	2.74	1
Mn (D)	0.07938	0.00130	0.00025	3.90000	0.39406	8.67	33
Mn	0.08936	0.00300	0.00026	3.40000	0.36097	7.56	27
Na	17.9	13.9	3.5	108.0	15.7	3.69	0
NH_4	0.033	0.005	0.005	1.430	0.146	8.33	91
NO_3	5.5	3.6	0.0	31.0	6.3	1.83	4
Ph	6.6	6.5	5.0	8.1	0.5	0.43	0.0
Sb	0.0003	0.0001	0.0001	0.0021	0.0005	3.08	97
Si (D)	23.5	22.0	4.4	47	11.0	0.13	0
Si	50.3	47.0	9.4	101	23.7	0.13	0
SO_4	13.8	7.6	0.3	85	15.7	1.90	3
TDS	150	118	35	830	104	3.25	0
Temp.	15.6	15.6	11.5	21.4	1.7	0.16	0.0
Zn	0.1320	0.0088	0.0006	3.9000	0.5419	6.00	10

3.2 Comparison of regional results with drinking water standards and guidelines

The quality of groundwater in the regional network has been compared against drinking water standards in Table 9 and aesthetic guidelines in Table 10. These are reported as exceedances of Maximum Acceptable Value (MAV) and half MAV (inclusive of those exceeding the MAV) for measured determinands of health significance. The latter is an arbitrary level used by the Ministry of Health to identify chemicals which ought to be monitored (priority two after micro-organisms) as they are more likely to reach the MAV over time.

It is evident from Table 9, that the most commonly occurring contaminant of concern in respect to health is nitrate. It is also highly mobile and is the most feasible to manage, given it is the result of land-use activities. Given the above, the groundwater monitoring reported here is focused primarily on nitrate occurrence and trends. It should be noted that all groundwater contamination is very difficult to remediate and hence protection is a more effective strategy.

Table 9: Regional groundwater quality comparison of number of wells and percentage of wells with the drinking-water standards

Determinand	>MAV	>half MAV
Antimony	0 (0%)	0 (0%)
Arsenic	5 (4.7 %)	13 (11.7 %)
Boron	0 (0%)	1 (0.9 %)
Manganese	5 (4.5 %)	9 (8.1%)
Nitrate	17 (15.3%)	36 (32.4%)
Copper	0 (0%)	0 (0%)

Arsenic is a determinand of particular concern for human health (Appendix V) and exceeds the drinking-water standards in about 5% of wells in the regional network. Exceedences often occur in wells with geothermal influence (Piper and Kim, 2006). Although its occurrence is natural, concentrations can be exacerbated by drainage and pumping.

Manganese is naturally occurring and now classified as a parameter of health significance. It exceeded the drinking water guideline at nearly 5% of regional wells monitored. It is typically associated with iron and occurs in anaerobic conditions. Manganese can be readily treated, typically with aeration and sand or other filters.

Antimony has been monitored as a one-off check. The MAV for antimony is 0.02 g m^{-3}. Antimony trioxide (one of its compounds), is classified by theInternational Agency for Research on Cancer (IARC) as a possible human carcinogen. This is based on animal inhalation studies. Little information is available, however, about the toxicity of this metal when ingested orally. Antimony is known to occur at significant concentrations at some wells in Coromandel not monitored as part of these networks.

Comparison of regional groundwater quality with aesthetic guideline values shows that pH most commonly falls outside the ideal range. This is indicative of corrosion concerns relating to typically acidic waters.

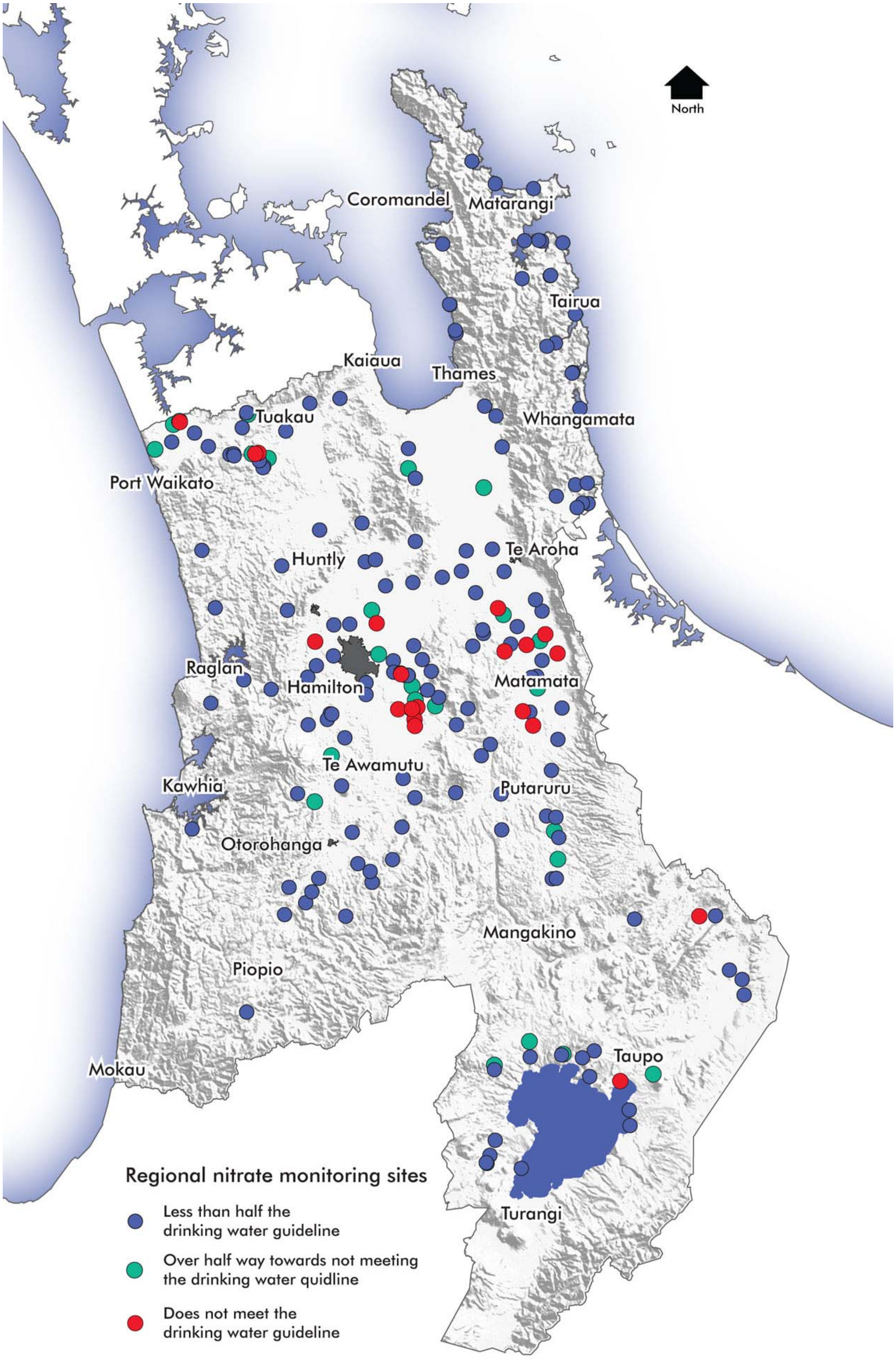
Iron and manganese, which typically are elevated together (Daughney, 2003) are common nuisance chemicals causing staining and scaling problems. High concentrations occur in anaerobic and peat influenced waters.

Table 10: Regional groundwater quality comparison with aesthetic guideline values (GV)

Determinand	>GV[1]
Ammonia	3 (2.7%)
Chloride	1 (0.9%)
Copper	0
Hardness	4 (3.6%)
Iron	40 (36%)
Manganese	19 (17%)
pH	93 (83.8%)
Sodium	0
Sulphate	0
Zinc	1 (0.9%)

[1] or outside range for pH

Groundwaters in the Waikato are typically slightly acid and hence often fall outside the aesthetic guideline range. Acid waters can be problematic for corrosion. It has no direct health concern but may influence the solubility and occurrence of other ions.



Digital Elevation Model layers derived by Environment Waikato. Topographic information derived from Land Information New Zealand's data. COPYRIGHT RESERVED.

Figure 2: **Regional monitoring network nitrate concentrations**

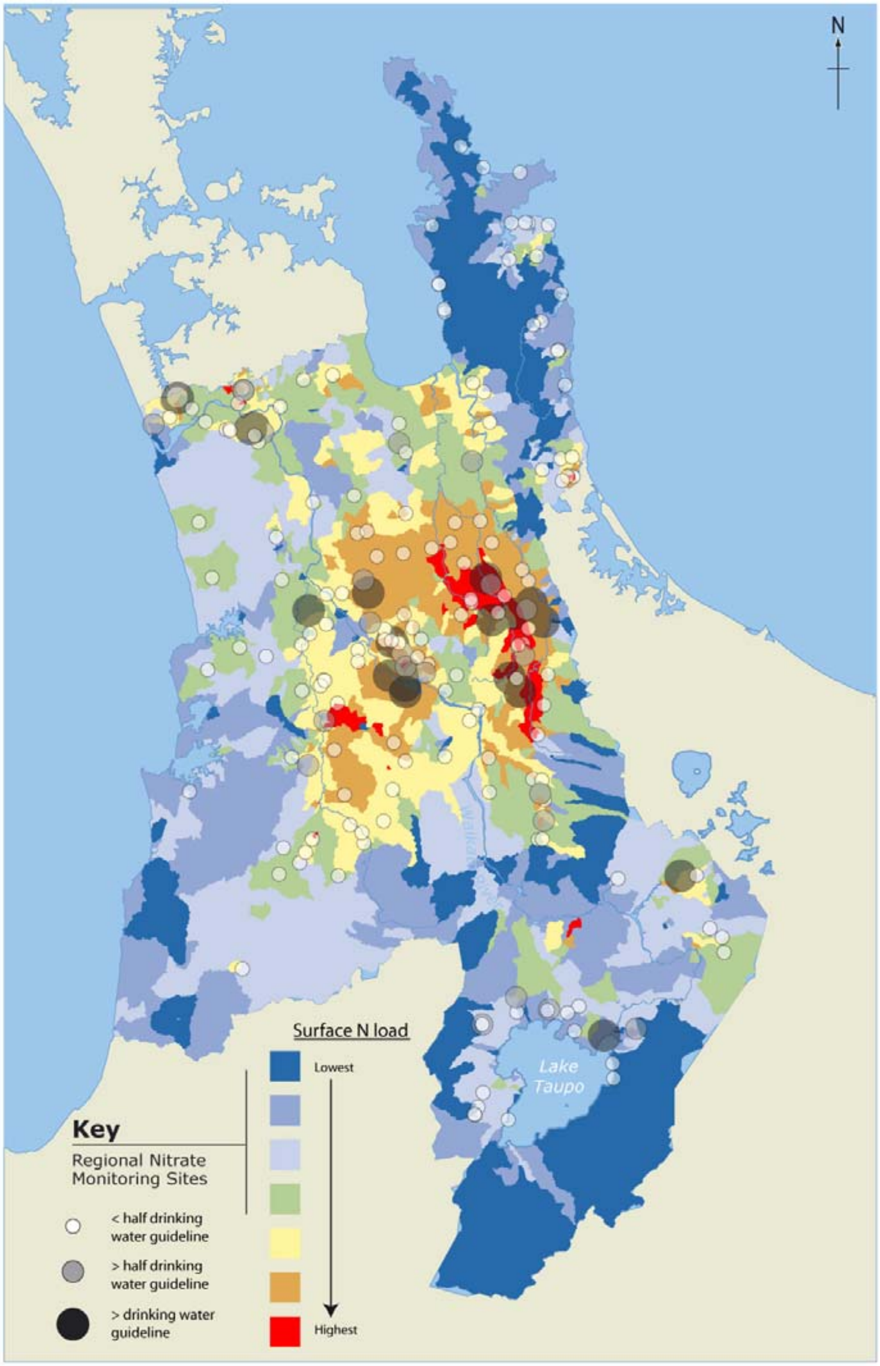


Figure 3: **Spatial nitrate leaching and regional nitrate results**

3.3 Community network results and summary statistics

Water quality analyses results for the community network in 2012/13 are listed in Table 11 and summary statistics are presented in Table 12. Non-detect results are given the half detection value for analysis purposes.

Again there is clear evidence in community well groundwater of land-use impacts on quality. Nitrate exceeded the drinking water standards at 1 supply (1.2%) and eight wells (9.9%) are ‘impacted’ (> half MAV). About 33 per cent of wells are land-use ‘influenced’ and just over half the wells (45 or ~55%) have nitrate at ‘ambient’ concentrations. Many of these are due to the existence of anaerobic conditions. The greater proportion of wells with ‘ambient’ concentrations is likely to reflect the more objective nature of this dataset and at least some localised exclusion of farming influence on school land.

Table 11: Community (school) groundwater quality network monitoring results (concentrations in g m^{-3}, conductivity in mS m^{-1}, (D) indicates dissolved rather than total concentrations).

Well Number	School	Date	Alkalinity	As	B	Ca	Cl	Cond.	Cu	Fe (D)	Fe	Free CO_2	Hardness	K	Mg	Mn (D)
Coromandel																
60-13	Coroglen	17/12/12	145	0.0059	0.095	3.9	15.6	31.8	< .00053	< .02	< .021	< 1	11	1.54	0.3	0.012
60-236	Manaia	17/12/12	75	0.0178	0.037	10.0	17.7	21.8	0.0065	4.6	30	26	57	3.1	7.7	0.39
60-260	Tapu	13/12/12	230	0.0011	0.240	65.0	34	63.7	0.0034	< .02	< .021	34	220	3.8	13.9	0.165
60-290	Opoutere	18/12/12	55	0.0024	0.018	10.2	17.1	17.1	< .00053	< .02	0.04	10	44	5.2	4.5	0.54
60-393	Hikuai	18/12/12	21	< .0011	0.011	2.0	13.2	9.6	0.0008	< .02	< .021	39	9.1	4.1	0.97	0.0014
60-478	Matatoki	13/12/12	34	0.0058	0.041	8.5	19.5	16.2	0.0081	0.05	116	26	32	1.68	2.7	0.147
72-640	Te Puru	13/12/12	133	0.0026	0.144	250	610	301	< .00053	< .02	1.86	8	710	3.5	24	0.28
Franklin																
61-1255	Pukekawa	16/11/12	62	0.0016	0.018	10.3	22	19.8	0.0107	< .02	2.1	9	56	2.9	7.4	0.0045
61-1679	Naike	15/11/12	95	< .0011	0.015	39.0	16.1	25.3	0.133	< .02	17.4	13	103	1.09	1.25	0.0068
61-1680	Waikaretu	15/11/12	210	0.0015	0.032	85.0	58	58.8	0.027	< .02	50	21	240	1.24	5.4	0.023
61-1727	Aka Aka Primary	16/11/12	84	< .0011	0.061	16.5	31	26.6	< .00053	< .02	0.063	< 1	57	4.2	3.8	0.023
61-1728	Mercer	16/11/12	96	< .0011	0.028	19.7	25	28.8	< .00053	< .02	0.36	23	85	5.1	8.8	0.0049
61-1729	Otaua Primary	21/11/12	115	0.0026	0.019	18.6	54	40.6	0.0022	< .02	1.64	6	131	3.1	21	0.098
61-1730	Mangatangi	21/11/12	15	< .0011	0.012	1.2	11.6	9.7	0.0024	< .02	0.033	34	7.3	4	1.03	0.0017
61-1731	Mangatawhiri	21/11/12	17	< .0011	0.014	1.3	15.8	10.2	0.0098	0.08	0.43	28	7.2	3.7	0.95	0.0073
61-182	Onewhero	16/11/12	65	< .0011	0.015	8.6	19.5	21.5	0.0032	< .02	0.31	3	67	2	11.1	< .0005
61-761	Harrisville	16/11/12	12	< .0011	0.017	2.2	15.0	13.8	0.00097	< .02	0.103	4	25	0.87	4.8	0.0007
72-1857	Te Kohanga Primary	16/11/12	99	< .0011	0.020	15.2	24	27.4	0.00091	0.03	0.095	5	90	2.8	12.7	0.0011
Hauraki																
63-390	Kaihere	21/11/12	24	0.0027	0.013	2.9	13.5	10.2	0.0113	< .02	38	43	14.6	2.2	1.77	0.0122
63-392	Waimata	19/12/12	78	0.0032	0.016	10.2	9.7	18.2	0.0048	0.02	0.028	3	57	3.1	7.8	0.034
Matamata-Piako																
64-32	Hoe-O-Tainui	21/11/12	20	< .0011	0.010	1.89	18.5	11.5	0.0054	0.08	0.104	39	12.9	0.94	1.98	0.0073
64-456	Kiwitahi	20/11/12	35	< .0011	0.015	3.7	15.1	12.4	< .00053	< .02	0.25	31	24	5.1	3.5	0.0016
72-5981	Manawaru	20/11/12	8	< .0011	0.036	9.1	18.9	20.2	0.00055	0.58	0.46	15	45	6.6	5.3	0.088
64-744	Tauhei	23/11/12	23	< .0011	0.074	2.9	40	23.2	0.03	< .02	5.8	63	19.2	5.3	2.9	0.0063
64-751	Te Puninga	27/11/12	34	0.0108	0.007	16.8	55	46.8	< .00053	7.1	6.7	39	107	19.3	15.8	0.73
64-807	Walton	20/11/12	52	0.0103	0.014	8.5	9.2	14.0	0.142	0.46	51	18	46	5.8	6	0.064

Well Number	School	Date	Alkalinity	As	B	Ca	Cl	Cond.	Cu	Fe (D)	Fe	Free CO_2	Hardness	K	Mg	Mn (D)
64-879	Hinuera	23/11/12	27	0.003	0.027	6.0	8.6	13.8	0.0031	0.13	4.4	31	29	6.3	3.4	0.035
64-880	Kereone	20/11/12	21	< .0011	0.015	3.3	12.1	11.6	0.0052	0.02	0.135	25	16.3	5.5	1.97	0.0019
64-883	Richmond Downs	23/11/12	58	< .0011	0.010	5.7	8.7	14.2	0.0089	0.06	3.6	17	34	2.7	4.9	0.02
64-884	Tatuanui	27/11/12	21	< .0011	0.084	11.9	16.6	23.7	0.0023	< .02	0.023	20	61	5.9	7.6	0.0074
64-885	Waihou	27/11/12	24	< .0011	0.096	6.5	30	21.4	0.0168	< .02	0.58	15	32	5.7	3.8	0.0059
64-990	Springdale Primary	4/12/12	11	0.003	0.032	9.5	35	30.3	0.00108	15.7	16.7	19	52	5.1	6.8	1.07
64-993	Elstow Primary	27/11/12	250	0.009	0.570	11.1	17.9	51.5	0.00059	0.09	0.153	4	65	5.3	9	0.0005
72-2137	Ngarau	23/11/12	28	< .0011	0.045	16.8	27	29.0	0.0067	< .02	< .021	21	80	7.5	9.1	0.0008
64-995	Wardville Primary	20/11/12	21	< .0011	0.106	27.0	30	41.7	0.026	0.94	1.37	38	139	8	17.3	0.23
64-996	Te Poi Primary	13/12/12	20	< .0011	0.013	2.2	6.2	7.6	0.0076	< .02	0.024	6	8.8	4.2	0.77	0.0005
Otorohanga																
65-142	Maihihi	13/12/12	36		0.012	3.5	8.0	10.4	< .00053		0.29	17	24	2.9	3.7	
65-285	Ngutunui Primary	21/11/12	51	< .0011	0.008	9.7	7.3	12.3	0.065	< .02	1.61	15	43	1.56	4.6	0.0046
72-749	Otewa	13/12/12	55		0.013	8.8	8.2	14.0	0.00066		< .021	7	32	3.3	2.6	
South Waikato																
67-565	Okoroire	13/12/12	29	< .0011	0.012	2.2	5.2	7.7	0.0097	< .02	0.042	22	12.2	3.3	1.64	0.0008
67-566	Tapapa	13/12/12	26	< .0011	0.014	2.9	7.9	9.8	0.0053	< .02	0.55	9	14.7	4.2	1.82	0.0034
67-567	Te Waotu	12/12/12	53	< .0011	0.012	4.5	7.8	9.8	< .00053	< .02	< .021	37	22	4.2	2.5	< .0005
67-602	Puketurua Primary	12/12/12	27	< .0011	0.009	5.9	15.8	13.9	0.0054	< .02	0.049	27	28	4.8	3.1	0.0007
Taupo																
68-794	Waitahanui	14/12/12	41	0.005	0.013	2.1	2.5	10.4	< .00053	< .02	< .021	< 1	7.2	0.163	0.47	0.022
68-1000	Kuratau Primary	14/12/12	18		0.005	3.7	3.2	6.6	0.0036		< .021	5	14.5	2.6	1.25	
Waikato																
69-1349	Horsham Downs	26/11/12	25	< .0011	0.012	2.6	14.5	12.2	< .00053	< .02	< .021	13	12	3.8	1.34	< .0005
69-1446	Ohinewai	15/11/12	41	0.0053	0.076	5.0	30	17.8	< .00053	3.4	3.9	26	21	3.4	1.99	0.16
69-1809	Tauwhare	6/12/12	22	0.0029	0.011	8.8	6.5	13.3	0.0021	0.11	15.5	17	35	2.7	3.2	0.184
69-1816	Te Mata	26/11/12	123	< .0011	0.023	31.0	18.1	29.6	< .00053	< .02	0.47	6	112	2.1	8.2	0.22
69-1897	Waikokowai	15/11/12	115	< .0011	0.240	1.74	19.7	28.7	< .00053	0.04	0.23	< 1	7.7	2.7	0.82	0.0041
69-1902	Waiterimu	23/11/12	16	< .0011	0.011	3.4	19.5	15.4	0.033	< .02	0.61	25	18.3	5.6	2.4	0.0047
69-2071	Glen Massey	15/11/12	28	0.0014	0.015	3.4	14.5	10.9	0.0085	< .02	3.3	24	16.3	3	1.91	0.0017
69-2072	Matangi	14/12/12	42	< .0011	0.390	12.1	7.3	15.8	0.00089	< .02	0.067	26	47	2.9	4.1	0.0017

Well Number	School	Date	Alkalinity	As	B	Ca	Cl	Cond.	Cu	Fe (D)	Fe	Free CO_2	Hardness	K	Mg	Mn (D)
72-2047	Ngati Haua	20/11/12	137	< .0011	0.031	29.0	23	33.8	< .00053	< .02	< .021	13	111	1.46	9.4	0.029
69-2074	Orini	21/11/12	23	< .0011	0.019	3.7	18.1	12.8	0.0042	0.02	0.146	40	16.3	3.9	1.73	0.0013
69-2075	Rotokauri	17/01/13	34	0.0011	0.013	3.8	19.3	13.1	< .00053	< .02	0.22	28	15.8	4.6	1.51	0.0009
69-2076	Te Akau	15/11/12	230	< .0011	0.078	94.0	34	59.3	< .00053	< .02	0.031	19	260	1.42	6.3	0.0028
69-2077	Te Kowhai	26/11/12	45	0.0012	0.028	8.1	19.2	19.3	0.00089	< .02	0.39	33	41	6.1	5	0.67
69-2079	Waitetuna	26/11/12	54	< .0011	7.00	12.2	310	113.2	< .00053	0.15	0.171	< 1	34	1.24	0.79	0.063
69-2080	Whatawhata	26/11/12	20	< .0011	0.018	6.0	14.2	14.9	0.0122	< .02	0.032	5	30	3.9	3.6	0.0021
69-2081	Whitikahu	23/11/12	143	0.0044	1.33	15.6	54	44.1	0.0035	7.0	13.5	80	93	9.6	13.1	1.08
69-2187	Horotiu	26/11/12	33	0.0014	0.031	4.8	10.3	13.5	< .00053	< .02	< .021	18	25	5.6	3.2	0.0019
69-912	Gordonton	26/11/12	25	< .0011	0.008	17.8	29	44.0	0.00152	< .02	0.112	24	166	5.6	29	0.007
72-739	Te Uku	26/11/12	166	< .0011	0.068	31.0	18.1	36.5	0.00145	< .02	0.37	5	128	3	12.3	0.095
Waipa																
70-1156	Hora Hora	12/12/12	72	< .0011	0.012	9.1	8.3	16.8	< .00053	< .02	0.032	9	53	3.4	7.4	0.0011
70-1157	Karapiro	13/12/12	33	< .0011	0.015	6.7	9.3	11.3	0.0025	< .02	0.52	17	25	4.2	2	0.0007
70-1158	Ngahinapouri	10/12/12	10	< .0011	0.009	12.3	15.2	16.0	0.0035	< .02	< .021	11	50	2.8	4.6	0.0014
70-1159	Parawera	17/01/13	25	< .0011	0.011	3.4	11.3	10.4	0.036	< .02	0.99	22	14.9	5.8	1.58	0.0016
70-1161	Rukuhia	10/12/12	72	< .0011	0.012	7.2	16.6	20.2	0.0035	1.02	3	64	36	7.7	4.4	0.057
70-1162	Whitehall	14/12/12	22	< .0011	0.016	1.73	8.1	7.8	0.005	< .02	0.53	9	7.2	3.4	0.69	0.0015
70-1164	Puahue	12/12/12	22	< .0011	0.012	1.85	8.6	8.2	< .00053	< .02	< .021	21	10.3	4	1.39	0.0007
70-1187	Capernwray Bible College	11/12/12	26	< .0011	0.078	8.5	20	20.0	< .00053	0.02	0.24	38	39	6.2	4.4	0.0072
70-1231	Goodwood	11/12/12	31	< .0011	0.038	12.9	14.1	20.2	< .00053	< .02	< .021	21	58	4.2	6.3	< .0005
70-453	Hautapu	10/12/12	44	< .0011	0.023	21.0	23	31.9	0.0036	0.06	1.75	31	95	6.9	10.1	0.0109
70-778	Paterangi	10/12/12	45	< .0011	0.012	4.9	10.6	12.4	< .00053	0.07	0.28	26	19.7	4.2	1.83	0.0046
70-794	Pokuru	6/12/12	23	< .0011	0.012	1.97	7.6	7.4	< .00053	0.03	0.34	8	9.3	4.1	1.06	0.0006
70-804	Pukeatua	12/12/12	27	< .0011	0.013	3.5	11.4	9.6	0.0032	< .02	0.077	21	15.2	4.9	1.55	0.0028
70-951	Te Miro	6/12/12	59	< .0011	< .0053	14.2	14.8	16.0	< .00053	< .02	2.9	< 1	48	3.1	3	0.049
70-952	Te Pahu	14/12/12	63	< .0011	0.015	6.9	12.5	16.1	< .00053	< .02	2.5	14	45	4.3	6.8	0.107
Waitomo																
71-60	Kinohaku	21/11/12	169	0.0056	0.500	12.7	36	48.6	0.0027	< .02	0.29	14	45	1.04	3.2	0.23
71-63	Aria Primary	19/12/12	145	< .0011	0.400	2.2	15.7	32.7	0.0146	0.03	0.89	< 1	6.4	0.67	0.192	0.0011

Well Number		Date	Mn	Na	NH_4	NO_3	pH	Sb	Si (D)	Si	SO_4	TDS	Temp.	Zn
Coromandel														
60-13	Coroglen	17/12/12	0.0132	72	0.02	< .05	8.9	< .00021	17.9	38	3.0	210	21.3	0.0052
60-236	Manaia	17/12/12	0.49	20	0.24	< .05	6.8	< .00021	12.5	27	3.8	146	16.6	0.0032
60-260	Tapu	13/12/12	0.16	48	< .01	4.3	7.1	< .00021	14.8	32	46	430	19.8	0.0187
60-290	Opoutere	18/12/12	0.51	14.1	< .01	0.05	7.0	< .00021	44	94	4.2	114	20.3	0.0019
60-393	Hikuai	18/12/12	0.005	13.4	< .01	1.02	6.0	< .00021	24	51	2.2	64	17.4	0.0051
60-478	Matatoki	13/12/12	0.25	17.4	0.22	0.05	6.4	0.00032	19.6	42	13.7	108	17.9	0.032
72-640	Te Puru	13/12/12	0.28	350	0.09	< .05	7.6	< .00021	16	34	530	2000	20.2	< .0011
Franklin														
61-1255	Pukekawa	16/11/12	0.0057	16.7	< .01	0.73	7.2	< .00021	30	65	2.8	133	16.0	0.21
61-1679	Naike	15/11/12	0.061	10.8	< .01	1.84	7.2	0.00024	8.4	17.9	4.7	170	16.1	1.22
61-1680	Waikaretu	15/11/12	0.094	26	< .01	< .05	7.3	< .00021	4	8.6	18.4	390	15.2	0.71
61-1727	Aka Aka Primary	16/11/12	0.024	30	0.29	< .05	8.2	< .00021	19.2	41	1.4	178	22.1	0.0078
61-1728	Mercer	16/11/12	0.0051	23	< .01	1.95	6.9	< .00021	32	69	4.5	193	17.8	0.28
61-1729	Otaua Primary	21/11/12	0.139	30	0.02	0.06	7.6	< .00021	23	50	7.9	270	17.0	0.053
61-1730	Mangatangi	21/11/12	0.00172	12.6	0.61	2.2	5.9	< .00021	41	87	4.2	65	16.7	0.44
61-1731	Mangatawhiri	21/11/12	0.0078	14.7	0.01	0.57	6.1	< .00021	41	88	4.3	68	19.4	0.086
61-182	Onewhero	16/11/12	0.00058	15.9	< .01	3.7	7.6	< .00021	15.8	34	2.3	144	15.3	0.0113
61-761	Harrisville	16/11/12	0.00123	15.5	< .01	8.1	6.8	< .00021	7.9	16.9	1.6	93	16.6	0.008
72-1857	Te Kohanga Primary	16/11/12	0.00106	20	< .01	0.66	7.6	< .00021	25	54	3.8	184	16.2	0.146
Hauraki														
63-390	Kaihere	21/11/12	0.067	13.6	-	0.53	6.0	< .00021	23	49	14.8	68	18.7	0.041
63-392	Waimata	19/12/12	0.037	14.6	< .01	0.11	7.8	< .00021	32	69	1.8	122	18.7	0.30
Matamata-Piako														
64-32	Hoe-O-Tainui	21/11/12	0.0067	17.1	< .01	0.79	6.0	< .00021	19.7	42	4.0	77	16.0	0.030
64-456	Kiwitahi	20/11/12	0.00156	13.9	< .01	0.16	6.4	< .00021	42	90	2.0	83	17.4	0.0012
72-5981	Manawaru	20/11/12	0.076	15.5	< .01	3.1	6.0	< .00021	29	62	42	135	17.1	0.0139
64-744	Tauhei	23/11/12	0.0067	33	< .01	1.85	5.9	< .00021	42	90	13.9	155	17.0	0.034
64-751	Te Puninga	27/11/12	0.69	28	0.22	0.07	6.2	< .00021	29	62	98	310		0.0136
64-807	Walton	20/11/12	0.178	14.4	0.01	< .05	6.8	0.00164	36	77	2.9	93	16.9	0.21
64-879	Hinuera	23/11/12	0.036	11.3	< .01	1.03	6.2	< .00021	37	79	18.6	92	16.5	0.052
64-880	Kereone	20/11/12	0.0022	13.2	0.02	3.9	6.2	< .00021	43	91	2.3	78	18.8	0.036
64-883	Richmond Downs	23/11/12	0.02	16.4	< .01	0.12	6.8	< .00021	37	79	1.4	95	16.5	0.048
64-884	Tatuanui	27/11/12	0.0075	15.2	< .01	4.4	6.3	< .00021	33	72	46	159		0.0118

Well Number		Date	Mn	Na	NH_4	NO_3	pH	Sb	Si (D)	Si	SO_4	TDS	Temp.	Zn
64-885	Waihou	27/11/12	0.0183	23	< .01	3.3	6.5	< .00021	34	72	16.4	143		0.171
64-990	Springdale Primary	4/12/12	1.02	26	0.13	0.43	6.0	< .00021	36	76	61	200	15.5	0.0165
64-993	Elstow Primary	27/11/12	0.00191	96	< .01	0.54	8.2	< .00021	45	96	< .5	350		0.0024
72-2137	Ngarau	23/11/12	0.00079	16.9	< .01	10.8	6.4	< .00021	36	77	25	194	16.6	0.0187
64-995	Wardville Primary	20/11/12	0.23	19.4	0.02	9.9	6.0	< .00021	35	74	101	280	17.0	0.0189
64-996	Te Poi Primary	13/12/12	0.00059	9.1	< .01	1.32	6.8	< .00021	41	87	1.3	51	19.2	0.026
Otorohanga														
65-142	Maihihi	13/12/12	0.0033	9.4	< .01	0.22	6.6		36	76	2.8	70	16.3	0.0043
65-285	Ngutunui Primary	21/11/12	0.0053	8.1	< .01	0.23	6.8	< .00021	14.5	31	0.8	83	16.2	0.0169
72-749	Otewa	13/12/12	< .00053	13.2	< .01	0.14	7.2		32	68	2.7	93	19.4	0.0125
South Waikato														
67-565	Okoroire	13/12/12	0.00101	9.8	< .01	0.09	6.4	< .00021	41	87	0.8	52	17.4	0.0088
67-566	Tapapa	13/12/12	0.0035	11.4	< .01	1.99	6.8	< .00021	38	82	1.1	66	15.2	0.025
67-567	Te Waotu	12/12/12	< .00053	9	< .01	1.37	6.5	< .00021	35	75	2.1	66	15.7	0.096
67-602	Puketurua Primary	12/12/12	0.00067	12.3	< .01	3.6	6.3	< .00021	36	76	3.2	93	15.9	0.174
Taupo														
68-794	Waitahanui	14/12/12	0.022	20	< .01	< .05	8.7	< .00021	25	53	7.4	70	12.1	0.0143
68-1000	Kuratau Primary	14/12/12	< .00053	5.2	< .01	1.78	6.8		20	43	2.8	44	17.4	0.0073
Waikato														
69-1349	Horsham Downs	26/11/12	< .00053	15.8	< .01	1.32	6.6	< .00021	39	83	5.7	82		0.0041
69-1446	Ohinewai	15/11/12	0.16	22	0.24	< .05	6.5	< .00021	34	74	3.2	119	16.3	0.002
69-1809	Tauwhare	6/12/12	0.25	9.3	0.05	0.38	6.4	< .00021	23	50	27	89	15.2	0.0027
69-1816	Te Mata	26/11/12	0.22	14.5	0.02	< .05	7.6	< .00021	17.9	38	2.3	198		0.041
69-1897	Waikokowai	15/11/12	0.0058	61	0.55	< .05	8.5	< .00021	2.6	5.5	6.9	192	16.8	0.0013
69-1902	Waiterimu	23/11/12	0.0049	17.7	< .01	6.2	6.1	< .00021	40	85	1.3	103	16.5	0.073
69-2071	Glen Massey	15/11/12	0.0031	14	< .01	0.5	6.4	< .00021	27	57	3.3	73	15.1	0.0135
69-2072	Matangi	14/12/12	0.0039	11.4	< .01	4	6.5	< .00021	17.4	37	9.6	106	15.5	0.0107
72-2047	Ngati Haua	20/11/12	0.029	31	< .01	< .05	7.3	< .00021	21	44	4.3	230	18.3	0.186
69-2074	Orini	21/11/12	0.00151	17.5	< .01	1.62	6.1	< .00021	40	85	3.0	86	17.4	0.28
69-2075	Rotokauri	17/01/13	0.0013	17.6	< .01	0.09	6.4	< .00021	41	88	2.6	88	18.0	0.0067
69-2076	Te Akau	15/11/12	0.0047	26	< .01	1.22	7.4	< .00021	8.2	17.5	40	400	16.6	< .0011
69-2077	Te Kowhai	26/11/12	1.08	17.4	< .01	3.5	6.4	< .00021	27	58	4.4	129		0.0054
69-2079	Waitetuna	26/11/12	0.062	196	0.24	< .05	8.7	< .00021	10	21	< .5	760		< .0011
69-2080	Whatawhata	26/11/12	0.0024	13	< .01	1.8	6.9	< .00021	32	69	19.4	100		0.0142
69-2081	Whitikahu	23/11/12	1.05	49	< .01	< .05	6.6	< .00021	43	91	0.6	300	17.5	0.034

Well Number		Date	Mn	Na	NH_4	NO_3	pH	Sb	Si (D)	Si	SO_4	TDS	Temp.	Zn
69-2187	Horotiu	26/11/12	0.0023	13.1	< .01	2.2	6.6	< .00021	33	71	7.2	91		0.0062
69-912	Gordonton	26/11/12	0.0068	13.8	0.02	29	6.3	< .00021	20	44	31	290		0.021
72-739	Te Uku	26/11/12	0.1	24	0.59	< .05	7.8	< .00021	14.7	31	0.9	240		0.0041
Waipa														
70-1156	Hora Hora	12/12/12	0.00136	11.7	< .01	0.34	7.2	< .00021	35	74	2.4	113	17.9	0.23
70-1157	Karapiro	13/12/12	0.0144	11.1	< .01	1.43	6.6	< .00021	38	81	1.4	76	16.9	0.050
70-1158	Ngahinapouri	10/12/12	0.00145	7	< .01	5.8	6.2	< .00021	12.9	28	16.6	107	16.3	0.0043
70-1159	Parawera	17/01/13	0.0019	11.5	< .01	2.1	6.4	< .00021	37	78	1.6	70	17.3	0.044
70-1161	Rukuhia	10/12/12	0.058	24	< .01	0.05	6.4	< .00021	39	84	3.0	135	19.0	0.044
70-1162	Whitehall	14/12/12	0.00183	10.6	< .01	0.8	6.7	< .00021	38	81	2.1	52	18.4	0.143
70-1164	Puahue	12/12/12	0.00069	10.2	< .01	0.98	6.3	< .00021	40	86	2.3	55	15.5	0.0092
70-1187	Capernwray Bible College	11/12/12	0.0072	18	< .01	10.6	6.1	< .00021	30	64	2.2	134	15.3	0.124
70-1231	Goodwood	11/12/12	< .00053	13.1	0.02	7.3	6.5	< .00021	21	45	19.6	135	17.2	< .0011
70-453	Hautapu	10/12/12	0.0117	19	0.01	10.4	6.5	< .00021	32	68	31	210	17.0	0.0021
70-778	Paterangi	10/12/12	0.0045	16.2	< .01	0.09	6.5	< .00021	42	90	1.1	83	18.6	0.052
70-794	Pokuru	6/12/12	0.00098	9.9	< .01	0.17	6.7	< .00021	40	85	1.9	50	16.1	0.0098
70-804	Pukeatua	12/12/12	0.0045	10.2	< .01	0.55	6.4	< .00021	38	82	1.6	64	17.3	0.028
70-951	Te Miro	6/12/12	0.07	10.6	0.24	< .05	8.1	< .00021	0.79	1.68	< .5	107	16.6	0.003
70-952	Te Pahu	14/12/12	0.122	13.4	< .01	0.06	7.0	< .00021	38	82	2.1	108	17.5	0.052
Waitomo														
71-60	Kinohaku	21/11/12	0.24	95	< .01	1.4	7.4	0.00051	9.1	19.4	23	330	16.3	0.29
71-63	Aria Primary	19/12/12	0.0061	75	0.11	0.18	9.1	< .00021	7.1	15.3	8.0	220	18.4	0.21

Table 12: General groundwater quality statistics for the 81 community well network (concentrations in g m^{-3}, conductivity in mS m^{-1}, (D) indicates dissolved rather than total concentrations).

Determinand	Mean	Median	Min	Max	St dev	Skew	Non-detect
Alkalinity	60	35	8	250	55.56	1.77	0
As	0.0018	0.00055	0.00055	0.0178	0.00	3.41	53
B	0.159	0.016	0.00026	7	0.79	8.38	1
Ca	14.7	8.1	1.2	250	30.87	6.09	0
Cl	29.4	15.8	2.5	610	73.84	6.93	0
Cond.	25.8	16.2	6.6	301	35.17	6.35	0
Cu	0.0089	0.0023	0.00026	0.142	0.02	4.75	27
Fe (D)	0.54	0.01	0.01	15.70	2.16	5.47	51
Fe	5.01	0.29	0.01	116	15.83	5.18	14
Free CO_2	20.0	18.0	0.5	80	15.23	1.29	7
Hardness	58.7	34.0	6.4	710	89.45	5.27	0
K	4.06	3.90	0.16	19.30	2.53	2.85	0
Mg	5.36	3.60	0.19	29.0	5.41	2.15	0
Mn (D)	0.09	0.006	0.00025	1.08	0.21	3.39	4
Mn	0.11	0.007	0.0006	1.08	0.23	3.17	0
Na	27.1	15.5	5.2	350	44.72	5.62	0
NH_4	0.05	0.01	0.01	0.61	0.13	3.21	56
NO_3-N	2.117	0.660	0.025	29	4.01	4.35	15
pH	6.8	6.6	5.9	9.1	0.75	1.21	0
Sb	0.000134	0.000105	0.000105	0.00164	0.00	7.83	74
Si (D)	28.3	32.0	0.8	45.0	11.77	-0.58	0
Si	60.5	69.0	1.7	96.0	25.10	-0.59	0
SO_4	17.6	3.2	0.30	530	60.62	7.80	3
TDS	173	108	44	2000	234.09	6.32	0
Temp.	17.2	17.0	12.1	22.1	1.61	0.45	0
Zn	0.082	0.019	0.0005	1.22	0.17	4.53	3

3.4 Comparison of community results with drinking water standards and guidelines

Community groundwater supply quality is compared with drinking water standards and aesthetic guidelines in Table 13. Exceedances of MAVs and half MAVs (inclusive of those exceeding the MAV) are reported for measured determinands of health significance.

It is apparent from Table 13 that the most common exceedances in community groundwater supplies are for arsenic and manganese. There are also single exceedences for nitrate and boron. It should be emphasised that these concentrations are from source water sampling and hence measured prior to treatment. Also some school groundwater supplies are used for only non-potable purposes. The relatively lower nitrate exceedances reflect that supplies are typically abandoned once nitrate MAVs are exceeded due to the difficulty of treatment. There is some evidence for this in the community monitoring network history.

Manganese is the determinand that most commonly exceeds the DWS MAV in community supplies. Given it is naturally occurring, its source formation may not be able to be excluded during well design and hence treatment may be required. It can, however, be readily treated, typically with aeration and filtering.

Arsenic, as previously mentioned is a contaminant of particular concern for human health (Appendix V). Similar to the regional network it exceeds the drinking-water standards in about 4% of wells. Again the exceedences observed are in areas with geothermal influence.

As previously mentioned, antimony has been included as a one-off check. None of the supplies tested had concentrations exceeding the guideline value (MAV) of 0.02 g m^{-3}. Antimony is, however, known to occur at significant concentrations in some wells in Coromandel Peninsula not monitored in these networks.

Table 13: Community network groundwater quality comparison with drinking-water standards

Determinand	>MAV	>half MAV
Antimony	0 (0%)	0 (0%)
Arsenic	3 (3.84%)	8 (10.3%)
Boron	1 (1.2%)	1 (1.2%)
Manganese	6 (7.4%)	12 (14.8%)
Nitrate	1 (1.2%)	9 (11.1%)
Copper	0 (0%)	0 (0%)

Comparison of regional groundwater quality with aesthetic guideline values shows that pH most commonly falls outside the ideal range. This is indicative of corrosion concerns relating to typically acidic waters.

Iron and manganese, which typically are elevated together) are common nuisance chemicals causing staining and scaling problems. High concentrations occur in anaerobic and peat influenced waters.

Table 14: Community groundwater quality comparison with aesthetic guideline values (GV)

Determinand	>GV[1]
Ammonia	3 (3.7%)
Chloride	2 (2.5%)
Copper	0 (0%)
Hardness	4 (4.9%)
Iron	46 (57%)
Manganese	25 (31%)
pH	59 (70.0%)
Sodium	1 (1.2%)
Sulphate	1 (1.2%)
Zinc	0 (0%)

[1] or outside range for pH

3.5 Redox condition of groundwater at monitoring wells

The redox conditions of groundwater in the monitoring wells strongly influences its quality and importantly the occurrence of nitrate (previously reported in doc 2274183, Hadfield, 2011). Under anaerobic conditions nitrate concentrations are typically below detection. Dissolved oxygen is also typically very low, and dissolved iron and manganese are often relatively high. Nitrogen, if detectable, is generally present at low levels in the ammonium form. Nitrate-N typically volatilises to N_2 gas via a microbially mediated process provided that an electron donor such as carbon is available (Korom, 1992).

Although the occurrence of nitrate and dissolved iron are typically mutually exclusive, there are a few wells where a mixture of conditions may be occurring, most likely due to screening of both anaerobic and aerobic zones together.

Four categories have been used to classify groundwater monitored in the regional and schools networks. Apart from aerobic and anaerobic categories, mixed and indeterminate categories are also designated. The criteria for these are as follows:

- Aerobic: NH_4, dissolved Fe and dissolved Mn all non-detect and NO_3-N > 1 ppm
- Anaerobic: Two of NH_4, dissolved Fe and dissolved Mn detected and NO_3-N non-detect
- Mixed: Two of NH_4, dissolved Fe and dissolved Mn detected and NO_3 -N detected > 1 ppm
- Indeterminate: not meeting the criteria above

Detection limits of 0.01 g m^{-3} were used for Mn and NH_4 whereas 0.02 g m^{-3} was the detection limit for dissolved Fe.

Dissolved oxygen was not used as a criterion because measurements were not considered sufficiently reliable in the regional and schools monitoring (due primarily to pumping effects). Also although aerobic conditions exist where nitrate-N is lower than 1 ppm (e.g. in areas not developed for agriculture), these are grouped as indeterminate until further evidence is gathered.

The percentages of network wells in each of the redox categories are listed in Table 15. Anaerobic groundwater is more commonly found in the community network. The median depths of the regional and community supply networks are 16 m and 38 m respectively (means are 27 m and 50 m). Figure 4 and 5, show that higher nitrate concentrations are generally found in shallower wells. Aerobic conditions are also less likely at depth. Total depth is used in these figures due to a lack of screen depth information for some wells. Screen depths would give a more accurate indication of where the water is being sampled from. Community wells for which total depth is unknown are excluded.

Table 15: Redox category percentages for the monitoring networks

Redox categories	Regional Network	Community Network
Aerobic	57.66%	30.86%
Anaerobic	3.60%	13.58%
Mixed	11.71%	12.35%
Indeterminate	27.03%	43.21%

School supply wells have nitrate concentrations below the drinking water guideline with one exception (which is not used for potable supply). Hence this network is ‘skewed’ by the necessity to meet standards for potable supply. There are instances where supplies have been abandoned due to exceedances. The regional network may, by contrast, be ‘relatively skewed’ toward shallower wells given interest in substantially including younger groundwater which may be affected by land-use change.

It is apparent that mixed redox sites are relatively shallow. Indeterminate sites comprise a large part of the deeper wells where groundwater is more likely to be older and hence less impacted to date by agricultural effects. The median and standard deviations of total depth for the redox categories are listed in Table 16. These show a similar pattern for the Regional and Community networks.

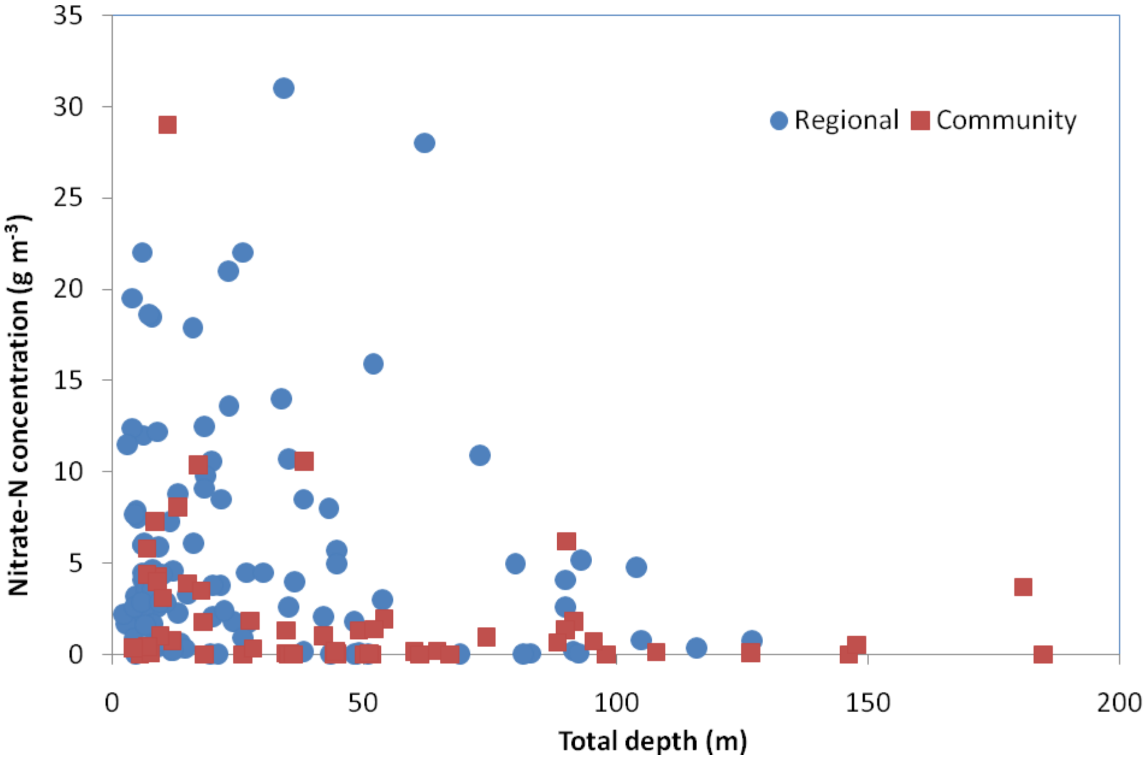


Figure 4: **Nitrate-N concentrations versus depth for the regional and community networks.**

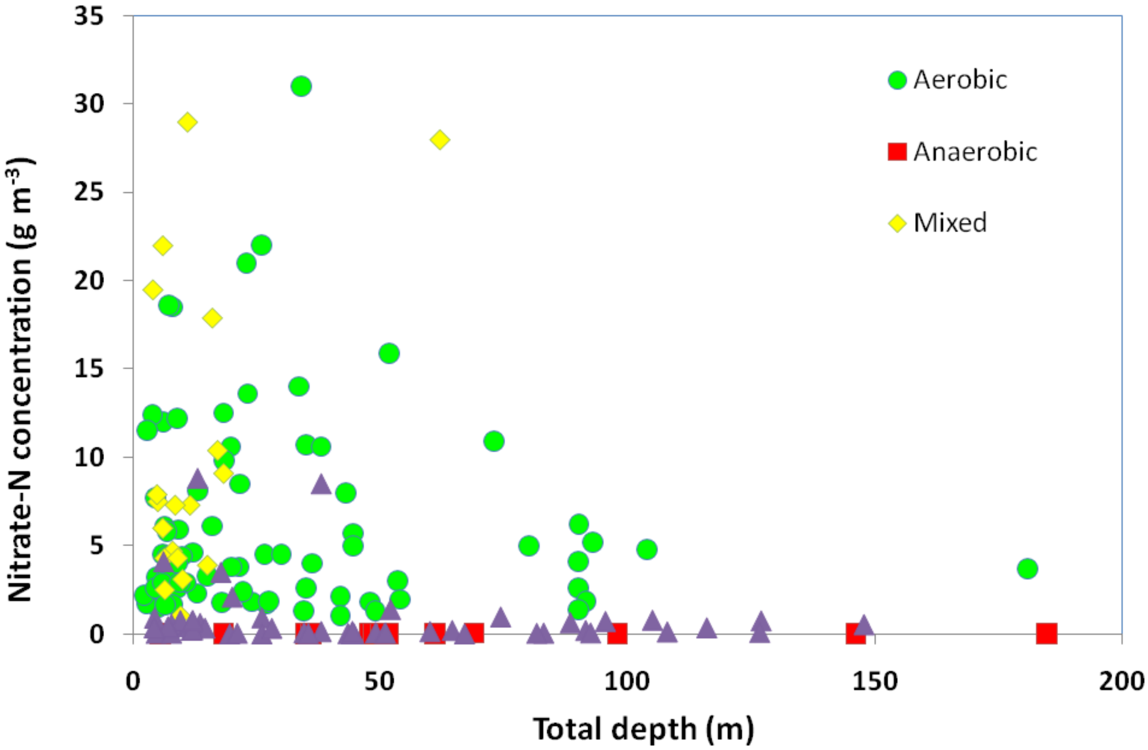


Figure 5: **Redox categories versus total well depth**

Table 16: Summary total depth statistics (median and standard deviation) for redox categories in the regional and community networks

Redox catagories	Regional Network (metres)	Community Network (metres)
Aerobic	18.33 (24.92)[1]	38.1 (46.92)
Anaerobic	48.5 (11.98)	50.75 (57.53)
Mixed	6.35 (15.56)	13.0 (27.98)
Indeterminate	19.75 (37.78)	44.6 (38.75)

[1] *standard deviation in brackets*

The resultant redox catagories (from doc. 2857305) are mapped for both networks in Figure 6. It appears that the ‘mixed’ status groundwaters occur most commonly in the southern Hauraki Plains and Hamilton Basin where there is intensive land-use (predominantly dairy) and the occurrence of occasional peaty sediments. The Coromandel Peninsula is characterised by common indeterminate waters and some anaerobic conditions. The former are likely to reflect the typical lack of intensive agriculture.

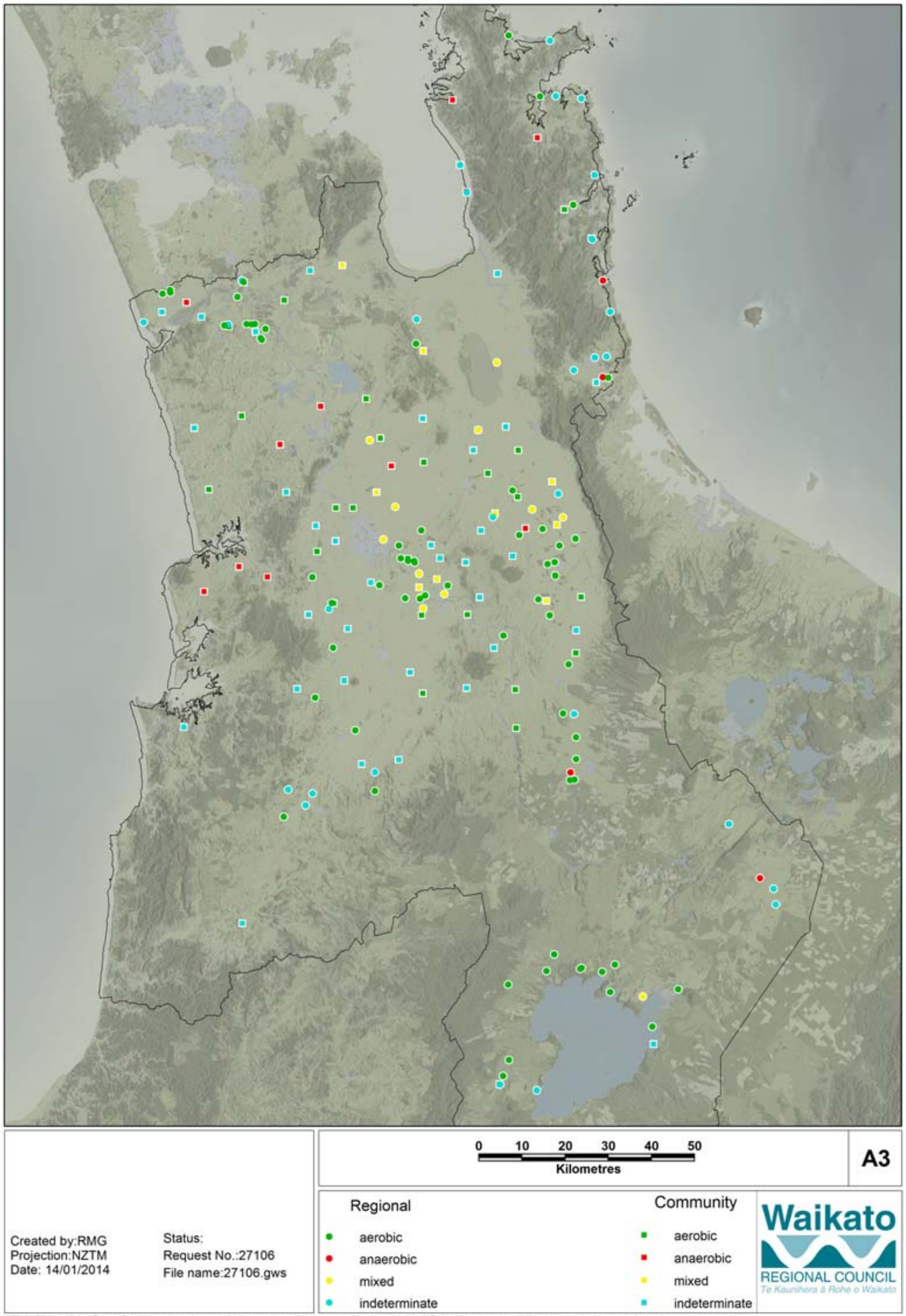


Figure 6 Distribution of redox categories for the regional and community networks.

3.6 Nitrate trends

Substantial variations in nitrate concentrations spatially across the region are evident in Figure 3. Nitrate is more likely to exceed drinking water guidelines in areas with a high proportion of market gardening (Pukekohe) and intensive dairy farming (Hamilton-Mangaonua).

There is a general trend of decreasing nitrate concentrations northward along the Hauraki Plains, with progressively low-lying, finer and peaty sediments. It is associated with a change from recharge to discharge flow regimes and more reducing groundwater conditions (i.e. lower redox). Nitrate concentrations are generally highest in shallow, vulnerable aquifers and are lowest in very deep or iron-rich waters.

There are few records available to indicate long-term nitrate trends. Monitoring data from some schools supplies, however, indicate a steady increase at several supplies since the 1950s.

Pressures on groundwater quality are generally increasing as land-use intensifies. The total volume of wastewater consented to discharge to land has steadily increased (it was 540,000 $m^3 d^{-1}$ in 1997).

National surveys of nitrate contamination of New Zealand have found some of the highest nitrate concentrations to be in parts of the Waikato region (Lincoln Environmental, 1998; GNS, 2007).

The ‘nitrate’ monitoring well network comprises wells listed in Table 17, which are monitored quarterly. These wells have generally been monitored since 1995 although some have longer records. The temporal trends of nitrate-N from these wells are illustrated in the following series of figures.

Table 17: Nitrate groundwater quality network (from doc 1529095)

Well	District	Map Reference	Depth (m)	Age[1] (years)	Land-use
60-12	Coromandel	T11:549-811	9	0.5	urban
61-113	Franklin	R12:831-387	13	4	market garden
61-126	Franklin	R13:607-298	6.09	5	dairy
61-208	Franklin	R12:668-365	18.3	9	drystock[2]
61-221	Franklin	R13:872-253	50	22	horticulture
61-59	Franklin	R13:791-285	26.6	11&59	dry stock
63-57	Hauraki	T13:414-204	5	11	dairy
64-108	Matamata-Piako	T14:465-802	23	62	dairy
64-117	Matamata-Piako	T14:565-844	16	7	dairy
64-12	Matamata-Piako	T14:496-863	11.5	7	dairy
64-20	Matamata-Piako	T14:531-738	9	8&46	urban, drystock
64-43	Matamata-Piako	T14:546-712	21.6	50	urban, drystock
64-46	Matamata-Piako	T14:557-780	12	17&43	dairy
64-50	Matamata-Piako	T14:595-797	16.1	15	dairy
64-70	Matamata-Piako	T14:557-901	11.8	27&59	dairy
64-120	Matamata-Piako	T15:510-655	22.2	27	market garden

Well	District	Map Reference	Depth (m)	Age[1] (years)	Land-use
66-6	Rotorua	U16:943-152	38	30	dairy
67-11	South Waikato	T15:535-620	18.5	62	dairy
67-15	South Waikato	T15:580-510	20	45	drystock[3]
69-173	Waikato	S14:151-871	6	3	dairy
69-365	Waikato	S13:123-022	4.2	2	dairy
69-81	Waikato	S14:982-739	2.25	1	drystock
70-44	Waipa	S15:244-635	18.3	39	drystock[2]
70-47	Waipa	T15:303-689	4.5	1	dairy
70-56	Waipa	S15:204-660	4.5	7	dairy
70-65	Waipa	S15:030-635	4.3	2	dairy
70-74	Waipa	S15:040-546	6.71	1	urban
70-76	Waipa	T15:430-574	30	31	dairy
70-21	Waipa	S15:238-661	6.41	5	berry farm
70-22	Waipa	S15:238-660	6.42	5	berry farm

[1] age expressed as mean residence time in years along with alternative ages where interpretation is non-unique

[2] market garden nearby

[3] dairy nearby

The following figures (7-36) show nitrate trends in individual monitoring wells. It can be seen that there is a range of responses to land-use and other factors. Linear trend analysis using seasonal Mann-Kendall test is reported in Table 18. This test is useful for detecting simple linear (monotonic) trends in variable environmental time-series data sets. It may suggest or discount the presence of an underlying trend which is not evident from visual inspection of the ground water record or summary statistics. This test generates probability (p) values that are used to assess the likelihood that the apparent relationship is ‘genuine’ rather than a random alignment of variables. The threshold (as conventionally used) for deciding a relationship is likely to be genuine where the probability (p) 5% or less (corresponding to a 95% confidence level or greater). A negative MK-Stat indicates a decreasing trend.

A total of 9 wells (30%) have significantly increasing nitrate concentrations while 12 (40%) are decreasing. This is an improvement from there being 37% reported to be increasing in 2011 and 23% decreasing. The significant decreases are typically from high concentrations (medians of 40% of these wells are above MAV and two thirds are above half MAV). Some of the temporal trends are clearly not monotonic (consistently increasing or decreasing), such as in wells 64_50, 64_120 and 70_44 (refer to Figures 20, 22 & 29 respectively). These wells show substantial and significant increases followed by similar declines.

Table 18: **Mann-Kendall trend analysis of nitrate concentrations** (red indicates increases and green decreases)

Well	Median (g m^{-3})	n	p-values (%)	trend (g m^{-3} y^{-1})
60-12	0.54	59	**<1**	**0.06**
61-113	5.50	70	**3.7**	**0.122**
61-126	6.5	67	**<1**	**0.132**
61-208	15.3	68	**<1**	**-0.246**
61-221	4.58	68	**<1**	**0.122**
61-59	4.17	64	**<1**	**0.033**
63-57	10.4	66	**<1**	**-0.14**
64-108	18.0	67	**<1**	**0.23**
64-117	14.4	66	**<1**	**0.389**
64-12	4.61	66	**<1**	**0.253**
64-20	5.86	67	60	0.038
64-43	8.08	67	**1.62**	**0.06**
64-46	4.42	68	**<1**	**-0.083**
64-50	7.21	68	**<1**	**-0.129**
64-70	0.75	64	**<1**	**-0.048**
64-120	6.57	71	13.36	-0.13
66-6	13.3	63	**<1**	**-0.80**
67-11	9.43	66	7.44	0.164
67-15	3.75	66	14.84	0.033
69-173	13.85	68	**1.83**	**-0.396**
69-365	6.42	68	**1.19**	**-0.109**
69-81	5.40	66	**<1**	**-0.35**
70-44	14.70	57	**<1**	**-0.32**
70-47	4.06	68	**<1**	**-0.215**
70-56	9.80	65	37.24	0.172
70-65	2.56	67	15.65	-0.056
70-74	3.75	68	**<1**	**0.109**
70-76	4.15	67	**<1**	**0.095**
70-21	9.70	67	9.62	-0.161
70-22	11.7	69	**<1**	**-0.336**

It is beyond the scope of this monitoring data report to relate these observed trends to land-use management. Factors such as groundwater age and attenuation mechanisms (denitrification) must be taken into account with land-use history. Contributing 'capture zones' are progressively being delineated for these sites. Ambient nitrate-N concentrations in aerobic conditions reflect vegetation and climate. Native forest and groundcover are likely to leach about 2 kg N ha^{-1} y^{-1} (Ledgard, 2000). Effective rainfall is typically greater than 300 mm y^{-1} and hence a nitrate-N concentration under ambient conditions is unlikely to be significantly greater than 0.6 g m^{-3}.

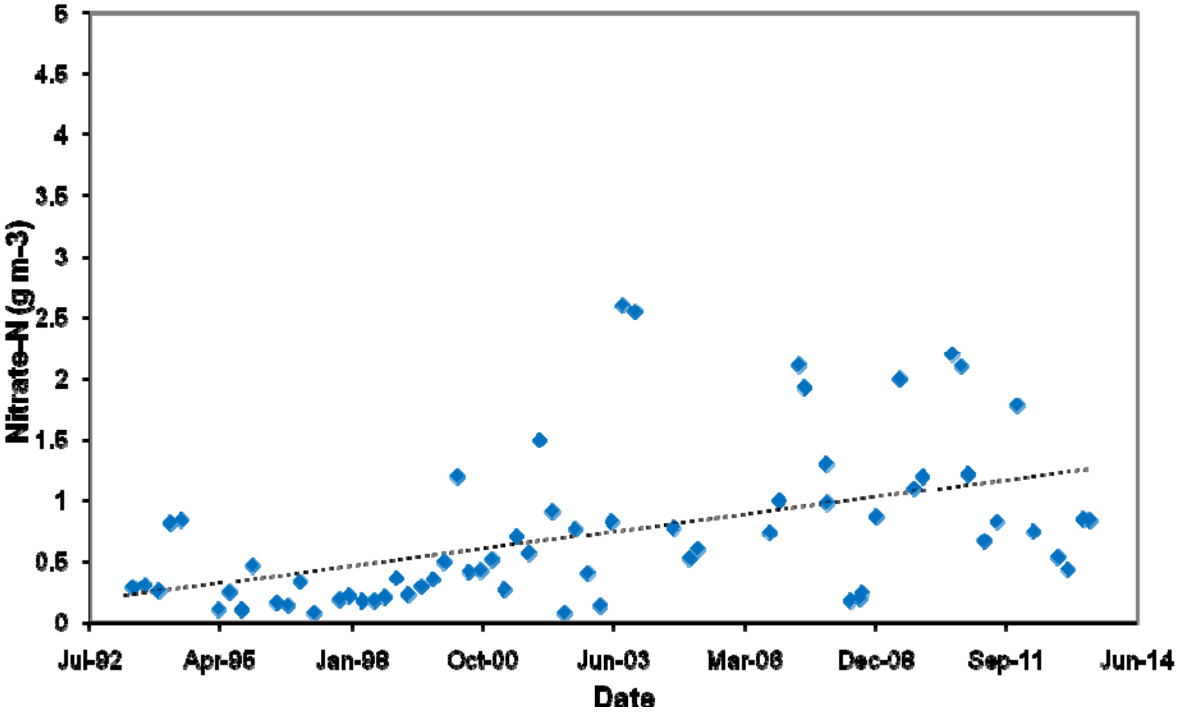


Figure 7: Nitrate concentration trend in well 60_12

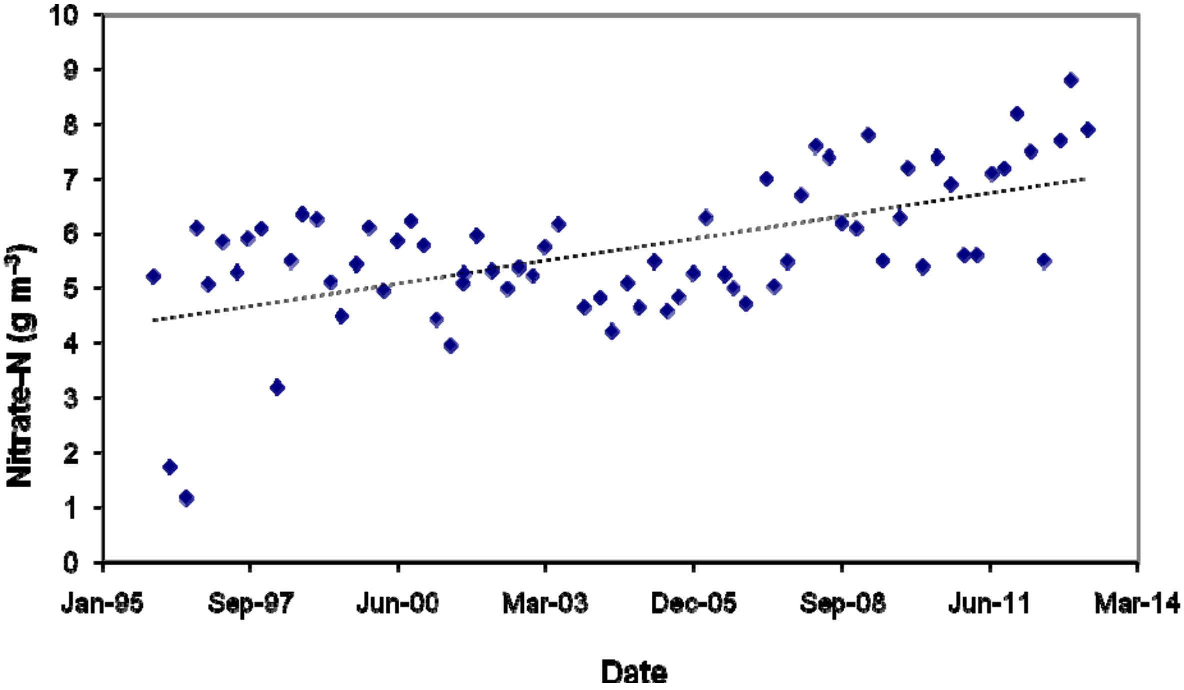


Figure 8: Nitrate concentration trend in well 61_113

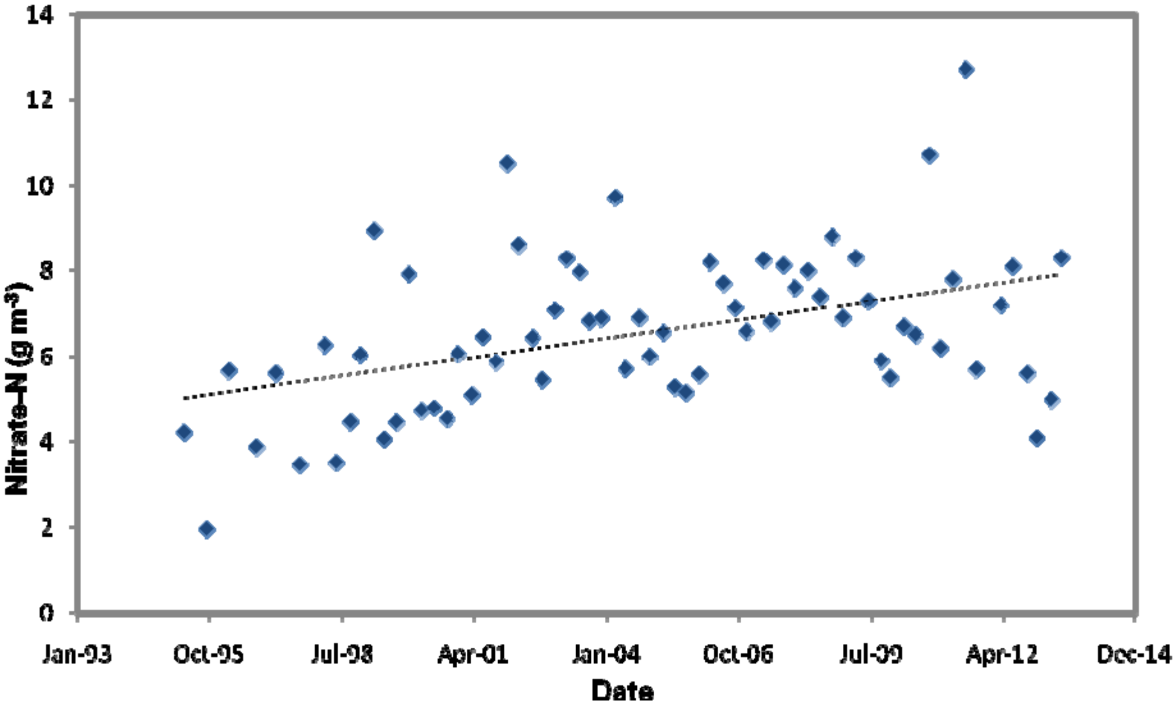


Figure 9: Nitrate concentration trend in well 61_126

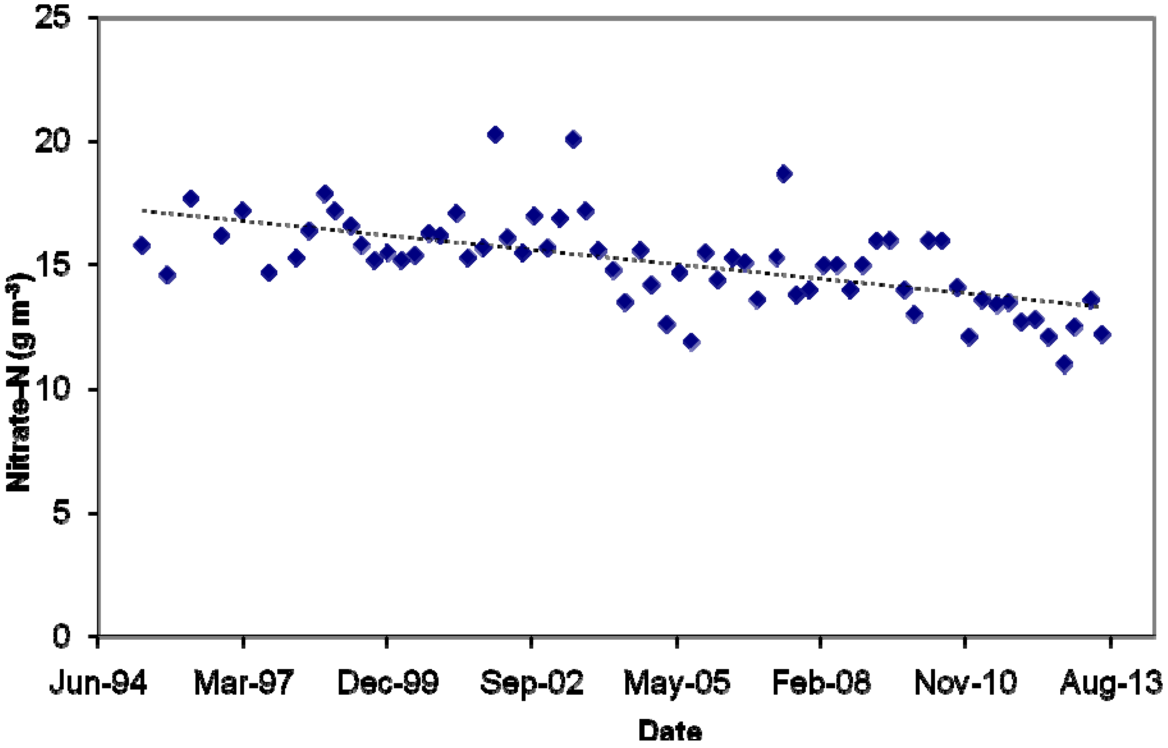


Figure 10: Nitrate concentration trend in well 61_208

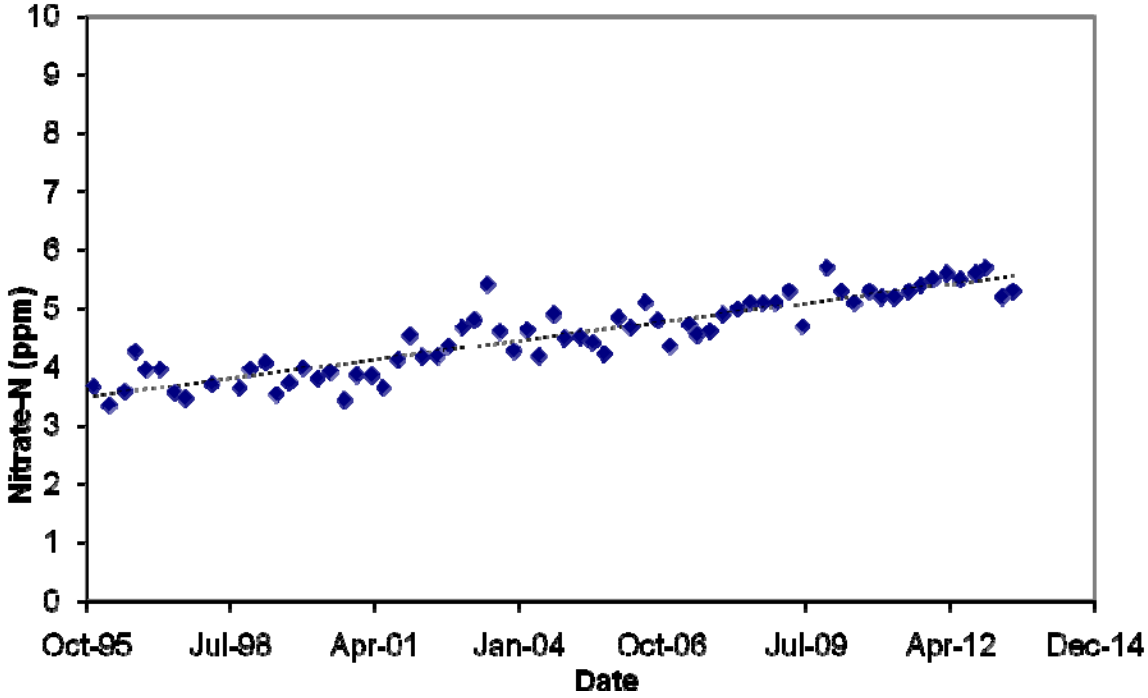


Figure 11: **Nitrate concentration trend in well 61_221**

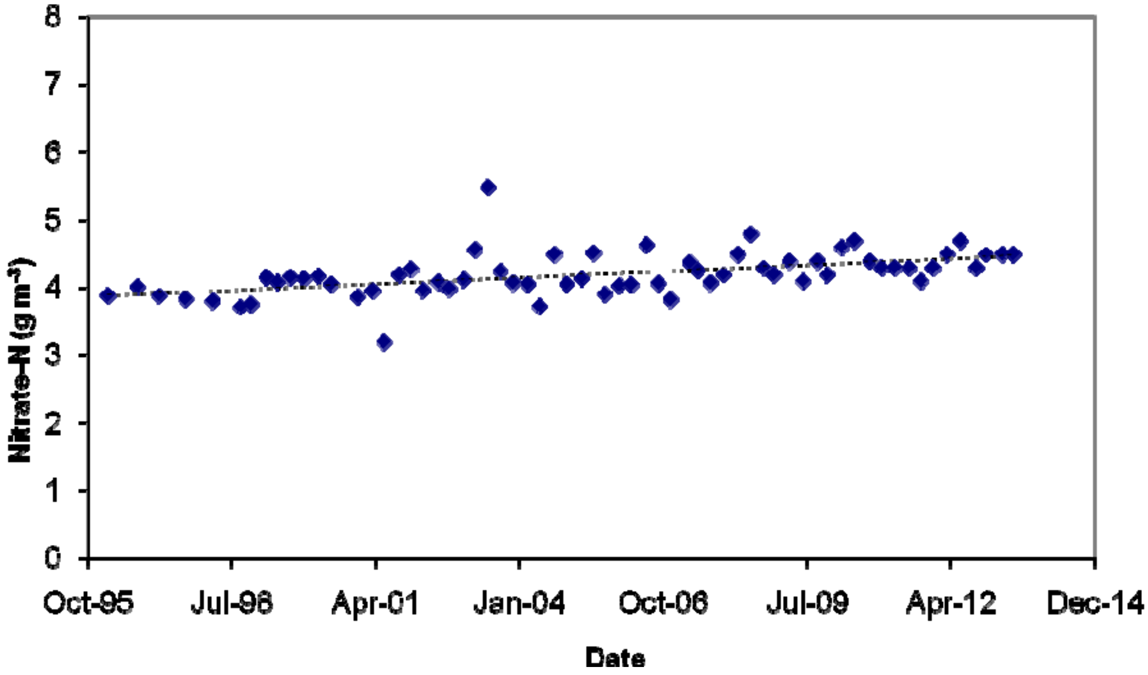


Figure 12: **Nitrate concentration trend in well 61_59**

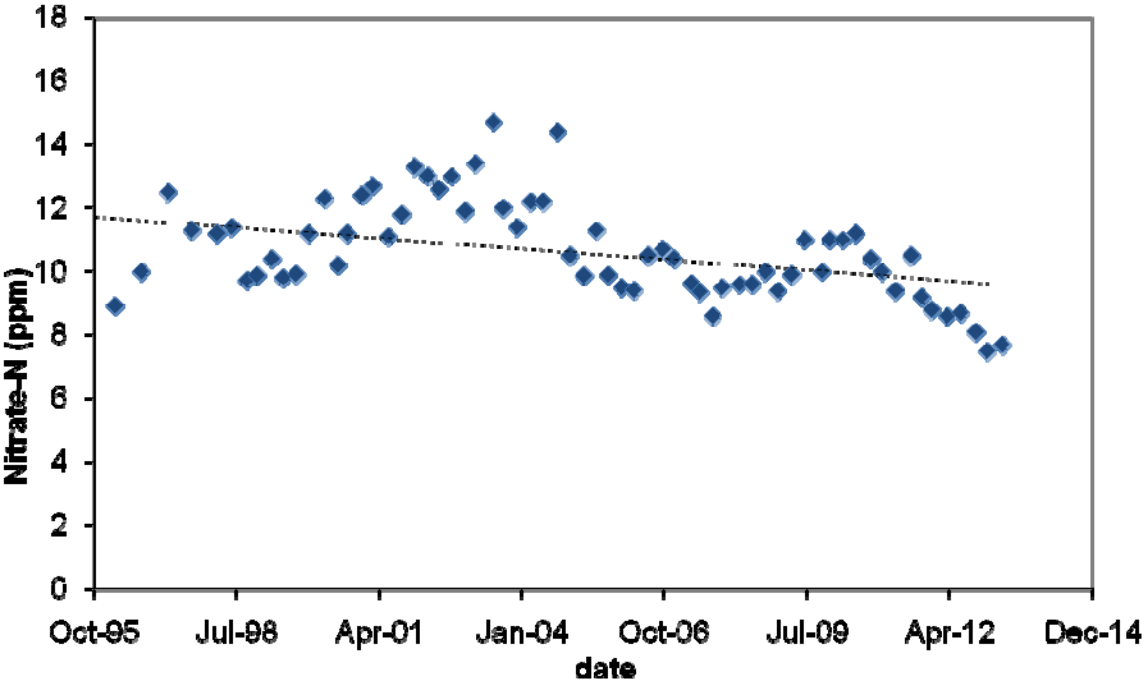


Figure 13: Nitrate concentration trend in well 63_57

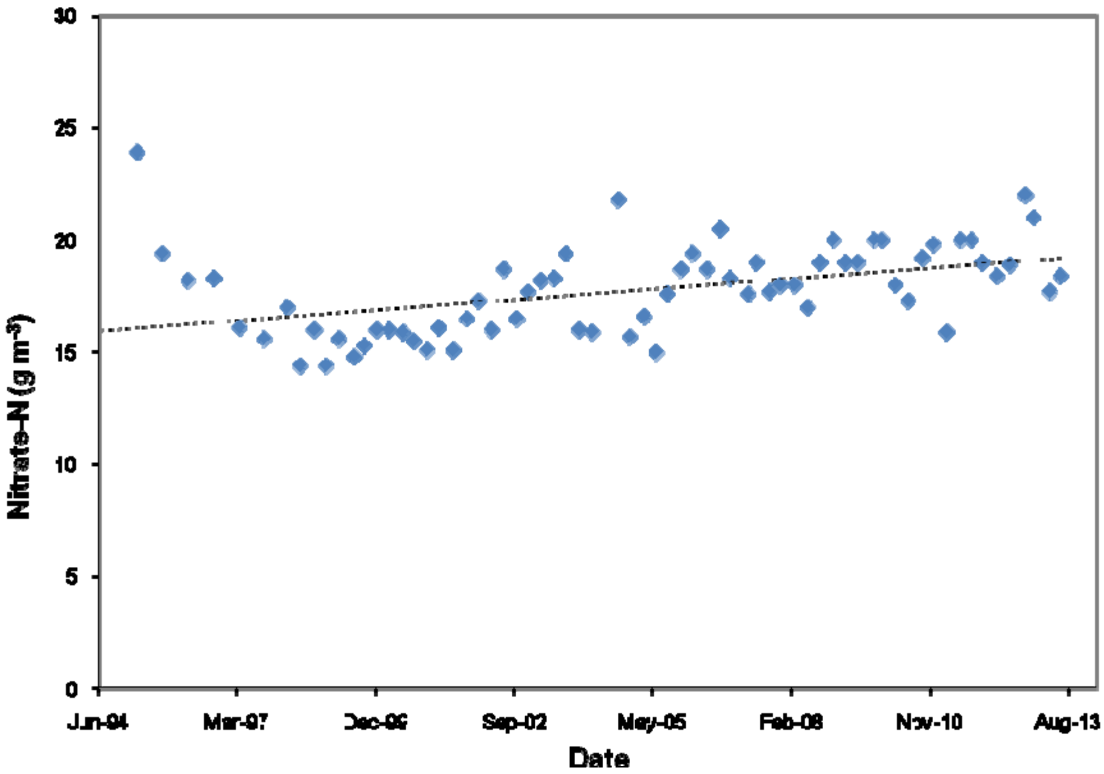


Figure 14: Nitrate concentration trend in well 64_108

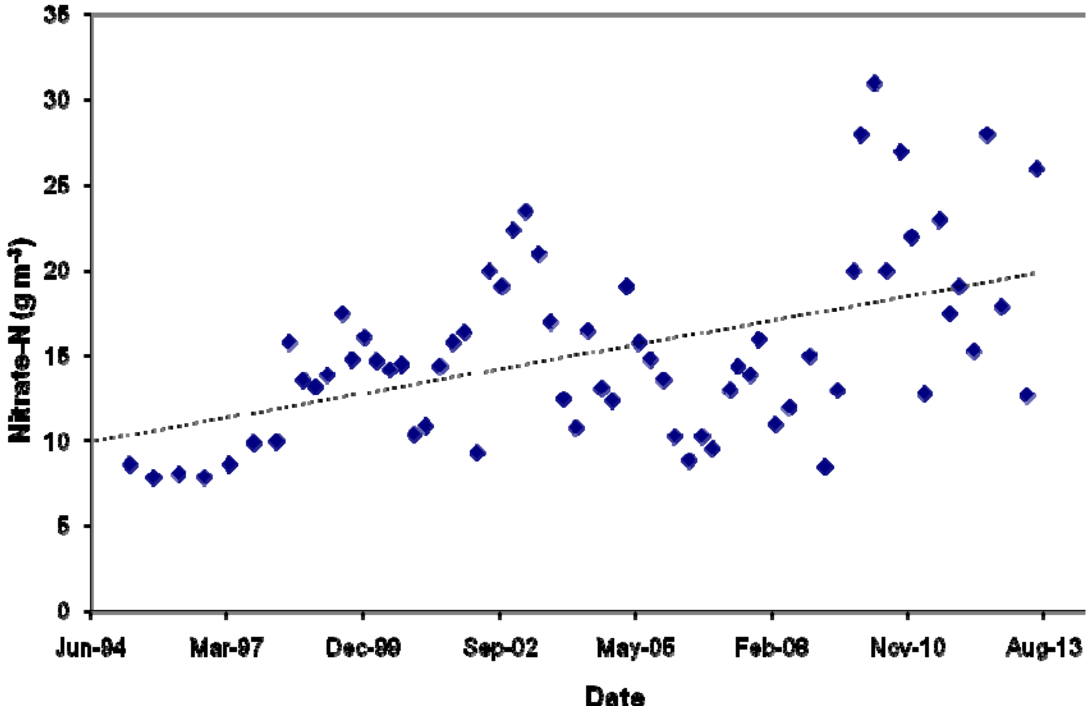


Figure 15: Nitrate concentration trend in well 64_117

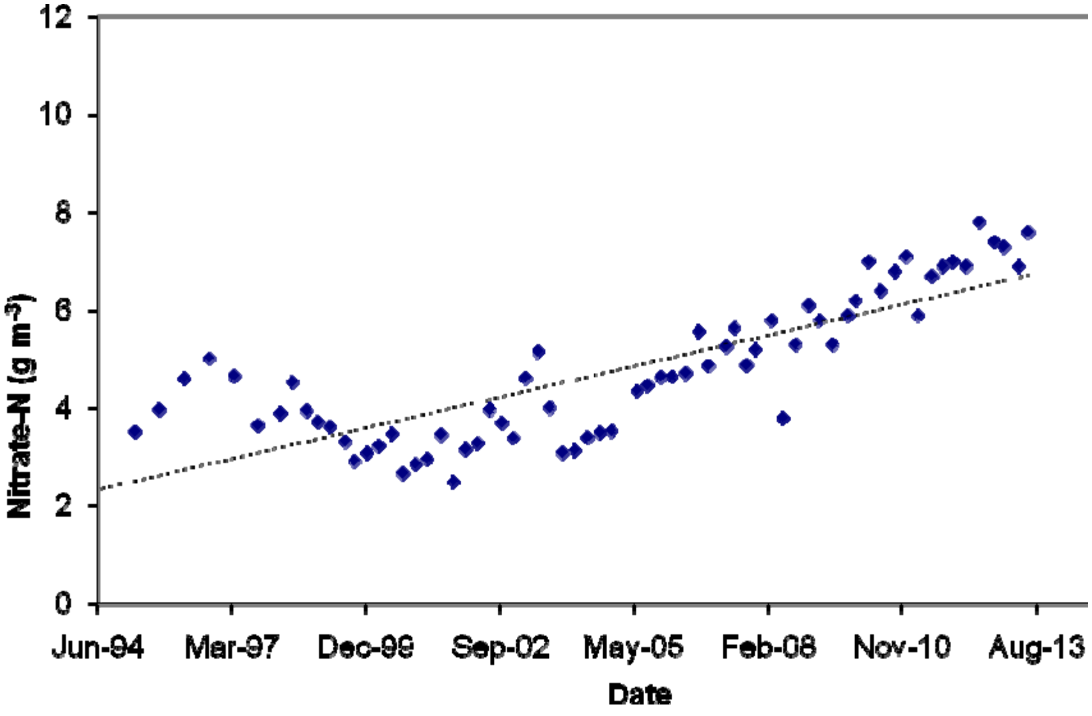


Figure 16: Nitrate concentration trend in well 64_12

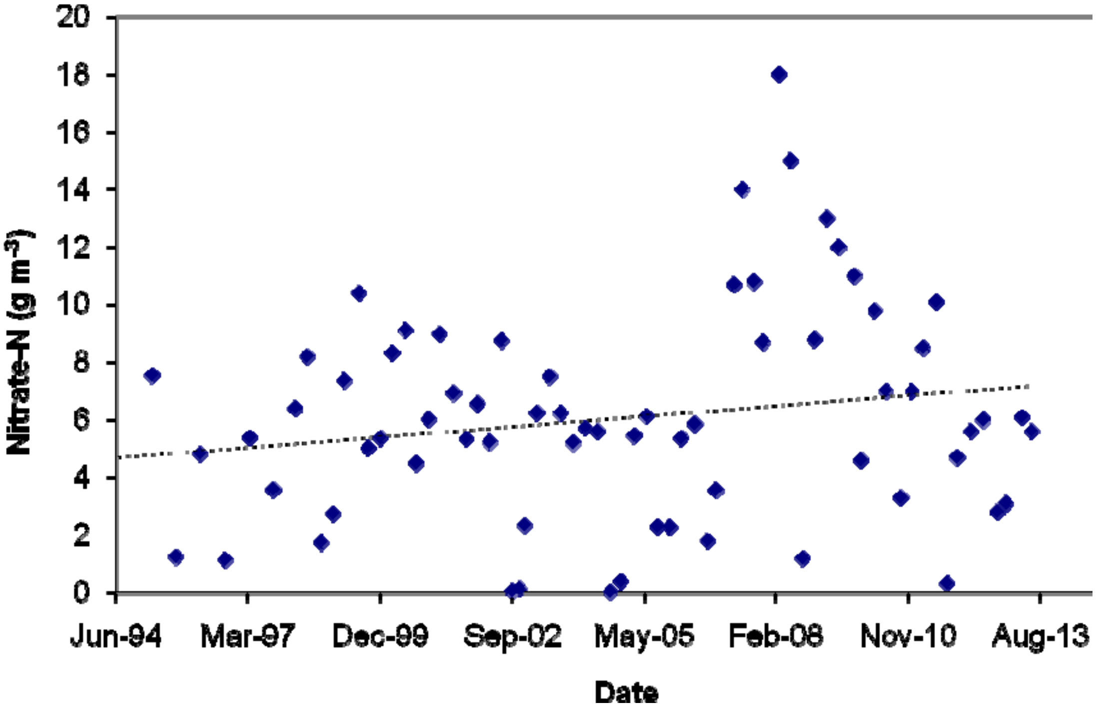


Figure 17: Nitrate concentration trend in well 64_20

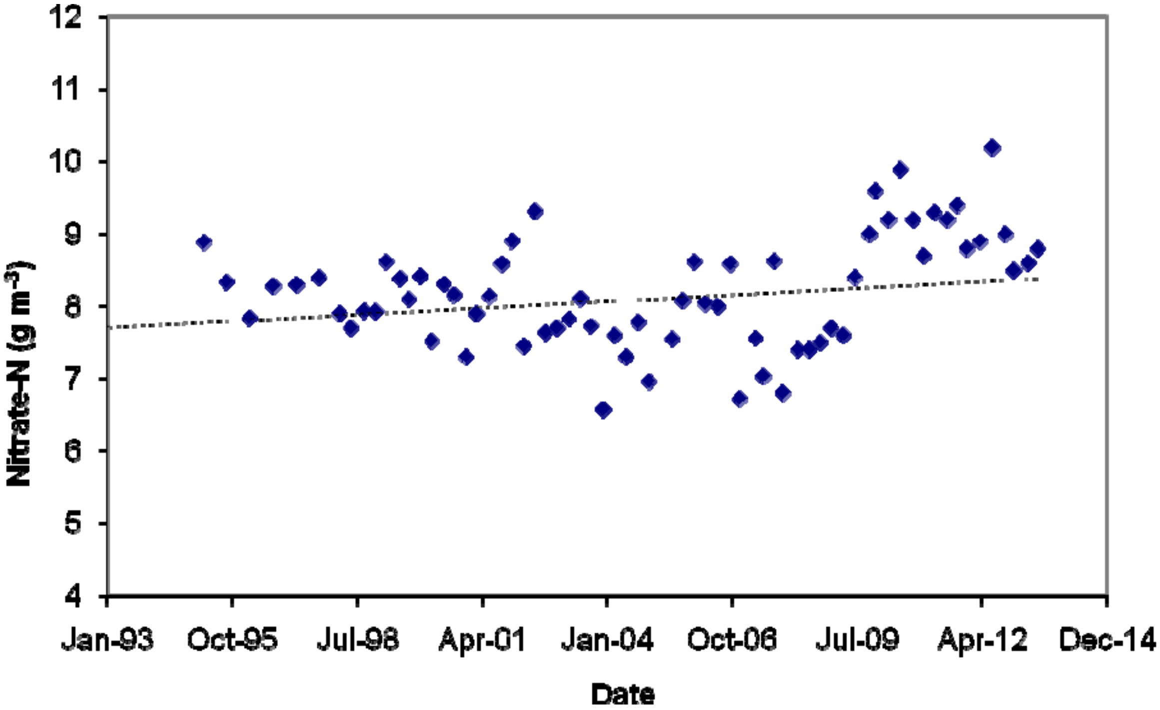


Figure 18: Nitrate concentration trend in well 64_43

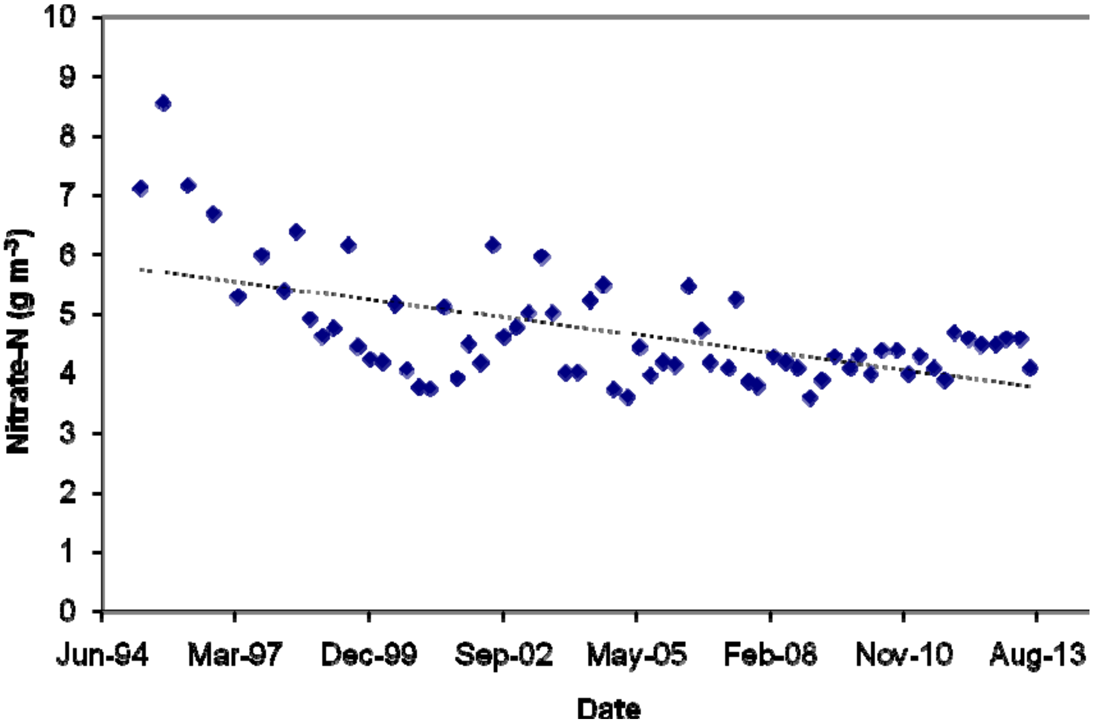


Figure 19: **Nitrate concentration trend in well 64_46**

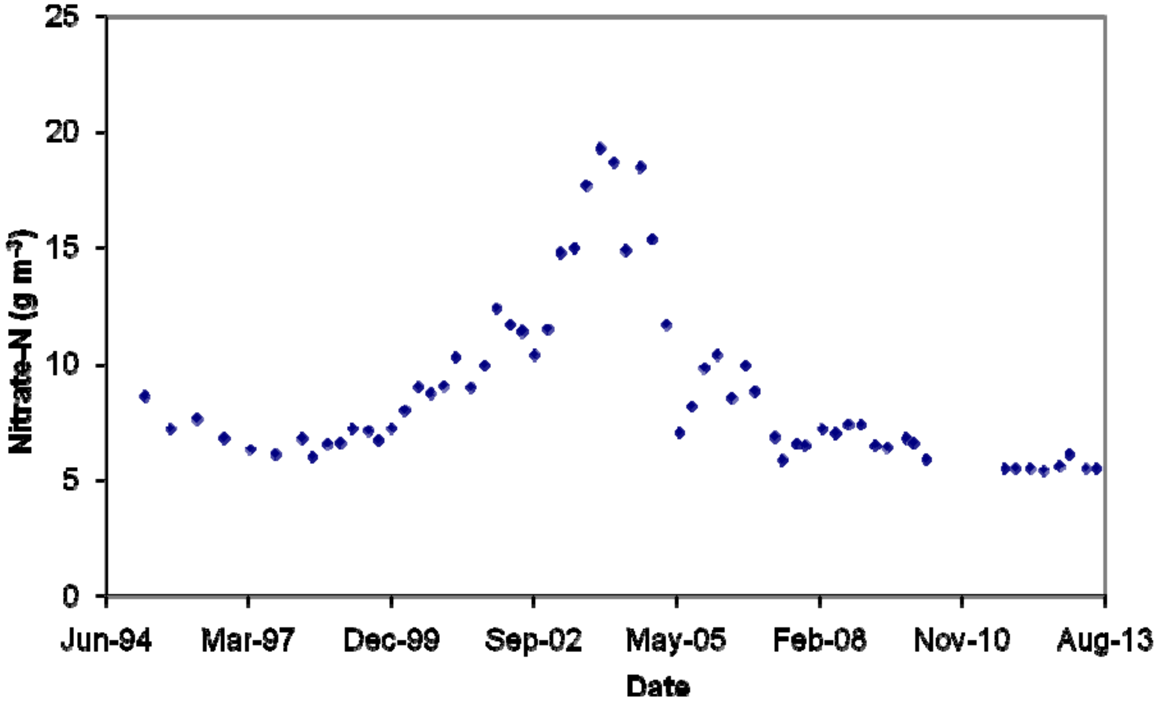


Figure 20: **Nitrate concentration trend in well 64_50**

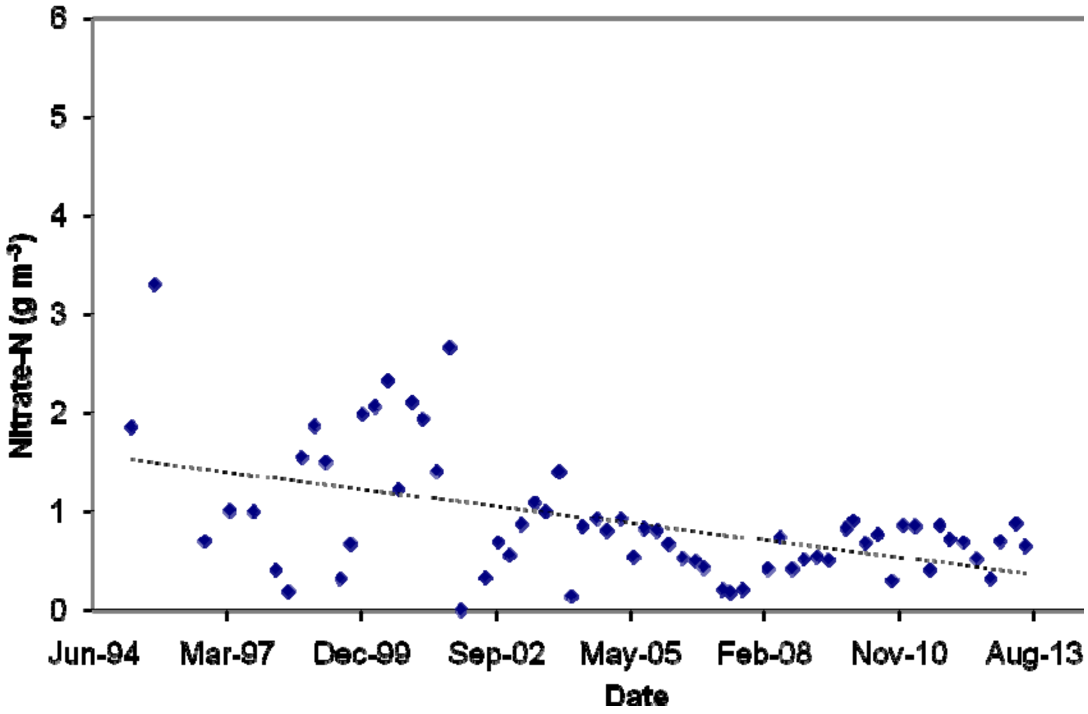


Figure 21: **Nitrate concentration trend in well 64_70**

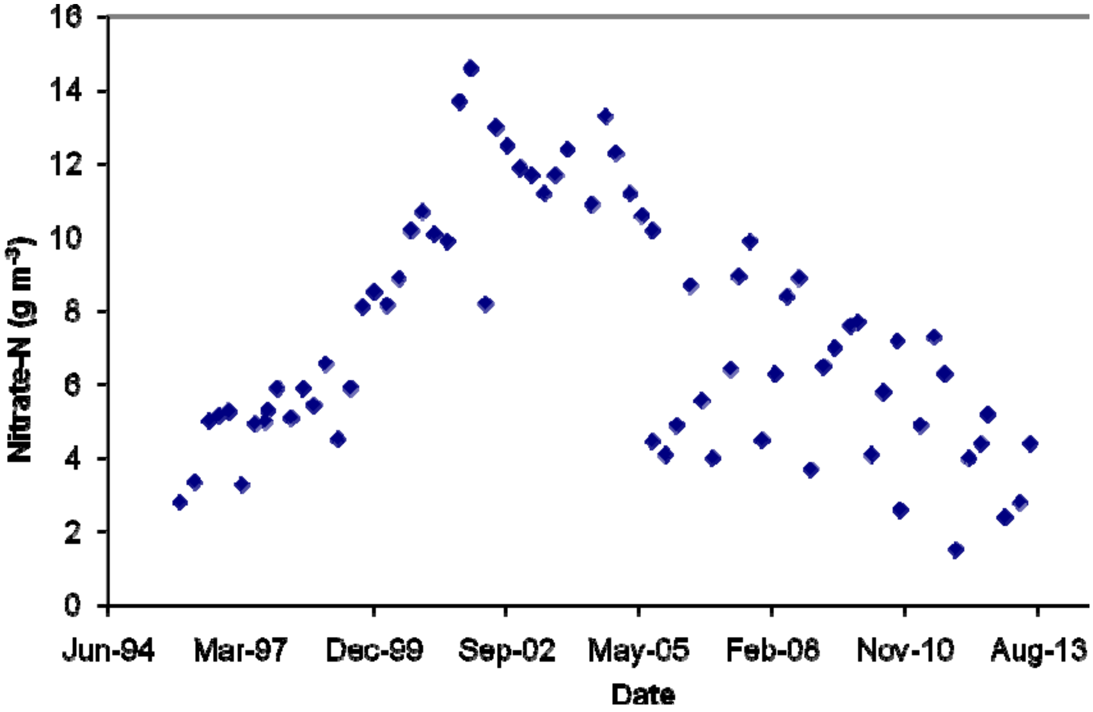


Figure 22: **Nitrate concentration trend in well 64_120**

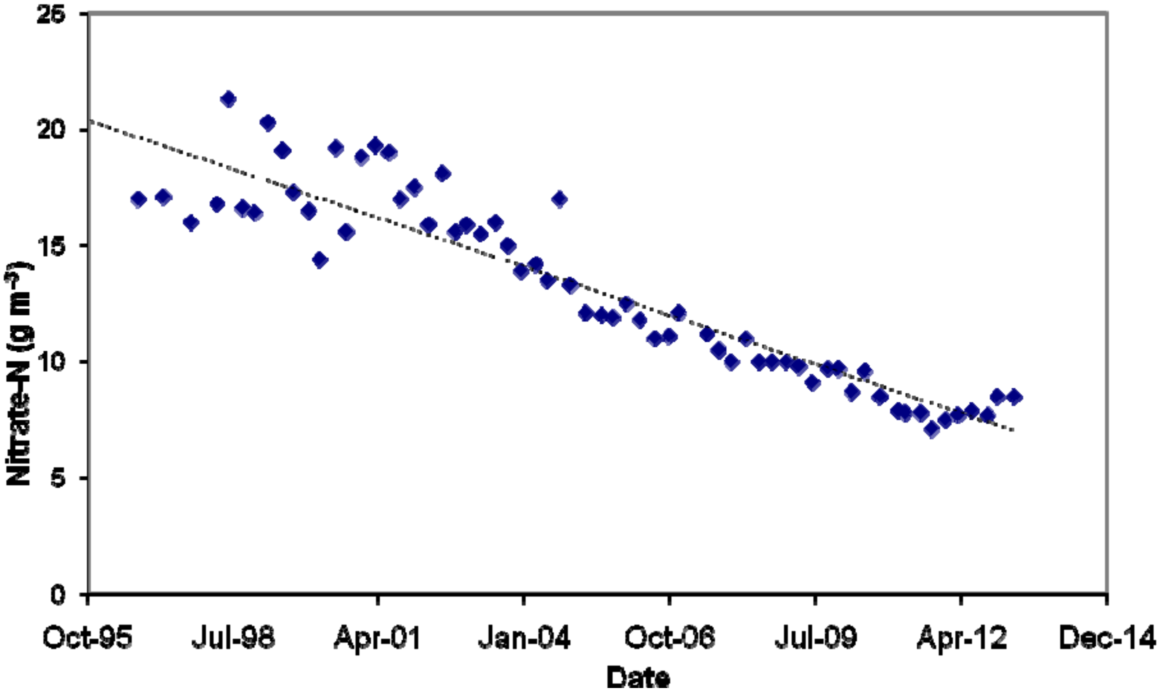


Figure 23: Nitrate concentration trend in well 66_6

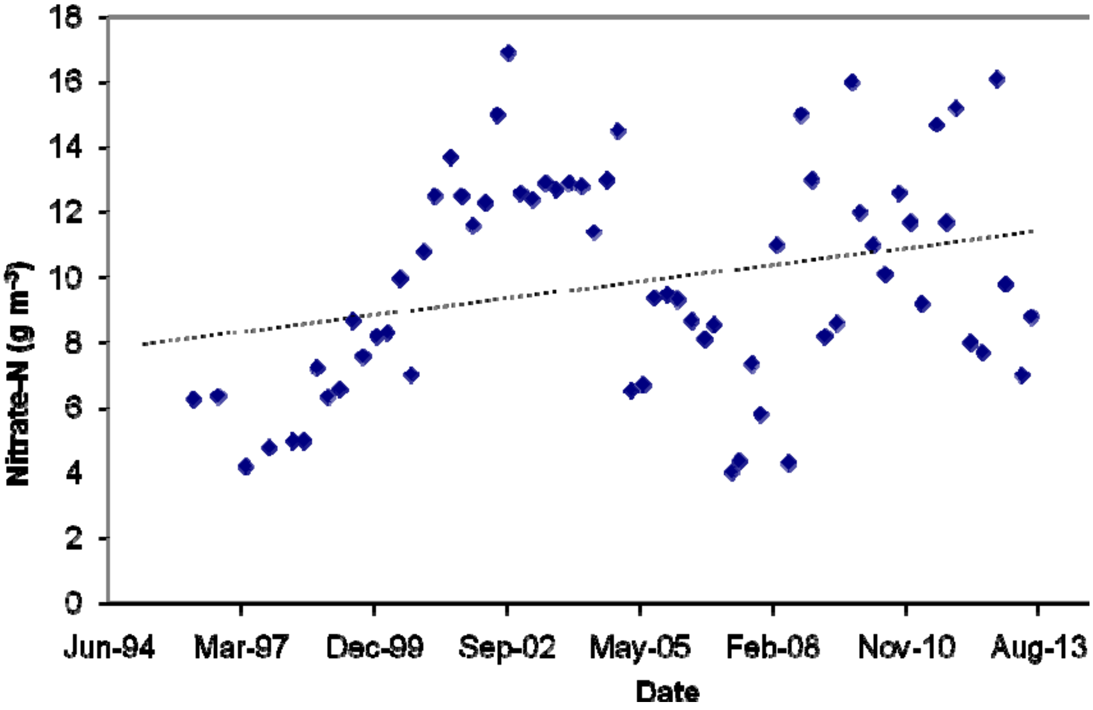


Figure 24: Nitrate concentration trend in well 67_11

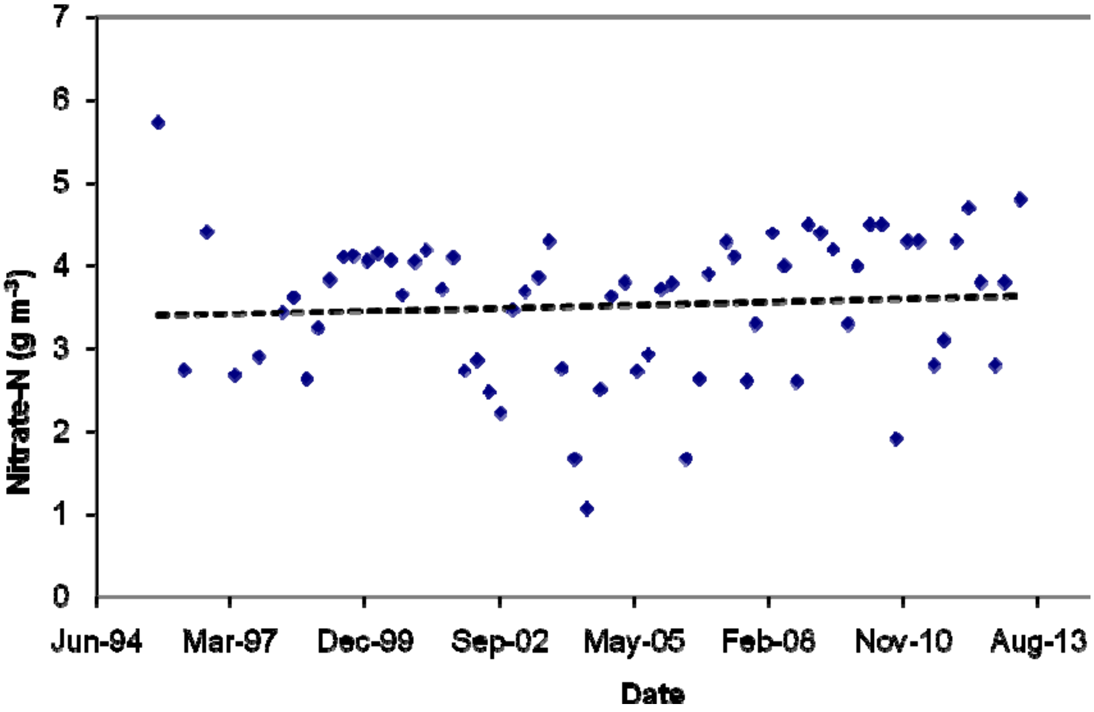


Figure 25: **Nitrate concentration trend in well 67_15**

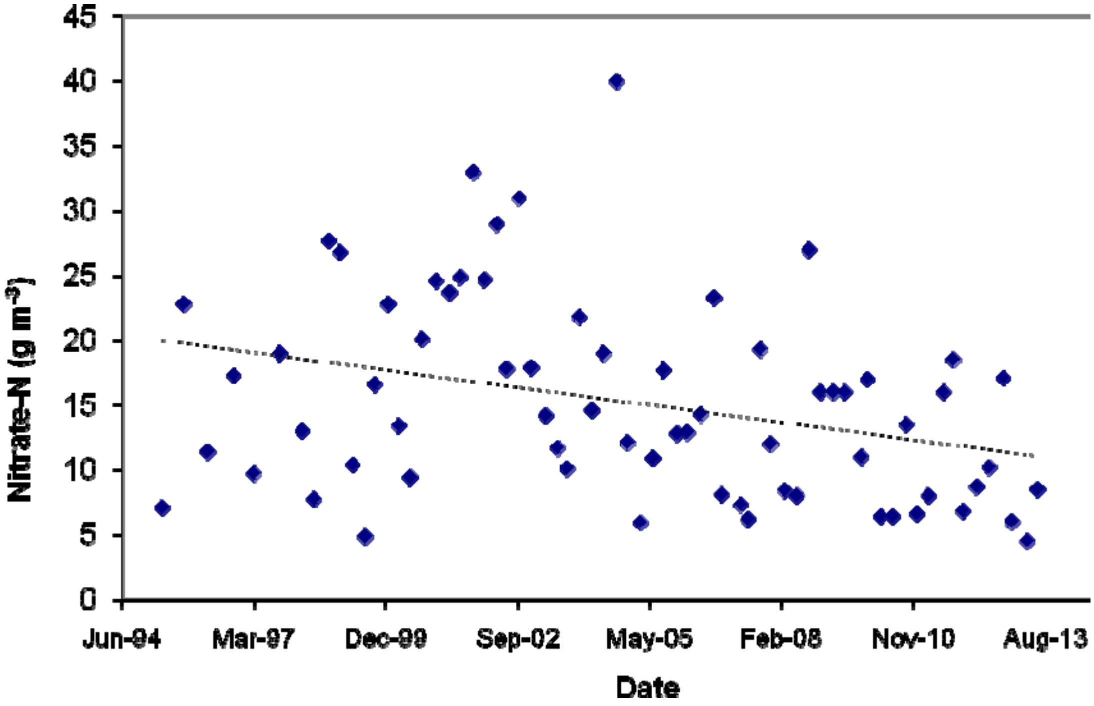


Figure 26: **Nitrate concentration trend in well 69_173**

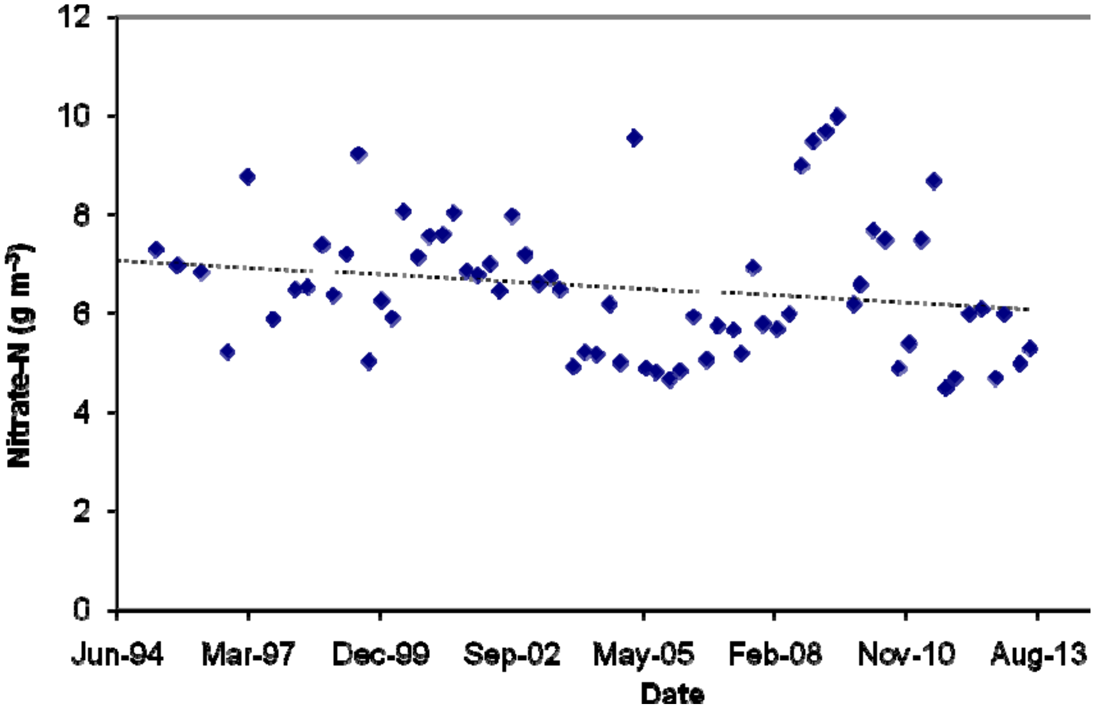


Figure 27: Nitrate concentration trend in well 69_365

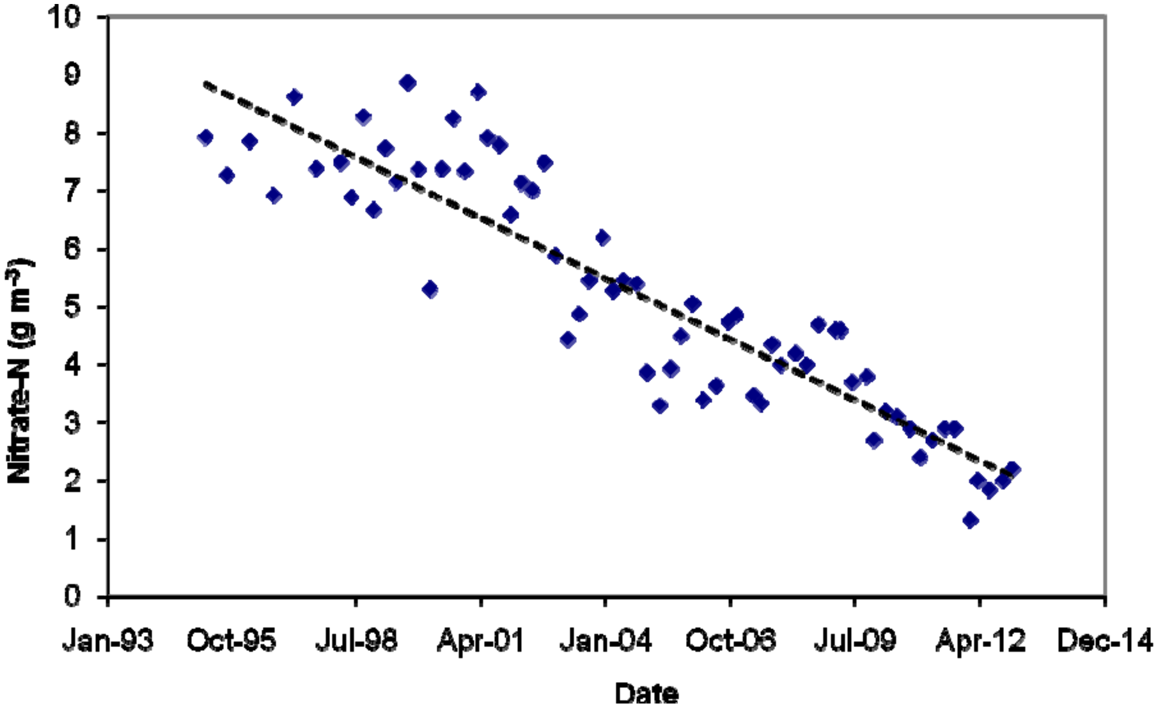


Figure 28: Nitrate concentration trend in well 69_81

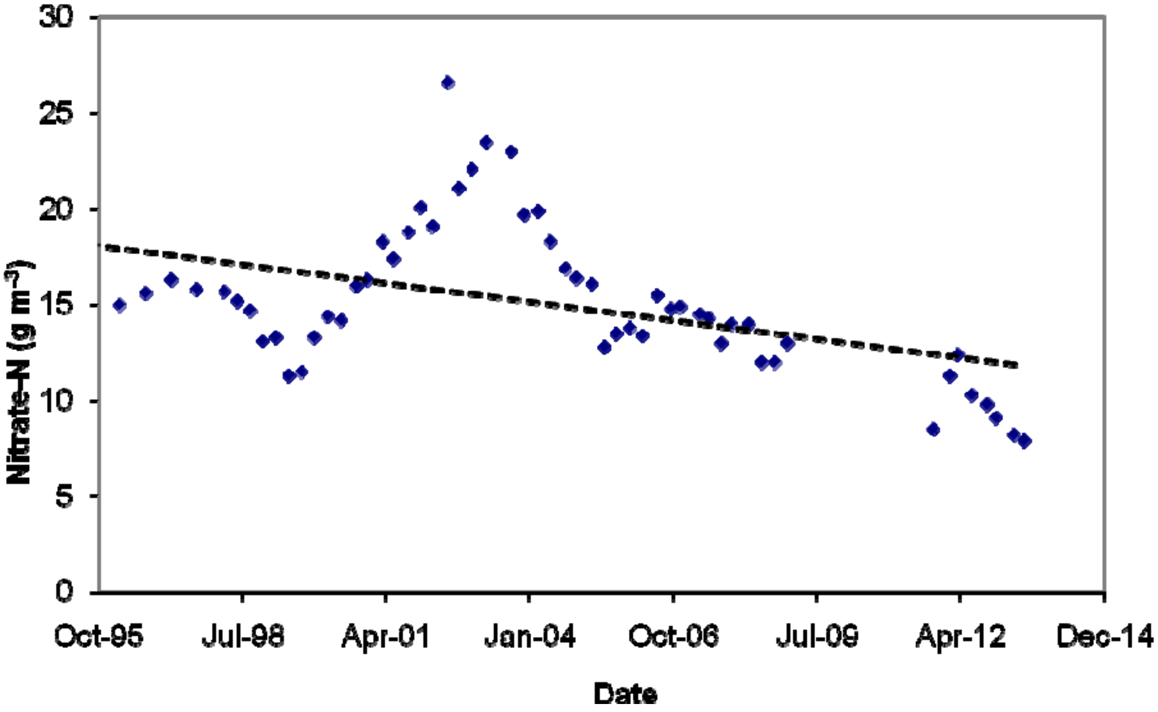


Figure 29: Nitrate concentration trend in well 70_44

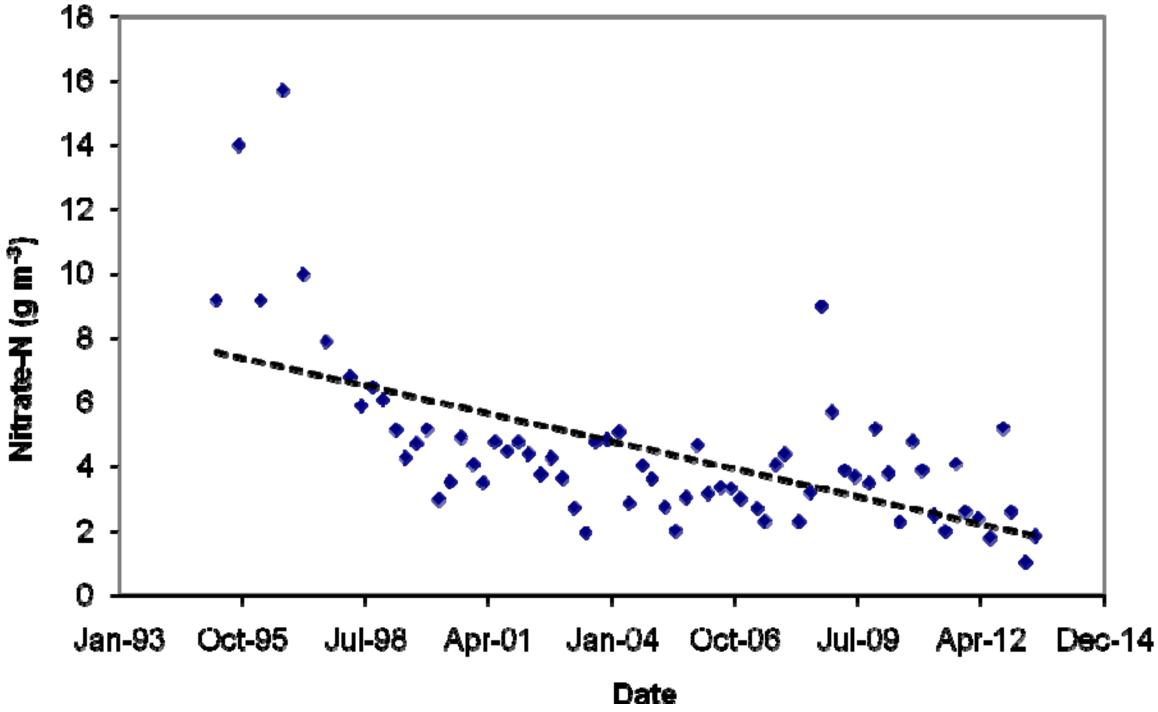


Figure 30: Nitrate concentration trend in well 70_47

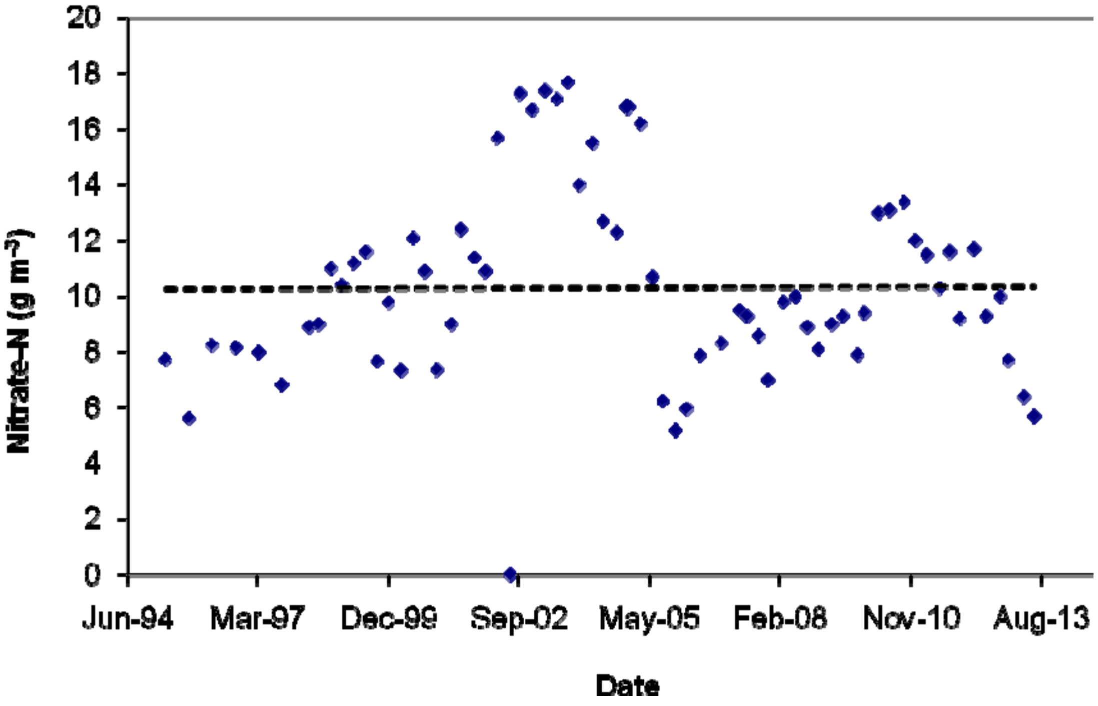


Figure 31: Nitrate concentration trend in well 70_56

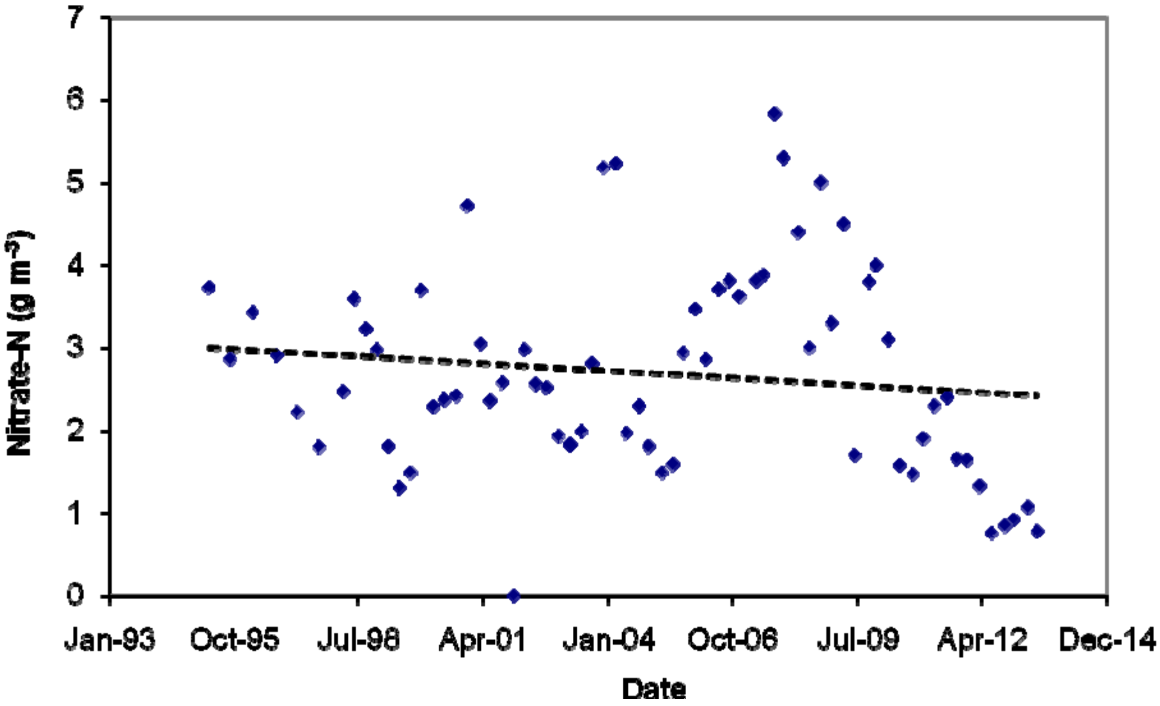


Figure 32: Nitrate concentration trend in well 70_65

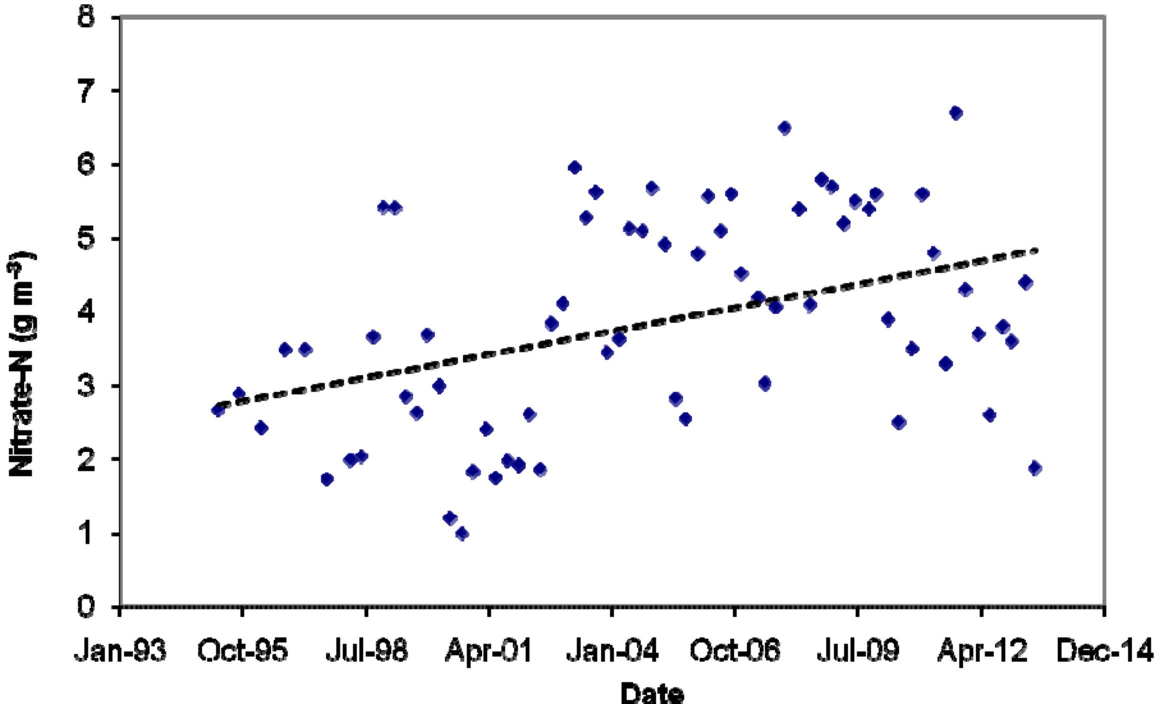


Figure 33: Nitrate concentration trend in well 70_74

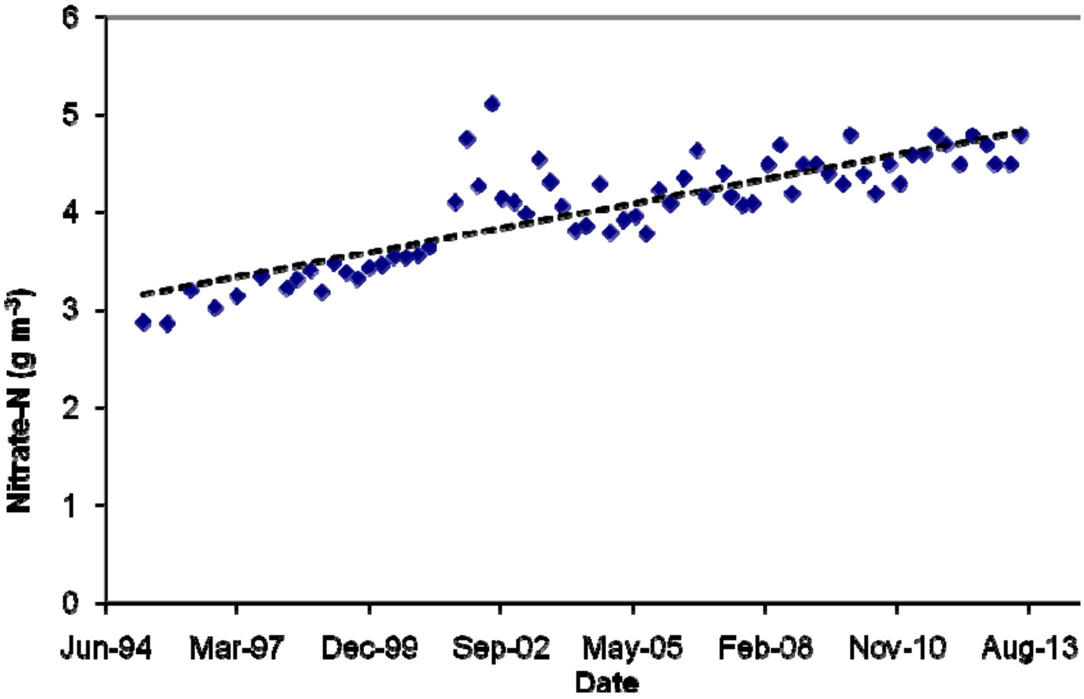


Figure 34: Nitrate concentration trend in well 70_76

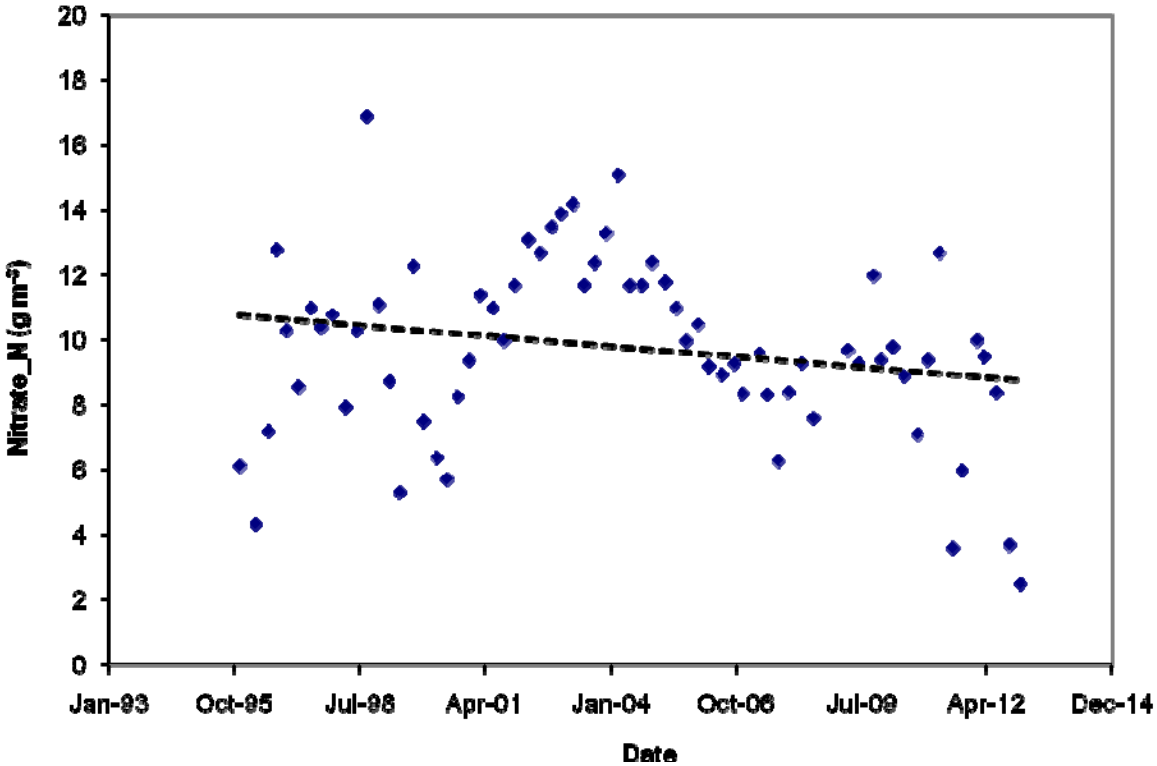


Figure 35: Nitrate concentration trend in well 70_21

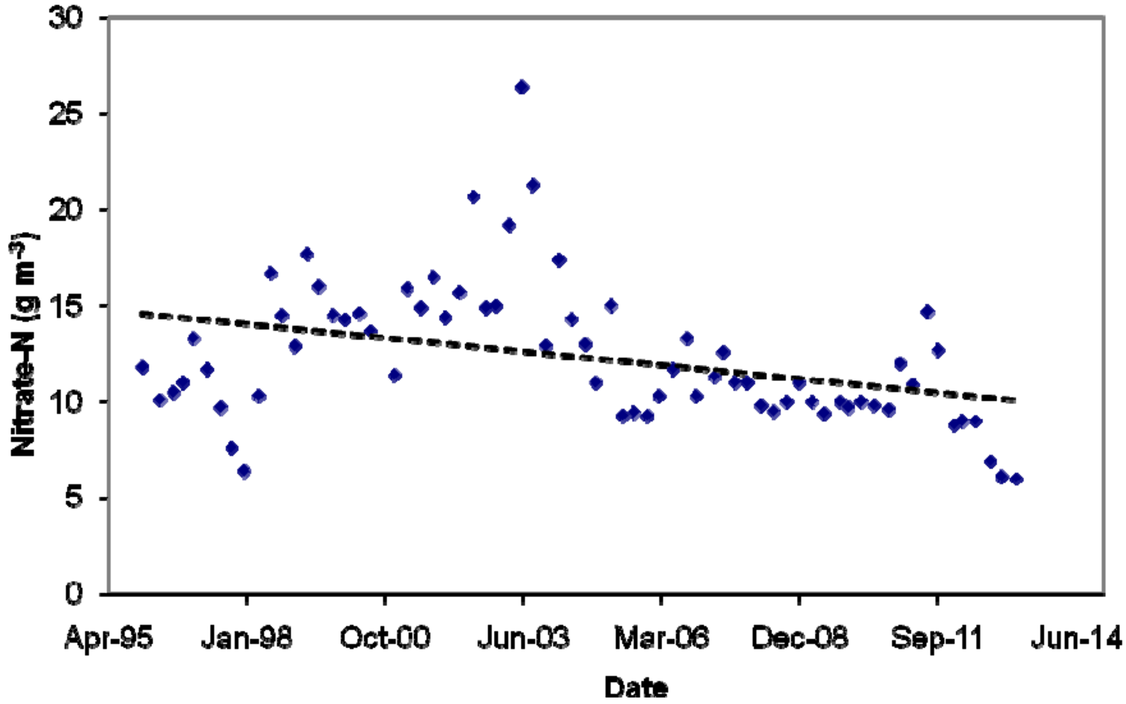


Figure 36: Nitrate concentration trend in well 70_22

3.7 Pesticide occurrence

Pesticide occurrence in groundwater is a concern for human health and may have implications for other uses such as stock watering and crop irrigation (s3.9 WRP). Poor management and use of agrichemicals may result in contamination of water supplies by hazardous substances. These may cause a range of both acute and or chronic health effects.

In 1995, Environment Waikato (now Waikato Regional Council) commenced an investigation into pesticide contamination of groundwater in high use areas of the Waikato. Aquifers considered to be particularly vulnerable to contamination were targeted by sampling groundwater at 35 sites in the Pukekohe/Pukekawa and Hamilton Basin/southern Hauraki Plains areas. Detectable pesticide residues were found at 74% of the wells sampled. A total of 20 different, mostly persistent and mobile, pesticide active ingredients were identified. Atrazine, alachlor, diuron, simazine, terbuthylazine and procymidone were most commonly detected (Hadfield and Smith, 2000).

The concentrations of pesticides detected were generally well below the maximum acceptable values (MAV) for drinking water. Notable exceptions were two sites where dieldrin (from nearby former sheep-dips) was detected above MAV. Subsequent quarterly monitoring of 20 of the sites, undertaken over three years, indicated considerable temporal variation in pesticide concentration and occurrence. A close relationship between pesticides detected in groundwater and those used at the site was apparent in five cases in the Hamilton Basin. The majority of pesticides in use, however, were not detected. Direct entry of pesticides into wells (e.g. during mixing) was indicated at some sites from relatively high concentrations and rapid response. There were also instances where detected pesticides were the result of historic use. Pesticides detected at several sites (at least five) apparently relate to chemical use at a neighbouring property. Much of the pesticide contamination detected is a legacy of past use or poor management practices. Careful chemical selection and management is needed to avoid adverse effects.

Four wells continue to be monitored quarterly to investigate temporal variation in pesticide occurrence. All of these wells abstract groundwater from shallow, unconfined aquifers and are located on properties where there is common pesticide use.

Pesticides were also analysed at a total of 80 wells, comprising 40 each from the regional and community networks (Table 3), and were reported as part of a four yearly indicator program on the Waikato Regional Council website www.waikatoregion.govt.nz. The percentage occurrences of pesticides in the regional and community networks relative to the drinking water guideline are listed in Table 19. Dieldrin was the pesticide which exceeded the drinking water guideline in both networks. This organochlorine has a very low MAV (0.04 ppb) because it bio-accumulates. Its occurrence typically relates to historic sheep dips or grass grub treatment. Other pesticides detected were predominantly of the triazine group which are relatively mobile and persistent.

Table 19: Occurrence of pesticides in the monitoring networks relative to the drinking water guidelines concentrations (data from doc. 2746519)

	Regional Network %	Community Network %
Non-detect	77.5	95
< half MAV[1]	20.0	2.5
> half MAV and < MAV	0	0
> MAV	2.5	2.5

[1] maximum acceptable value for drinking water

3.8 Microbial occurrence

The occurrence of micro-organisms in groundwater is the highest priority quality concern from a health perspective. Their presence can lead to rapid and major outbreaks of illness, potentially with fatal consequences.

E.-coli are the preferred indicator group for the occurrence of micro-organisms because they are easy to detect and count, and have better survival in fresh water than enterococci. *E. coli,* which is a common gut bacterium living in warm blooded animals, is an indicator of water contamination by excrement and the potential presence of pathogenic viruses, bacteria and protozoa. Specific measurement of pathogen occurrence such as viruses (e.g. MS2), is comparatively expensive and difficult. Total coliforms also were not used as they indicate more general bacterial occurrence, often unrelated to human health risk. The Ministry of Health (2005) drinking water guidelines specify a maximum acceptable value for *E*. coli of <1 organism per 100 ml.

Analysis for *E. coli* was undertaken on 82 samples from sites throughout the Waikato region, as part of a four yearly indicator program reported on the Waikato Regional Council website www.waikatoregion.govt.nz. Sites comprise 21 school supply wells and 61 regional monitoring wells. Fourteen of these were wide diameter wells (approximately 900 mm), only one of which is for school supply. Wide diameter wells are more likely to be contaminated as they are shallow and more difficult to seal than narrow (typically 100 mm) diameter wells.

The wells for which E-coli were analysed were selected from the larger networks, prioritised on the basis of the following criteria:

- vulnerability to contamination from the land surface assessed using the DRASTIC index (Aller et al., 1987) –
- availability of in-situ pumps to minimise the potential to introduce contamination during sampling
- availability of well log and construction information (with the exception of some wide diameter wells)
- spatial distribution and land-use representation (for further statistical comparison).

Microbial contamination is more likely in this group than a completely random sample. Samples were collected in sterile bottles which were kept cool and analysis was undertaken within 24 hours.

In the 2012 sampling, *E-coli* were detected in 5% of community water supply wells and 14.75 % of regional network wells. The results for wide and narrower diameter wells are compared in Table 20. Over half the wide diameter wells had E-coli detections whereas they were only detected in about 3% of other wells. The wide diameter wells are shallow and therefore located in the lowlands where the water table is near the surface.

Table 20: Occurrence of E-coli

	***E-coli* present %**	***E-coli* absent %**
Wide diameter	57.14	42.86
Narrow diameter	2.94	97.06

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Appendix I: Regional groundwater quality network sampling records and frequency

(grey shading signifies quarterly sampling and grey hashed is annual sampling).

Well	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Coromandel																				
60-12	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
60-124		▨							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
60-167									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
60-190									▨	▨	▨	■	■	■	■	■	■	■	■	
60-316									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
60-345									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
60-348	▨								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
60-4	■	■	■						▨	▨	▨	▨	▨							
72-3559														▨	▨	▨	▨	▨	▨	
60-407									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
60-480									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
60-483									▨	▨	▨									
72-2691													▨	▨	▨	▨	▨	▨	▨	
Franklin																				
61-113	▨	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
61-126	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
61-135	▨	▨							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
61-143	▨	▨	▨	▨				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
61-208	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
61-221	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
61-230	▨	▨	▨	▨				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
61-245	▨	▨						▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
61-258	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
61-280	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
61-54	▨	▨	▨	▨				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
61-59		■	■	■	■	■ 2	■	■	■	■	■	■	■	■	■	■	■	■	■	

Well	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
61-702									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
61-85			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
61-93				■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
Hauraki																				
63-201									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
63-240									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
63-328									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
63-43		▨	▨						▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
63-57	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
63-74								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
63-78									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
72-1223				▨					▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
Matamata-Piako																				
64-108	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-111								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
64-117	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-12	▨	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-120	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-20	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-43	▨	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-46	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-50	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-511	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-7	▨	▨	▨	▨					▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
64-70	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-720			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
64-831								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
Otorohonga																				
65-4	▨	▨	▨						▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
65-6	▨	▨	▨						▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
65-8	▨	▨	▨						▨	▨	▨	▨	▨	▨	▨	▨				
72-5510																	▨	▨	▨	
Rotorua																				
66-58	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	

Well	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
66-6	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
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66-93								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
66-96								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
South Waikato																				
67-11				■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
67-15	▨	▨	▨	▨	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
72-4500															▨	▨	▨	▨	▨	
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67-404									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
67-435									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
67-483									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
67-55									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
67-573			▨						▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
67-83									▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
Taupo																				
68-301							■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
68-317		▨					■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
68-320							■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
68-661								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		
72_3696																				
68-912								▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	
68-964					■	■	■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
72-1008							■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
72-1011							■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
72-1069								■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
72-1072								■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
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72-1082								■	■	■	■	■	■	▨	▨	▨	▨	▨	▨	
72-1087								■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
72-1089								■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
72-356							■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
72-392							■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	
72-431							■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨	

Well	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Waikato																				
69-163									▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
69-1709	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
69-173	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
69-19	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
69-248	▓	▒	▒	▒					▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
69-295									▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
69-365	▓	▓	▓	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
69-374	▓	▓	▓	▓					▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
69-62								▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
69-81	▓	▓	▓	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
69-97	▓	▓	▓	▓				▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
62-5	▒	▒	▒	▒					▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
Waipa																				
70-1134			▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
70-21	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
70-22	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
70-31									▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
70-44	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▓	▓	▒	▒	▒	
70-47	▓	▓	▓	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
70-50								▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
70-56	▓	▓	▓	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
70-65	▓	▓	▓	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
70-74	▓	▓	▓	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
70-76	▓	▓	▓	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	▒	
Waitomo																				
71-1	▓	▓	▓						▓	▓	▓	▓	▓	▓	▓	▓	▓	▓		
72_2138																			░	
71-26	▓	▓	▓						▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
71-3		▓	▓						▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
71-4	▓	▓	▓						▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
71-5		▓	▓						▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	

Appendix II: Groundwater quality analysis methods and detection limits

Determinand	Units	Detection limit	Method description
ALKT	g/m3-CaCO3	1	Potentiometric autotitration to pH 4.5. APHA 2320B.
As	g/m3	0.0011	ICP-MS after HNO3 digestion. APHA 3125 B.
B	g/m3	0.0053	ICP- MS after HNO3 digestion. APHA 3125B.
Ca	g/m3	0.053	ICP-MS after HNO3 digestion. APHA 3215 B.
Cd (D)	g/m3	0.00005	Filtered, ICP-MS APHA 3125B
Cd T	g/m3	0.053	ICP-MS after HNO3 digestion. APHA 3125B.
Cl	g/m3	0.5	Filtered sample, Ion chromotography. APHA 4110B.
Cond	mS/m @25"C	0.1	Measured in lab by meter @ 25"C. APHA Method 2510B
Cu	g/m3	0.00053	ICP-MS after HNO3 digestion. APHA 3125B.
F	g/m3	0.021	Specific ion electrode.APHA 4500-FC.
Fe (D)	g/m3	0.02	Filtered, ICP-MS APHA 3125B
Fe	g/m3	0.021	ICP-MS after HNO3 digestion. APHA 3125B.
Free CO2	g/m3-CO2	1	Free Carbon Dioxide Calculation from alkalinity & pH (APHA 4500 CO2D)
Hardness	g/m3-CaCO3	1	Calculation from Ca and Mg. APHA 2340B.
K	g/m3	0.053	ICP-MS after HNO3 digestion. APHA 3215 B.
Mg	g/m3	0.021	ICP-MS after HNO3 digestion. APHA 3215 B.
Mn (D)	g/m3	0.0005	Filtered, ICP-MS APHA 3125B
Mn	g/m3	0.00053	ICP-MS after HNO3 digestion. APHA 3125B.
Na	g/m3	0.021	ICP-MS after HNO3 digestion. APHA 3215 B.
NH_4	g/m3-N	0.01	Filtered Sample. Colorimetry, Phenolhypochlorite. Discrete Analyser.
NO_3-N	g/m3-N	0.05	Ion chromatography. APHA 4110B

pH	pH	0.1	Measured in lab by meter. APHA Method 4500-H+ B.
SO_4	g/m3	0.5	Filtered sample.Ion chromotography APHA 4110B
TDS	g/m3	2	Calculated from Electrical Conductivity
Temp.	DegC	0.1	Meter.Field measurement.
Zn (D)	g/m3	0.001	Filtered, ICP-MS APHA 3125B
Zn	g/m3	0.0011	ICP-MS after HNO3 digestion. APHA 3125B/US EPA 200.8

Appendix III: Groundwater sampling protocol Summary[1]

Pre-sampling:

- Gather site sheets with specific instructions
- Prepare and check sampling equipment and bottles
- Calibrate probes – conductivity, temperature & DO as required
- Plan sample delivery and prepare field sheets

Sample collection:

- Confirm site details and update as required
- Check probe calibration and bottle labels
- Measure depth to water
- Calculate or check purge volume2
- Install pump if necessary3
- Commence pumping and measure conductivity and temperature using a flow cell
- Pump 3 annular volumes (or as otherwise specified & noted)
- Ensure temperature is stabile within 0.2oC
- Ensure conductivity is stabile within 3%
- Measure D.O. if required minimising aeration
- Note field parameters and sampling details on field sheet
- Collect samples in bottles labelled with site number and name
- All filtering will be carried out in the lab unless specified
- Microbial samples should retain a small air space4
- Clean and rinse all sampling equipment and leave site as before

Storage and delivery:

- Store sample bottles in chilli bin with ice or refrigerated container
- Keep sample bottles cool below 4oC but do not freeze microbial samples
- Samples should be delivered to the lab within 24 hours for microbial analysis and preferably for all analyses
- Chain of custody sheets should be provided and suite of analyses checked

Microbial specific:

- Take water level with sterilised probe
- Wear disposable sterile gloves
- Sterilise sample pump (if required to introduce) using 60-70% ethanol and take blank sample before sampling
- Tap/discharge end should be dried with sterile wipes and flamed
- Use sterile sample bottles with small air space
- Deliver cooled but unfrozen to lab within 24 hours

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[1] For more information refer to document 1464180 however where different this summary should be followed

[2] Pi r^2 x saturated well depth – similar riser pipe volume e.g. 100 mm diameter well is ~ 8L per m; 50 mm diameter well is ~ 2L per m; see site sheets for detail and suggested purge volume

[3] Pumping equipment introduced for microbial sampling must be sterilised

[4] For further consideration of microbial sampling requirements see specific section below

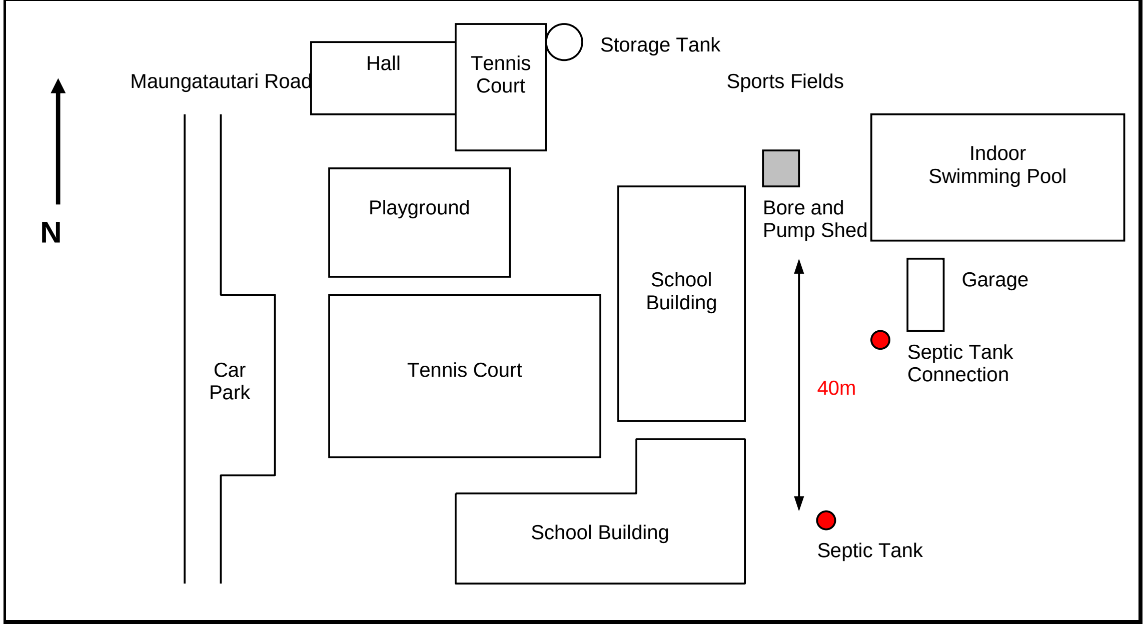
Appendix IV: Example site sheets

SCHOOL WATER SUPPLY
SITE DETAILS

Site Name:	**Hora Hora Primary**	**Site (Hydrol) No:**	**70.1156**
Map Reference:	T15:408-546	Well No./Type:	7783
Address:	Maungatautari Road	Bore Log? (y/n)	Yes
	Horahora	Driller:	Rotorua
Person to Contact:	Lyn (S)	Year of Construction:	-
		Depth (m):	28
		Diameter (mm):	150
	(07) 827 2823	Casing depth (m):	14
Number of People Served:	49 children	Casing type:	100
Aquifer Geology:	Gravel	Pump details:	Deep well cylinder
Drastic Index:	141	Sample method:	Bore and office tap
Registered Supply? (y/n)	Yes	Sampling regime:	2 monthly (Medlab)
Topography:	Strongly rolling	Static water level (m):	**4** (borelog) / 11 (00)
Land Use:	Farming, gullies	Water Quality:	Good

Site Map

(p.t.o. for site photo)



COMMENTS[1]

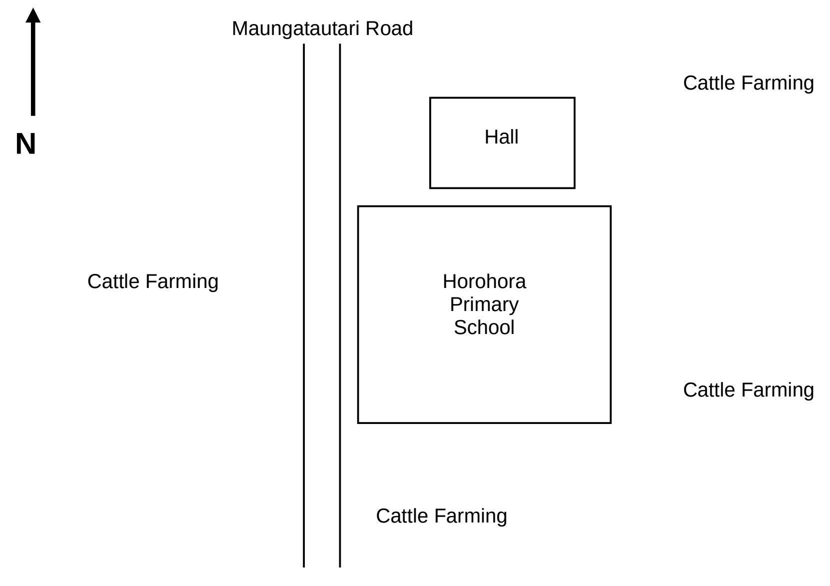
Bore water is used for everything including drinking.
No water treatment systems installed.
To sample - attach plastic sheeting to the tap in the pump shed to divert water out of the shed. Turn the tap on, then flick the float switch on the storage tank in the trees on the hill to start the pump. Flush for 10 - 15 minutes and sample. Turn off the tap and reset float switch.

OSH HAZARD IDENTIFICATION

Hazards	Location	Risk	Action Required
Children	In driveway and carpark		Keep an eye out
Storage tank	In trees on the hill	Falling off and or in	Be careful

Notes: 1 Current Water Quality Sampling Regime, Sampling Method and Access

LAND USE[2]



Notes: 2 Potential threats and details regarding distances.

Photograph numbers: 501 - 504 & 1073

501. Location of Pump shed

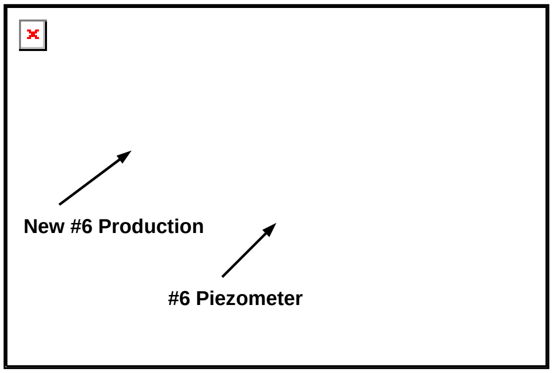
502. Pump and bore setup

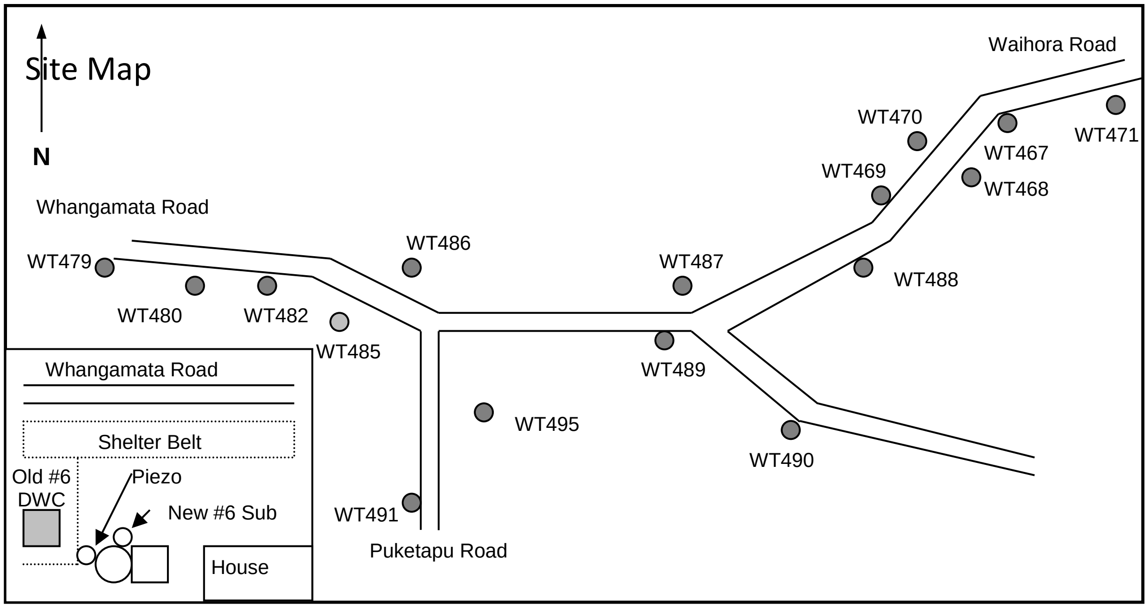
504. Landuse and topography

1073. Sampling technique

Lake Taupo groundwater
site details

Site Name:	Waihora #6 New Production	Site (Hydrol) No:	72.514
Map Reference:	T17:546-844	Wells on property:	16
Address:	Whangamata Road	Bore log available?	Yes
	RD1, Taupo	Driller:	Benton & Son
Person to contact:	Peter Booth / Ken Burt	Year of Construction:	2001
ph:	Ken: (025) 468224	Bore Depth (m):	171
	Peter: (025) 945066	Casing Diameter (mm):	100
Survey Date:	19/02/2002	Casing depth (m):	78
Aquifer geology:	Rhyolite	Casing type:	Steel
Drastic Index:	-	Screen diameter (mm)	-
Topography:	Gently rolling	Screen depths (m)	78 – 171
Land Use:	Sheep and beef	Screen type:	-
Water Use:	Stock	Pump details:	Submersible
Level probe access (y/n)	Yes	Well yield (m^3d^{-1})	90
Static water level (m chf)	8.095 (19/02/2002)	Drawdown for above	79.6
Water quality comment:	High in manganese	Aquifer test info (y/n)	Yes
Water quality sampled	Yes	Water supply?	Bore





Comments

New #6 is suitable for groundwater level monitoring, groundwater quality sampling and aquifer flow testing. Samples have high concentrations of manganese.

Appendix V: Selected MoH determinand data sheets

(Excerpted from Ministry of Health 2005a Guidelines for drinking water quality management in New Zealand)

Arsenic

Updated July 2005.

Maximum acceptable value (provisional)

Based on health considerations, the concentration of arsenic in drinking-water should not exceed 0.01 mg/L. The WHO guideline value is designated as provisional in view of the scientific uncertainties. The maximum contaminant level (USEPA 2004) is 0.01 mg/L.

Sources to drinking-water

1 To source waters

Arsenic can enter the aquatic environment by the weathering of minerals and rocks, run-off from soils, from geothermal fluids or atmospheric deposition. The mineralised zones of sulphitic ores probably contain the highest concentrations of arsenic although high levels of arsenic may also occur in some coals and peats. In New Zealand, arsenic occurs in greywacke and schists and in tertiary volcanics. In greywacke and schist it occurs as arsenopyrite and loellingite in gold-bearing lodes of the Reefton and Otago Goldfields. It also occurs in auriferous quartz lodes associated with volcanics in the Hauraki goldfield, especially in the Tokatea-Coromandel area. Geothermal fluids contain elevated concentrations of arsenic and water bodies such as the Waikato River subjected to their discharge have typically high arsenic concentrations.

Arsenic can also be released to the aquatic environment via the discharge of wastes from industries in which it is used. Arsenic and its compounds are used in the production of semiconductors, pigments, for medical purposes, in glassmaking, in alloys with lead and copper, rodenticides, insecticides, herbicides, and as timber preservatives.

2 From treatment processes

No known sources.

3 From the distribution system

No known sources, despite the use of arsenical brasses.

Forms and fate in the environment

The most common oxidation states of arsenic are +3 and +5 although it can also exist in the 0 and -3 states. Arsenic (V) is the stable form of arsenic in aerobic water while arsenic (III) is the predominant form of arsenic under anaerobic conditions such as in groundwaters. In surface waters, the majority of arsenic occurs in a soluble form which can be removed from the water by co-precipitation with hydrated iron and aluminium oxides, or adsorbed/chelated by suspended organic matter in water or humic substances in bottom sediments.

Typical concentrations in drinking-water

Arsenic was routinely measured in New Zealand drinking-water supplies as part of the Department of Health three yearly surveillance programme. Of 1895 samples analysed between 1983 and 1989, 13 samples (1.3% of supplies) had concentrations equal to or exceeding the 1984 guideline value of 0.05 mg/L. The majority of drinking-water

supplies in New Zealand have arsenic concentrations of less than 0.001 mg/L. However, supplies using source waters significantly contaminated with arsenic such as the Waikato River, that do not fully treat their water have been reported to contain up to 0.15 mg/L in reticulated water.
The P2 Chemical Determinand Identification Programme, sampled from 342 zones, found arsenic concentrations to range from ‘not detectable’ (nd) to 0.10 mg/L, with the median concentration being ‘nd’ (limit of detection = 0.001 mg/L).

Levels in natural waters generally range between 0.001 and 0.002 mg/L, although concentrations may be elevated (up to 12 mg/L) in areas containing natural sources (WHO 2004).

Removal methods

Conventional coagulation treatment with iron or aluminium can achieve good removal of arsenic. The effectiveness depends on: the oxidation state of the arsenic (trivalent arsenic should be converted to pentavalent arsenic by oxidation with chlorine or potassium permanganate); the pH at which the process is carried out; and whether iron or aluminium is used as the coagulant.

Lime-softening, ion exchange resins, and activated alumina can also be used to remove arsenic. The removal of arsenic from water by ion exchange and alumina depends upon the arsenic being present as the negatively-charged arsenate ion, AsO_4^{3-}. This ion contains arsenic in the highest oxidation state (5+), and oxidation of any arsenic in the 3+ oxidation state is required if it is to be removed by these two processes.

Analytical methods

Referee method

Electrothermal Atomic Absorption Spectrometric Method (APHA 3113).

Some alternative methods

1 Hydride Generation/Atomic Absorption Spectrometric Method (APHA 3114B).
2 nductively Coupled Plasma – Mass Spectrometry (EPA Method 200.8).

Health considerations

The health considerations apply mainly to the inorganic arsenic compounds. These are more likely to be present in drinking-water supplies than the organic compounds. Except for individuals who are occupationally exposed to arsenic, the most important route of exposure is through the oral intake of food and beverages.

Ingested elemental arsenic is poorly absorbed and is largely eliminated unchanged. Soluble arsenic compounds are readily absorbed from the gastro-intestinal tract. Inorganic arsenic may accumulate in skin, bone and muscle. In humans, inorganic arsenic does not appear to cross the blood-brain barrier but transplacental transfer of arsenic has been reported.

Early symptoms of acute arsenic intoxication include abdominal pain, vomiting, diarrhoea, pain in the muscles, weakness and flushing of the skin. Signs of chronic arsenicalism include dermal lesions, peripheral neuropathy, skin cancer and peripheral vascular disease.

Arsenic does not appear to be mutagenic in bacterial and mammalian assays although it can induce chromosomal aberrations in a variety of cultured cell types, including human cells.

Arsenic has not been demonstrated to be essential in humans. It is an important drinking-water contaminant, as it is one of the few substances shown to cause cancer in humans through consumption of drinking-water. There is overwhelming evidence from epidemiological studies that consumption of elevated levels of arsenic through drinking-water is causally related to the development of cancer at several sites, particularly skin, bladder and lung. In several parts of the world, arsenic-induced disease, including cancer, is a significant public health problem. Because trivalent inorganic arsenic has greater reactivity and toxicity than pentavalent inorganic arsenic, it is generally believed that the trivalent form is the carcinogen. However, there remains considerable uncertainty and controversy over both the mechanism of carcinogenicity and the shape of the dose-response curve at low intakes. Inorganic arsenic compounds are classified by IARC in Group 1 (carcinogenic to humans) on the basis of sufficient evidence for carcinogenicity in humans and limited evidence for carcinogenicity in animals.

Derivation of maximum acceptable value

Data on the association between internal cancers and ingestion of arsenic in drinking-water are insufficient for quantitative assessment of risk. Instead, owing to the documented carcinogenicity of arsenic in the drinking-water of human populations, the lifetime risk of skin cancer has been estimated using a multistage model that is both linear and quadratic in dose. On the basis of observations in a Taiwanese population ingesting arsenic contaminated drinking-water, the levels associated with lifetime skin cancer risks of 10^{-4}, 10^{-5} and 10^{-6} are 1.7, 0.17 and 0.017 μg/L. These values may, however, overestimate the actual risk of skin cancer owing to the possible contribution of other factors to disease incidence in the Taiwanese population and to possible dose-dependent variations in the metabolism that could not be taken into consideration. Moreover, 1–14% of arsenic-induced skin cancers are fatal.

WHO has established a provisional guideline value of 0.01 mg/L for arsenic in drinking-water. The estimated lifetime skin cancer risk associated with exposure to this concentration is six per 10,000 (6×10^{-4} or $6 \times 10^{-6} - 8.4 \times 10^{-5}$ lifetime risk of fatal skin cancers).

The WHO provisional guideline value agrees with the value derived on the basis of the provisional maximum tolerable daily intake for inorganic arsenic of 2 μg/kg body weight, established by the Joint FAO/WHO Expert Committee on Food Additives in 1983, and assuming a 20% allocation to drinking-water.

WHO stated in 2004 that there remains considerable uncertainty over the actual risks at low concentrations, and available data on mode of action do not provide a biological basis for using either linear or non-linear extrapolation. In view of the significant uncertainties surrounding the risk assessment for arsenic carcinogenicity, the practical quantifcation limit in the region of 0.001–0.01 mg/L and the practical difficulties in removing arsenic from drinking-water, the guideline value of 0.01 mg/L is retained. In view of the scientific uncertainties, the guideline value is designated as provisional.

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Boron

Updated July 2005.

Maximum acceptable value

Based on health considerations, the concentration of boron in drinking-water should not exceed 1.4 mg/L. In 2001 the Australian Drinking Water Guidelines considered that boron may be an essential trace element for humans and based on an acceptable range of oral intake, a concentration of up to 4 mg/L in water would not pose a human health risk.

Sources to drinking-water

1 To source waters

The most common boron containing mineral is tourmaline which is present in igneous and some sedimentary rocks. The weathering of both of these rock types releases boron, which is then transported in solution. Soil leaching and volcanic activity may also add boron to water. Boron has been found in hot springs and brines at high concentrations, indicating that hydrothermal and geothermal fluids are also a source of boron.

Boron may also be released to water from the discharge of industrial and domestic wastewaters, or in agricultural run-off. In industry, boron is used in fire retardants, borosilicate glass, enamels and antioxidants for soldering, detergents and in the photographic, cosmetic, leather, textile, paint and wood-processing industries. It is also used in the preparation of disinfectants and drugs and in some synthetic rocket fuels. Elemental boron is used to harden metals, in nuclear reactors for neutron absorption and in agriculture to improve crop yields.

2 From treatment processes

No known sources.

3 From the distribution system

No known sources.

Forms and fate in the environment

The chemical behaviour of boron in the aquatic environment is poorly understood, but it is thought that the predominant species is boric acid which is moderately soluble in water and does not dissociate readily.

Typical concentrations in drinking-water

Boron was routinely measured in New Zealand drinking-water supplies as part of the Department of Health three-yearly surveillance programme. Of 1904 samples analysed between 1983 and 1989, 35 samples (1.3% of supplies) contained concentrations equal to or exceeding the 1984 guideline value of 0.5 mg/L.

The P2 Chemical Determinand Identification Programme, sampled from 297 zones, found boron concentrations to range from ‘not detectable’ (nd) to 11 mg/L, with the median concentration being ‘nd’ (limit of detection = 0.06 mg/L).

Removal methods

There are, at present, no economically feasible methods of removing boron from source waters, other than changing the source. Boron concentrations can be reduced by granular activated carbon, anion exchange or lime-softening.

Analytical methods

Referee method

Colorimetric Method, Azomethine-H Parts C, D (Boron in Waters, Effluents, Sewage and Some Solids, 1980, HMSO, UK).

Some alternative methods

1 Colorimetric Method (APHA 4500-B B).

Health considerations

Boron, when administered as borates or boric acid, is rapidly and almost completely adsorbed from the gastrointestinal tract. Boron excretion occurs mainly through the kidney. Boron is present naturally in many food products, with high amounts found in foods of plant origin, especially fruits, leafy vegetables, nuts and legumes. It has been estimated that intake of boron from food is about 10 times that from water.

Long term exposure of humans to boron compounds leads to mild gastrointestinal irritation. In short-term and long-term animal studies and in reproductive studies with rats, testicular atrophy was observed. Boric acid and borates were not mutagenic in various *in vitro* test systems. No increased tumour incidence was observed in long-term carcinogenicity studies in mice and rats.

Acute boron poisoning has been reported after application of dressings, powders or ointments containing borax and boric acid to large areas of abraded skin and following ingestion. Symptoms of boron poisoning include gastrointestinal disturbances, skin eruptions, and central nervous system stimulation followed by depression.

Tests for mutagenicity using bacteria and mammalian cells have been mostly negative. Neither boric acid nor borate induce chromosomal aberrations in mammalian cells.

Derivation of maximum acceptable value

A tolerable daily intake approach has been used for the derivation of the MAV for boron in drinking-water. Benchmark dose methodology (based on the influence of boron of foetal body weight affecting 5 per cent of the animals, in a rat study) has been used to derive a tolerable daily intake value. This value has been used for the derivation of the MAV of boron in drinking-water.

The MAV for boron in drinking-water was derived as follows:

$$\frac{10.3 \text{ mg/kg body weight per day} \times 70 \text{ kg} \times 0.2}{2 \text{ L per day} \times 50} = 1.4 \text{ mg/L}$$

where:

- benchmark dose (5%) = 10.3 mg/kg body weight per day
- average weight of an adult = 70 kg
- the proportion of tolerable daily intake assigned to the consumption of water = 0.2
- uncertainty factor = 50
- average amount of water consumed by an adult = L per day.

NB: Here the benchmark dose is used in place of the NOAEL.

References

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World Health Organization. 2004. *Guidelines for Drinking-water Quality* (3rd ed).

Cadmium

Updated July 2005.

Maximum acceptable value

Based on health considerations, the concentration of cadmium in drinking-water should not exceed 0.004 mg/L (4 μg/L). The maximum contaminant level (USEPA 2004) is 0.005 mg/L.

Sources to drinking-water

1 To source waters

Cadmium can enter water from the weathering of rocks and minerals and run-off from soils. The only naturally-occurring cadmium compound of significance, the sulphide greenockite, CdS, which is fairly rare, is almost always associated with the polymetallic sulphide ores of zinc, lead and copper.

Cadmium has a wide range of sources and may enter water in industrial and domestic discharges or from street and agricultural run-off. Domestic discharges generally contain high levels of cadmium. Its principal industrial uses are in electroplating other metals or alloys for corrosion protection, in solders and in amalgam used in dentistry. It is also used in the manufacture of pigments, nickel-cadmium storage batteries, electronic equipment, lubricants, photography supplies, glass, ceramics, biocides and as a stabiliser in plastics. It is likely to be present in waste discharged from fertiliser factories using phosphate ores containing cadmium. In agriculture, farm run-off containing these fertilisers are an important source of diffuse pollution by cadmium. Exhaust emission and tyre wear contribute a significant amount of cadmium to street run-off.

2 From treatment processes

No known sources.

3 From the distribution system

Cadmium may enter drinking-water from the dissolution of galvanised pipes in which it is an impurity associated with the zinc. It may also be present as a result of cadmium-containing solders in fittings, water heaters, water coolers and taps.

Forms and fate in the environment

In fresh waters, cadmium exists principally as the free Cd(II) ion, cadmium chloride and cadmium carbonate. Adsorption is probably the most important process for removal of cadmium from the water column. Exchange of cadmium for calcium ions in the lattice structure of carbonate minerals can remove cadmium from solution. In natural waters, co-precipitation with hydrous iron, aluminium and manganese oxides occurs. Alternatively, in waters of high organic content, adsorption of cadmium to humic substances and other organic complexing agents can be significant.

Typical concentrations in drinking-water

Cadmium was routinely measured in New Zealand drinking-water supplies as part of the Department of Health three yearly surveillance programme. Typical concentrations of cadmium in New Zealand drinking-water supplies are <0.005 mg/L (<5 μg/L).

The P2 Chemical Determinand Identification Programme, sampled from 898 zones, found cadmium concentrations to range from 'not detectable' (nd) to 0.26 mg/L, with the median concentration being 'nd' (limit of detection = 0.0005 mg/L).

Removal methods

Lime-softening achieves good removal of cadmium, provided it is applied to hard waters.

Ion exchange resins can remove cadmium, provided the resins are not overwhelmed by other cations such as calcium and magnesium. This form of treatment may be useful for the removal of heavy metals that have entered the water post-treatment.

Adsorption of cadmium on to PAC, GAC and oxides of Mn(IV), Fe(III) and Al(III) has been reported.

Chemical coagulation with aluminium and iron salts is limited as a viable option for the removal of soluble cadmium. The effectiveness of removal is dependent on the pH at which the process is carried out. In both cases, the effectiveness increases with increasing pH.

In situations where the dissolution of poor-quality zinc from galvanized pipes is a source of cadmium, adjustment of the water chemistry to reduce its corrosiveness will minimise cadmium concentrations.

Analytical methods

Referee method

Electrothermal Atomic Absorption Spectrometric Method (APHA 3113).

Some alternative methods

1. Inductively Coupled Plasma (ICP) Method (APHA 3120).
2. Inductively Coupled Plasma – Mass Spectrometry (EPA Method 200.8).

Health considerations

Absorption of cadmium compounds is dependent on the solubility of the compounds. Cadmium accumulates primarily in the kidneys and has a long biological half-life in humans of about 10–35 years.

The kidney is the main target organ for cadmium toxicity. In humans long-term exposure can cause kidney dysfunction leading to the excretion of protein in the urine. This may occur in about 10 per cent of the population if the amount of cadmium exceeds 200 mg/kg. Other effects may include the formation of kidney stones and softening of the bones (osteomalacia).

Itai-Itai disease has been reported in Japan among people exposed to cadmium via food and drinking-water. Symptoms were similar to osteomalacia accompanied by kidney dysfunction.

Evidence concerning the mutagenicity of cadmium is unclear with many tests reporting negative results although some report gene mutation and chromosome abnormalities in mammalian cells. However the positive results are reported as being weak and seen only at high concentrations.

There is evidence for the carcinogenicity of cadmium by the inhalation route, and the International Agency for Research on Cancer has classified cadmium and cadmium compounds in Group 2A (probably carcinogenic to humans). However, there is no evidence of carcinogenicity by the oral route. Food is the main source of daily exposure to cadmium. The daily oral intake is 0.01–0.035 mg. Smoking is a significant additional source of cadmium exposure.

Derivation of maximum acceptable value

As there is no evidence of carcinogenicity by the oral route and no evidence for the genotoxicity of cadmium, a provisional tolerable weekly intake (PTWI) approach has been used for the derivation of the MAV. Assuming an absorption rate for dietary cadmium of 5 per cent and a daily excretion rate of 0.005 per cent of body burden, the Joint FAO/WHO expert Committee on Food Additives concluded that, if levels of cadmium in the renal cortex are not to exceed 50 mg/kg, a total intake of cadmium should not exceed 0.001 mg/kg body weight per day. This total daily intake has been used to derive the MAV.

The MAV for cadmium in drinking-water was derived as follows:

$$\frac{0.001 \text{ mg/kg body weight per day} \times 70 \text{ kg} \times 0.1}{2 \text{ L per day}} = 0.0035 \text{ mg/L (rounded to 0.004 mg/L)}$$

where:

- PTWI = 0.007 mg/kg, so the tolerable daily intake = 0.001 mg/kg body weight per day
- average weight of an adult = 70 kg
- the proportion of tolerable daily intake assigned to the consumption of water = 0.1
- average amount of water consumed by an adult = 2 L per day.

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Manganese

Updated July 2005.

Maximum acceptable value

Based on health considerations, the concentration of manganese in drinking-water should not exceed 0.5 mg/L. Based on aesthetic considerations, the concentration of manganese in drinking-water should not exceed 0.04 mg/L. The USEPA has a secondary drinking water regulation of 0.05 mg/L for manganese.

Sources to drinking-water

1 *To source waters*

Manganese can reach the aquatic environment from the weathering of rocks and minerals and runoff from soils. Manganese is not an essential constituent of any of the more common silicate rock minerals, but it can substitute for iron, magnesium or calcium in silicate structures. Many igneous and metamorphic minerals contain manganese as a minor constituent. It is a significant constituent of basalt and many olivines and of pyroxene and amphibole. Small amounts are present in dolomite and limestone, substituting for calcium.

Manganese may enter water from industrial discharges and agricultural runoff. Manganese and its compounds are used in the steel industry in the manufacture of metal alloys, in the manufacture of dry cell batteries, paints, varnishes, inks, dyes, glass, ceramics, matches, fire works and fertilisers. Manganese is also used in animal feeds.

Bottom waters in lakes and reservoirs can become very low in dissolved oxygen. Under these conditions iron and manganese leach out from the sediments and begin to circulate through the water column, resulting in raw water concentrations that may be too high for the treatment process to handle. Uncontaminated rivers and streams generally have low concentrations of manganese, ranging from 0.001 mg/L to 0.6 mg/L.

2 *From treatment processes*

No known sources.

3 *From the distribution system*

There are situations in which manganese concentrations in the water at the consumers' taps can be higher than those entering the distribution system. This is not the result of manganese being dissolved from reticulation materials. It arises from manganese, in either soluble or insoluble form, passing into the distribution system. Insoluble manganese may settle out in pipes, and soluble manganese may be oxidized to insoluble forms, by oxygen or other chemical oxidants, such as chlorine, and also settle. Changes in water flows through the system may then resuspend the particulate manganese, which may lead to 'black' water at the consumers' taps.

Certain nuisance organisms concentrate manganese and give rise to taste, odour and turbidity problems in distributed water.

Forms and fate in the environment

Manganese has three valence states in natural environments (2+, 3+, 4+). In the absence of dissolved oxygen Mn(II) predominates, otherwise it is readily oxidised to Mn(IV). In natural oxygenated waters, a substantial fraction of manganese is present in suspended form. In surface waters, divalent manganese will be oxidised to manganese dioxide which will undergo sedimentation. In the presence of complex-forming inorganic and organic compounds, the colloidal stability of manganese oxides will be enhanced. Alternatively, in areas of low dissolved oxygen or in anaerobic areas at low pH, soluble manganese forms may persist. Many of the groundwaters reported to carry large manganese concentrations are from thermal springs.

Typical concentrations in drinking-water

Manganese was measured routinely in New Zealand drinking-water supplies as an aesthetic parameter as part of the Department of Health three yearly surveillance programme. It is now classified as an inorganic parameter of health significance. Of 1143 samples analysed from 913 supplies between 1983 and 1989, 91 samples (9.3 per cent of supplies) were equal to or exceeded the highest desirable level (ie, GV) of 0.05 mg/L.

The P2 Chemical Determinand Identification Programme, sampled from 400 zones, found manganese concentrations to range from 'not detectable' (nd) to 1.7 mg/L, with the median concentration being 0.002 mg/L (limit of detection = 0.001 mg/L).

Removal methods

Oxidation of Mn(II) to insoluble Mn(IV) compounds is a commonly employed technique. Aeration uses oxygen from the air to achieve oxidation. This precipitates the manganese, which is either allowed to settle or is removed by filtration. The rate at which oxidation occurs is pH dependent, becoming faster as the pH is increased. Some Mn(II) is adsorbed on to higher oxidation states of Mn in slightly alkaline solution. A coating of higher oxides of manganese on filter granules acts to catalyse the removal of lower oxidation states. Organically-bound manganese is not removed by aeration.

Other oxidising agents such as chlorine and potassium permanganate may be used for the removal of manganese. A pH of 8 is required for chlorine oxidation, and pH 7 to 8 is optimum for permanganate oxidation.

Sand or anthracite filters can be used to filter the precipitated manganese from the water. Before the removal process becomes efficient, a coating of iron and manganese oxides must develop on the grains of the filter medium. Until this coating develops, removal may be poor. Natural zeolites (ion exchange materials) treated with manganese can be used as the filter medium. This medium is known as greensand, and requires periodic regeneration of the iron and manganese oxide coating. Mn(II) ions come into contact with the zeolite and are converted to the insoluble oxide which is filtered out by the filter bed.

Natural zeolites or synthetic resins can also be used to remove manganese by a true ion-exchange process. Sodium attached to the zeolite is exchanged for Mn(II) ions in the incoming water. It is important that the water is free of oxygen that might lead to oxidation and precipitation of the manganese, as this will foul the zeolite.

Manganese, in the absence of oxygen, can be removed effectively by raising the pH above approximately 10 to precipitate manganese hydroxide. This can be exploited if the lime-soda ash process is being used for hardness reduction.

Analytical methods

Referee method

Electrothermal Atomic Absorption Spectrometric Method (APHA 3113).

Some alternative methods

1. Flame Atomic Absorption Spectrometric Method (APHA 3111).
2. Inductively Coupled Plasma Method (APHA 3120B).
3. Inductively Coupled Plasma – Mass Spectrometry (EPA Method 200.8).

Health considerations

Manganese is an essential trace element with an estimated daily nutritional requirement of 30–50 µg/kg body weight. The greatest exposure to manganese is usually from food. Its absorption rate can vary considerably according to actual intake, chemical form, and presence of other metals such as iron and copper. Typically, only about 3–8 per cent of ingested manganese is absorbed by the gastro-intestinal tract. In infants and young animals, very high absorption rates of manganese have been observed. After absorption it is concentrated in the liver and eventually excreted in faeces. It has a relatively short biological half-life of 13 to 37 days in humans. Manganese deficiency affects bone, the brain and reproduction in a number of species.

Evidence of manganese neurotoxicity has been seen in miners following prolonged exposure to manganese dusts. There is no convincing evidence of toxicity in humans associated with the consumption of manganese in drinking-water, but there are only limited studies available. By the oral route, manganese is often regarded as one of the least toxic elements.

In one case, the symptoms associated with consuming drinking-water containing a manganese concentration of close to 28 µg/L included lethargy, increased muscle tone, tremor and mental disturbances. However, the concentrations of other metals were also high and the reported effects may not be due to manganese alone.

Experiments with animals have shown no adverse effects, other than a change in appetite and a reduction in the metabolism of iron in haemoglobin synthesis. Some *in vitro* studies have reported mutagenic activity for manganese on mammalian cells and bacteria.

There is no firm evidence that manganese is carcinogenic. Some studies indicate that it may, in fact, have an anti-carcinogenic effect.

Derivation of maximum acceptable value

The MAV for manganese in drinking-water is based on the upper range value of manganese intake of 11 mg/day, identified using dietary surveys, at which there are no observed adverse effects (ie, considered a NOAEL), using an uncertainty factor of 3 to take into consideration the possible increased bioavailability of manganese from water. This results in a TDI of 0.06 mg/kg of body weight. The MAV was derived as follows:

$$\frac{0.06 \text{ mg/kg body weight per day x 70 kg x 0.2}}{2 \text{ L per day}} = 0.42 \text{ mg/L (rounded to 0.4 mg/L)}$$

where:

- tolerable daily intake = 0.06 mg/kg body weight per day
- average adult weight = 70 kg
- the proportion of tolerable daily intake assigned to the consumption of water = 0.2
- average amount of water consumed per day = 2 L per day.

The aesthetic guideline value for mangansese is 0.1 mg/L due to the fact that it deposits in water mains and causes discoloration when scoured out. Some water supplies may need to aim for a lower concentration to prevent the build-up.

At concentrations exceeding 0.1 mg/L, manganese can impart an undesirable taste to water.

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Nitrate and nitrite

Updated July 2005.

Maximum acceptable value for nitrate (short-term)

Based on health considerations, the concentration of nitrate (as NO_{3-}) in drinking-water should not exceed 50 mg/L.

Maximum acceptable value for nitrite (short-term)

Based on health considerations, the short-term concentration of nitrite (as NO_{2-}) in drinking-water should not exceed 3 mg/L.

Maximum acceptable value for nitrite (long-term and provisional)

Based on health considerations, the long-term concentration of nitrite (as NO_{2-}) in drinking-water should not exceed 0.2 mg/L. The WHO guideline value for chronic effects of nitrite is considered provisional owing to uncertainty surrounding the relevance of the observed adverse health effects for humans and the susceptibility of humans compared with animals.

Maximum acceptable value for combined nitrate plus nitrite

The sum of the ratios of the concentrations of each to its Maximum acceptable value (short-term) should not exceed 1. The maximum contaminant level for nitrate (USEPA 2004) is 10 mg/L as N, and 1 mg/L for nitrite as N, or a total of 10 mg/L.

Sources to drinking-water

1 To source waters

Nitrate and nitrite can enter the aquatic environment from the oxidation of vegetable and animal debris and animal excrement.

Nitrate and nitrite can also enter water from agricultural, domestic and industrial discharges. Nitrate is used in chemical fertilisers, oxidising agents in the chemical industry, in the manufacture of glass, enamels for pottery, matches, pickling meat and in the production of explosives. A major source of nitrate is from municipal wastewaters and septic tanks. Nitrite is also used as a corrosion inhibitor in industry, and for curing meats.

2 From the treatment processes

The chlorination of raw waters containing significant amounts of ammonia or nitrite may lead to increases in nitrate through their oxidation. As 70 per cent or more of the chlorine consumed during the oxidation of ammonia leads to N_2 production, the increase in nitrate concentrations is likely to be small unless ammonia concentrations are high.

3 From the distribution system

Chloramination may give rise to the formation of nitrite within the distribution system if the formation of chloramine is not sufficiently controlled. The formation of nitrite is as a consequence of microbial activity and may be intermittent. Nitrification in distribution systems can increase nitrite levels, usually by 0.2–1.5 mg/L.

Forms and fate in the environment

Nitrate and nitrite are naturally occurring ions which make up part of the nitrogen cycle. Nitrate is the oxidised form of combined nitrogen found in natural waters and in dilute aqueous solutions is chemically unreactive. Under anaerobic conditions nitrate may be reduced to nitrite and ammonia. Nitrite is seldom present in surface waters at significant concentrations but may be present in ground waters. High nitrite levels are generally indicative of contamination. Incomplete nitrification of ammonia and denitrification of nitrate result in the biochemical production of nitrite which is generally present only under anaerobic conditions.

Typical concentrations in drinking-water

Nitrate

Nitrate was routinely measured in New Zealand drinking-water supplies as part of the Department of Health three yearly surveillance programme. Of 1908 samples analysed between 1983 and 1989, 14 samples (0.7%) contained concentrations equal to or exceeding the 1984 MAV of 10 mg/L (N).

The P2 Chemical Determinand Identification Programme, sampled from 673 zones, found nitrate concentrations to range from 'not detectable' (nd) to 30 mg/L as NO_{3}-N, with the median concentration being 0.2 mg/L (limit of detection = 0.1 mg NO_{3}-N/L).

Nitrite

Nitrite was not measured routinely in New Zealand drinking-water supplies as part of the Department of Health three yearly surveillance programme.

The P2 Chemical Determinand Identification Programme, sampled from 227 zones, found nitrite concentrations to range from 'not detectable' (nd) to 0.088 mg/L, with the median concentration being 'nd' (limit of detection = 0.005 NO_{2}-N mg/L).

Removal methods

Nitrate

Nitrate is not removed from water by classical methods of treatment. Ion exchange systems have been developed for removing nitrate, but dilution with water of lower nitrate concentration from another source is commonly used, where one is available.

Nitrite

Treatment of the water with an oxidising agent such as chlorine will convert the nitrite to nitrate. The nitrate can then be treated as explained for nitrate. The USEPA Maximum Concentration Level for nitrite indicates that the concentration at which it might be of concern is ten times less than the guideline for nitrate. The oxidation of high nitrite levels to nitrate therefore will not create an unacceptably high nitrate concentration in the water, unless the nitrate level is already high, or the nitrite level is extremely high.

Analytical methods

Nitrate

Referee method

Cadmium Reduction Method (APHA-NO_3-E).

Some alternative methods

1 Ion Chromatography Method (APHA 4110).
2 Nitrate Electrode Method (APHA 4500-NO_3 D).

Nitrite

Referee method

Colorimetric Method (APHA 4500-NO_2 B).

Some alternative methods

1 Ion Chromatography Method (APHA 4110).

Health considerations

Ingested nitrate is absorbed readily and completely from the upper small intestine. Nitrite may be absorbed directly from the stomach as well as from the small intestine. Sodium nitrite is used as a food preservative, especially in cured meats.

The toxicity of nitrate in humans is thought to be due solely to its reduction to nitrite. The primary health concern regarding nitrate and nitrite is the formation of methaemoglobinaemia, so-called blue-baby syndrome. Nitrate is reduced to nitrite in the stomach of infants, and nitrite is able to oxidise haemoglobin (Hb) to methaemoglobin (metHb), which is unable to transport oxygen around the body. The reduced oxygen transport becomes clinically manifest when metHb concentrations reach 10% or more of normal Hb concentrations; the condition, called methaemoglobinaemia, causes cyanosis and, at higher concentrations, asphyxia. The normal metHb level in infants under three months of age is less than 3%. Other susceptible groups include pregnant women and people with a deficiency of glucose-6-phosphate dehydrogenase or methaemoglobin reductase. Methaemoglobinaemia in infants also appears to be associated with simultaneous exposure to microbial contaminants (eg, Addison and Benjamin 2004).

Nitrate is not mutagenic in bacteria and mammalian cells in vitro. Chromosomal aberrations were observed in the bone marrow of rats after oral nitrate uptake, but this could have been due to exogenous N-nitroso compound formation. Nitrite is mutagenic.

The weight of evidence is strongly against there being an association between nitrite and nitrate exposure in humans and the risk of cancer.

Derivation of maximum acceptable values

Nitrate (short-term)

The MAV of 50 mg/L (as NO_3) is to protect against methaemoglobinaemia in bottle-fed infants (short-term exposure). In epidemiological studies, methaemoglobinaemia was not reported in infants in areas where drinking-water consistently contained less than 50 mg of nitrate per litre.

The epidemiological evidence for an association between dietary nitrate and cancer is insufficient, and the MAV for nitrate in drinking-water is established solely to prevent methaemoglobinaemia, which depends upon the conversion of nitrate to nitrite. Although bottle-fed babies are the most susceptible, occasional cases have been reported in some adult populations.

Nitrite (short-term)

The short-term MAV of 3 mg/L (as NO_2) is to protect against methaemoglobinaemia in bottle-fed infants. Animal studies were inappropriate to establish a firm no observable adverse effect level for methaemoglobinaemia in rats. Therefore, a pragmatic approach was followed, accepting a relative potency for nitrite and nitrate with respect to methaemoglobin formation of 10:1 (on a molar basis), and a provisional MAV of of 3 mg/L has been adopted for nitrite.

Nitrite (long-term)

The 0.2 mg/L (as NO_2) MAV for long-term exposure for chronic effects of nitrite is considered provisional owing to uncertainty surrounding the relevance of the observed adverse health effects for humans and the susceptibility of humans compared with animals. The occurrence of nitrite in the distribution system as a consequence of chloramine use will be intermittent, and average exposures over time should not exceed the provisional MAV. The nitrite MAV (long-term exposure) is based on allocation to drinking-water of 10% of JECFA ADI of 0.06 mg/kg of body weight per day, based on nitrite-induced morphological changes in the adrenals, heart and lungs in laboratory animal studies.

Nitrate : nitrite ratio

Because of the possibility of simultaneous occurrence of nitrite and nitrate in drinking-water, the sum of the ratio of the concentration of each to their short-term MAVs, as shown in the following formula, should not exceed 1:

$$\frac{C(NO_2)}{MAV(NO_2)} + \frac{C(NO_3)}{MAV(NO_3)} \leq 1$$

where C = concentration, and MAV = maximum acceptable value.

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