

Drinking Water Quality in the Horizons Region

November 2014

Horizons Report 2014/EXT/1405

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1.0 Introduction

Pattle Delamore Partners have been engaged by Horizons Regional Council to review groundwater chemistry data to describe the patterns of groundwater quality in the region and if breaches of Maximum Acceptable Values (MAVs) or Guideline Values (GVs) in the Drinking Water Standards for New Zealand 2005 (revised 2008) (DWSNZ). Information gleaned from these analyses will be used to provide recommendations to groundwater users in the area. Horizons Regional Council provided data from their Hilltop and Qualarc databases for the analysis. The PDP (2013) report highlighted some bores which breach national drinking water standards, this report uses more recent data to provide an updated assessment of where any breaches occur.

Detailed analysis was conducted on 27 boreholes from the Hilltop database, with data records extrapolated back in time using information from the Qualarc database. At all monitoring sites, field measurements were made of groundwater temperature, electrical conductivity, pH, dissolved oxygen, and redox potential. Laboratory analysis was then generally undertaken for a selection or all of the following:

- : Major cations (Ca, Mg, Na, K);
- Major anions (HCO₃, SO₄, Cl);
- : Other chemical species that often affect water quality (Fe, Mn, As, F, B);
- Other indicative chemical parameters (SiO₂, Br) and;
- : Indicators of bacterial contamination (Escherichia coli (E. coli), total coliforms).

Groundwater quality data from 2013-2014 has been assessed for breaches of New Zealand drinking water standards (NZDWS) of 14 water quality parameters according to New Zealand Ministry of Health guidelines (2008). This data has been examined spatially, and using historical data any recent trends have been highlighted. Reasons for breaches and trends are also discussed.

2.0 Groundwater Quality Analysis

2.1 Methods

Firstly, the number of records and the length of the time series data for each bore were assessed. This data is presented in Table 1 together with the well depths and locations. Next, water quality parameters in the Hilltop database were chosen for analysis if NZDWS guideline values (GVs) and maximum acceptable values (MAVs) exist. A total of 14 water quality parameters were selected. Table 2 presents the list of parameters used and the NZDWS GVs and MAVs for each. Any necessary corrections to the data were then made; Nitrate and Nitrite were converted into Nitrate-N and Nitrite-N respectively. This is because data for both Nitrate-N and Nitrate existed, with the same being the case for Nitrite and DWS are often reported in terms of nitrogen content. In low pH environments, ammonia (NH₃) becomes ammonium (NH₄), and so for simplicity, all data was

converted into ammoniacal nitrogen. To calculate hardness, the calcium and magnesium concentrations were converted into molar equivalents of calcium carbonate, and then summed.

For some species in the Qualarc and Hilltop databases, different chemical analyses have been undertaken on the same parameter at different times, for example "total arsenic" and "soluble arsenic". A brief analysis was undertaken to determine any differences in the calculated values from these methods, by plotting results from the differing analyses against one another for each borehole. No obvious trend was identified from any of the resultant plots, and all results were included in the subsequent analysis. Detection limits vary between the differing analyses, and only some are reported. The detection limits in the Hilltop database are consistent, and these have been added to the figures in Appendix B. Where samples returned results below the detection limit, half the detection limit was used in statistical analysis.

For each bore and each species, the mean, median, maximum and minimum values, and total number of beaches were calculated for all data prior to 2013 and for 2013-14. Bores were then segregated based on their redox characteristics (oxidising or reducing) according to the findings of PDP (2013). Finally, time series of data for each redox environment and for each chemical species were plotted, and maps showing where breaches of NZDWS GVs, and MAVs occur spatially were constructed.

One bore in the Hilltop database (352271), was not analysed as this is screened in the deeper basement rock and the groundwater has a high electrical conductivity making it unsuitable for potable supply, contrasting with the sand and gravel screened bores.

			Depth	Screened				No.	No.	
Bore	Easting	Northing	(m)	Lithology	Data Source	Start Date	End Date	Sampling	Samples Analysed	
			(11)	Litilology				rounds		
209005	1769434	5580221	68.6	Sand	Qualarc/Hilltop	29/10/1996	22/10/2013	26	571	
301011	1783606	5562485	27	Gravel	Qualarc/Hilltop	28/09/1998	22/10/2013	18	389	
312001	1793730	5548926	18	Gravel	Qualarc/Hilltop	7/11/1994	22/10/2013	29	605	
312007	1790026	5553997	62.8	Sand	Qualarc/Hilltop	25/05/1992	22/10/2013	37	779	
312020	1795327	5555177	116.7	Gravel	Qualarc/Hilltop	25/03/1996	22/10/2013	26	561	
314025	1807712	5553874	7.2	Gravel	Qualarc/Hilltop	7/11/1994	22/10/2013	29	631	
316037	1823563	5548965	26.5	Gravel	Qualarc/Hilltop	8/11/1994	22/10/2013	30	649	
332009	1794013	5528889	25.37	Unknown	Qualarc/Hilltop	29/04/1991	22/10/2013	44	908	
332025	1791935	5536397	8.6	Sand	Qualarc/Hilltop	26/01/1996	22/10/2013	47	673	
334091	1810906	5527654	19	Gravel	Qualarc/Hilltop	8/11/1994	22/10/2013	30	633	
336114	1825664	5530018	12.3	Gravel	Qualarc/Hilltop	8/11/1994	22/10/2013	30	655	
336333	1824995	5534744	96	Gravel	Qualarc/Hilltop	31/10/2000	29/08/2012	14	322	
337005	1833657	5533098	83	Sand	Qualarc/Hilltop	29/04/1991	22/10/2013	43	885	
338005	1843312	5527219	10.52	Unknown	Qualarc/Hilltop	8/11/1994	22/10/2013	30	616	
339001	1853985	5530488	4.7	Gravel	Qualarc/Hilltop	8/11/1994	22/10/2013	31	645	
342051	1793343	5516722	65.5	Gravel	Qualarc/Hilltop	29/04/1991	22/10/2013	44	905	
343125	1795990	5525373	10.6	Sand	Qualarc/Hilltop	2/05/1995	22/10/2013	30	648	
352099	1792465	5504131	9.15	Unknown	Qualarc/Hilltop	20/04/1995	20/03/2014	65	191	
352271	1790598	5506044	93.2	Unknown	Qualarc/Hilltop	29/04/1991	22/10/2013	43	899	
352312	1787361	5508117	86	Unknown	Qualarc/Hilltop	1/05/1995	22/10/2013	27	571	
353015	1798610	5507731	22.3	Sand	Qualarc/Hilltop	21/06/1995	19/03/2014	78	837	
353251	1796578	5506824	20	Unknown	Qualarc/Hilltop	21/05/2002	16/12/2013	35	120	
357109	1833475	5511160	14.45	Unknown	Qualarc/Hilltop	23/03/1999	22/10/2013	22	471	
362001	1787778	5496985	16.3	Sand	Qualarc/Hilltop	20/07/1995	19/03/2014	63	191	
362003	1786529	5495500	11.1	Unknown	Qualarc/Hilltop	29/04/1991	22/10/2013	42	886	
363112	1796876	5500893	19.2	Unknown	Qualarc/Hilltop	2/08/1995	19/03/2014	65	197	
372071	1787202	5490231	26	Sand	Qualarc/Hilltop	28/10/1994	20/03/2014	69	228	
430005	1857643	5534613	17	Unknown	Qualarc/Hilltop	8/11/1994	22/10/2013	31	650	

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Chemical Species	NZDWS	NZDWS Maximum	Justification
	Guideline Value	Acceptable Value (MAV)	
	(GV)		
Arsenic	n/a	0.01 mg/L	Health and environmental hazard.
Boron	0.5 mg/L	1.4 mg/L	Health and environmental hazard.
Iron	0.2 mg/L	n/a	Aesthetics (potability and encrustation, staining).
Manganese	0.04 mg/L	0.4 mg/L	Aesthetics (taste, and staining), health and environmental hazard.
Sodium	200 mg/L	n/a	Health hazard, and affects water usability for irrigation. Indicator of seawater intrusion.
Hardness	200 mg/L & < 100 mg/L if pH < 7	n//a	Aesthetic and water usability, can cause encrustation if > 200 mg/L, and corrosion if < 100 mg/L and pH < 7 .
Fluoride	0.7 mg/L	1.5 mg/L	Health hazard (skeletal disorders)
Chloride	250 mg/L	n/a	Potability, corrosiveness, and indicator of seawater intrusion
Sulphate	250 mg/L	n/a	Aesthetic and health hazard.
Ammoniacal Nitrogen	1.24 mg/L	n/a	Environmental hazard (toxic to aquatic life)
Nitrite Nitrogen	n/a	0.91 mg/L (short term) 0.06 mg/L (long term)	Pollution indicator, health and environment hazard
Nitrate Nitrogen	n/a	11.3 mg/L	Pollution indicator, health and environment hazard
рН	< 7 & > 8.5	n/a	Water usability and contamination indicator
E. Coli	n/a	< 1 per 100 ml	Health risk, and indicator of contamination.

3.0 Location of DWS breaches in 2013-2014

3.1 Data Available for 2013-2014

For most bores, two sampling rounds were undertaken in March and October 2013 across the Horizons region for all parameters. However, additional samples were taken for nitrate and pH at some bores and some of these were taken in 2014 as well as 2013. Conversely, some bores were sampled only annually for arsenic. Table 3 summarises the sampling dates in bores where one or

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more parameters were not sampled biannually in 2013 (March and October). No samples were taken from the 96 m deep bore 336333 in 2013-2014, which is located north-east of Palmerston North.

	onitoring bores not sample	ed biannually in 2013-20	014 showing the dates of
sampling r Borehole	ounds. Sampling rounds	Sampling rounds	Sampling rounds remaining
	Nitrate and pH	Arsenic	parameters
301011	October 2013	•	
312007	October 2013		
332009	October 2013		
336333	Last sampled August 2012		
337005	March & October 2013	March 2013	March & October 2013
338005	March & October 2013	March 2013	March & October 2013
339001	March & October 2013	March 2013	March & October 2013
352099	March 2013 – March 2014 tri-monthly (5 samples)	No samples taken	
353015	March 2013 – March 2014 tri-monthly (6 samples – extra sample taken in March 2013)	March & October 2013	
353251	March 2013 – March 2014 tri-monthly (5 samples)	No samples taken	
357109	March & October 2013	March 2013	March & October 2013
362001	June 2013 – March 2014 tri-monthly (4 samples)	No samples taken	
363112	March 2013 – March 2014 tri-monthly (5 samples)	No samples taken	
372071	March 2013 – March 2014 tri-monthly (5 samples)	Last sampled May 2008 (E	. coli last sampled August 2009)
430005	March & October 2013	March 2013	March & October 2013

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3.2 Redox Conditions

Figure A.1 shows a map of the Horizons region and the analysed wells, separating the boreholes according to their redox conditions and depth (< 20 m deep and > 20 m deep). Redox bores were defined in the PDP (2013) report based on the concentrations of several water quality parameters. Bores with high iron, manganese, arsenic and ammonia were classed as reducing, while bores with high nitrate, and low arsenic, iron and, manganese were classified as oxidising. Generally, most of the oxidising bores are shallow (\leq 27 m deep), while deeper bores tend to be reducing. This is because deeper groundwater is older, and dissolved oxygen in the water is consumed by redox reactions through time. Oxidising wells predominantly occur to the east and south-west, with the reducing wells mostly occurring close to the coast. A total of 13 oxidising wells and 14 reducing wells were analysed.

3.3 Major Cations and Anions

Five major ions were analysed; Sodium, Magnesium and Calcium (combined as Hardness), Chloride, and Sulphate. Typically these ions are present in groundwater in the highest concentrations.

3.3.1 Sodium

Figure A.2 shows a map of median sodium concentrations and redox conditions in 2013. No Sodium breaches are found to occur, and all but one analysis produced a median value < 55 mg/L.

- Oxidising bores all had low (<27 mg/L median value) sodium concentrations, which is expected in shallow groundwater environments.
- Reducing bores had similar concentrations to oxidising bores (≤ 55 mg/L), with the exception of bore 337005 located close to the Manawatu gorge. This well produced a median value of 178 mg/L, however this concentration is still below the NZDWS GV of 200 mg/L.

3.3.2 Hardness

The NZDWS optimum range for hardness is 100-200 mg/L. Soft water is characterised as being below this optimum range, whilst hard water is characterised as exceeding it. Figure A.3 shows a map of median hardness concentrations and where breaches of the NZDWS GV occurred in 2013 (i.e. where concentrations were outside the 100-200 mg/L range). In general, harder potentially encrusting waters occur in deeper, reducing bores while softer potentially corrosive waters occur in shallower oxidising bores.

- Fourteen breaches of hardness < 100 mg/L were identified occurring in all sampled oxidising wells. The softest waters occurred in wells 362003 and 357109, and 430005, with the remaining wells having median hardness values of > 71 mg/L.
- Eight breaches of hardness > 200 mg/L were identified in 6 of the 13 sampled reducing wells. Three of these breaches were borderline, yielding median values of 195-201 mg/L. The greatest median hardness was 562 mg/L in the 117 m deep bore, 312020 to the

north west of Bulls and the other hard water bores > 201 mg/L also lie immediately to the west of this bore in the Rangitikei groundwater management zone.

3.3.3 Chloride

Figure A.4 shows a map of median chloride concentrations and redox conditions in 2013. No breaches of the chloride NZDWS GV were detected.

- Chloride in oxidising bores is ≤ 39 mg/L throughout the region, far below the NZDWS GV of 250 mg/L/.
- The maximum median chloride concentrations are at bore 337005 (152 mg/L), located adjacent to the Manawatu gorge east of Palmerston North and 312020 (143 mg/L), northwest of Bulls. These wells are relatively deep, 83 m and 117 m respectively. Bore 337005 is proximal to the Pohangina anticline and basement aquifers which have high salinities. Mixing with these deeper groundwaters could cause greater chloride concentrations.
 - 3.3.4 Sulphate

Figure A.5 shows a map of median sulphate concentrations and redox conditions in 2013. No breaches of the sulphate NZDWS GV were detected.

- In oxidising wells, sulphate is always > 5 mg/L which is expected as sulphate reduction cannot occur in oxidising conditions. However, the maximum median sulphate concentration is < 39 mg/L, far below the NZDWS GV of 250 mg/L.</p>
- In 7 of the 13 reducing wells, sulphate concentrations are < 0.05 mg/L. The greatest sulphate concentrations (105.5 mg/L) occur in 312020 and chloride concentrations are also high in this well. This is a deep (117 m deep), reducing well and could indicate that mixing with saline groundwaters is occurring at depth, or it may be an indication of the local geology. The presence of gypsum for example can give rise to high sulphate concentrations.</p>

3.4 Minor Determinands

Minor determinands are ions which are often present in groundwater but in typically much lower concentrations than major ions, except in exceptional cases. Five minor determinands were assessed, including two metals (iron and manganese), two metalloids (arsenic and boron), and one anion (fluoride).

3.4.1 Manganese

Figure A.6 shows a map of median manganese concentrations and where breaches of the NZDWS GV and MAV occurred in 2013. A total of 24 breaches of the manganese NZDWS GV (0.04 mg/L) were detected, 17 of which also exceeded the MAV (0.4 mg/L).

Only one oxidising well had a manganese concentration exceeding the NZDWS GV, this well is shallow (7.2 m) and located close to the Rangitikei River. This is an exception and could be caused by a connection to the river or local geology. All of the remaining 8 sampled oxidising bores had manganese concentrations typically below the detection limit.

As expected, manganese concentrations exceed the GV in all reducing wells, and exceed the MAV in bores close to the coast and along the Manawatu River. Over 74% of samples taken in 13 reducing wells exceeded the NZDWS MAV. This is a consequence of the reducing conditions, where the low oxygen content of the groundwater allows dissolution of metals and metalloids in the strata.

3.4.2 Iron

Figure A.7 shows a map of median iron concentrations and where breaches of the NZDWS GV occurred in 2013. Fourteen of the twenty one sampled wells yielded iron concentrations exceeding the GV of 0.2 mg/L.

- Only oxidising well 338005 had iron concentrations exceeding the NZDWS GV. This well is 10.52 m deep and adjacent to the Manawatu River, this exceedance could again be due to a connection with the river or due to the local geology.
- As with manganese, all reducing wells exceeded the iron GV. Concentrations are greatest along the coast and the Manawatu River.

3.4.3 Arsenic

Figure A.8 shows a map of median arsenic concentrations and where breaches of the NZDWS MAV occurred in 2013. Five of the twenty one bores had at least one sample taken which exceeded the MAV.

- No breaches of the MAV were observed in oxidising bores, with concentrations below or just above the analytical detection limit.
- Nine breaches of the NZDWS MAV occurred in five reducing wells close to the coast, a total of 39% of samples from the 13 reducing wells. These breaches of the MAV for arsenic are consistent with the reducing / oxidising groups of bores, with breaches of the MAV only occurring in reducing bores, where higher concentrations of arsenic are typically found. Away from the zone where breaches are found to occur, concentrations are at least an order of magnitude lower.

3.4.4 Boron

Figure A.9 shows a map of median boron concentrations and where breaches of the NZDWS GV and MAV occurred in 2013. Only one of the twenty one sampled bores breached the GV, and no exceedances of the MAV were detected.

- : Oxidising bores had median boron concentrations \leq 0.05 mg/L, consistent with the groundwater redox conditions found in these bores.
- As with oxidising wells, 85% of the 13 sampled reducing wells had median boron concentrations ≤ 0.05 mg/L, and only one well exceeded the boron GV. No exceedances of the MAV occurred. The only identified GV breach occurred in bore 337005, which is located close to the Manawatu gorge, east of Palmerston North. This well is 83 m deep and has a median Boron concentration of 1.19 mg/L. No other wells surrounding this borehole have high boron concentrations and since these are all shallow (< 20 m deep)

this implies that the high boron levels may be a result of the nature of the deep strata and reflect local conditions around that particular bore. Mixing with groundwaters from the basement aquifers of the Pohangina anticline, which have a different geochemistry could produce these high boron concentrations. The next greatest median boron concentration is 0.12 mg/L, far below the NZDWS GV of 0.5 mg/L.

3.4.5 Fluoride

Figure A.10 shows a map of median fluoride concentrations in 2013. No exceedances of the GV or MAV occurred, in any of the samples collected.

- The highest median concentration in oxidising bores is 0.2 mg/L, far below the fluoride GV of 0.7 mg/L.
- The greatest median concentration in reducing bore is 0.35 mg/L, half that of the NZDWS GV. Concentration are generally higher in reducing wells closer to the coast.

3.5 Nutrients

Nutrients are present in groundwater from natural sources, such as organic matter within the aquifer, or from anthropogenic sources such as fertilizer. Concentrations of ammonia, nitrite, and nitrate are examined here.

3.5.1 Ammoniacal Nitrogen

Figure A.11 shows a map of median ammoniacal nitrogen concentrations and where breaches of the NZDWS GV occurred in 2013. Ammonia occurs naturally from the breakdown of organic matter in anaerobic conditions, from animal waste or anthropogenic fertilizer application.

- Ammoniacal nitrogen is low (always ≤ 0.01 mg/L) in oxidising wells, this is because in oxidising conditions ammonia is oxidised to nitrite or nitrate.
- In total 43.5% of samples from the 13 sampled reducing wells breach the NZDWS GV.
 Exceedances of the GV in reducing bores occur in wells ranging in depth from 10.6-83 m.
 These wells are mostly sited in the agricultural regions of the Manawatu and Rangitikei groundwater management zones.

3.5.2 Nitrite Nitrogen

Figure A.12 shows a map of median nitrite N concentrations in 2013. No wells breached the long term NZDWS MAV of 0.06 mg/L.

- Concentrations of nitrite N in oxidising wells are always at least an order of magnitude below the NZDWS MAV. This is perhaps because nitrite oxidises to nitrate in the oxidising conditions of these wells.
- The highest concentrations of nitrite N in reducing wells occurred in deeper bores (63-117 m) close to the coast. The maximum of these values though remains an order of magnitude below the MAV concentration. In general nitrite N concentrations are higher in reducing wells than oxidising wells. Possibly as a by product of nitrate reduction.

3.5.3 Nitrate Nitrogen

Figure A.13 shows a map of median nitrate N concentrations in 2013-2014, and where the NZDWS MAV was breached. Three of the twenty seven sampled bores exceeded the MAV of 11.3 mg/L

- Two oxidising wells (352099 and 353251) had median nitrate nitrogen concentrations exceeding the maximum acceptable nitrate nitrogen concentration, with a further well (372071) having one of five samples which breached this value. These wells are all located to the south of the region, around Levin. All concentrations > 9 mg/L were in oxidising wells < 27 m deep, suggesting that agricultural affects may be significant in causing high concentrations at these points.</p>
- The maximum nitrate nitrogen concentration in the reducing wells was 0.08 mg/L, which is expected as denitrification (reductive breakdown of nitrate) occurs in anaerobic environments.

3.6 Bacteria

The detection limit for E.Coli at the laboratory where samples were analysed was 4 MPN / 100 ml, which is greater than the drinking water standard (< 1 MPN / 100 ml). Therefore, the E.Coli data have been split into three groups. One group contains bores with detections of > 4 MPN / 100 ml, which represent confirmed detections of E.Coli in a sample. The second group contains bores that have detections of 4 MPN / 100 ml or less. The detection limit means that the presence or absence of E.Coli cannot be confirmed in bores in the second group. The final group contains samples with results of < 1 or 0 MPN / 100 ml, which indicates that samples from the bores did not breach drinking water standards.

Figure A.14 shows a map of the maximum most probable E. coli numbers per 100 ml in 2013, and where the NZDWS MAV were exceeded (in bores where the count of E.Coli was > 4 MPN / 100 ml), and possibly exceeded (where the count was 1-4 MPN / 100 ml). Only 2 of the 21 sampled wells contained confirmed detections of E coli in either of the two sampling rounds that took place in 2013, both of which are 11 m deep. Shallow bores are vulnerable to contamination from surface sources, so detections of E.Coli in the two bores is not surprising. A further 16 bores contain possible exceedances (between 1 and 4 MPN / 100 ml, while in the remaining 3, results were reported as < 1 MPN / 100 ml, meaning NZDWS were not breached.

3.7 pH

The acceptable range for pH is 7-8.5, with values outside of this range breaching the DWSNZ GV. Figure A.15 shows a map of median pH values and where NZDWS GV breaches occur in 2013-2014.

pH is on average < 7 in all oxidised wells. The cause of the low pH is actually likely to be related to the effect of rainfall recharge, which can become acidic as it passes through the soil zone. A total of 79% of samples taken from 20 wells < 27 m deep reported pH values < 7 across both oxidising and reducing bores.

 pH of reducing wells is always > 7 with the exception of two wells (301011 and 334091) both wells are < 27 m deep. No samples were taken where the pH exceeds 8.5.

3.8 Summary

Figure A.16 shows a summary map of where exceedances of NZDWS have been detected in 2013-2014. Table 5 summarises data from 2013-2014, and where breaches of NZDWS have occurred. The lower thresholds of pH and hardness GV was breached in all of the 13 sampled oxidising bores. The lower threshold of hardness was breached in all but one of the 8 sampled oxidising bores. The MAV for nitrate N was also exceeded in 3 of the 13 sampled bores. In reducing bores, the GV for iron and manganese was breached in all 13 sampled bores. All but one of the reducing wells also exceeded the manganese MAV. Five bores had hardness and ammoniacal nitrogen concentrations above the GV, and arsenic concentration exceeded the MAV in three bores.

Median E. coli concentrations exceeded the MAV value in 18 of the 21 sampled bores, although as noted above, these results may not be reliable. Boron concentration exceeded the NZDWS GV in reducing bore 337005 sited adjacent to the Manawatu gorge. This is possibly due to mixing with deeper groundwater in the basement. Overall, there are no new exceedances which are exceptional when compared to previous data reported in PDP (2013).

4.0 Groundwater Quality Trend Analysis

4.1 Major Cations and Anions

Figures B.1 to B.8 show time series graphs of sodium, chloride, hardness, and sulphate concentrations in both oxidising and reducing boreholes.

Sodium and chloride concentrations appear to be predominantly stable across all boreholes, with some bores showing high variability between sampling rounds. The reducing bore 332025 shows a slight decreasing trend from 2007 for chloride and 2007 for sodium to 2011 but this has now levelled out. Bore 337005 (83 m deep, located close to the Manawatu Gorge, north east of Palmerston North), which is also reducing, shows a steady increasing trend in chloride concentrations since 2001, but this seems to be flattening in recent years. This is consistent with the trends noted by PDP previously. There is also a corresponding increasing trend for sodium in bore 337005 (and hardness, see below) but the trend for sodium is less pronounced and shows more variability.

Chloride is a useful indicator of general water quality and therefore the trends in this parameter are useful indicators of any longer term in groundwater quality. Trends in chloride were analysed in the groundwater quality report (PDP, 2013) and of the other increasing chloride trends highlighted by PDP (2013), most appear to have stabilised in recent years, and none are of immediate concern. Table 3 summarises any changes in the identified trends from 2013.

Table 4: C	hanges in Ch	loride concentrations in well	s with trends identified in PDP (2013)						
Borehole	PDP (2013) trend	Current Trend	Concern						
209005	Increasing	Very slight (0.67 mg/L) increase since 2012.	No, insignificant recent change, median 2013 concentration of 50.6 mg/L well below GV.						
314025	Increasing	Highly variable since 2005, first result (36.6 mg/L) of 2013 greatest since 2010.	No, variability likely related to changes in recharge or connection to surface water bodies (shallow well). Maximum recent concentration well below past maximum of 120 mg/L.						
332025	Decreasing	Stabilised only minor changes since 2012.	No, current decreasing trend has stabilised median of 51.1 mg/L well below GV.						
336333	Increasing	No data since 2013.							
337005	Increasing	Median 2013 concentration increased by 6.5 mg/L since 2013.	Yes, most recent concentration (152.6 mg/L) is highest recorded.						
339001	Increasing	Increased since last monitoring but within historic ranges.	No, insignificant recent change, median 2013 concentration of 39.3 mg/L well below GV.						
342051	Increasing	Most recent result highest since 2009, slight increase.	No, insignificant recent change, median 2013 concentration of 22 mg/L well below GV.						
343125	Decreasing	Slight decrease since 2012, last result is lowest since 2010.	No, decreasing trend.						
353015	Increasing	Continued very slight (< 0.2 mg/L) increase since 2012.	No, concentrations increasing at minor rate, median 2013 concentration of 32.6 mg/L well below GV.						
430005	Increasing	Variable, early 2013 result (31.1 mg/L) highest recorded.	No, most recent result significantly lower (21.9 mg/L) than early 2013 result.						

Over the past 5 years, hardness concentrations have also remained predominantly stable when the variability between sampling rounds is averaged out. The main exception is the reducing bore 337005, which has shown a clear increase in hardness concentrations from 2002-2011, but has

since remained relatively stable. The pattern of increasing concentration of hardness, chloride and sodium in bore 337005, together with unusually high concentrations of Boron (above the GV, but below the MAV)) may be caused by local conditions around the bore. These trends could be caused by long term trends in recharge and ion exchange. Whilst the concentrations are not yet high enough to be of serious concern, the long term increasing trend in this bore is worth highlighting and keeping under review.

With regards to sulphate, there are only three years of available data for sulphate concentrations (from 2011 to 2013), and concentrations have not varied significantly over that time period.

4.2 Minor Determinands

Figures B.9 to B.18 show time series graphs of manganese, iron, arsenic, boron, and fluoride concentrations in both oxidising and reducing boreholes.

For manganese, all of the oxidising bores have shown a declining trend since 2008-2009 with the exception of 314025, which is highly variable between sampling rounds, yielding the highest recorded concentration in early 2013. Many of the manganese concentrations in oxidising bores now fall below the detection limit, with the decreasing trend causing an overall decrease of over an order of magnitude. Prior to the change the sampled wells were yielding similar results. The reason for this decrease across oxidising bores may be caused by increasing analysis accuracy or changes in sampling techniques to include filtering samples. In reducing bores, all manganese concentrations have been predominantly stable over the last 4 years.

Iron concentrations in oxidising bores are highly variable between sampling rounds, and there is no consistent identifiable trend for any of the bores. In reducing bores, iron concentrations have been relatively stable since 2012, with some minor increases and decreases. Results for almost all boreholes showed a large decrease in 2011, this could be due to a systematic sampling or laboratory error. Since 2011, the concentration of iron in reducing bores shows a consistent and spatially widespread increasing pattern, although the absolute value of concentrations is within the range of historical variability. However, the pattern is noteworthy, since it may reflect region wide drivers for changes in hydrochemistry.

Concentrations of arsenic and boron in oxidising bores are mostly stable, with many reported results below the detection limit. Reducing bores also show mostly stable arsenic and boron concentrations, although results from 332025 have been highly variable. The maximum concentration ever recorded in this bore was taken in late 2012. This variability could reflect the shallow depth (< 9 m) of the bore meaning it is influenced by the diluting effects of surface water recharge to a greater extent.

Boron concentrations in reducing well 337005 have been steadily increasing since sampling began in 2002 (although the most recent three samples are all stable) and the concentration of Boron is over the NZDWS GV, but currently concentrations are still below the MAV. The reason for this increase is unclear, and since there is little data prior to 2010 confidence in the trend prior to this date is low. However, given the trends in chloride, hardness and sodium in bore 337005 continued review of the hydrochemistry observed in this bore is recommended.

All wells show no consistent increases or decreases in fluoride concentrations, rather steady inconsistent fluctuations between sampling rounds.

4.3 Nutrients

Figures B.19 to B.24 show time series graphs of ammoniacal N, nitrite N, and nitrate N concentrations in both oxidising and reducing boreholes.

Ammoniacal N concentrations in oxidising bores show a high variability between sampling rounds, which is likely due to the proximity of the concentrations to the detection limit. In most reducing wells concentrations have been declining since 2011, but concentrations remain within the historical range for each bore. This widespread declining trend is similar but opposite to that observed with iron and may perhaps reinforce the possibility of some region wide driver for temporal hydrochemical patterns in the reducing bores.

Nitrite N concentrations in both oxidising and reducing bores are highly variable, mostly around or close to the detection limit, with no consistent trends. A series of nitrite N spikes are present when the long term NZDWS MAV is exceeded, particularly in reducing bores. It is often the case that spikes from a number of bores coincide, such as in 2011 for reducing wells. Spikes from 2011 correlate well with spikes in ammonical N concentrations. This might suggest that contamination during sampling might be occurring.

Nitrate N concentrations in reducing bores behave in a similar manner to nitrite N concentrations, being predominantly low but variable with a series of spikes.

In oxidising bores, nitrate concentrations in most wells appear stable although a variable but increasing trend appears to be present in the time series of bore 314025, with the highest value yet being recorded in the most recent sampling round in late 2013. Bore 362001 does exhibit a decreasing trend beginning in 2005, and this well has been consistently below the NZDWS MAV since 2010. A comparison of current trends with the trends highlighted in PDP (2013) is given in Table 4. Most recent (i.e. 2013) concentrations are stable or slightly decreasing, but these decreases are not significant, and a reversal to an increasing trend could occur.

Borehole	PDP (2013) trend	Current Trend	Concern						
314025	Stable	Most recent data suggests an increasing, but variable, trend.	Potentially. Maximum concentrations are beginning to approach the MAV.						
338005	Increasing	Current decreasing trend since 2012, most recent result (0.15 mg/L) lowest recorded.	No, trend is decreasing and concentrations well below MAV.						
352099	Decreasing	Continuing slight decreasing trend, current result is lowest since 2010.	Yes, concentrations still consistently greater than MAV.						
353015	Increasing	Stabilised only minor changes since 2012, median has decreased by 0.17 mg/L.	Yes, concentrations have exceeded MAV in the past						
353251	Increasing	Very slight decreasing trend since 2012, median has decreased by 0.17 mg/L.	Yes, concentrations still consistently greater than MAV. Decreasing trend is not significant.						
362001	Increasing	Decreasing trend since 2005, most recent result (6.6 mg/L) second lowest recorded.	Decreasing trend appears consistent in most recent data, but concentrations in this bore should be kept under review due to past exceedances of the MAV.						
363112	Increasing	Mostly stable since 2007.	No, concentrations have never exceeded MAV and appear stable. Current median of 2.94 mg/L well below MAV.						
372071	Increasing	Mostly stable since 2009, slight increasing trend in last 3 results.	Yes, has breached the MAV in early 2013.						
430005	Increasing	Variable, results within historic ranges.	No, concentrations are variable but have never breached MAV.						

4.4 Bacteria

Figures B.25 and B.26 show time series graphs of E. coli in oxidising and reducing bores respectively. There is no distinct trend in E. coli concentrations, although since 2008 more wells are reporting values of < 4 per 100 ml and since 2010 the number of results of < 1 per 100 ml

has increased, which may reflect an improvement in well head security, sampling procedures, or laboratory analysis. However, some of these results may still represent an NZDWS exceedance of the < 1 MPN / 100 ml criterion. In 2013, only two shallow (11 m deep) bores unequivocally breached NZDWS criteria, as mentioned above this is not unexpected for these shallow bores. Exceedances of NZDWS in a number of bores remains uncertain due to the high detection limit.

4.5 pH

Figures B.27 and B.28 show time series graphs of pH in oxidising and reducing bores respectively. No consistent pH trend is observed, except in bore 362001, which shows a consistent increasing trend since 2005. However, there is much variability, some of which could be due to seasonal recharge changes. Some of the extreme pH spikes often coincide and could be related to inadequate pH meter calibration. The most extreme spike dates to the April 2008 sampling round, when readings reached improbable pH values of 12.5-16.1. These results have been omitted from the time series plot.

5.0 Conclusions

A review of 14 water quality parameters across 27 regularly sampled boreholes in the Horizons region has been completed. The majority of bores were sampled on two occasions in 2013 although some additional samples were taken from certain bores and, conversely, some bores were only sampled once for some parameters. A summary of the results derived from the analysis of water quality data in the Horizons region is given below:

- NZDWS guideline values for pH (< 7) and the lower guideline value for hardness (< 100 mg/L) were breached in all sampled oxidising bores, and 1 bore (13%) exceeded the guideline value for iron concentration;
- NZDWS maximum acceptable values were breached for nitrate in 23 % of oxidising bores respectively;
- NZDWS guideline values for iron, ammoniacal N, hardness, manganese, and boron were breached in 100 %, 38 %, 38 %, 15 %, and 8 % of 13 sampled reducing bores respectively;
- NZDWS maximum acceptable values were breached for manganese and arsenic in 77 % and 23 % of 13 sampled reducing bores respectively;
- With the exception of borehole 337005, only slight increasing and decreasing trends in water quality exist, and water quality parameters appear to be predominantly stable. There are multiple trends in this bore which may be related to long term trend in recharge or mixing with deeper basement groundwater;
- Generally, where the oxygen content of the groundwater is low (i.e. reducing conditions), dissolution of metals (e.g manganese and iron) and metalloids (e.g. arsenic) in the strata occurs and concentrations of these elements are greater;
- Generally there have been no significant changes since in GV and MAV exceedances since 2012.

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DRINKING WATER QUALITY IN THE HORIZONS REGION

Borehole	Depth (m)	Max E. Coli (n/100 ml) ¹	Median Nitrate- N (mg/L)	Max Nitrate- N (mg/L))	Median Nitrite- N (mg/L)	Median Arsenic (mg/L)	Median Boron (mg/L)	Median Manganese (mg/L)	Median Iron (mg/L)	Median Ammonial N (mg/L)	Median Hardness (mg/L)	Median pH	Median Chloride (mg/L)	Median Fluoride (mg/L)	Median Sulphate (mg/L)	Median Sodium (mg/L)	GV Exceeded	MAV Exceeded
			•						Oxidisin	g Conditions	•	•						
339001	5	4	5.4	7.0	0.001	0.0005	0.05	0.00075	0.11	0.013	73.1	5.9	39.3	0.10	38.49	26.6	Hardness, pH	E Coli
314025	7	4	1.8	3.5	0.002	0.00125	0.05	0.049	0.09	0.005	121.1	6.9	27.2	0.09	17.97	19.3	pH, Mn	E Coli
352099	9		18.6	20.6								6.7					pН	N03
338005	11	4	0.2	0.2	0.001	0.0005	0.04	0.0025	0.49	0.005	71.1	6.4	31.9	0.14	12.03	17.3	Hardness, pH, Fe	E Coli
362003	11	68	0.7	0.8	0.002	0.0005	0.02	0.0005	0.01	0.008	19.5	6.5	11.8	0.06	5.37	8.3	Hardness, pH	E Coli
357109	14	4	4.9	5.8	0.001	0.0005	0.01	0.004	0.02	0.0105	34.0	5.4	15.2	0.03	13.23	8.3	Hardness, pH	E Coli
362001	16		7.3	7.5								6.9					pН	
430005	17	4	2.2	2.9	0.001	0.0005	0.03	0.0005	0.01	0.008	57.5	6.6	26.5	0.15	21.94	14.9	Hardness, pH	E Coli
363112	19		2.9	3.0								6.1					pН	
353251	20		17.7	18.6								6.6					pН	N03
353015	22	4	10.0	10.8	0.012	0.0005	0.01	0.0005	0.02	0.0075	74.2	6.6	32.6	0.04	6.38	23.8	Hardness, pH	E Coli
372071	26		9.9	11.4								6.6					pН	NO3
316037	27	4	10.8	11.1	0.001	0.00075	0.01	0.003	0.05	0.005	71.6	5.9	26.0	0.21	13.07	23.0	Hardness, pH	E Coli
									Reducin	g Conditions								
332025	9	4	0.00	0.003	0.002	0.009	0.04	0.646	9.02	0.793	193.3	7.1	51.1	0.23	3.54	37.1	Fe	E Col, Mn
343125	11	58	0.00	0.004	0.002	0.017	0.04	0.464	6.44	4.458	142.4	7.6	39.3	0.20	0.02	29.7	NH3, Fe	E Coli, As, N
336114	12	4	0.02	0.03	0.002	0.001	0.02	0.076	0.35	0.354	143.7	7.6	34.2	0.07	19.14	17.3	Fe, Mn	E Coli
312001	18	4	0.01	0.01	0.002	0.013	0.03	1.55	13.15	1.985	242.4	7.1	70.9	0.32	0.03	34.4	Hardness, NH3, Fe	E Coli, As, M
334091	19	4	0.01	0.01	0.001	0.048	0.03	1.2	6.23	2.004	155.5	6.8	45.3	0.28	0.01	26.6	pH, NH3, Fe	E Col, Mn
332009	25	0	0.00	0.002	0.001	0.001	0.04	0.655	0.71	0.176	201.1	7.7	29.2	0.16	0.01	24.3	Hardness, Fe	Mn
301011	27	0	0.01	0.01	0.002	0.009	0.03	0.739	0.20	0.157	149.8	6.9	44.5	0.35	4.82	35.8	pH, Fe	Mn
312007	63	0	0.00	0.001	0.003	0.001	0.02	0.869	0.44	0.243	223.6	7.6	20.2	0.07	0.01	19.9	Hardness, Fe	Mn
342051	66	4	0.00	0.003	0.001	0.014	0.12	0.236	1.39	2.7435	118.9	7.7	22.0	0.15	0.01	35.4	NH3, Fe, Mn	E Coli, As
209005	69	4	0.08	0.16	0.002	0.007	0.02	0.6205	0.64	0.014	200.5	7.7	50.6	0.08	16.73	27.2	Hardness, Fe	E Coli, Mn
337005	83	4	0.01	0.01	0.001	0.001	1.19	0.4565	3.49	4.5895	33.4	7.4	152.1	0.35	3.27	177.5	NH3, Fe, B	E Coli, Mn
352312	86	4	0.00	0.003	0.008	0.010	0.05	0.4255	2.89	0.754	194.6	7.3	36.4	0.16	0.01	37.3	Fe	E Coli, Mn
336333	96																	
312020	117	4	0.04	0.08	0.005	0.001	0.03	0.171	0.44	0.387	562.4	7.7	143.0	0.04	105.50	55.2	Hardness, Fe, Mn	E Coli

Notes: 1. The lab detection limit for E.Coli is < 4 MPN/100ml. Therefore, results of 4 MPN/100 ml may not represent actual detections of E.Coli

6.0 References

- New Zealand Ministry of Health (2008). Drinking-water Standards for New Zealand 2005 (Revised 2008). October, 2008.
- Pattle Delamore Partners Ltd. (2013). Report on Horizons Groundwater Quality Monitoring Network. Report prepared for Horizons Regional Council. May, 2013.

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DRINKING WATER QUALITY IN THE HORIZONS REGION

BoreNumber	Depth	Max E. coli	Median	Max nitrate	Median	Median	Median iron	Median total	Median	Median	Median	Median	Median	Median	Median	Median	Reducing -	MAV exceeded	GV exceeded	Piper Diagram
borentamber	Deptii	(n/100 ml)	nitrate	nitrogen	arsenic	Manganese	(mg/L)	ammonial	total	conductivity		phosphate		sulphate	total	sodium	oxidising	ing to exceeded	er exceeded	Grouping
		(, ,	nitrogen	(mg/L)	(mg/L)	(mg/L)		nitrogen	hardness	(mS/m)		(mg/L)	(mg/L)	(mg/L)	alkalinity	(mg/L)	conditions			
			(mg/L)		(0, ,			(mg/L)	(mg/L	(-, ,		(0, ,	(0, ,	(0, 7	(mg/L					l l
			(<u>G</u> ,)						CaCO ₂)						HCO3)					
Oxidisi	ng cond	litions		<u> </u>		<u> </u>			565537			I	<u> </u>	<u> </u>	<u> </u>					
339001	5		3.6	12.7	0.000	0.002	0.01	0.005	70	31	5.9	0.06	40	28	32	28	0	NO3	рН	1
314025	7		0.1	2.5	0.001	0.015	0.02	0.009	92	27	7.2	0.12	21	16	113	16	0			2
352099	9		23.9	32.4						52	6.8						0	NO3	рН	
338005	11		0.2	2.1		0.006	0.07	0.008	64	23	6.3	0.03	26	13	73	17	0		рН	2
362003	11		1.2	5.8	0.000	0.001	0.01	0.005	25	10	6.5	0.04	12	6	22	8	0		рН	l
357109	14		4.5	6.6	0.000	0.010	0.03	0.010	33	13	5.4	0.03	12	11	11	8	0		рН	1
362001	16		14.2	22.2						34	6.7						0	NO3	рН	1
430005	17		2.3	9.7	0.000	0.002	0.01	0.008	52	20	6.2	0.07	23	18	40	15	0		рН	1
363112	19		2.9	3.6						17	6.1						0		рН	
353251	20		16.7	<i>89.9</i>						27	6.6						0	NO3	рН	
353015	22	4	10.0	11.1	0.000	0.003	0.02	0.007	66	27	6.8	0.11	29	7	51	24	0	E. coli	рН	
372071	26		11.0	13.1	0.001	0.006	0.03	0.005	84	25	6.6		24	10	77	25	0	NO3	рН	
316037	27		11.7	16.0	0.000	0.006	0.01	0.005	69	29	6.4	0.05	26	13	41	25	0	NO3	рН	1
Reduci	ng cond	litions							•											
332025	9		0.0	1.6	0.007	0.72	9.88	0.95	220	63	7.2	0.06	73	4	269	45	R	Mn	Fe, Hard	2
343125	11	240	0.0	0.3	0.019	0.51	2.43	3.27	145	47	7.4	0.05	50	0	232	33	R	E. coli, As, Mn	Fe, NH3	2
336114	12	7	0.0	0.3	0.000	0.07	0.10	0.36	150	38	7.6	0.26	31	17	160	19	R	E. coli	Mn	2
312001	18		0.0	0.8	0.009	1.16	10.42	1.61	207	74	7.1	0.03	70	0	290	38	R	Mn	Fe, NH3, Hard	2
334091	19		0.0	0.3	0.048	1.10	5.39	1.97	151	45	6.9	0.94	45	0	207	28	R	As, Mn	Fe, NH3, pH	2
332009	25	1	0.0	0.1	0.001	0.71	0.27	0.17	192	50	7.4	0.66	29	0	281	28	R	E. coli, Mn	Fe	2
312007	63		0.0	0.1	0.000	0.91	0.43	0.27	217	54	7.6	0.13	20	0	305	22	R	Mn	Fe, Hard	2
342051	66		0.0	0.1	0.015	0.25	1.00	2.80	123	43	7.6	2.10	24	0	250	39	R		Mn, Fe, NH3, Hard	
209005	69		0.0	0.3	0.007	0.63	0.33	0.06	186	54	7.6	0.26	50	17	206	28	R	Mn	Fe	2
337005	83	4	0.0	0.1	0.000	0.33	2.20	4.25	26	92	7.5	1.32	126	4	274	157	R	E. coli?	Mn. Fe, NH3	other
352312	86	4	0.0	0.7	0.010	0.43	2.48	0.75	199	29	7.0	0.30	36	0	302	41	R	E. coli?, Mn	Fe	2
352271	93	L	0.0	0.1	0.130	0.52	1.92	17.60	930	557	7.5	0.02	1854	0	188	685	R	As, Mn	Fe, NH3, Hard	other
336333	96		0.0	0.2	0.000	0.14	0.14	0.12	162	43	7.9	0.28	39	14	178	24	R		Mn	2
312020	117	1	0.1	1.6	0.000	0.17	0.07	0.46	527	133	7.7	0.11	145	114	448	58	R	E. coli?	Mn, Hard	other

Copy of summary water quality data from PDP (2013) for comparison with updated data.

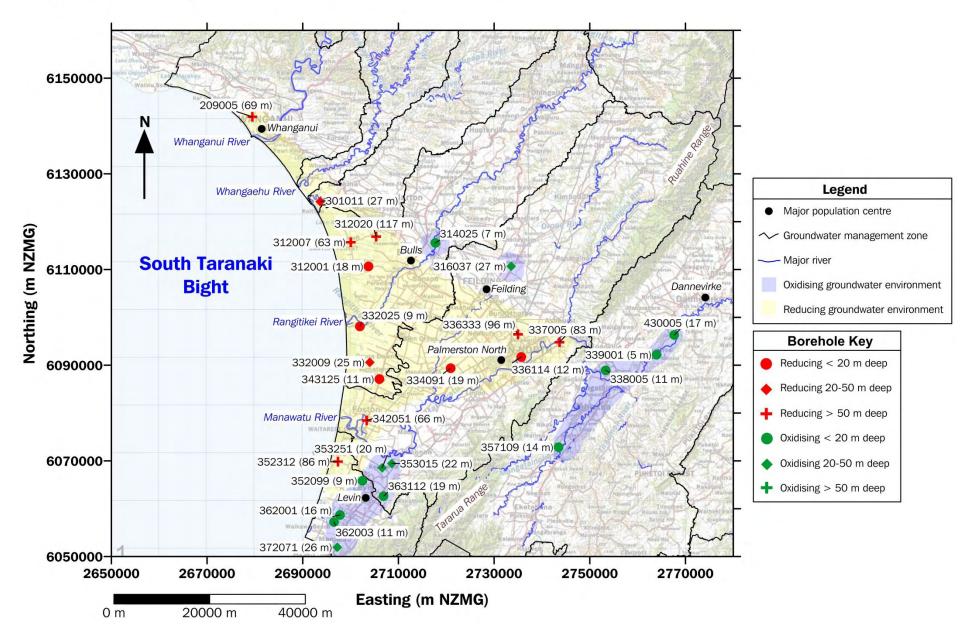


Figure A.1: Plot of analysed boreholes showing depth, redox conditions and geographical features.

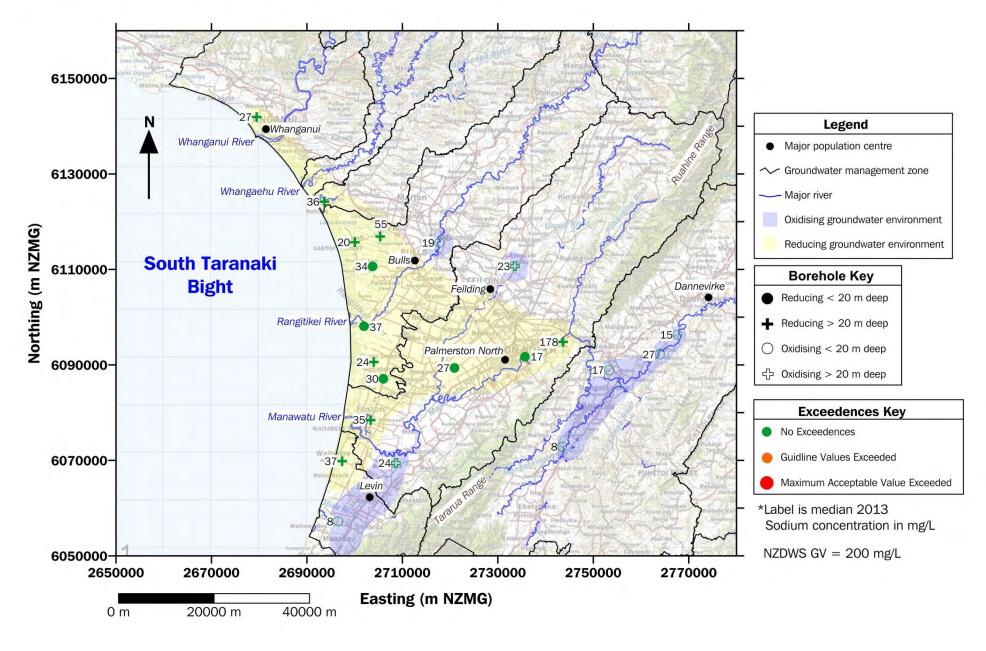


Figure A.2: Plot of Sodium concentrations and locations of GV exceedances for all bores sampled in 2013.

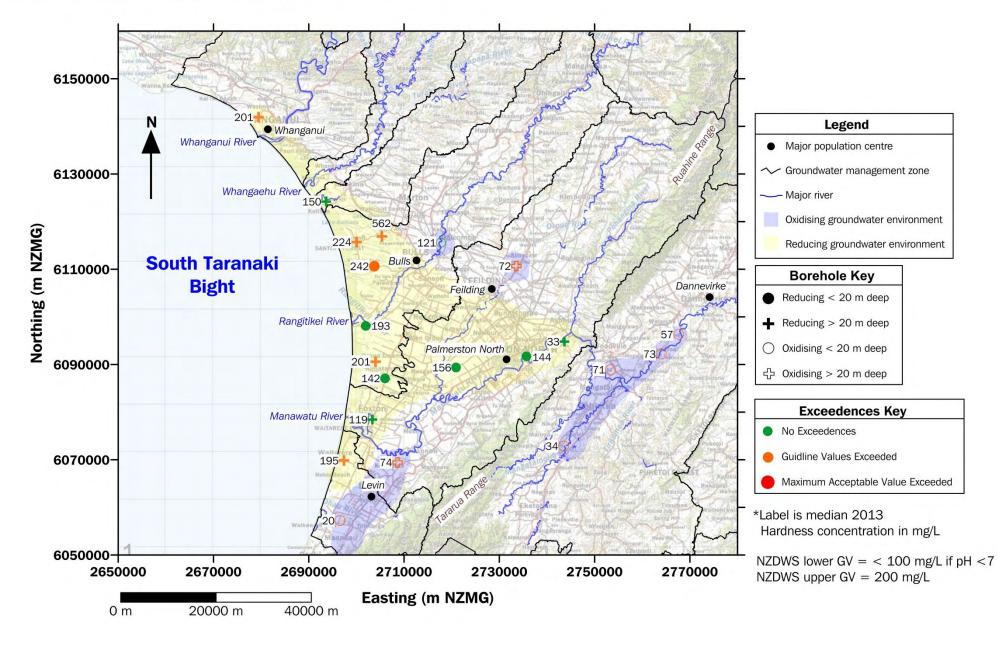


Figure A.3: Plot of Hardnesss concentrations and locations of GV exceedances for all bores sampled in 2013.

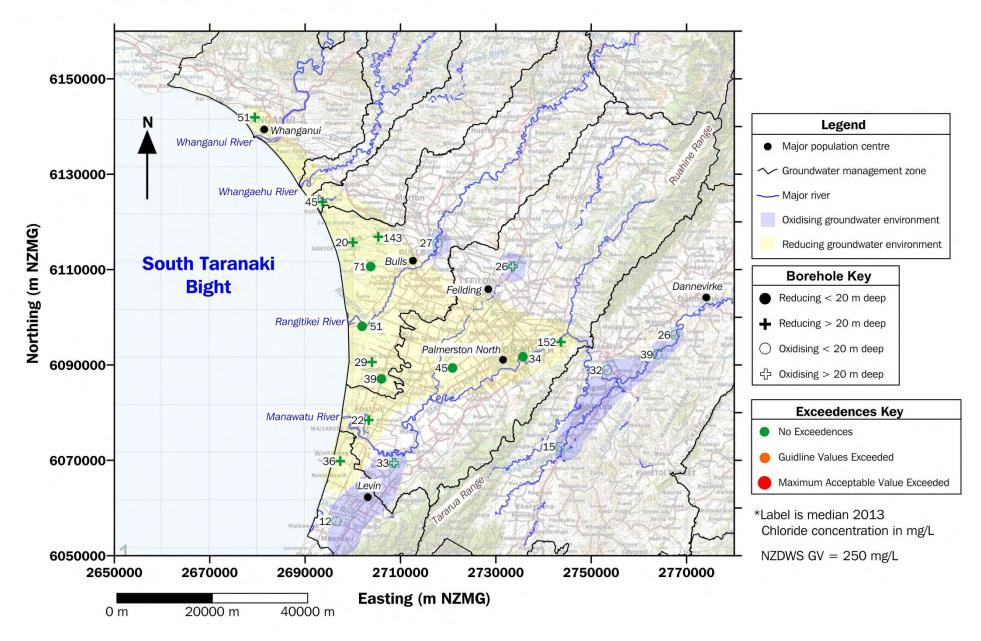


Figure A.4: Plot of Chloride concentrations and locations of GV exceedances for all bores sampled in 2013.

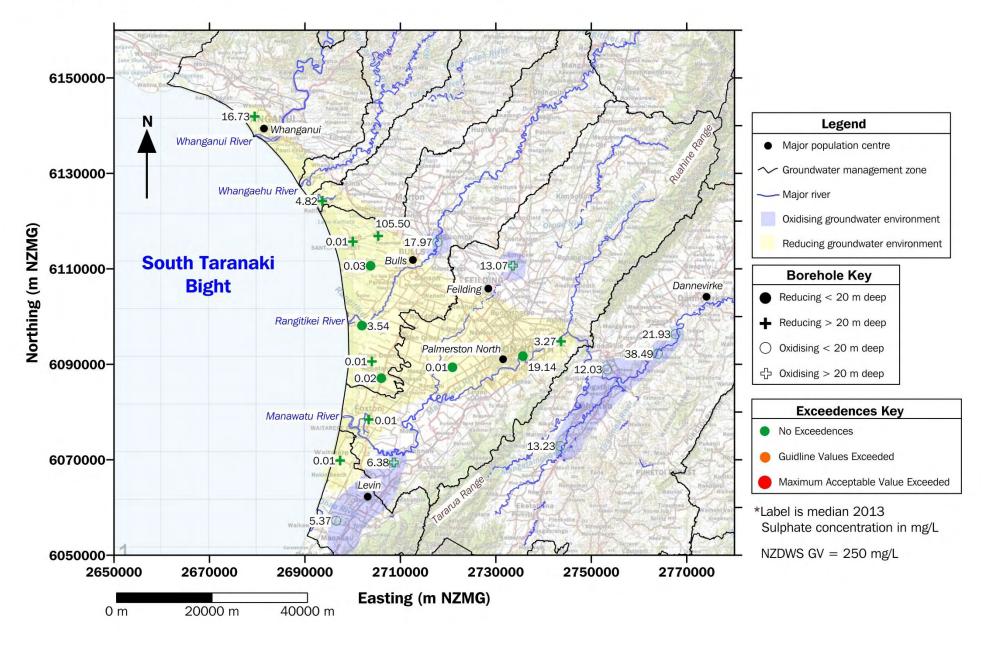


Figure A.5: Plot of Sulphate concentrations and locations of GV exceedances for all bores sampled in 2013.

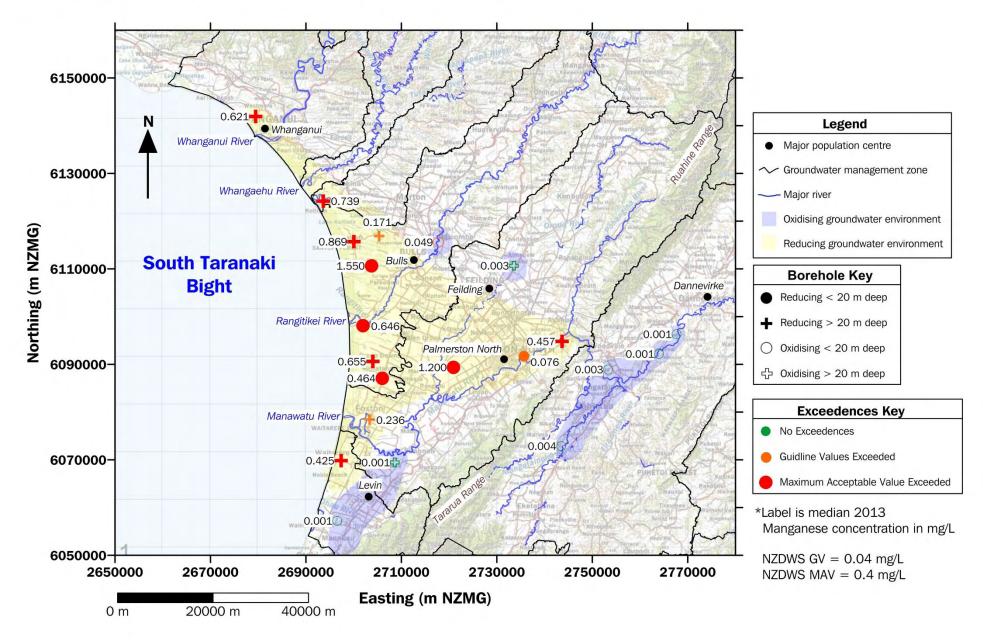


Figure A.6: Plot of Manganese concentrations and locations of MAV and GV exceedances for all bores sampled in 2013.

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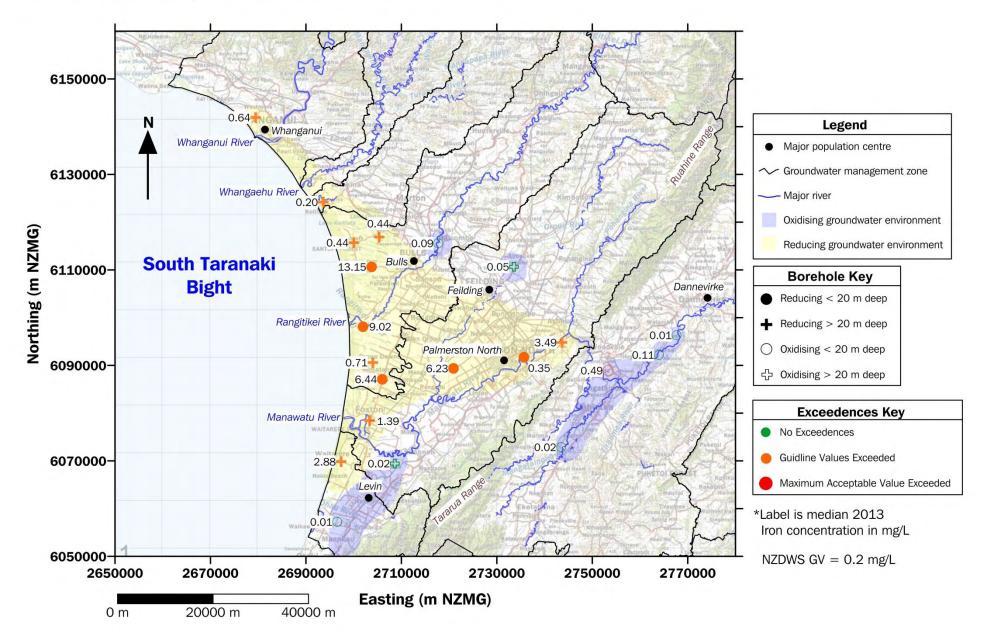


Figure A.7: Plot of Iron concentrations and locations of GV exceedances for all bores sampled in 2013.

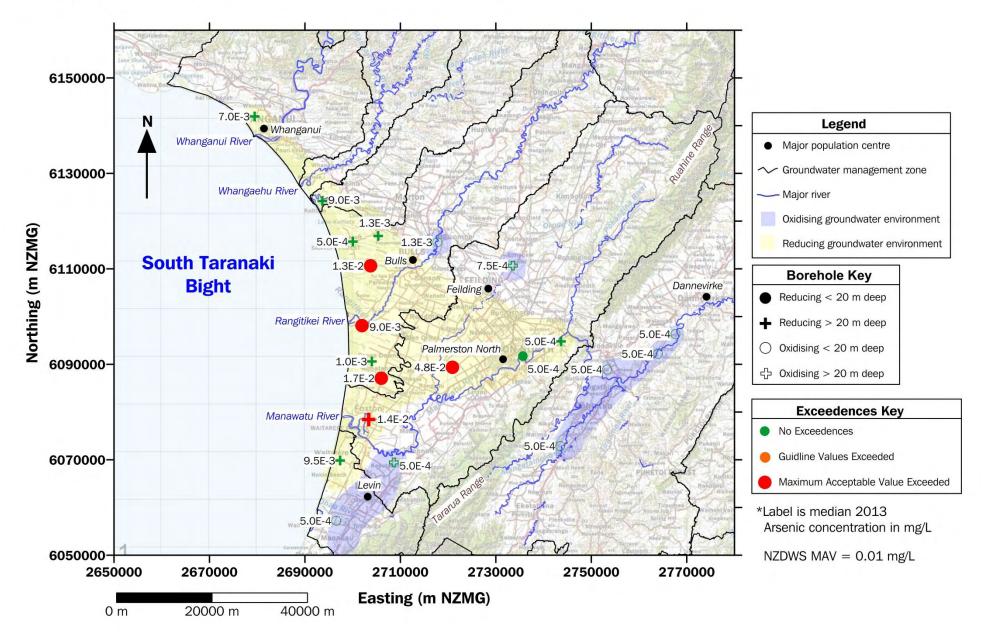


Figure A.8: Plot of Arsenic concentrations and locations of MAV exceedances for all bores sampled in 2013.

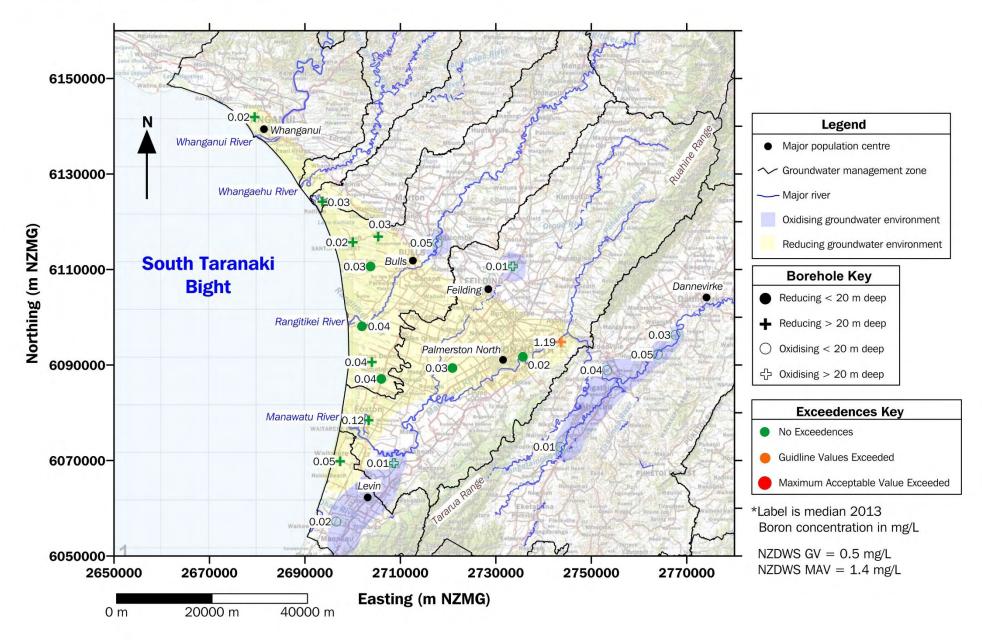


Figure A.9: Plot of Boron concentrations and locations of MAV and GV exceedances for all bores sampled in 2013.

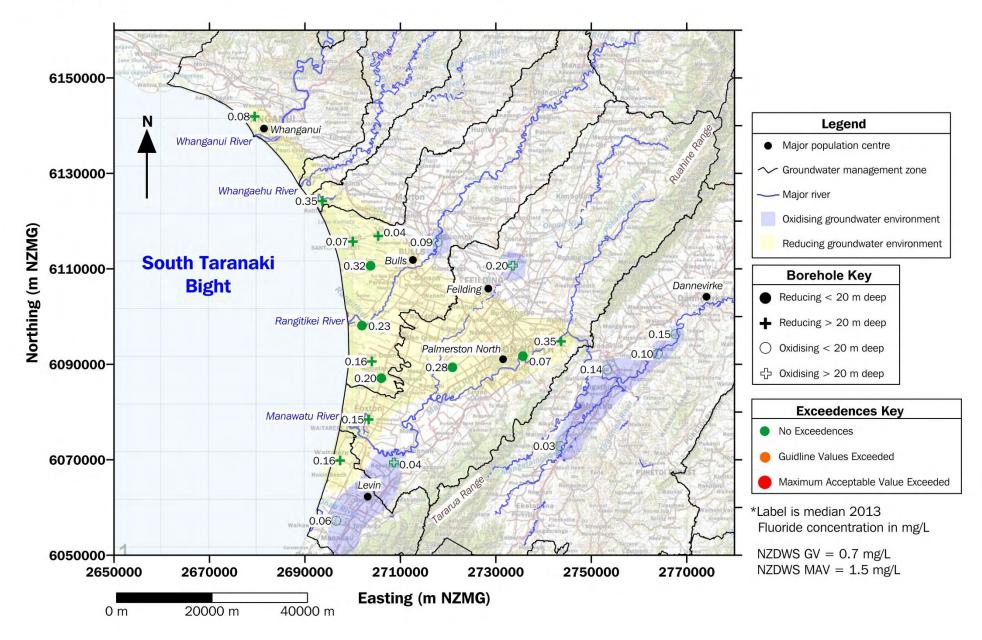


Figure A.10: Plot of Fluoride concentrations and locations of MAV and GV exceedances for all bores sampled in 2013.

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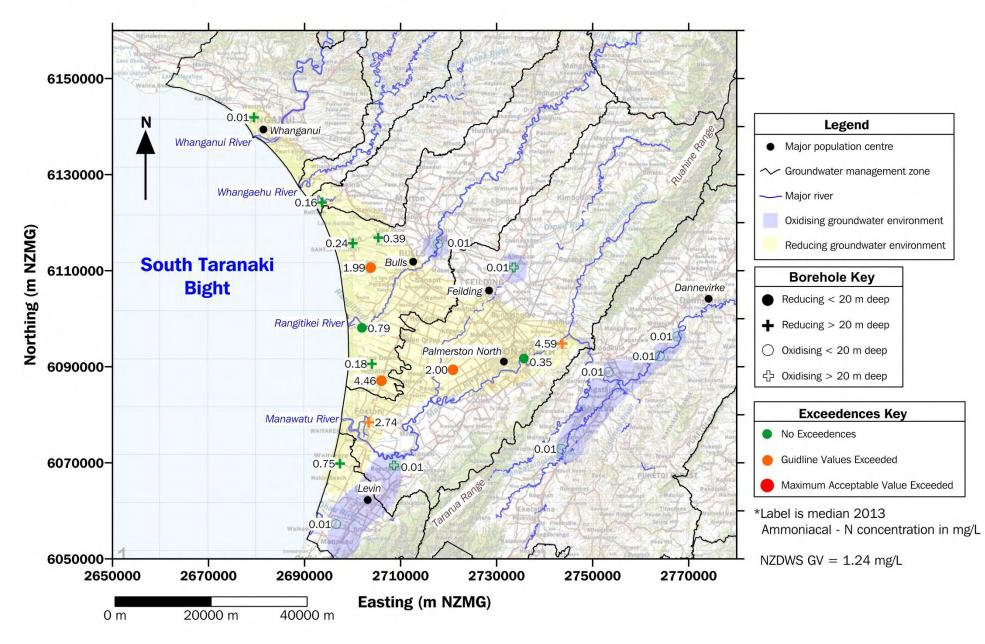


Figure A.11: Plot of Ammoniacal - N concentrations and locations of GV exceedances for all bores sampled in 2013.

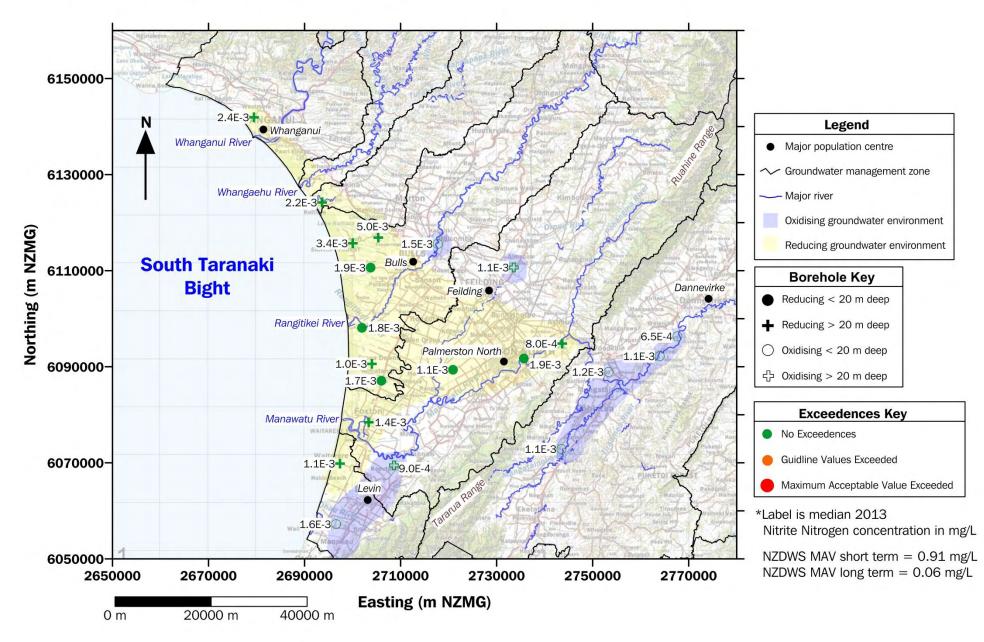


Figure A.12: Plot of Nitrite Nitrogen concentrations and locations of MAV exceedances for all bores sampled in 2013.

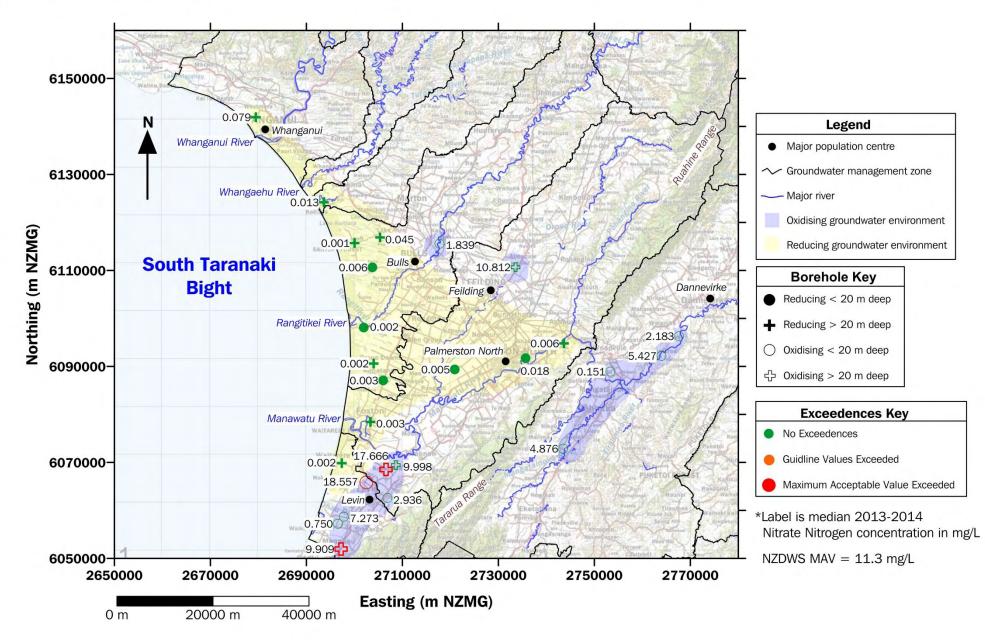
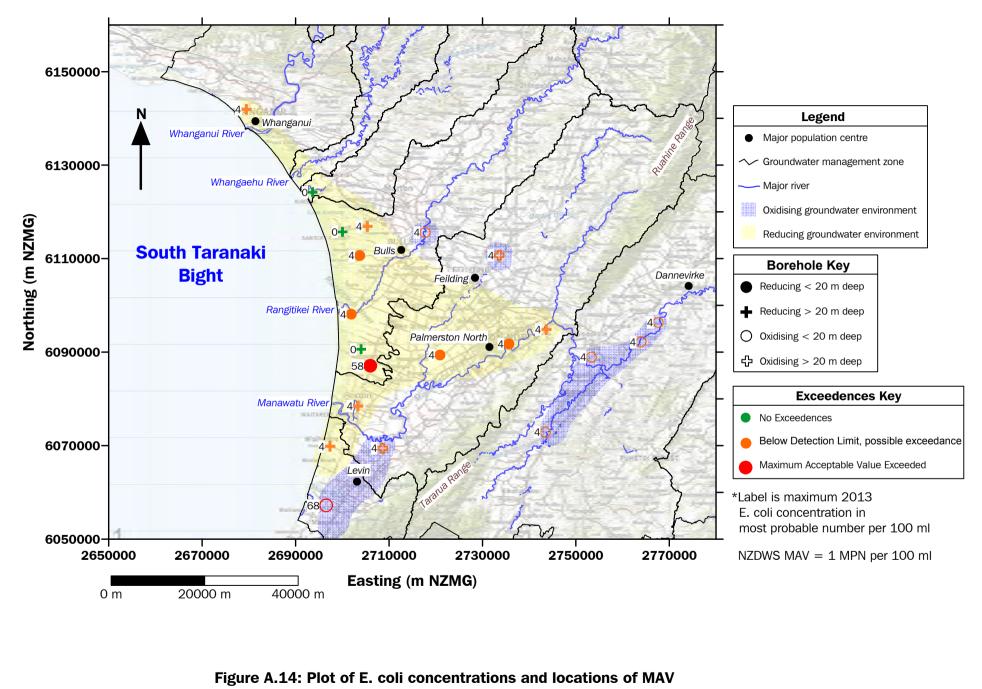


Figure A.13: Plot of Nitrate Nitrogen concentrations and locations of MAV exceedances for all bores sampled in 2013-2014.

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exceedances for all bores sampled in 2013.

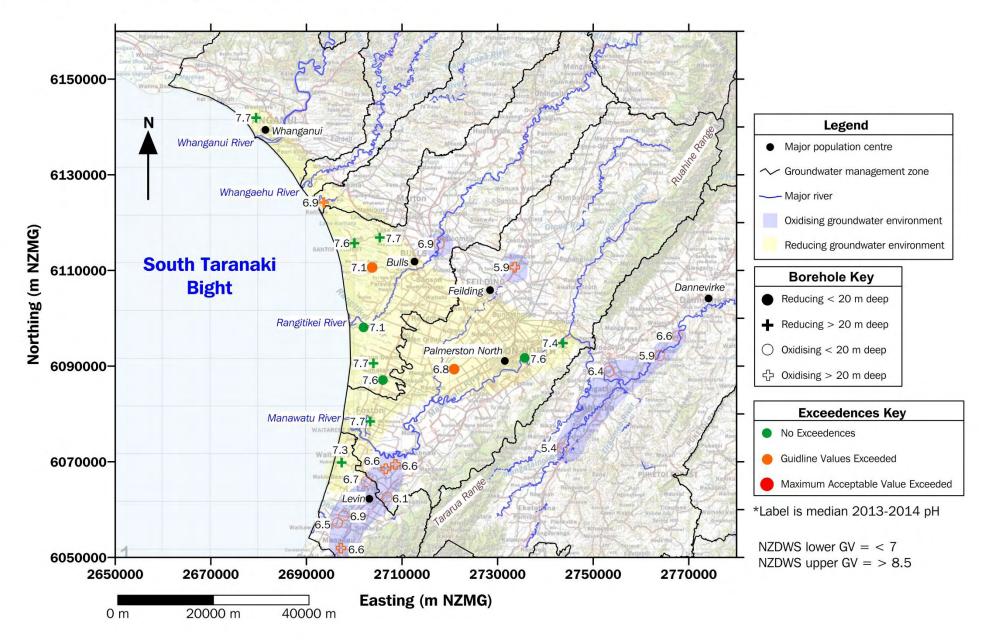


Figure A.15: Plot of pH values and locations of GV exceedances for all bores sampled in 2013-2014.

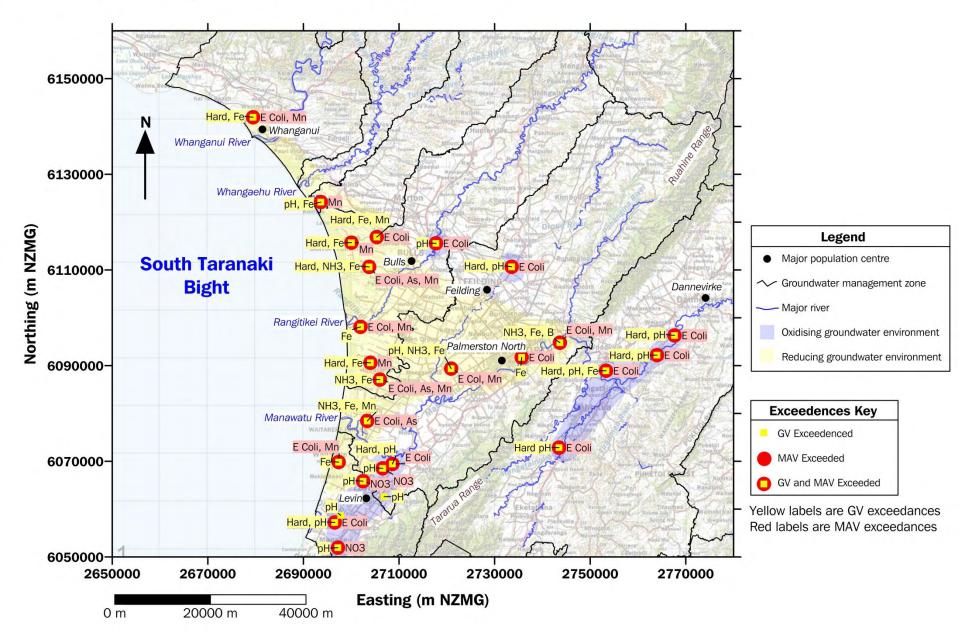


Figure A.16: Summary plot of all NZDWS GV and MAV exceedances in 2013-2014



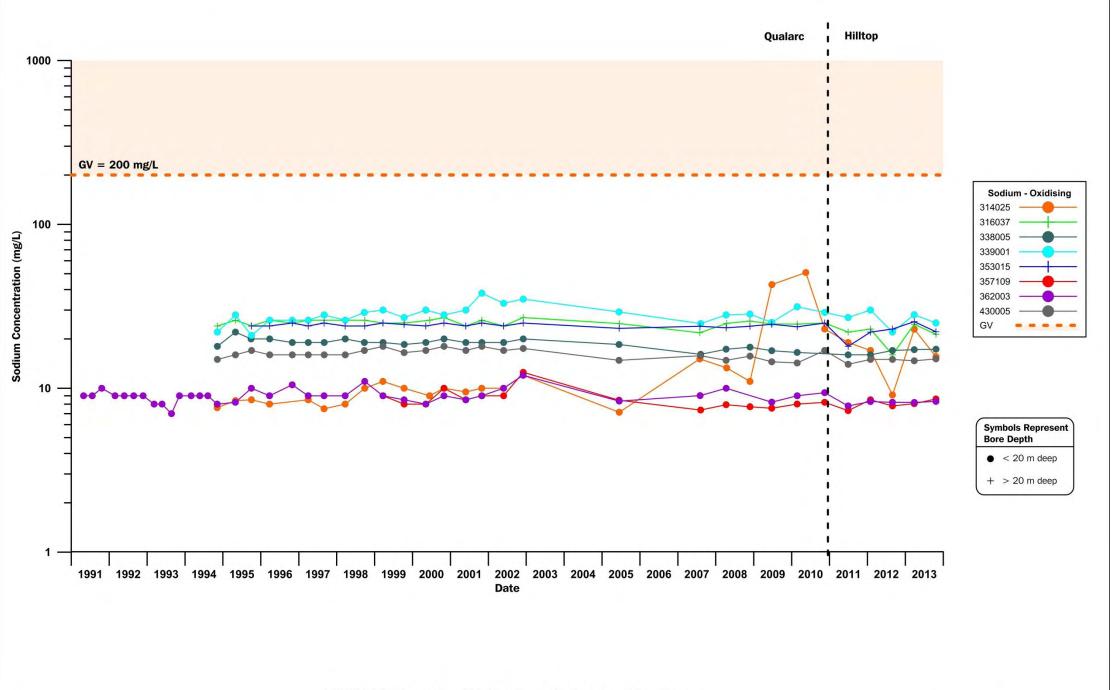
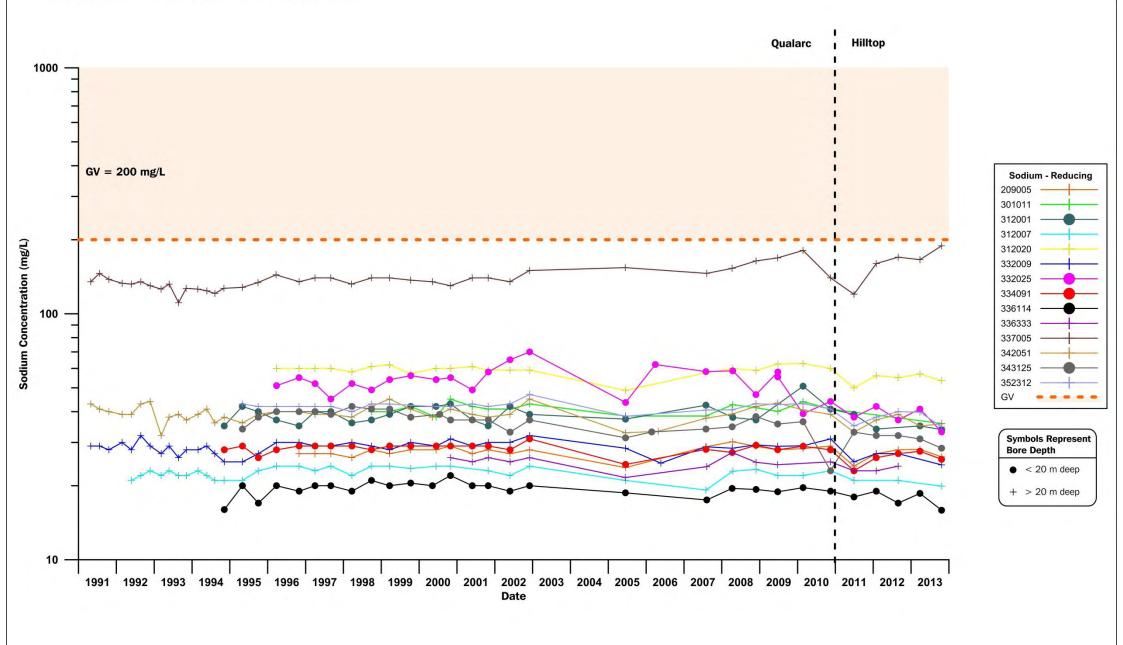
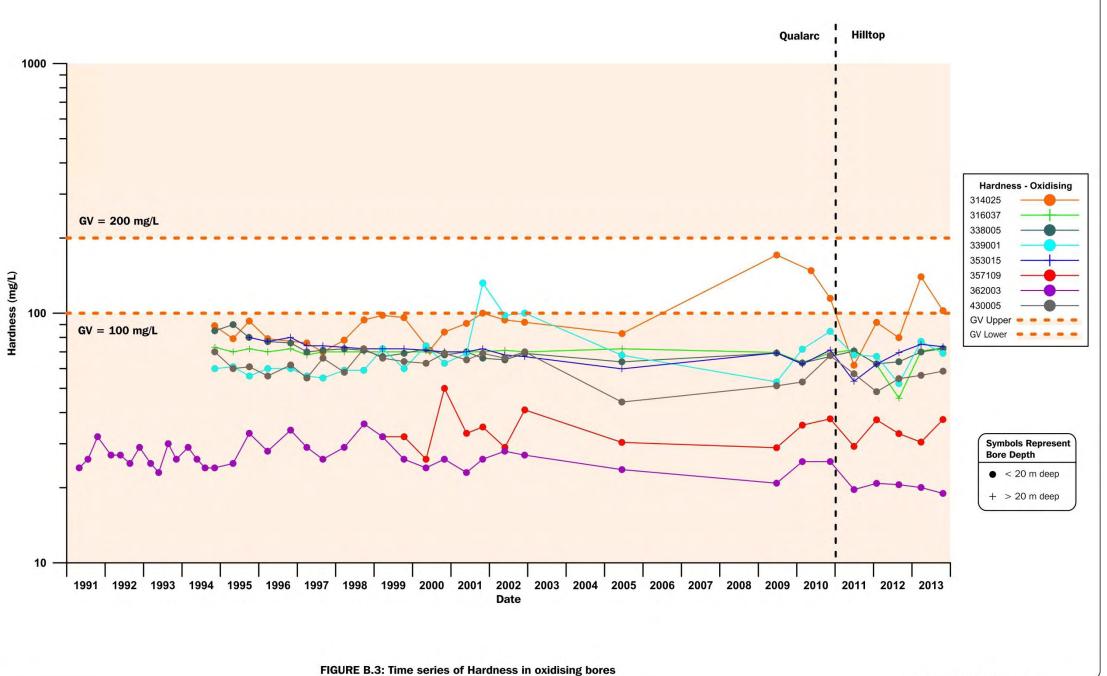
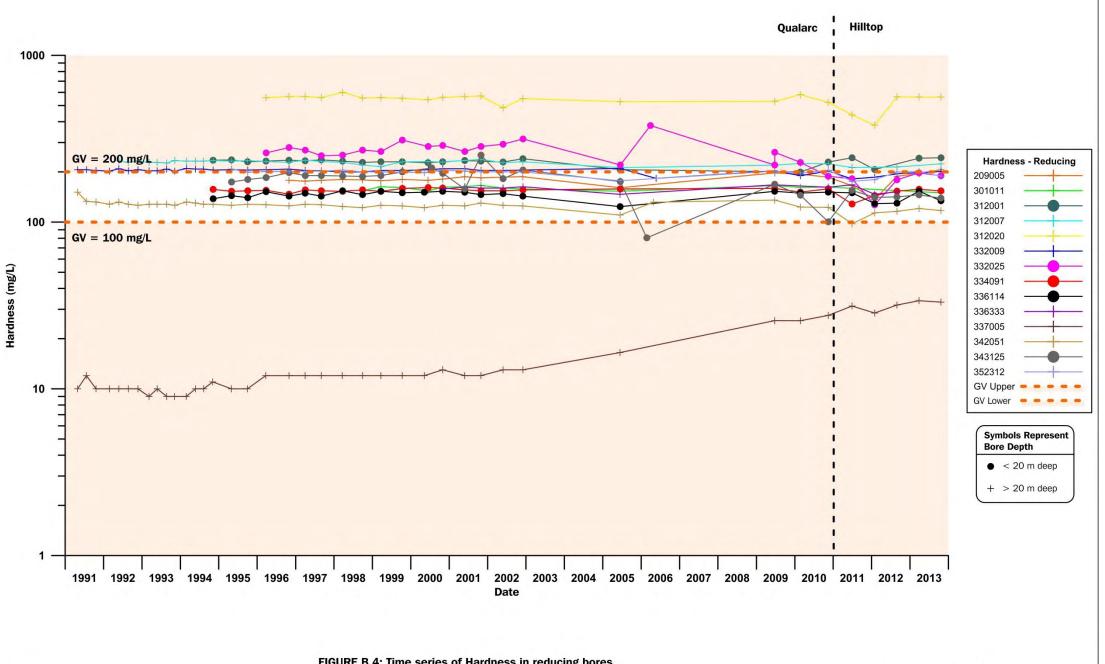
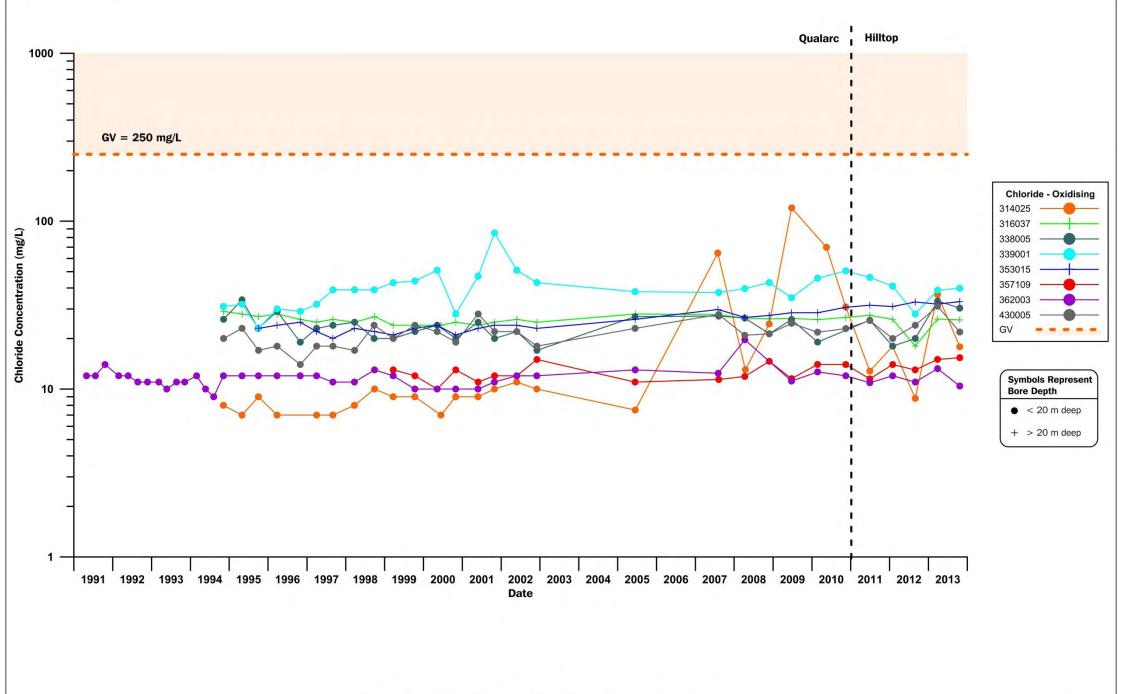


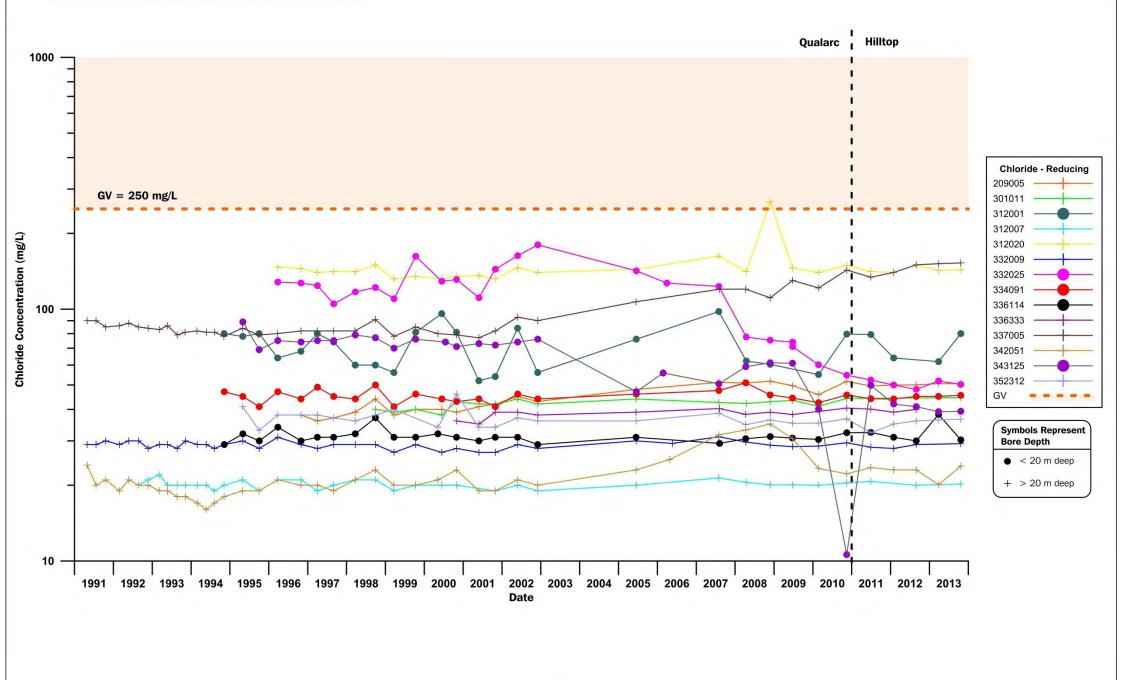
FIGURE B.1: Time series of Sodium Concentrations in oxidising bores

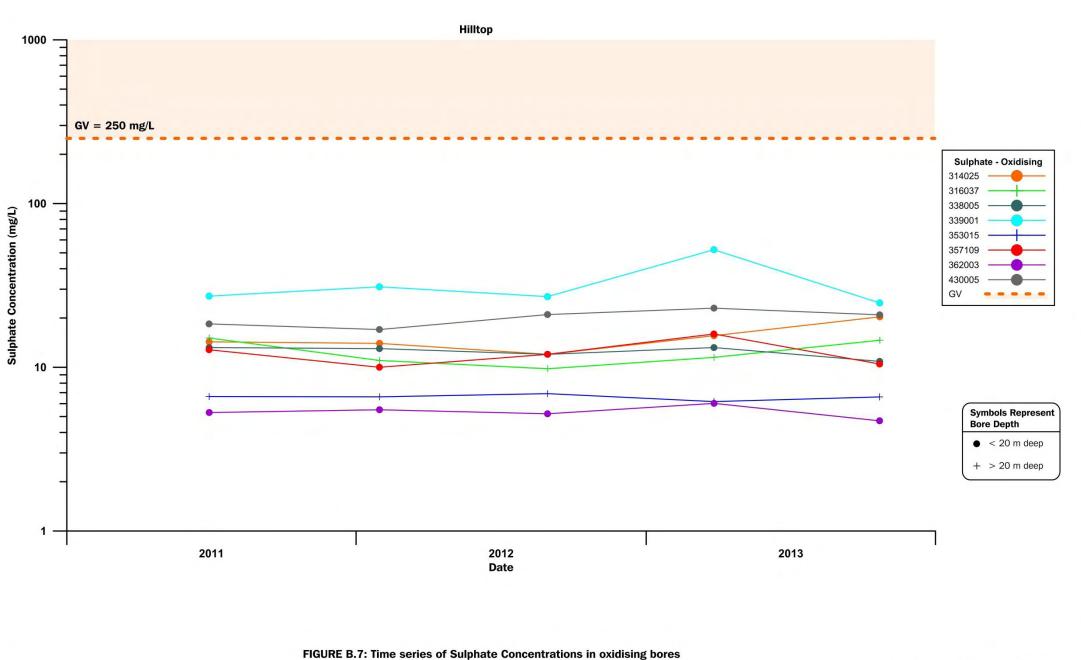


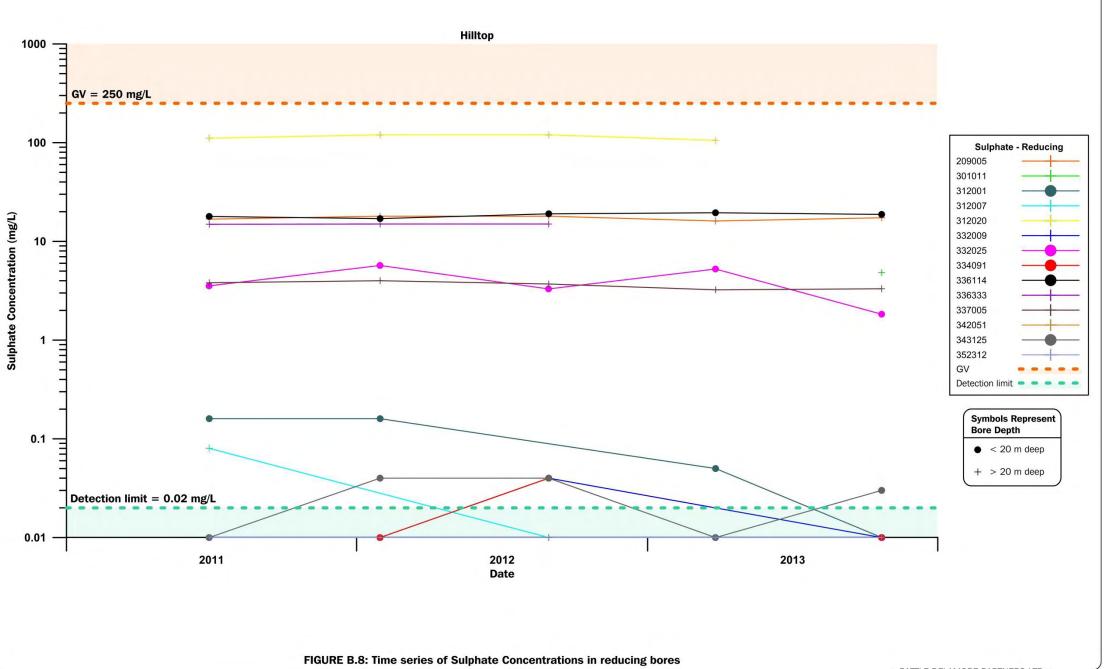


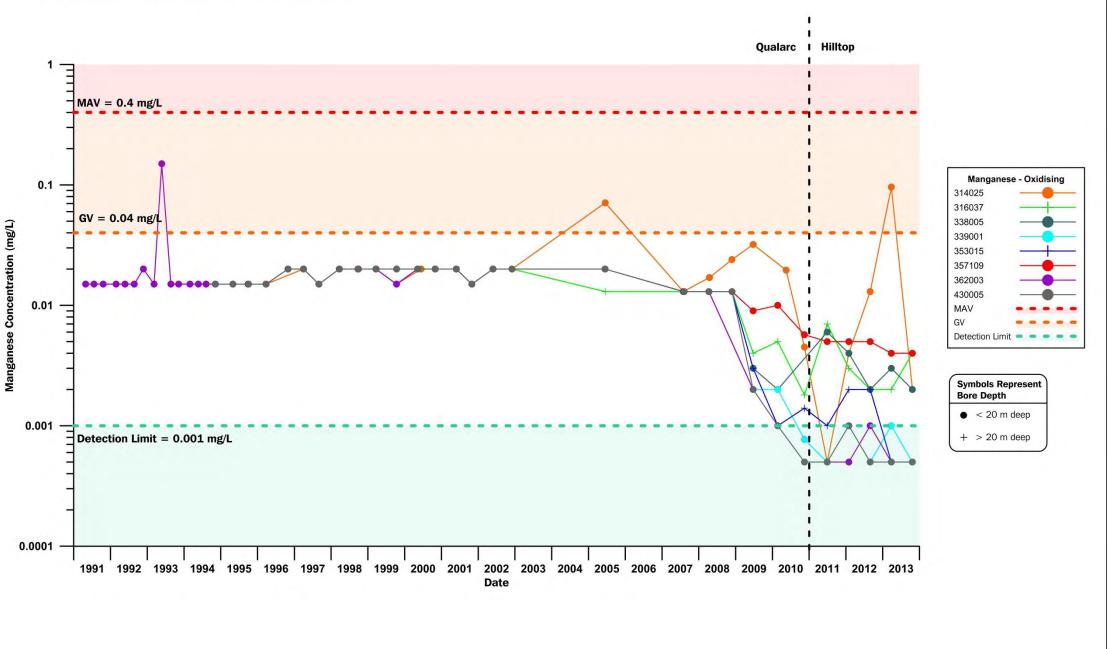














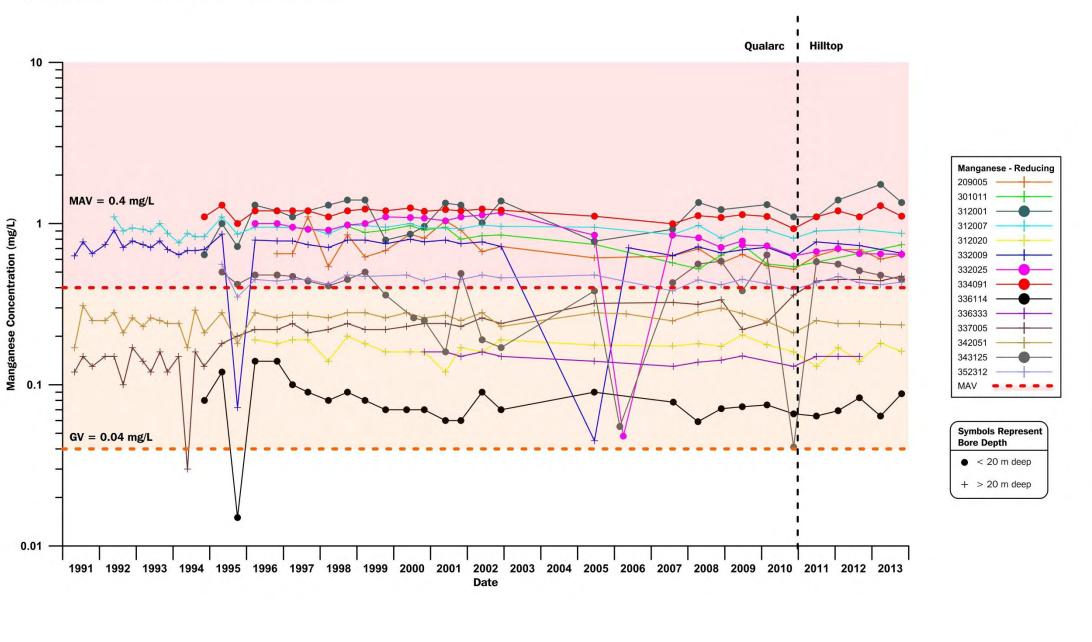
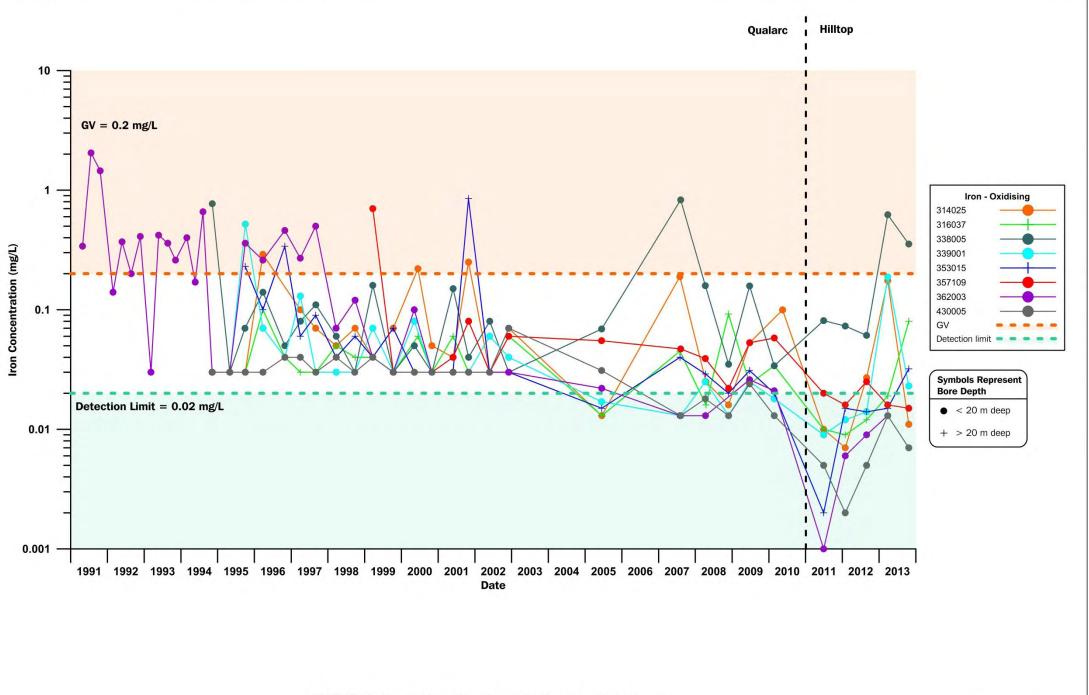
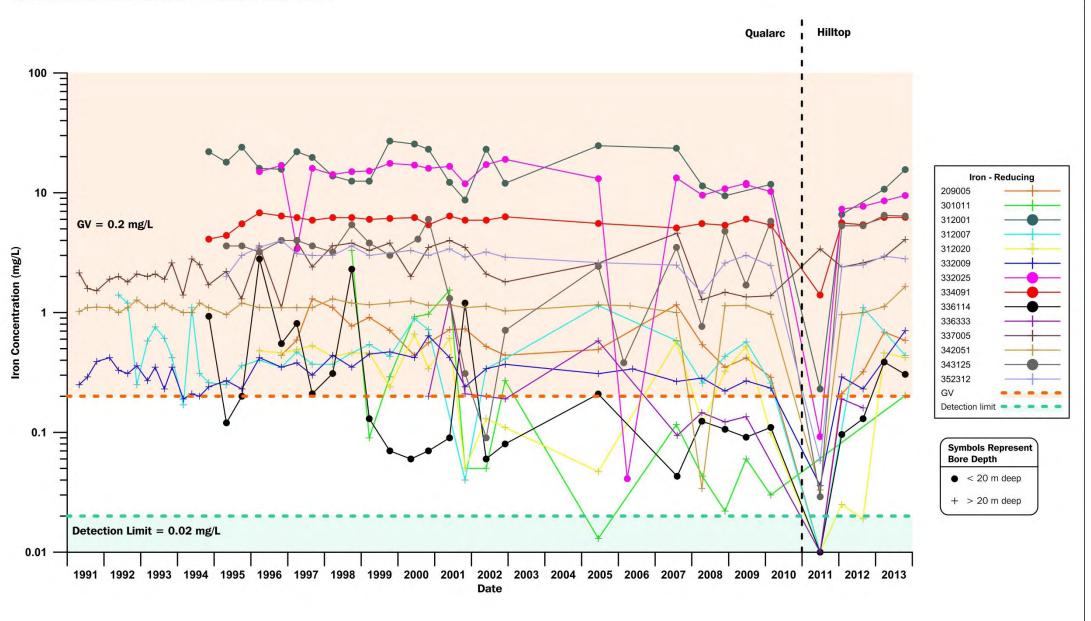


FIGURE B.10: Time series of Manganese Concentrations in reducing bores





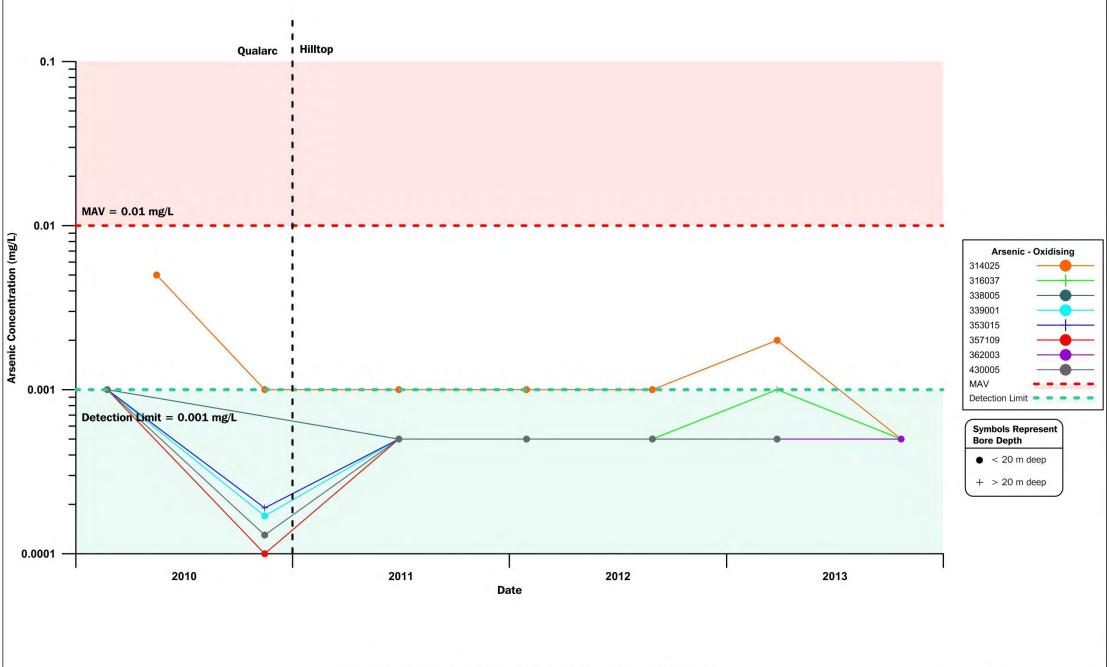
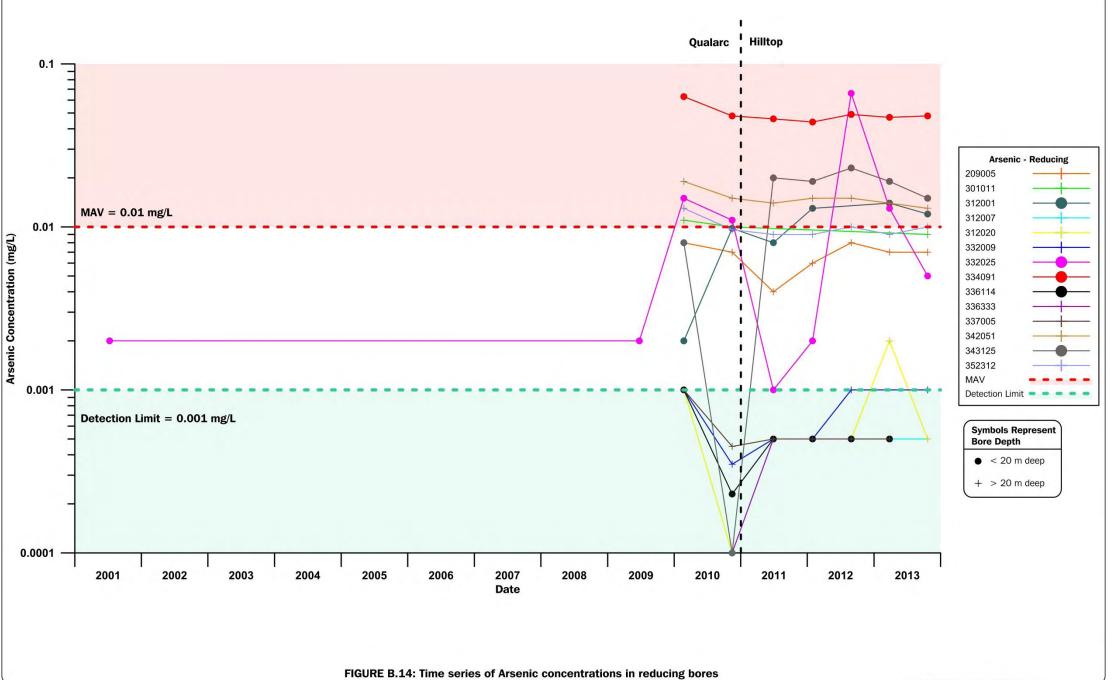


FIGURE B.13: Time series of Arsenic concentrations in oxidising bores



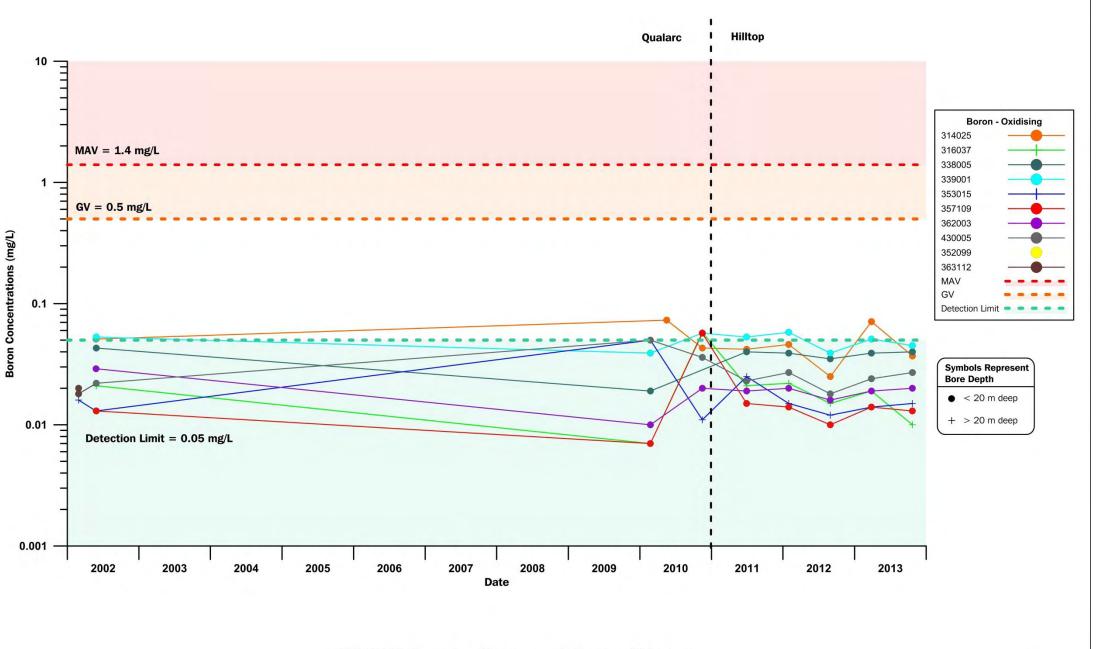


FIGURE B.15: Time series of Boron concentrations in oxidising bores

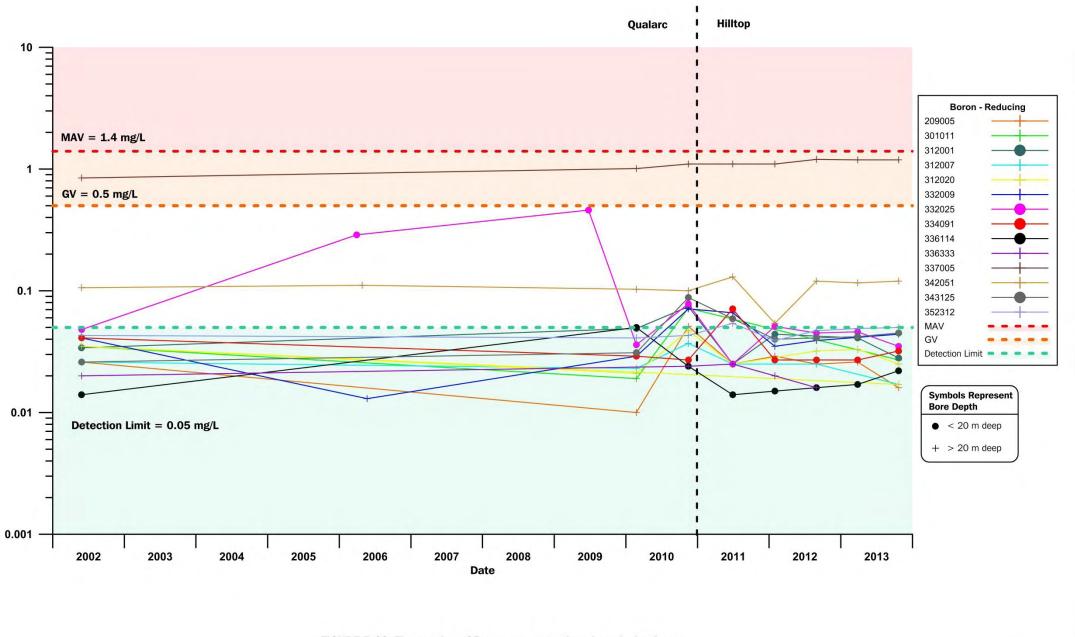
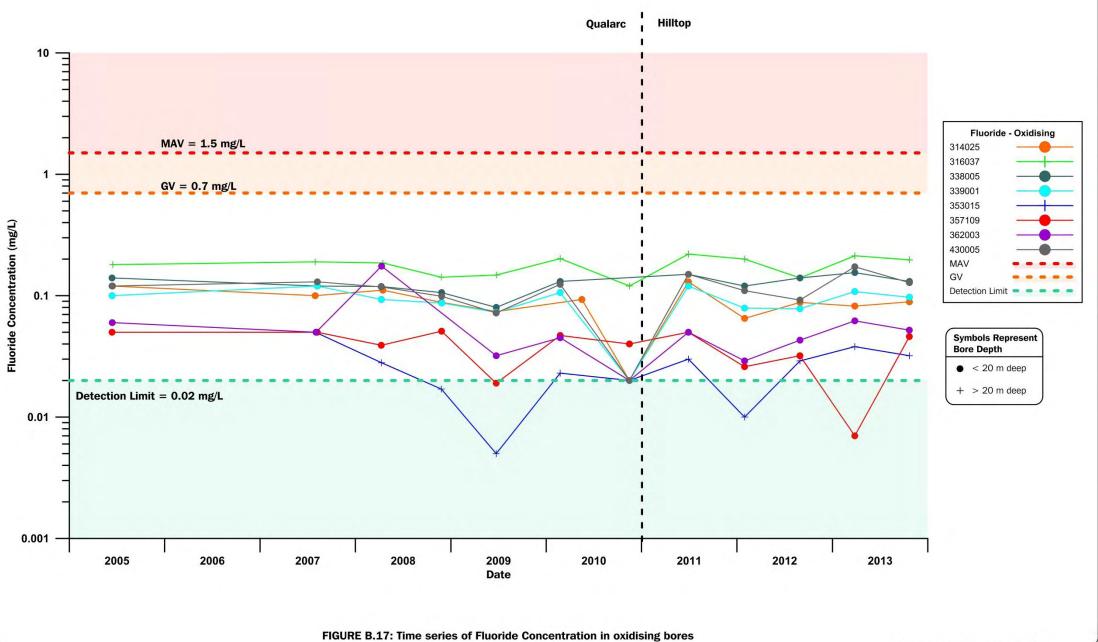
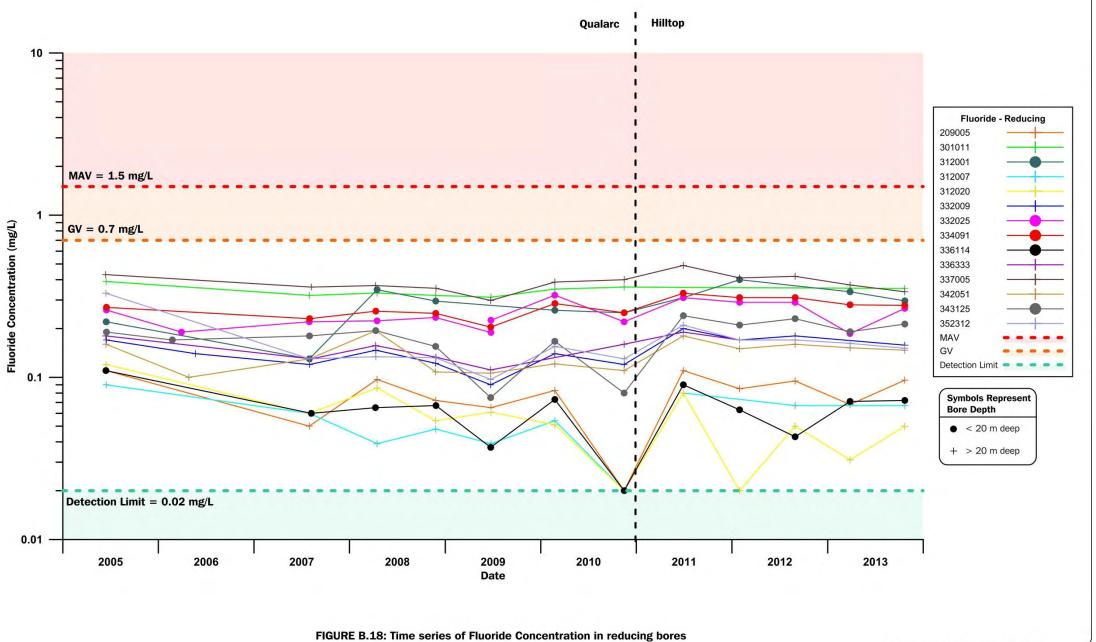
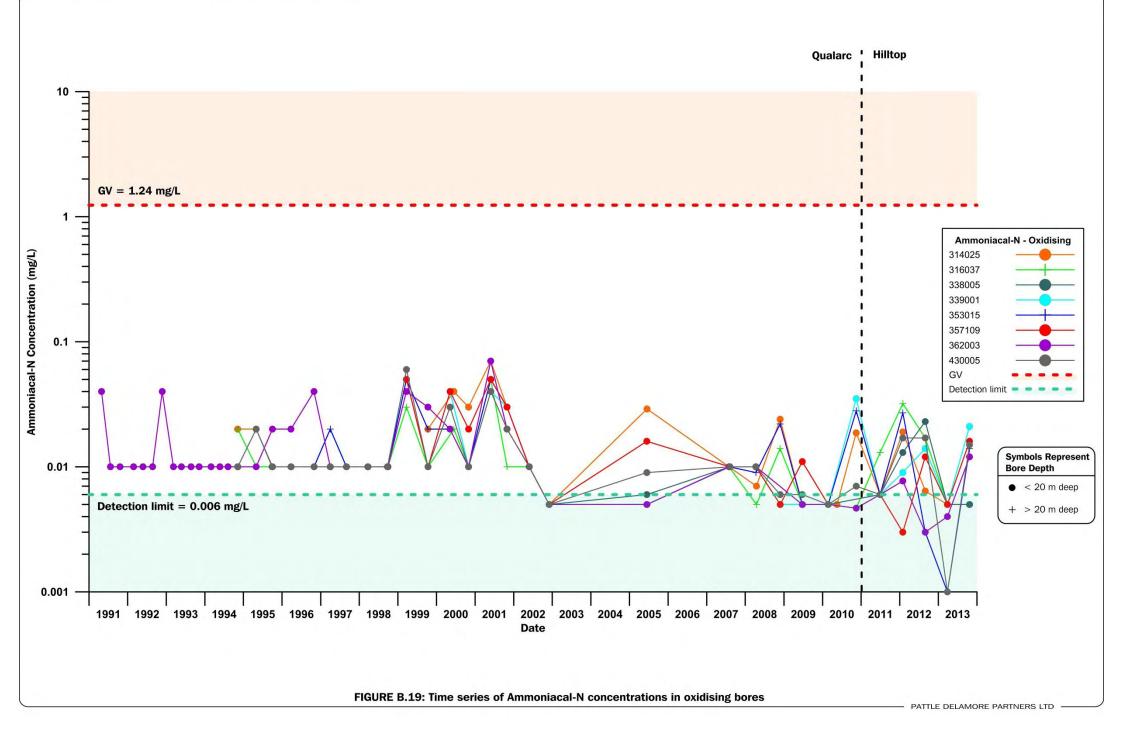
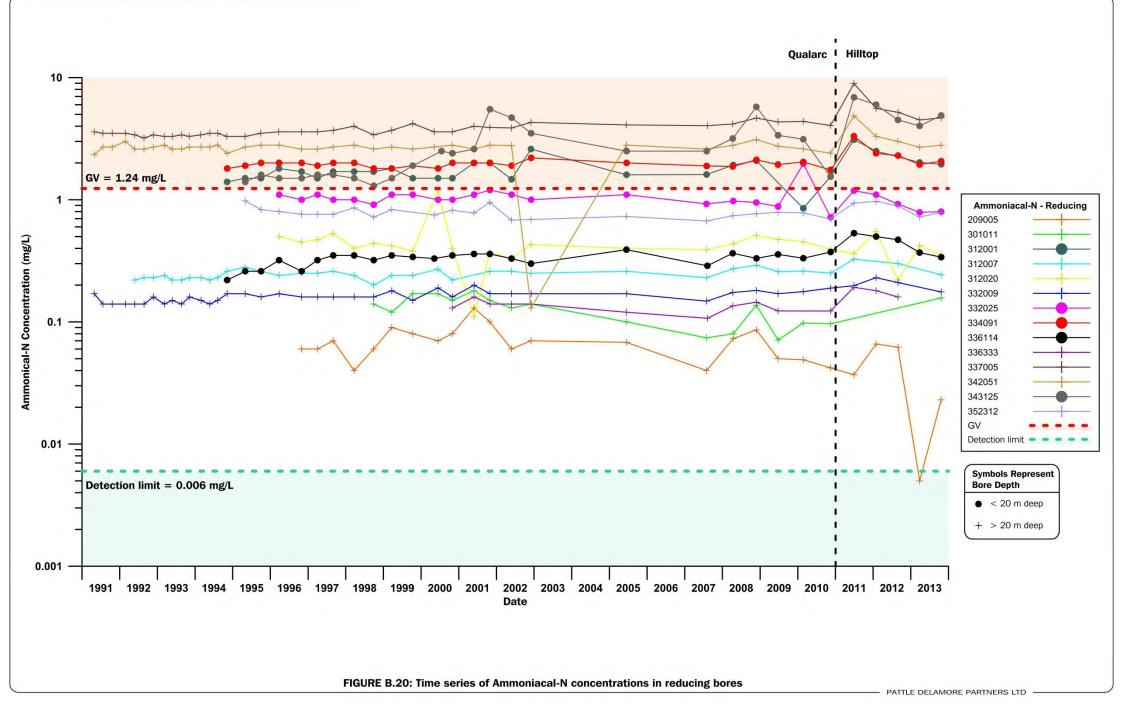


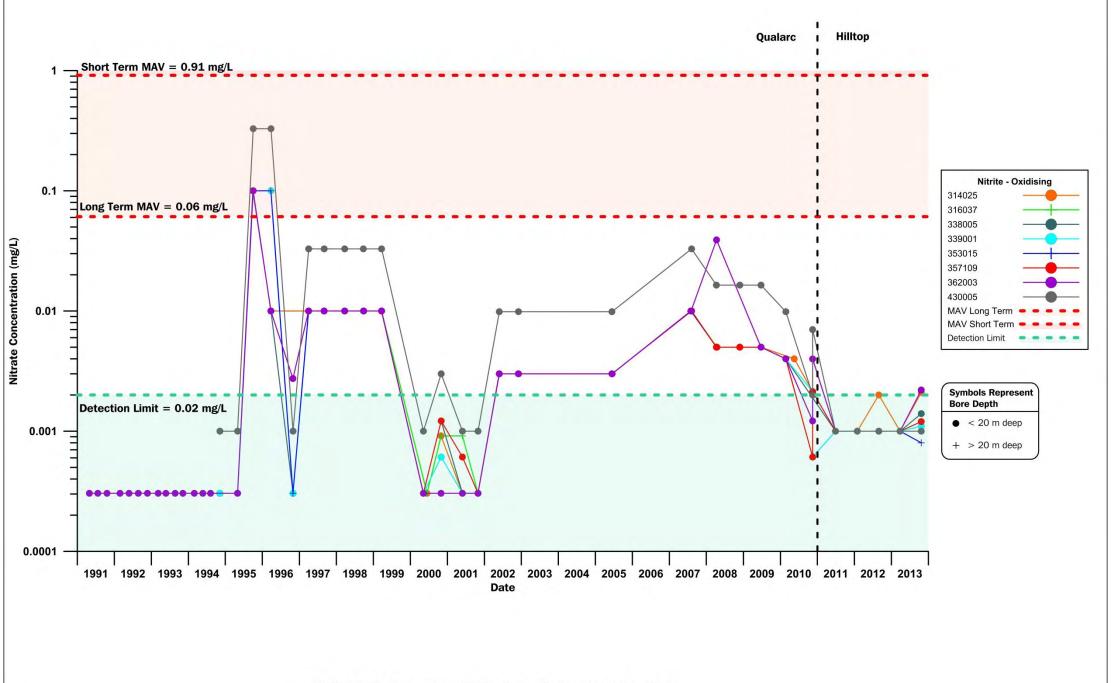
FIGURE B.16: Time series of Boron concentrations in reducing bores

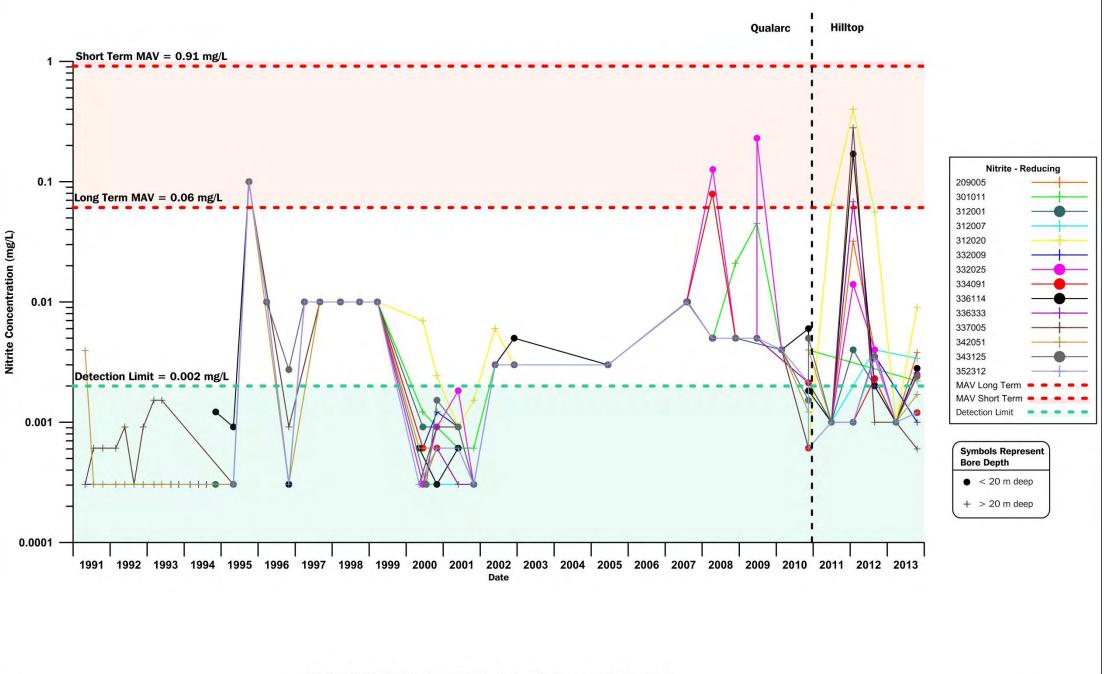




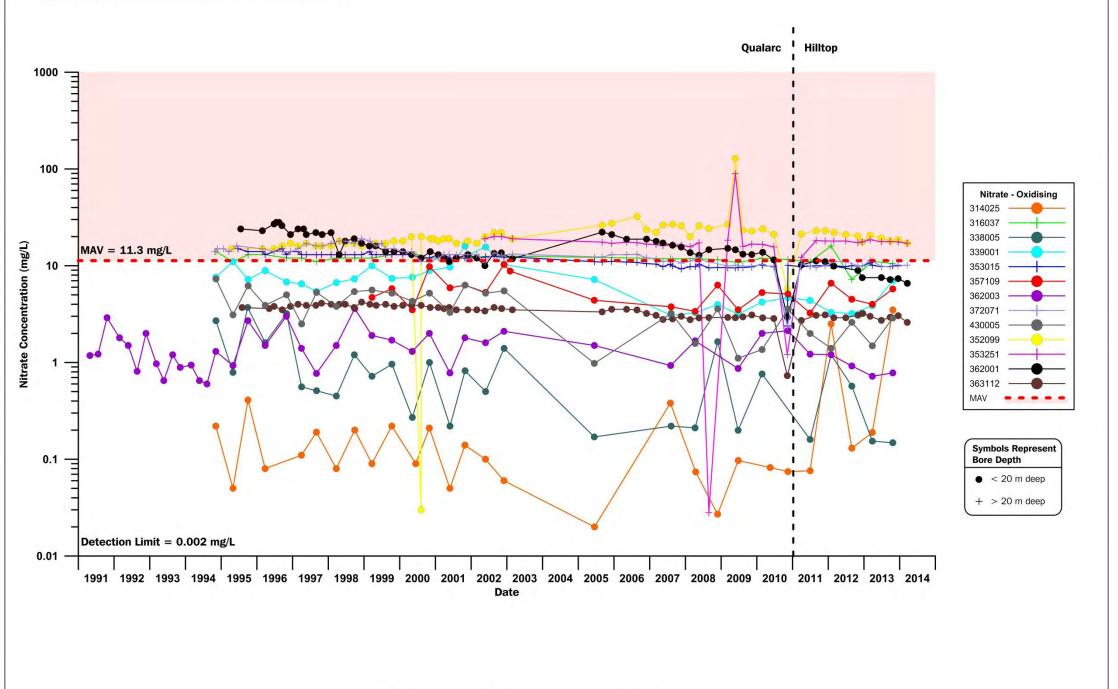


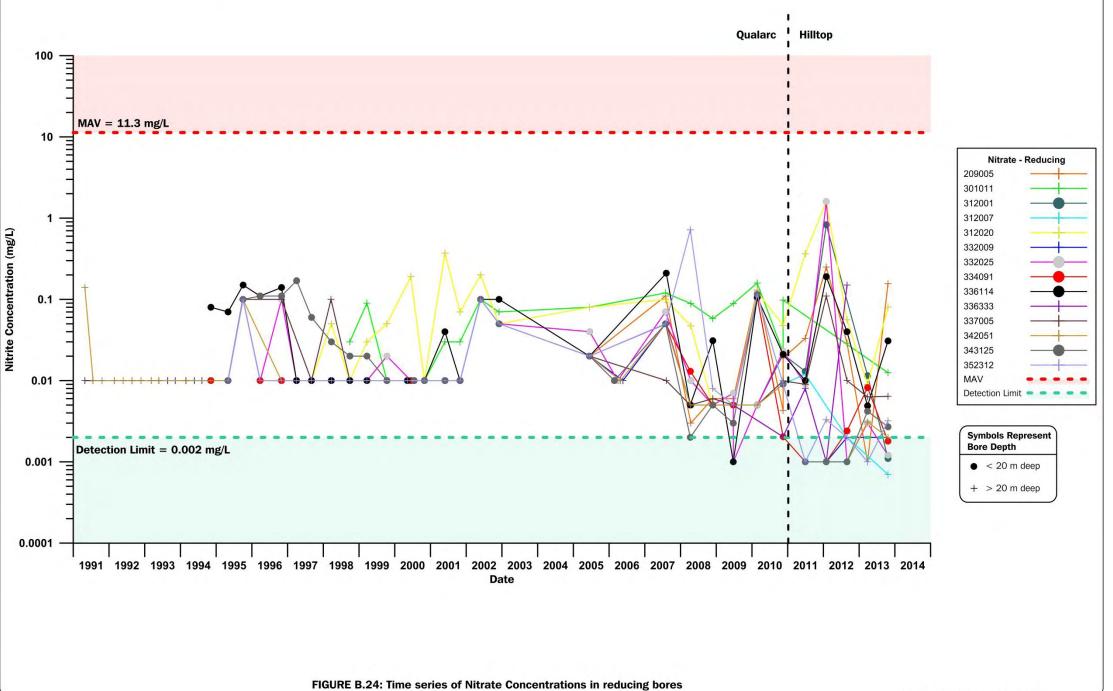












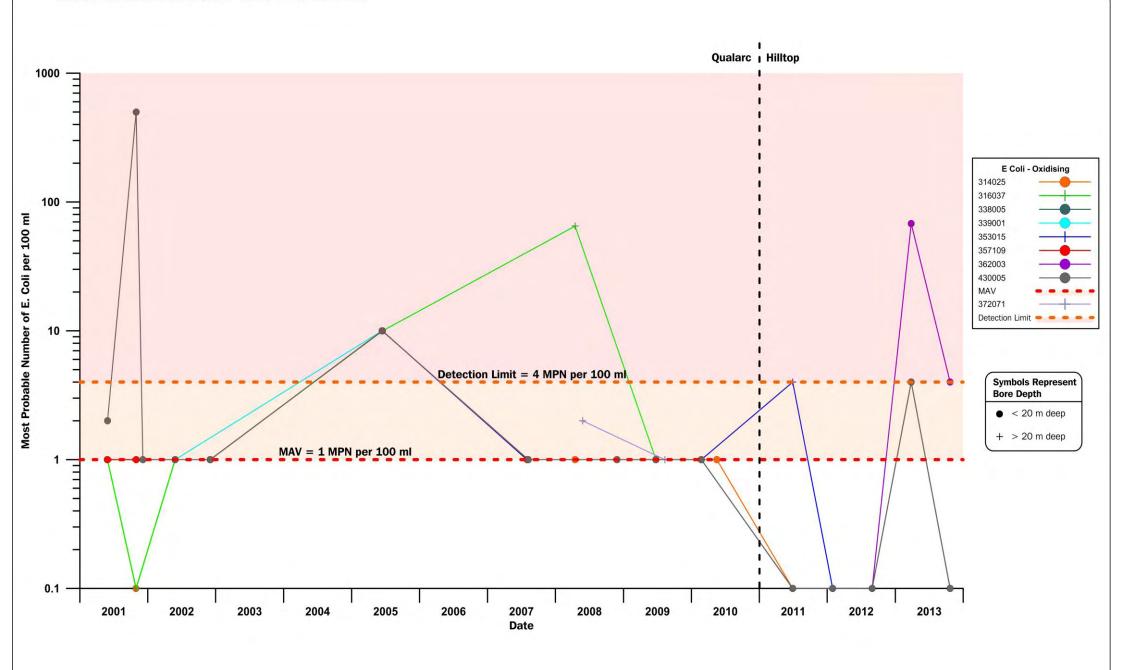
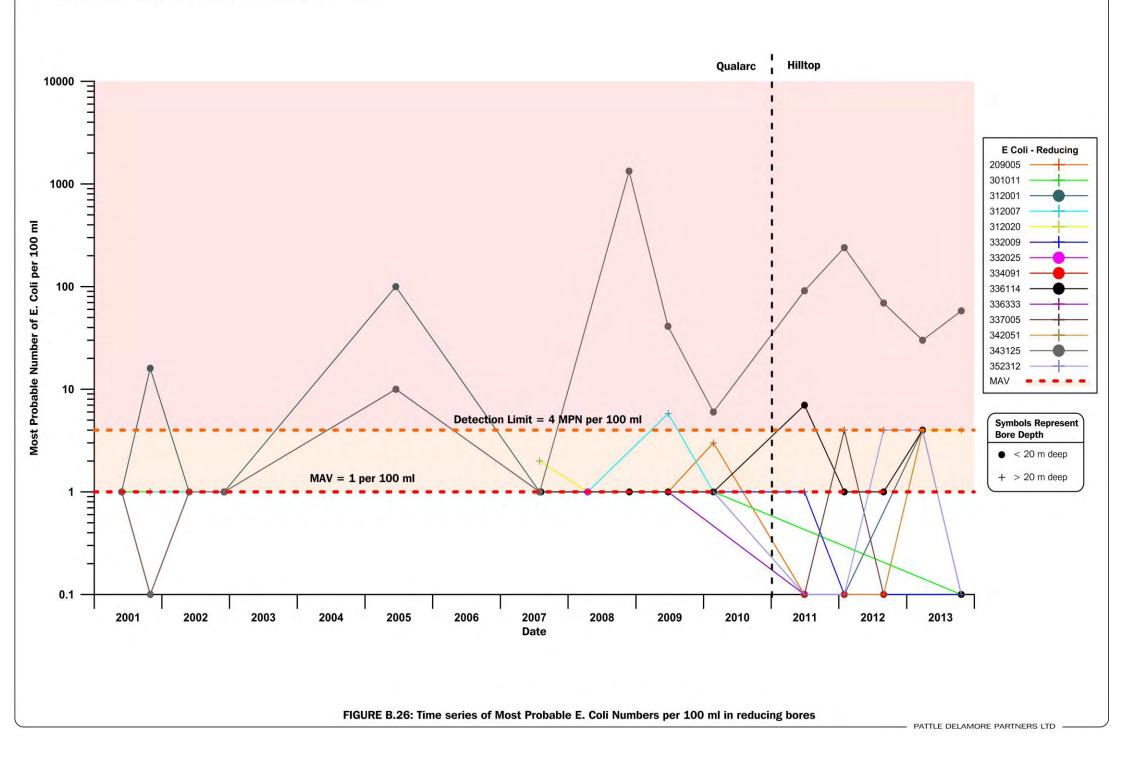
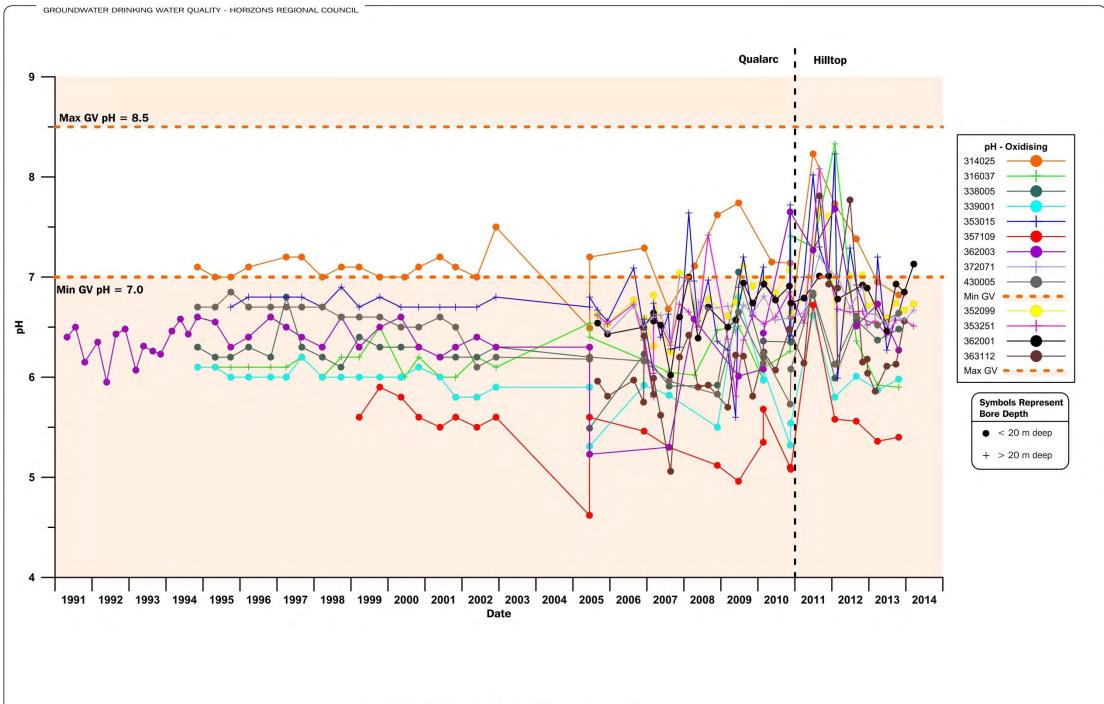


FIGURE B.25: Time series of Most Probable E. Coli Numbers per 100 ml in oxidising bores









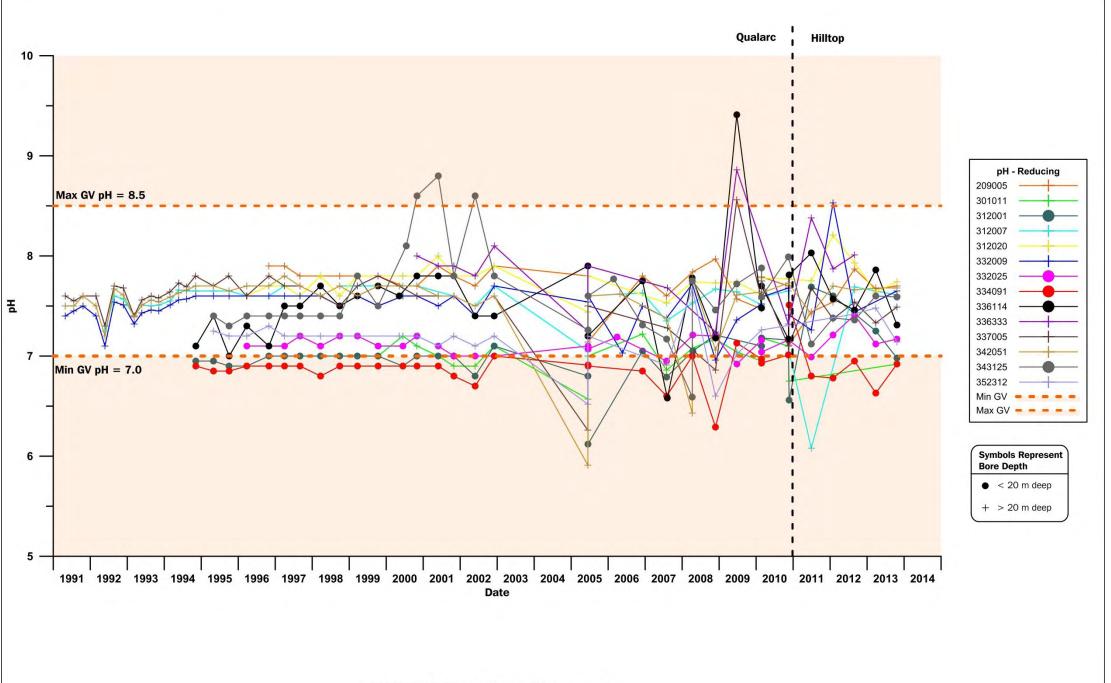


FIGURE B.28: Time series of pH in reducing bores



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