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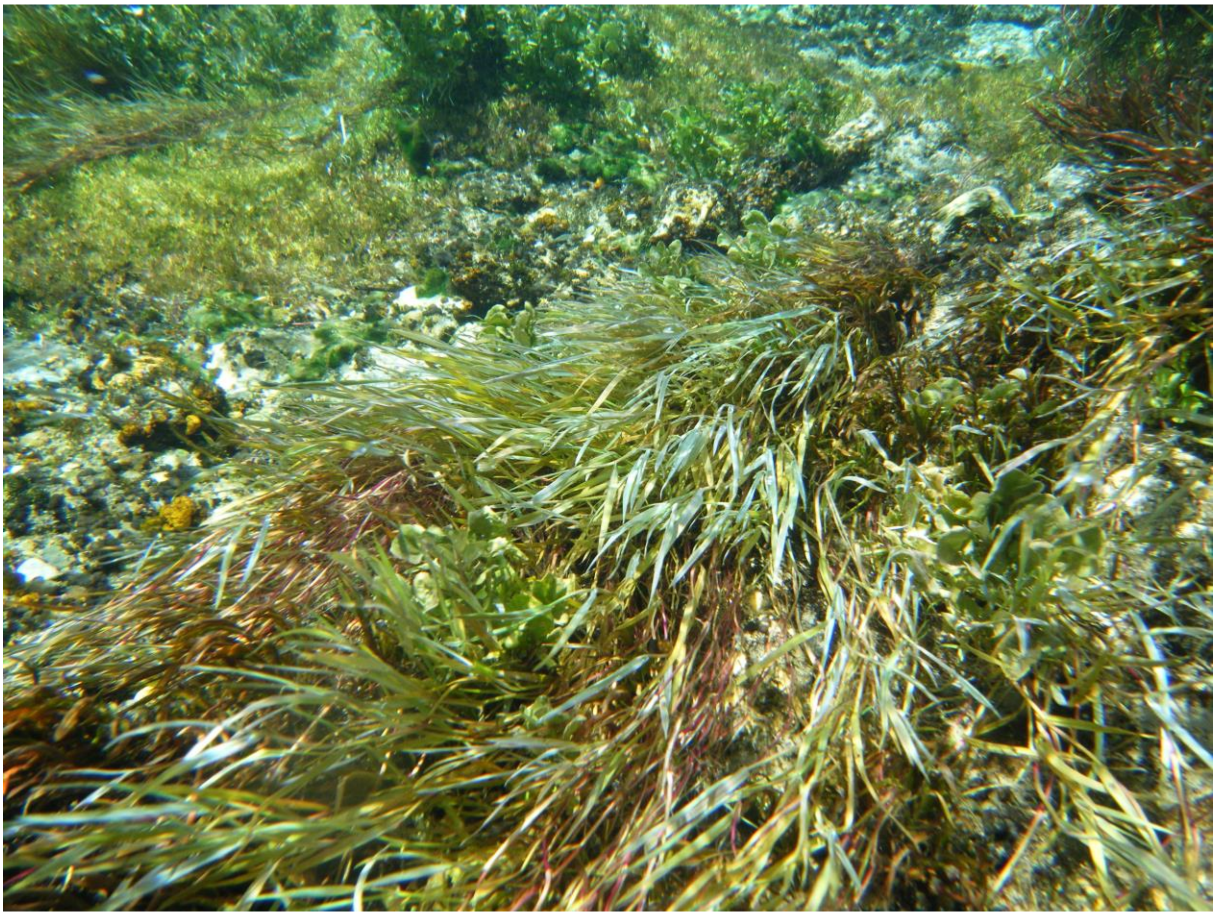
# The nutrient status of Waikoropupu Springs with particular reference to nitrate-N levels



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Cover Photograph: Submerged aquatic vegetation in the Springs River downstream of Waikoropupu Springs. JD Stark, 26 November 2012.

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# The nutrient status of Waikoropupu Springs with particular reference to nitrate-N levels


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Prepared for

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# INTRODUCTION

Concerns have been raised recently about increasing nitrate concentrations in the waters of Waikoropupu Springs. Consequently, Tasman District Council (TDC) has commissioned Stark Environmental Limited (SEL) to undertake a brief evaluation of the significance of this trend and to recommend a nitrate limit.

Nitrate is the dominant form of nitrogen in well-oxygenated surface waters and enters waterways directly from the atmosphere, runoff from farmland, septic tanks, industrial and municipal wastewater discharges. Excess nitrate in rivers can cause proliferations of nuisance periphyton and aquatic plants.

Care must be taken when interpreting guidelines for nitrate because nitrate can be expressed as nitrate or nitrate-N. Nitrate ($NO_3$) contains both nitrogen and oxygen, but the term nitrate-N refers only to the nitrogen portion of the nitrate molecule. The nitrate molecule contains one nitrogen atom (atomic weight 14) and three oxygen (atomic weight 16) atoms, so the percentage of nitrogen in the nitrate molecule is 14/(16*3 + 14) or 22.6%. Theses formulae convert concentrations between nitrate and nitrate-N:-

nitrate * 0.226 = nitrate-N    or    nitrate-N * 4.425 = nitrate

In this report all concentrations are the nitrate-N form of nitrate.

## Nitrate-N data

Michaelis (1974, 1976) sampled water quality four-weekly (15 occasions) in Waikoropupu Springs between July 1970 and September 1971 although nitrate-N analyses were undertaken on only four of these occasions. TDC /Geological & Nuclear Sciences (GNS) provided nitrate-N concentrations for groundwater emanating from Waikoropupu Springs for the period 25 September 1990 to 5 December 2014. Available nutrient data for Waikoropupu Springs are summarised in Appendix 1.

Frances Michaelis (1974), in her M.Sc. thesis, reported nitrate-N concentrations of 0.29 – 0.34 g/m$^3$ for the main spring based on four sampling occasions between January 1970 and March 1971.

Nitrate-N concentrations in the TDC dataset range from 0.12 g/m$^3$ to 0.92 g.m$^3$, but there are several nitrate-N values in the data record that are much higher than adjacent values. These comprised concentrations of 0.902 g/m$^3$ (5 June 1996), 0.62 g/m$^3$ (20 September 1999), 0.8 g/m$^3$ (4 December 2007), 0.91 g/m$^3$ (4 March 2008), and 0.92 g/m$^3$ (15 December 2008). There is also a series of low nitrate-N values (*i.e.*, 0.12 – 0.20 g/m$^3$) recorded between November 1990 and September 1992 that seem out of step with other data values. I believe that these data are almost certain to be erroneous (a view shared by Magali Moreau-Fournier – a groundwater scientists with GNS (see Appendix 2)) so these data values have been excluded from the data set prior to further statistical analyses. Remaining nitrate-N concentrations range from 0.29 g/m$^3$ to 0.51 g/m$^3$ (Appendix 1).

## NITRATE-N TRENDS IN PUPU SPRINGS

Given that concerns have been expressed about increasing nitrate levels in the waters of Pupu Springs, let us first examine the trend.

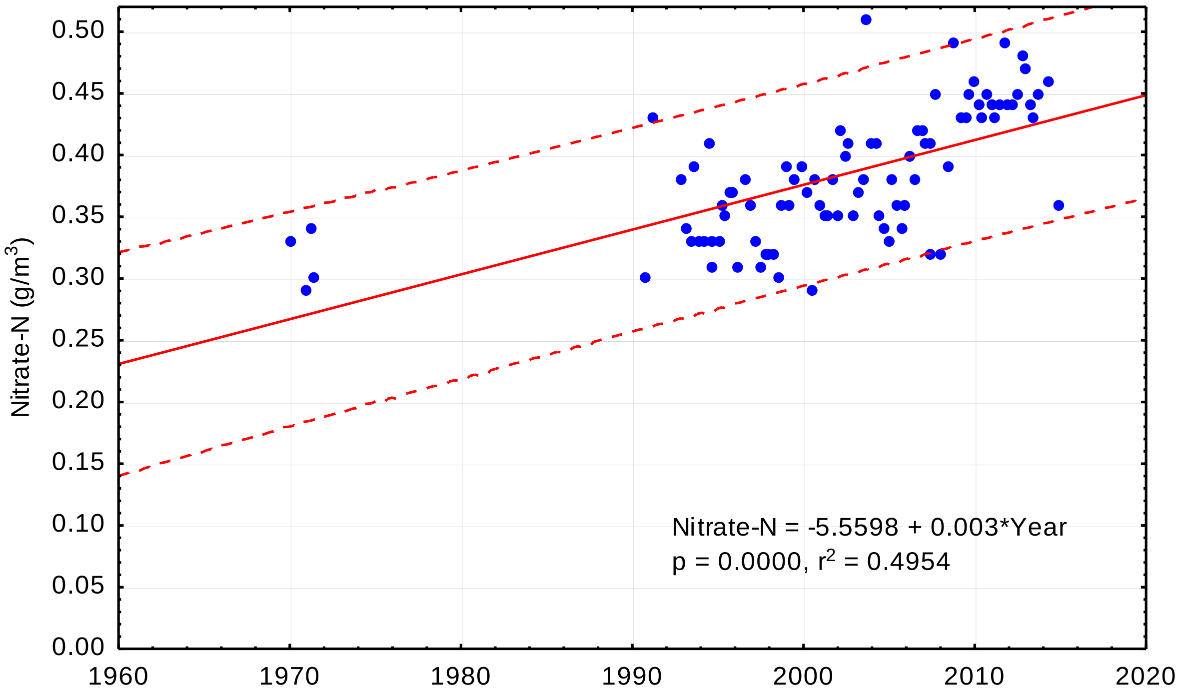


**Figure 1** Trend in nitrate-N concentrations in Waikoropupu Springs from Michaelis (1974) for 1970-71 and TDC/GNS data from 1990 to 2014. The dashed lines are 95% prediction limits about the regression line.

Figure 1 shows a plot of nitrate-N concentrations in Pupu Springs with data from Michaelis (1976) for 1970 – 71 and from TDC/GNS for 1990 – 2014.

Time series analysis on the data plotted on Figure 1 reveals that there has been a statistically significant the positive temporal trend in nitrate-N concentrations between 1970 and 2014 (Kendall Tau = 0.517, $P < 0.000001$, N = 90).

On average, nitrate-N values have increased by about 40 – 50% in 44 years. However, from 2010 to 2014 inclusive, although the trend is still positive, it is not statistically significant (Kendall Tau = 0.088, P = 0.622, N = 17) (Figure 1).

The nitrate-N concentrations of 0.29 – 0.34 g/m$^3$ reported by Michaelis (1974) for 1970 – 71 are within the range of concentrations recorded between 1990 and 2009. Since 2009 almost all nitrate-N concentrations have been higher than those recorded in 1970 – 71 (Figure 1). Although nitrate-N concentrations recorded in the last five years mostly are higher than those recorded previously, there is a suggestion that the trend may have flattened off slightly in the last five years. Time will tell.

Springs in karst regions (such as north-west Nelson) are prone to increases in discharge during high rainfall due to infiltration of surface water close to the source (Death *et al.* 2004). This could also explain some of the temporal variability in nutrient concentrations in water collected from Waikoropupu Springs.

## NITRATE-N GUIDELINES FOR PROTECTING FRESHWATER ENVIRONMENTS

ANZECC (2000) provided guidelines expressed in terms of nitrate nitrogen (nitrate-N) but there were errors in the calculations as pointed out by Chris Hickey (NIWA, Hamilton) (see Appendix 3 in Hickey & Martin (2009)). The nitrate guidelines provided by Hickey & Martin (2009) in their review of nitrate toxicity to freshwater aquatic species (which was prepared for Environment Canterbury), in Hickey (2013), and in the National Policy Statement for Freshwater Management (NPS-FWM) (NZ Govt 2014) are the most up-to-date and relevant guidelines for nitrate-N in New Zealand's freshwaters. Upland and lowland rivers were defined by ANZECC (2000) as those above and below 150m altitude respectively.

Table 1 summarises guidelines for nitrate-N in freshwaters depending on the purpose, the type of environment, and/or the degree of protection required.

**Table 1** Published guidelines for Nitrate-N in freshwaters of relevance to Waikoropupu Springs.

| Guideline Value (mg/L or g/m$^3$) | Purpose | Reference |
|---|---|---|
| 20 | Very localised point source discharges | Hickey & Martin (2009) |
| 11.3 | Freshwater aquaculture | ANZECC (2000) |
| 10 | Recreation | ANZECC (2000) |
| 2.4 – 3.6 | Highly disturbed systems (80-90% protection) | Hickey & Martin (2009) |
| 1.7 | Environments subjected to disturbance from human activity (95% protection) | Hickey & Martin (2009) |
| 1.5 | Toxicity Surveillance Value for pristine environments with high biodiversity and conservation values (99% protection) | Hickey (2013), NZ Govt (2014) |
| 1.0 | Toxicity Grading Value for pristine environments with high biodiversity and conservation values (99% protection) | Hickey & Martin (2009)<br>Hickey (2013), NZ Govt (2014) |
| 0.444 | Prevent nuisance algal growth in lowland rivers | ANZECC (2000) |
| 0.167 | Prevent nuisance algal growth in upland rivers | ANZECC (2000) |

Hickey (2013) recommended nitrate toxicity guidelines for different management classes of New Zealand freshwaters based upon statistically-derived no-observed-effect concentrations (NOEC) and threshold-effect concentration (TEC) thresholds for 22 species (including fish, amphibians, invertebrates, and algae). A two-number guideline management framework (*i.e.*, grading and surveillance values) for use with compliance monitoring programmes was proposed that is consistent with the ANZECC (2000) risk-based methodology to provide various levels of ecosystem protection. The terms 'grading' and 'surveillance' were derived from the compliance descriptors applied to microbiological standards. Hickey's (2013) recommended toxicity guidelines were adopted for the NPS-FWM (NZ Govt 2014).

The *Grading Values*, derived from the species NOEC values, are recommended for compliance assessments based on the annual median concentrations. These are equivalent to trigger values derived using the ANZECC (2000) procedure. The *Surveillance Values*, derived from the species TEC values, are recommended for compliance assessments based on monitoring data annual 95$^{th}$ percentile concentrations.

Hickey's (2103) guidelines for nitrate-N toxicity are conservative because they are based on the most sensitive species in the database that was used to derive the nitrate guidelines. Furthermore, the guidelines were based on long-term toxicity tests in low hardness waters (which would be expected to result in the highest nitrate toxicity). The management classes ranged from 'pristine environments with high biodiversity and conservation values' at one extreme to 'significantly degraded environments with probable chronic effects on multiple species' at the other. There is no question that Waikoropupu Springs would warrant the highest level of protection.

## Comparisons with nitrate-N guidelines

### *For prevention of nuisance periphyton growth*

Figure 2 compares the nitrate-N concentrations from Pupu Springs with the ANZECC (2000) guidelines for prevention of nuisance algal growths in upland and lowland rivers.

All nitrate-N data values recorded from Pupu Springs (including all but one of the dubious low values recorded in 1990 – 92 excluded from subsequent analyses – see Appendix 1) exceed the ANZECC (2000) guideline value of 0.167 g/m$^3$ designed to prevent nuisance algae proliferations in upland rivers (Figure 2).

Waikoropupu Springs is located at an altitude of 14 metres above sea level (Michaelis 1974), so, according to the ANZECC (2000) criterion, the Springs River is a lowland waterway (*i.e.*, < 150m above mean sea level), and the guideline concentration of 0.444 g/m$^3$ would apply. However, the Springs River is not a typical lowland river given that it is spring-fed with a near-constant water temperature of 11.7$^o$C (Michaelis 1976). Water temperature is among the most important factors affecting the rate of accrual of periphyton biomass (although nutrients and carbon are required also (Olsen *et al.* 2012)). In many rivers, nuisance algal blooms are at their worst when elevated water temperatures occur in the warmer months. However, given the cool temperature regime of the Springs River I would expect there to be less of a problem with nuisance algal or aquatic plant proliferations for given nutrient concentrations compared with a non-spring-fed lowland river. One could speculate, therefore, that a slightly higher guideline than 0.444 g/m$^3$ might be acceptable.

On the other hand, large freshes (exceeding three times median flow or five or six times the preceding baseline) that are known to flush out accumulated periphyton proliferations in rivers (Biggs & Close 1989), are likely to occur less frequently downstream of a spring-fed system like Waikoropupu Springs where the usual flow statistics do not apply. Never-the-less, the flow is variable enough (with extreme flood and one day average drought flows of 57.9 and 3.6 m$^3$/s respectively - TDC website) to have significant impacts on aquatic plant and algal communities in the Springs River whenever large freshes or extreme low flows occur. However, the basin immediately around the main springs would not be affected appreciably by freshes and could be especially vulnerable to the occurrence of nuisance periphyton growths stimulated by addition of plant nutrients. It could be prudent, then, to keep nutrient inputs to the system below the levels known to cause undesirable growths.

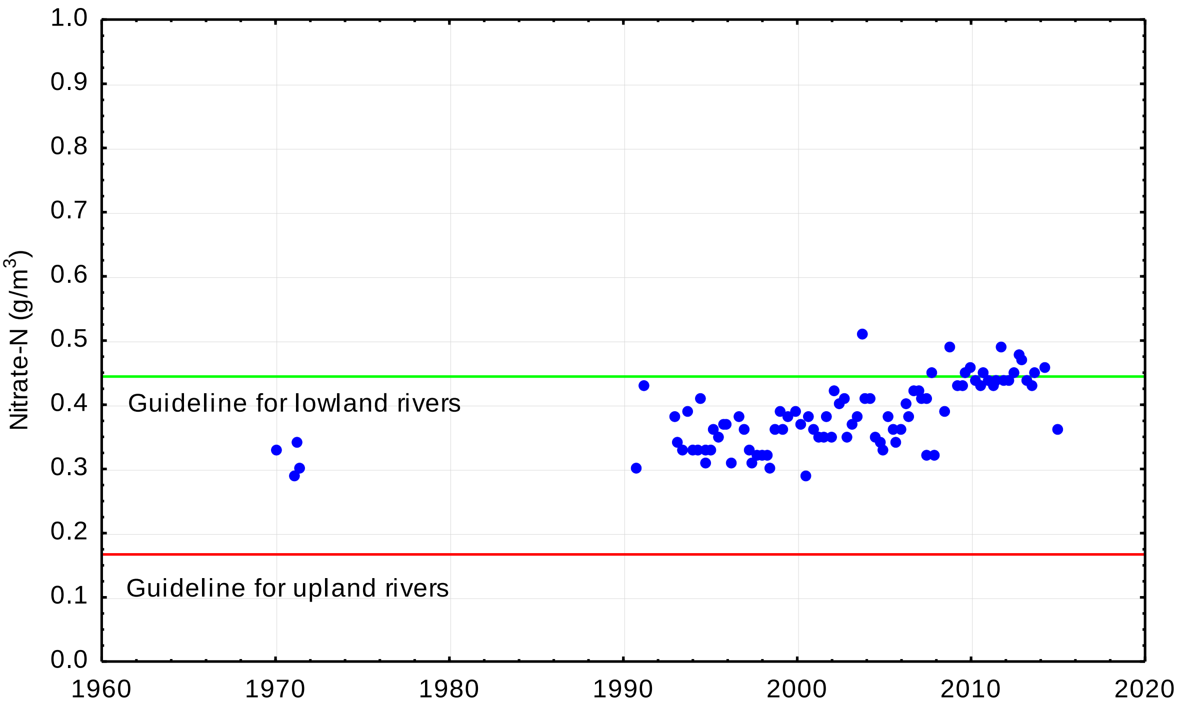


**Figure 2** Comparison of nitrate-N concentrations in Waikoropupu Springs with ANZECC (2000) guidelines to prevent nuisance algal growths in upland (red) and lowland (green) rivers. Data from Michaelis (1974) for 1970-71 and TDC/GNS data from 1990 to 2014.

### *For prevention of nitrate toxicity*

Figure 3 shows the comparisons with the grading and surveillance guidelines for prevention of nitrate toxicity in pristine environments with high biodiversity and conservation values (Hickey 2013). The horizontal green line represents the grading guideline nitrate-N concentration of 1.0 g/m$^3$. The fitted green line shows calculated annual median nitrate-N values from Pupu Springs data (which are compared to the grading guideline to assess compliance). The horizontal blue line on Figure 3 is the surveillance guideline for nitrate toxicity set at a nitrate-N concentration of 1.5 g/m$^3$. The other blue line on the plot shows the annual 95$^{th}$ percentiles, which are compared to the surveillance guideline to assess compliance.

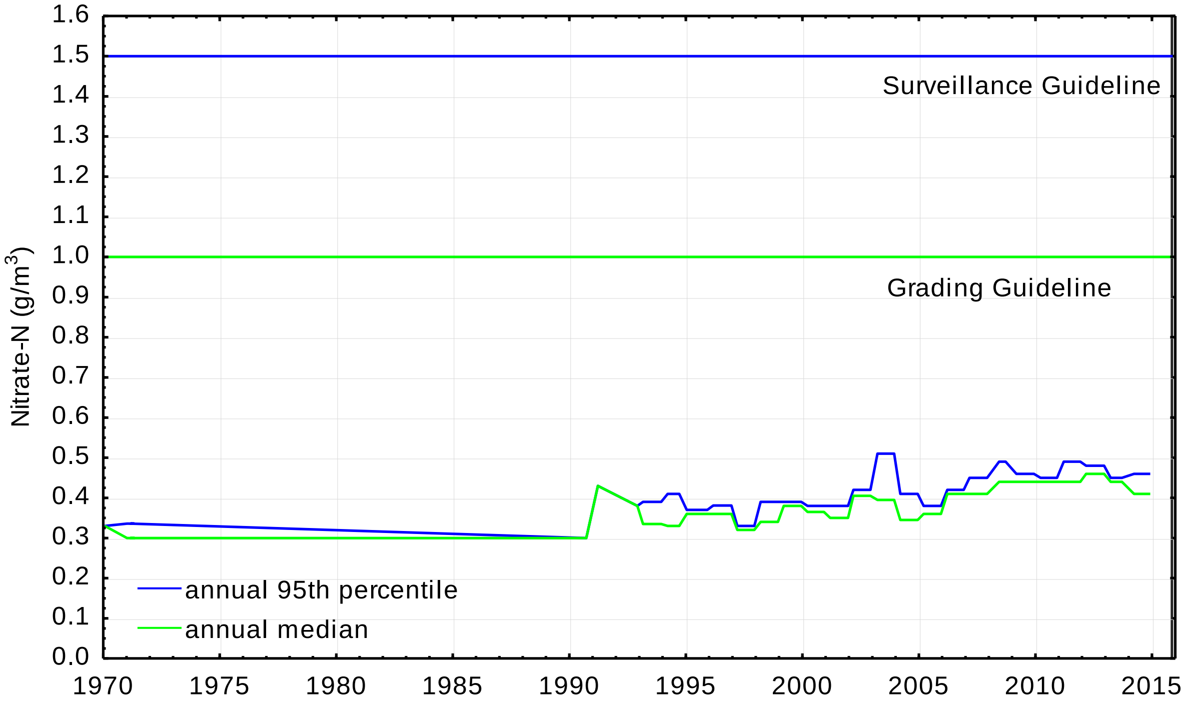


**Figure 3** Nitrate-N trend in Waikoropupu Springs (1990 – 2014) showing grading and surveillance guidelines for avoiding nitrate toxicity in pristine environments with high biodiversity and conservation values.

In general, the annual median and annual 95th percentile nitrate-N values are well below the grading and surveillance guidelines. Consequently, although nitrate levels in Pupu Springs have increased over the past 44 years, concentrations remain well below the levels that are likely to have any significant toxicity effects because they are below the grading and surveillance guidelines that have been proposed by Hickey (2013) specifically to protect the integrity of pristine freshwater environments (such as Waikoropupu Springs) with high biodiversity and conservation values.

## NITROGEN : PHOSPHORUS RATIOS FOR AQUATIC PLANT GROWTH

Extensive and diverse aquatic plant communities of healthy appearance are present in Waikoropupu Springs and the Springs River downstream (Figure 4) at least as far as the confluence with Bells Creek. I am very familiar with this area having been involved with the biomonitoring programme for the NZ King Salmon (NZKS) farm for the last 29 years. Although I have observed some differences in the plant communities at the monitoring sites over the years (mainly the appearance of the emergent species such as water cress (Figure 5)), I am certain that these have been related to the flow regime (*i.e.*, the influence of low flows and freshes, and exposure of previously submerged plants when flows decrease). I have not seen any change that I would attribute to water quality. [I am not very familiar with the Springs River further downstream than about 200m below the Bells Creek Confluence, and if I was to make informed comment on that part of the river I would need to undertake further investigations and sampling.]

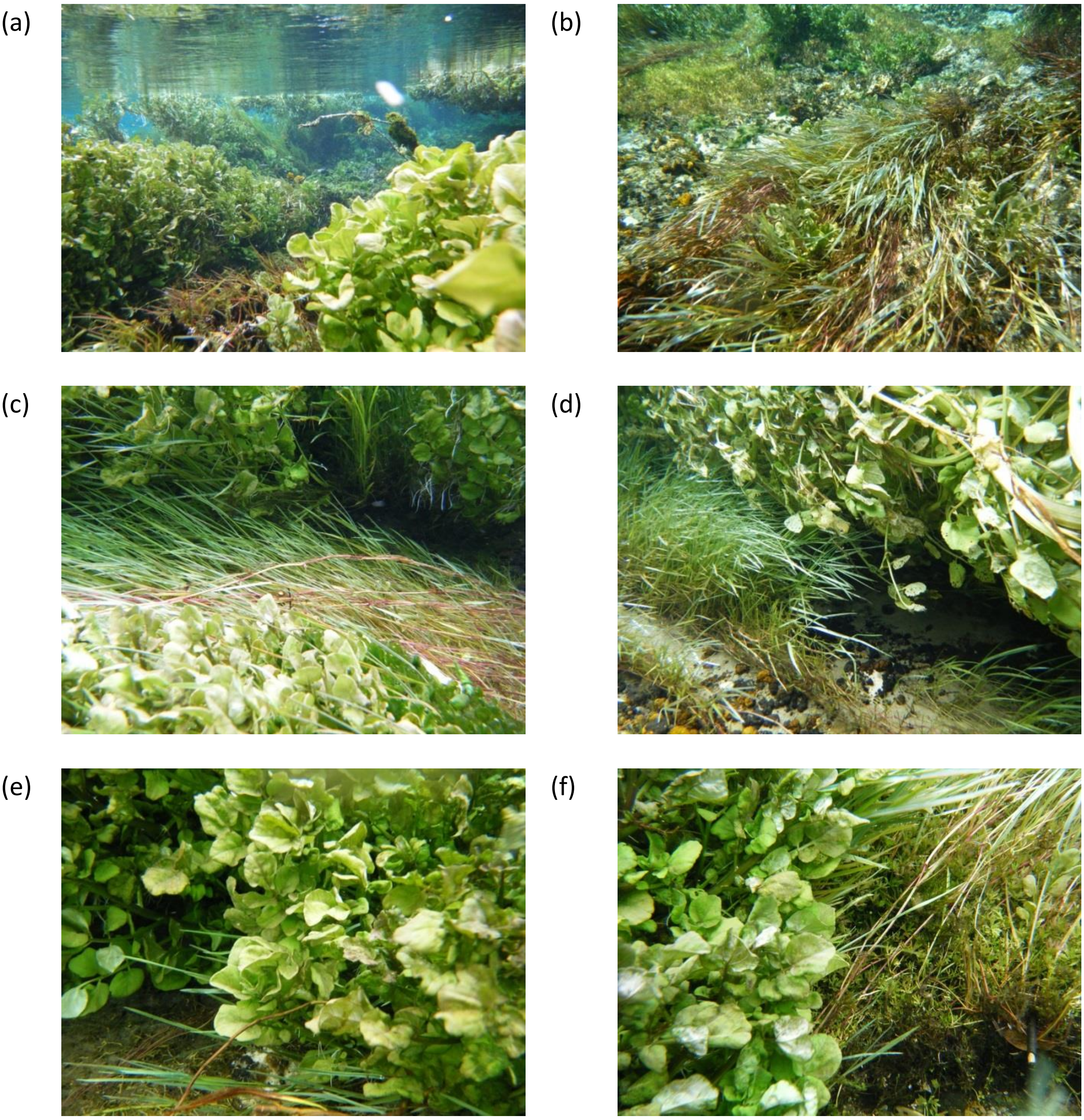


**Figure 4** A selection of underwater photographs from the Springs River immediately upstream of the NZKS farm discharge. (a) 3 February 2011, (b) 26 November 2012, (c) – (e) 16 December 2013, (f) 29 December 2014.

(a)

(b)

**Figure 5** Photographs of NZKS biomonitoring Site 3a on the Springs River upstream of the NZKS discharge. (a) 29 January 2009, (b) 2 February 2010.

Plants, including nuisance periphyton, require nutrients to grow and not just nitrogen alone. Nitrogen (and phosphorus) compounds are plant nutrients – like fertilisers – so what are the likely consequences of the increase in nitrate-N on plant growth in Pupu Springs?

A ratio of bioavailable nitrogen to phosphorus between 10:1 and 15:1 generally is regarded as the normal balance for aquatic plant growth (Biggs & McBride 1980). A ratio below this is indicative of nitrogen limitation, with phosphorus limitation likely at higher ratios. Davies-Colley (1985) defined potentially bioavailable phosphorus as all of the dissolved reactive phosphorus (DRP) plus 20% of the total particulate phosphorus (TPP). The TPP is defined as total phosphorus (TP) - DRP. Bioavailable nitrogen is the sum of the ammoniacal and nitrate forms of nitrogen (Biggs & McBride 1980).

Table 2 summarises the concentrations of nitrogen and phosphorus species from Waikoropupu Springs and provides calculated values for the minimum, median, and maximum bioavailable N and P and N:P ratios. Censored data (*i.e.*, concentrations below detection limit expressed as 'less-than' values (*e.g.*, < 0.001)) were replaced by half the detection limit (*e.g.*, 0.0005) prior to these analyses.

**Table 2** Minimum, median, and maximum nitrate-N, ammoniacal-N, bioavailable-N, DRP, TPP, bioavailable-P, and N : P ratios for Wakoropupu Springs based on data collected between 1970 and 2014.

| | Nitrate-N | Ammoniacal-N | Bioavailable N | DRP | TPP | Bioavailable P | N:P ratio |
|---|---|---|---|---|---|---|---|
| **Minimum** | 0.29 | 0.001 | 0.295 | 0.002 | 0.002 | 0.0014 | 5:1 |
| **Median** | 0.37 | 0.005 | 0.395 | 0.018 | 0.020 | 0.0100 | 18:1 |
| **Maximum** | 0.51 | 0.05 | 0.540 | 0.080 | 0.050 | 0.0400 | 165:1 |
| **N** | 101 | 70 | 66 | 22 | 19 | 19 | 10 |

Bioavailable nitrogen concentrations in Waikoropupu Springs can be determined for 66 sampling occasions compared with only 19 occasions for bioavailable phosphorus. N:P ratios can be calculated for only 10 occasions between 1996 and 2003 when the necessary analyses were undertaken on the same samples. The median bioavailable N:P ratio during this period was 18:1 (range 5:1 – 165:1) with 70% of N:P ratios suggestive of phosphorus limitation, and the remainder indicative of normal balance for plant growth.

Bioavailable N concentrations in Waikoropupu Springs have increased (Kendall tau = 0.523, P < 0.000001, N= 66) faster that bioavailable P concentrations (Kendall tau = 0.253, P = 0.129, N = 19). If this trend continues then phosphorus limitation could continue to be the norm.

With nitrate-N concentrations exceeding the ANZECC (2000) guideline of 0.444 g/m$^3$ for prevention of nuisance algal growths in lowland rivers on 43% (9 of 21) sampling occasions since 2008, phosphorus-, temperature-, or flow-mediated limitation may be required if nuisance periphyton or plant growth is to be avoided. However, Waikoropupu Springs and the Springs River (at least as far downstream as Bell's Creek) is well-vegetated and it could be that any additional nutrients serve to increase the productivity of these communities without changing their character appreciably or causing enrichment further downstream.

The ANZECC (2000) DRP guideline for prevention of nuisance growths in lowland rivers (< 150m above mean sea level) is 0.01 $g/m^3$ (Table 3). Since March 2005, DRP concentrations in the Springs have been measured annually and have ranged from <0.004 to 0.026. Prior to that date the DRP detection limits were greater than 0.01 $g/m^3$, so data cannot be compared to the guideline value. Since March 2005, on 11% (1/9) of sampling occasions the ANZECC (2000) guideline has been exceeded, and equalled on two (22%) other occasions (in March 2012 and 2013) (Figure 6).

**Table 3** Published guidelines for Dissolved Reactive Phosphorus (DRP) in freshwaters.

| **Guideline Value** | **Purpose** | **Reference** |
|---|---|---|
| 0.01 $g/m^3$ | Prevent nuisance algal growth in lowland rivers | ANZECC (2000) |
| 0.009 $g/m^3$ | Prevent nuisance algal growth in upland rivers | ANZECC (2000) |

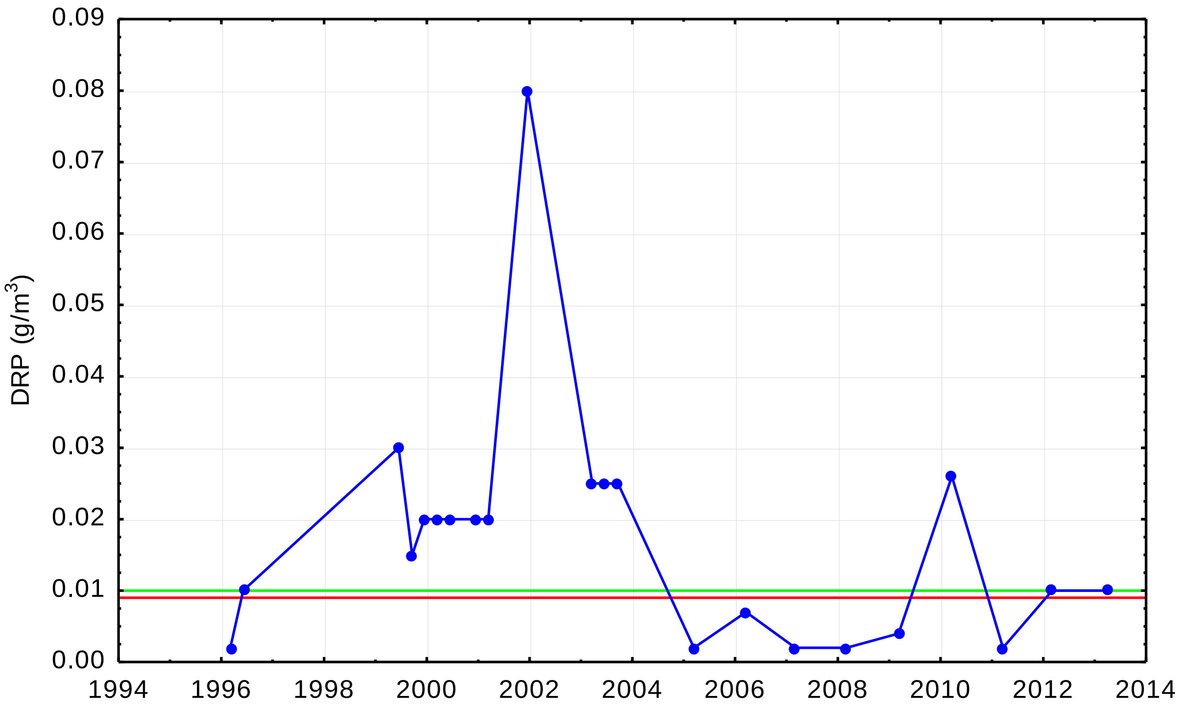


**Figure 6** DRP concentrations recorded from Waikoropupu Springs showing the ANZECC (2000) guidelines for prevention of nuisance algal growths in upland (0.009 $g/m^3$ red line) and lowland (0.01 $g/m^3$ green line) rivers.

Several studies have shown positive relationships (although not necessarily statistically significant) between nitrate and phosphate concentrations in freshwaters (e.g., Dike *et al*. 2010, Young *et al*. 2010), and phosphorus is much less soluble in water than nitrogen (Davies-Colley & Wilcock 2004, Parliamentary Commissioner for the Environment 2012) so it is unlikely that high phosphorus concentrations would be associated with low nitrate concentrations).

The N:P ratio analyses and the comparisons with ANZECC (2000) guidelines suggest that low DRP is more likely than nitrate to limit nuisance algal growth in Pupu Springs, although this was not the case on 30% of sampling occasions.

Data from Waikoropupu Springs reveal strong linear relationships between bioavailable N and nitrate-N and bioavailable P and DRP.

Bioavailable N = 1.0700 * Nitrate-N – 0.0174 ($r^2 = 0.9563$, $p < 0.0001$)
Bioavailable P = 0.8874 * DRP + 0.0021 ($r^2 = 0.9973$, $P < 0.0001$)

The ANZECC (2000) limits applied to the above relationships result in and N:P ratio of 42:1 consistent with phosphorus limitation.

If we insert the maximum values (*i.e*., Nitrate-N = 0.49 g/$m^3$, DRP = 0.026 g/$m^3$) recorded in the last five years into the above equations we get a bioavailable N:P ratio of 20:1 which is also consistent with phosphorus limitation. However, the maximum DRP value is much higher than most other DRP concentrations recorded in the last nine years, which have all been 0.01 g/$m^3$ or less.

## DRINKING WATER STANDARDS

The Ministry of Health (2008) Maximum Acceptable Value (MAV) for nitrate is 50 mg/L, which is equivalent to a nitrate-N concentration of 11.3 mg/L (or 11.3 g/$m^3$). This is a short-term MAV intended to protect against methaemoglobinaemia in bottle-fed infants. The maximum (reliable) nitrate-N concentration of 0.51 g/$m^3$ recorded from Pupu Springs is less than 5% of the MAV, so there is no cause for concern in this respect.

## EFFECTS ON MACROINVERTEBRATE COMMUNITIES

Biological monitoring undertaken in the Springs River since August 1986 can provide some indication whether or not river health has changed over the years and, in particular, whether or not the change (if any) could be related to deteriorating water quality (Stark 2015).

Figure 7 shows Macroinvertebrate Community Index (MCI) values versus time for a site on the Springs River that is upstream of the influence of the NZKS salmon farm (except for the water abstraction that does not have a measurable impact on MCI values). It is, however, affected by flow variability from the Springs and Fish Creek and possible contamination from activities in the catchment upstream.

From 1986 to 1999 biomonitoring at Pupu Springs was undertaken twice per year – nominally February and August. From 2000 to 2011 biomonitoring was annual (normally February) and from 2011 to date (following NZKS's re-consenting) monitoring has been undertaken in December. In the early years, MCI values from around August – September tended to be higher than those recorded around February, so the August – September data have been removed prior to analysis so that the trends testing remains unbiased.

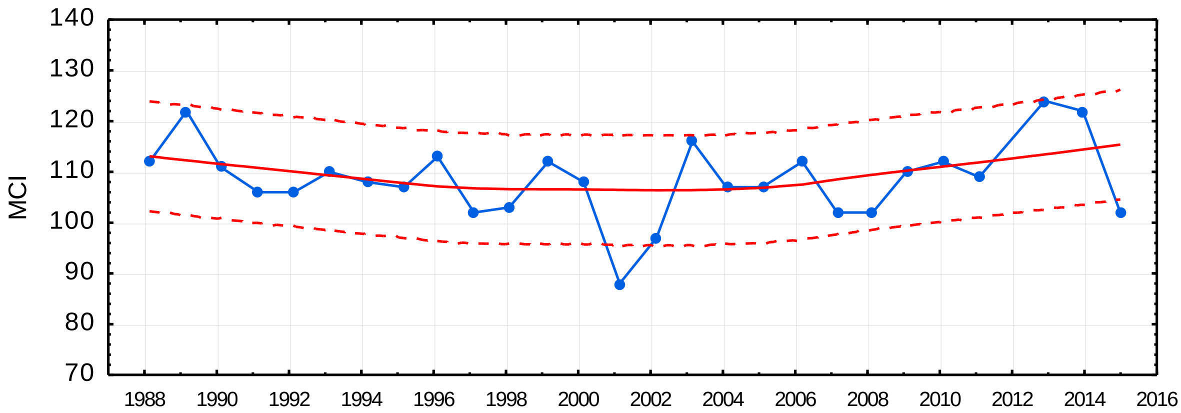


**Figure 7** MCI versus time (23 February 1988 – 29 December 2014) for Site 3/3a in the Springs River upstream of the NZKS discharge. Data from August – September collected prior to 2000 have been excluded. The fitted line is a LOWESS trend (tension = 0.7) with dashed red lines indicated error of ±10.83 MCI units.

Overall there has been no statistically significant trend in MCI values at Site 3/3a in the Springs River upstream of the salmon farm outflow channel (Kendall Tau = -0.018, P = 0.898, N = 27).

Incidentally, with the August – September data collected prior to 2000 included, there was a statistically significant negative trend (*i.e.*, a decrease) in MCI values in the Springs River at Site 3a between 1986 and 2014 (Kendall Tau = -0.266, P = 0.014, N = 41). However, this is a consequence of seasonality in MCI values with higher values recorded in August – September compared with December – February.

It should be noted that MCI values from single D-net samples have an error of ±10.83 units (Stark 1998). This has not been taken into account in the above analysis, but to put this into perspective, the dashed red lines on Figure 5 show the approximate error about the LOWESS fit. MCI values on only two sampling occasions (*i.e.*, 23 February 2001 & 29 December 2014) are further from the LOWESS fit than the error (± 10.83) associated with calculating MCI from a single D-net sample. All other MCI values recorded during December – February from Site 3/3a are unlikely to be significantly different from one another. When biomonitoring is based on single samples per site (which is most cost-effective), it is unwise to place too much reliance on single MCI values, which is why I tend to rely on trends testing. Consequently, the low MCI values are not necessarily of great concern unless the run of low values persists (which, to date, has not been the case).

Almost all of the variability in MCI shown on Figure 7 is likely to be within the error associated with calculating MCI from single D-net samples. The low MCI in 2001 was considered to be due to a prolonged period of low flows prior to sampling (Stark & Crowe 2001). We can conclude from the biomonitoring data that the increased nutrient content of the waters of the Springs River does not seem to have had any noticeable effect on macroinvertebrate communities or river 'health' as determined by the MCI.

# CONCLUSIONS AND RECOMMENDATIONS

Although there has been a statistically significant increase in the nitrate-N concentrations in the waters of Waikoropupu Springs from 1970 to 2014 (but very little increase over the last five years), in absolute terms the nitrate-N concentrations are well below levels likely to have any toxicity implications for human or farm animal health or for the ecological health of the Springs and the river downstream. However, nitrate-N concentrations have exceeded the ANZECC (2000) limit of 0.444 g/m$^3$ for prevention of nuisance algal growths in lowland (< 150m above sea level) rivers on 43% (9 of 21) sampling occasions since 2008. Prior to 2008, the ANZECC limit was exceeded only once (0.51 g.m$^3$ on 23 September 2003), although this concentration was at least 0.10 g/m$^3$ higher than concentrations measured on adjacent sampling occasions (0.38 – 0.41 g/m$^3$), which could raise some concern regarding the reliability of that value. The bottom line, however, is that prior to 2008, nitrate-N values generally were below the ANZECC guideline but since then nitrate-N concentrations have been close to, or above, the guideline of 0.444 g/m$^3$. The obvious question (which is beyond the scope of this brief report), is "Why?"

Phosphorus appears to be nutrient limiting plant growth in the system on most sampling occasions. Phosphorus concentrations are increasing in Springs water too, but at a slower rate than nitrate, so phosphorus limitation is likely to persist if this trend continues. With both bioavailable N and P increasing and phosphorus limitation most likely, it does not mean that there will not be any increase in the enriching effect and consequently an increase in the productivity of submerged plant communities. It means, simply, that not all of the N will be taken up by plants and that productivity would increase if more P was available. It means also, that if excess nitrogen is exported downstream then nuisance periphyton growths could occur in the Springs River downstream should there be further phosphorus additions into downstream reaches.

It would be helpful to understand WHY nitrate-N and DRP concentrations in the waters of Waikoropupu Springs have increased. For example, is it due to contamination of deep groundwater and/or infiltration of contaminated surficial waters during periods of high rainfall? It could be that the increasing trend has plateaued (given the results over the last five years), but if future monitoring continues to show an increase, then understanding why it is occurring, and any time lag been activities on land and effects on groundwater will be essential if TDC wishes to justify implementation of measures aimed at halting or reversing the trend.

Despite the ANZECC guidelines for N and P being exceeded occasionally in recent years I have not observed changes to the aquatic plant communities that I would term 'adverse' or a consequent of enrichment, or any suggestion that enrichment has affected the health of macroinvertebrates in the Springs River upstream of the salmon farm discharge. It could be, then, that higher limits than the ANZECC (2000) guidelines of 0.444 g/m$^3$ (nitrate-N) and 0.01 g/m$^3$ (DRP) could be sufficient to protect the integrity of the Waikoropupu Springs ecosystem. Perhaps if nutrient concentrations in the Springs continue to increase without any obvious adverse effects, then slightly higher limits might be appropriate. Meantime, however, prevention is better than cure, so it could be wise to adopt the ANZECC (2000) limits.

In my view, the most appropriate nitrate-N guideline value for preventing nuisance algal growth is 0.444 g/m$^3$, which is the limit for lowland rivers. Waikoropupu Springs is not a typical lowland river (being spring fed), but the ANZECC (2000) guidelines define a lowland river as one located less than 150 m above mean sea level (which, at 14m above mean sea level, Waikoropupu Springs certainly is). Besides, the nitrate-N limit for upland rivers of 0.167 g/m$^3$ is lower than any nitrate-N concentrations recorded from the Springs over the past 44 years (with the exception of the dubious low values recorded in 1991 – 92).

Wilcock *et al.* (2007) advised against focussing on just one nutrient (such as nitrate), so any efforts to manage nutrient inputs to Waikoropupu Springs should consider both nitrogen and phosphorus. To that end, I recommend that's the ANZECC (2000) guideline of 0.01 g/m$^3$ for DRP should be adopted too.

In summary, I recommend that monitoring of nitrate-N and DRP concentrations in Waikoropupu Springs should be undertaken at least four times per year. I suggest that annual median concentrations (based on at least four sampling occasions) could be compared for compliance purposes with limits of 0.444 g/m$^3$ (Nitrate-N) and 0.01 g/m$^3$ (DRP). Trends testing should also be undertaken to determine whether or not nutrient levels are continuing to increase (or not).

## ACKNOWLEDGMENTS

Helpful comments on earlier drafts of this report were provided by Andrew Fenemor (Landcare Research), Joseph Thomas, Trevor James, and Rob Smith (all TDC).

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**Appendix 1** Nutrient concentrations in groundwater from the Waikoropupu Springs (25 September 1990  27 March 2014). Data for 1970-71 from Michaelis (1974). Remaining data supplied by Tasman District Council (all concentrations are $g/m^3$). Data values in red are dubious (Magali Moreau-Fournier, GNS – see Appendix 2).

| Date | DRP | Nitrate-N | Nitrite-N | Phosphate | TN | TP | Ammonia-N |
|---|---|---|---|---|---|---|---|
| 26-Jan-70 | | 0.33 | - | | | | 0.069 |
| 10-Jan-71 | | 0.29 | 0.001 | | | | 0.050 |
| 2-May-71 | | 0.30 | | | | | 0.004 |
| 8-Mar-71 | | 0.34 | | | | | |
| 25-Sep-90 | - | 0.3 | - | - | - | - | - |
| 28-Nov-90 | - | 0.2 | - | - | - | - | - |
| 26-Mar-91 | - | 0.43 | - | - | - | - | - |
| 19-Jun-91 | - | 0.15 | - | - | - | - | - |
| 23-Sep-91 | - | 0.17 | - | - | - | - | - |
| 3-Dec-91 | - | 0.13 | - | - | - | - | - |
| 24-Mar-92 | - | 0.12 | - | - | - | - | - |
| 13-Jul-92 | - | 0.12 | - | - | - | - | - |
| 15-Sep-92 | - | 0.12 | - | - | - | - | - |
| 2-Dec-92 | - | 0.38 | - | - | - | - | - |
| 2-Mar-93 | - | 0.34 | - | - | - | - | - |
| 21-Jun-93 | - | 0.33 | - | - | - | - | - |
| 26-Aug-93 | - | 0.39 | - | - | - | - | - |
| 13-Dec-93 | - | 0.33 | <0.002 | - | - | - | - |
| 23-Mar-94 | - | 0.33 | <0.002 | - | - | - | - |
| 7-Jun-94 | - | 0.41 | <0.002 | - | - | - | - |
| 31-Aug-94 | 0.005 | 0.31 | <0.001 | - | 0.37 | 0.007 | <0.005 |
| 20-Sep-94 | - | 0.33 | 0.016 | - | - | - | - |
| 16-Jan-95 | - | 0.33 | 0.008 | - | - | - | - |
| 20-Mar-95 | - | 0.36 | 0.009 | - | - | - | - |
| 21-Jun-95 | - | 0.35 | 0.002 | - | - | - | - |
| 3-Oct-95 | - | 0.37 | 0.01 | - | - | - | - |
| 5-Dec-95 | - | 0.37 | 0.01 | - | - | - | - |
| 6-Mar-96 | <0.004 | 0.31 | <0.002 | <0.004 | - | <0.004 | 0.02 |
| 5-Jun-96 | 0.01 | 0.902 | <0.005 | 0.01 | - | 0.01 | <0.01 |
| 4-Sep-96 | - | 0.381 | <0.005 | - | - | - | 0.005 |
| 17-Dec-96 | - | 0.36 | - | - | - | - | <0.01 |
| 19-Mar-97 | - | 0.33 | - | - | - | - | <0.01 |
| 17-Jun-97 | - | 0.31 | - | - | - | - | 0.02 |
| 23-Sep-97 | - | 0.32 | - | - | - | - | <0.01 |
| 10-Dec-97 | - | 0.32 | - | - | - | - | <0.02 |
| 19-Mar-98 | - | 0.32 | - | - | - | - | <0.02 |
| 23-Jun-98 | - | 0.3 | - | <0.1 | - | <0.100 | <0.02 |
| 9-Sep-98 | - | 0.36 | - | - | - | - | <0.01 |
| 15-Dec-98 | - | 0.39 | - | - | - | - | <0.01 |
| 16-Mar-99 | - | 0.36 | - | - | - | - | <0.01 |
| 15-Jun-99 | 0.03 | 0.38 | - | 0.03 | - | 0.03 | 0.05 |
| 20-Sep-99 | <0.03 | 0.62 | - | <0.03 | - | - | <0.01 |
| 15-Dec-99 | <0.04 | 0.39 | - | <0.04 | - | <0.04 | 0.04 |
| 21-Feb-00 | - | - | - | - | - | - | - |
| 22-Mar-00 | <0.04 | 0.37 | - | <0.04 | - | <0.04 | <0.01 |
| 7-Jun-00 | <0.04 | 0.29 | - | <0.04 | - | <0.04 | <0.01 |
| 6-Sep-00 | - | 0.38 | - | <0.04 | - | <0.04 | <0.01 |
| 6-Dec-00 | <0.04 | 0.36 | - | <0.04 | - | <0.040 | <0.01 |
| 13-Mar-01 | <0.04 | 0.35 | - | <0.04 | - | <0.040 | <0.01 |
| 19-Jun-01 | - | 0.35 | - | <0.04 | - | <0.040 | <0.01 |
| 11-Sep-01 | - | 0.38 | - | <0.04 | - | - | <0.01 |
| 18-Dec-01 | 0.08 | 0.35 | - | 0.08 | - | 0.08 | <0.01 |
| 12-Mar-02 | - | 0.42 | - | <0.10 | - | <0.100 | <0.01 |

| Date | DRP | Nitrate-N | Nitrite-N | Phosphate | TN | TP | Ammonia-N |
|---|---|---|---|---|---|---|---|
| 12-Jun-02 | - | 0.4 | - | <0.10 | - | <0.100 | <0.01 |
| 3-Sep-02 | - | 0.41 | - | <0.10 | - | <0.100 | <0.01 |
| 3-Dec-02 | - | 0.35 | - | <0.05 | - | <0.050 | <0.01 |
| 24-Mar-03 | <0.05 | 0.37 | - | <0.05 | - | - | <0.01 |
| 18-Jun-03 | <0.05 | 0.38 | - | <0.05 | - | <0.050 | 0.04 |
| 23-Sep-03 | <0.05 | 0.51 | - | <0.05 | - | <0.050 | 0.03 |
| 10-Dec-03 | - | 0.41 | - | - | - | - | 0.01 |
| 17-Mar-04 | - | 0.41 | - | - | - | - | <0.01 |
| 15-Jun-04 | - | 0.35 | - | - | - | - | <0.01 |
| 21-Sep-04 | - | 0.34 | - | - | - | - | <0.01 |
| 13-Dec-04 | - | 0.33 | - | - | - | - | <0.01 |
| 15-Mar-05 | <0.004 | 0.38 | - | <0.004 | - | - | <0.01 |
| 15-Jun-05 | - | 0.36 | - | - | - | - | <0.01 |
| 13-Sep-05 | - | 0.34 | - | - | - | - | <0.01 |
| 12-Dec-05 | - | 0.36 | - | - | - | - | <0.01 |
| 21-Mar-06 | 0.007 | 0.4 | - | 0.007 | - | - | <0.01 |
| 12-Apr-06 | - | 0.42 | - | - | - | - | - |
| 20-Jun-06 | - | 0.38 | - | - | - | - | <0.01 |
| 5-Sep-06 | - | 0.42 | - | - | - | - | <0.01 |
| 4-Dec-06 | - | 0.42 | - | - | - | - | <0.01 |
| 6-Mar-07 | <0.004 | 0.41 | - | <0.004 | - | - | <0.01 |
| 3-Jun-07 | - | 0.41 | - | - | - | - | - |
| 12-Jun-07 | - | 0.32 | - | - | - | - | <0.01 |
| 4-Sep-07 | - | 0.45 | - | - | - | - | <0.01 |
| 4-Dec-07 | - | 0.8 | - | - | - | - | <0.01 |
| 6-Dec-07 | - | 0.32 | - | - | - | - | - |
| 4-Mar-08 | <0.004000 | 0.91 | - | <0.004 | - | - | 0.02 |
| 10-Jun-08 | - | 0.39 | - | - | - | - | <0.01 |
| 22-Sep-08 | - | 0.49 | - | - | - | - | - |
| 15-Dec-08 | - | 0.92 | - | - | - | - | <0.01 |
| 10-Mar-09 | 0.004 | 0.43 | - | 0.004 | - | - | <0.01 |
| 16-Jun-09 | - | 0.43 | - | - | - | - | <0.01 |
| 15-Sep-09 | - | 0.45 | - | - | - | - | <0.01 |
| 8-Dec-09 | - | 0.46 | - | - | - | - | <0.01 |
| 23-Mar-10 | 0.026 | 0.44 | - | 0.026 | - | - | <0.01 |
| 22-Jun-10 | - | 0.43 | - | - | - | - | <0.01 |
| 22-Sep-10 | - | 0.45 | - | - | - | - | <0.01 |
| 7-Dec-10 | - | 0.44 | - | - | - | - | 0.03 |
| 21-Mar-11 | <0.004 | 0.43 | - | <0.004 | - | - | <0.01 |
| 15-Jun-11 | - | 0.44 | - | - | - | - | <0.01 |
| 16-Sep-11 | - | 0.49 | - | - | - | - | 0.03 |
| 6-Dec-11 | - | 0.44 | - | - | - | - | 0.02 |
| 5-Mar-12 | 0.01 | 0.44 | - | 0.01 | - | - | 0.05 |
| 15-Jun-12 | - | 0.45 | - | - | - | - | <0.01 |
| 4-Oct-12 | - | 0.48 | - | - | - | - | 0.05 |
| 13-Dec-12 | - | 0.47 | - | - | - | - | 0.004 |
| 26-Mar-13 | 0.01 | 0.44 | - | 0.01 | - | - | 0.04 |
| 6-Jun-13 | - | 0.43 | - | - | - | - | 0.008 |
| 18-Sep-13 | - | 0.45 | - | - | - | - | <0.003 |
| 27-Mar-14 | 0.0047 | 0.46 | <0.002 | - | - | - | <0.005 |
| 5-Dec-14 | - | 0.36 | - | - | - | - | 0.004 |

**Appendix 2** Possible explanations for unusually low and high nitrate-N concentrations in the waters of Waikoropupu Springs (email to Joseph Thomas (TDC) from Magali Moreau-Fournier, GNS dated 14 September 2013).

**From:** Magali Moreau-Fournier [mailto:M.Moreau-Fournier@gns.cri.nz]
**Sent:** Saturday, 14 September 2013 1:28 p.m.
**To:** Joseph Thomas
**Subject:** NO3-N at NGMP site 7

Hi Joseph,

Thanks for your enquiry regarding nitrate-nitrogen ($NO_3$-N) concentrations at the Waikoropupu main spring (GGW site ID 7).

The spring has been quarterly monitored from November 1990 to present. All groundwater chemical analyses exhibit an acceptable charge balance error (acceptability threshold is 5%; APHA/AWWA/WEF, 2005).

$NO_3$-N concentrations at this site range from 0.12mg/l to 0.92mg/l, with a median of 0.38 mg/l (median absolute deviation of 0.04mg/l) as shown in Figure 1. A statistically significant increasing trend of +0.006 mg/l per year has been detected (Mann-Kendall test, p-value<0.005; outliers excluded for trend magnitude calculation). The $NO_3$-N median concentration at this site is well below the corresponding national median for groundwater of 1.3mg/l (Ministry for the Environment, 2007) and the maximum acceptable value for drinking water of 11.5mg/l (Ministry of Health, 2005)

The following outliers were identified (concentrations below or above 4 times the median absolute deviation, Figure 1):

- Consistent low $NO_3$-N concentrations (<0.22mg/l) from 1990 to September 1992.
- Sporadic high $NO_3$-N concentrations (>0.54mg/l) for water samples collected on the following days: 5/06/1996, 20/09/1999, 4/12/2007, 4/03/2008 and 15/12/2008).

Low $NO_3$-N concentrations may be linked to the state of oxygenation of groundwater. Nitrogen is found in the form of nitrate-nitrogen in oxygenated groundwater, whereas in reduced groundwater, nitrogen is found as ammonium-nitrogen ($NH_4$-N) (Ministry for the Environment, 2007). At this site ammonium-nitrogen ($NH_4$-N) was monitored only from 6/03/1996. There is no information in the GGW database on the laboratory or the analytical method used for determination of $NO_3$-N concentration prior to June 1999. As NH4-N was not measured in the early 1990ies, it is not possible to say if the nitrogen form of N changed due to more reducing conditions, however, this would be unlikely due to the hydrology of the site and there is no indication of such change in redox from the iron (Fe) and manganese (Mn) results over this time period (Figure 2). There is only one Mn concentration measurement above the detection limit over the entire monitoring period (0.006 mg/l on 23/09/2003; Figure 2). Occasional Fe measurements above the detection limit occurred over the entire monitoring period (0.1 mg/l). The variable detection limits in the Fe and Mn datasets may reflect changes in either laboratory used or analytical method, it may also be explained by analytical improvement of a method with time. Results measured at the detection limit may fall within analytical errors.

The low $NO_3$-N concentrations observed in the early 1990s are odd, although consistent until September 1992. It is possible that these low concentrations are linked to the sampling collection method (the national standard protocol for sampling groundwater was not developed until 2006; Daughney et al. 2006), or the analytical method or laboratory. The high concentrations are isolated events. Neither the low or high $NO_3$-N outlier concentrations are consistently linked with either high or low concentrations in the other major ions (Figure 3).

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Kind regards,

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