NIWA
Taihoro Nukurangi

Sustainability of Te Waikoropupu Springs' aquifer ecosystems

Prepared for Andrew Yuill

March 2015

Corrected July 2016

Prepared by:
Graham Fenwick

For any information regarding this report please contact:
Graham Fenwick
Principal Scientist
Biodiversity
+64 3 343 8051
graham.fenwick@niwa.co.nz

National Institute of Water & Atmospheric Research Ltd
PO Box 8602
Riccarton
Christchurch 8011

Phone +64 3 348 8987

NIWA CLIENT REPORT No: CHC2015-020
Report date: March 2015
NIWA Project:

Quality Assurance Statement		
	Reviewed by:	Scott Larned
	Approved for release by:	Clive Howard-Williams

Contents

Tables

1 Introduction

1.1 Background

Te Waikoropupu Springs emerge from a complex of aquifers[1] (for convenience here called the Te Waikoropupu Springs aquifer complex (WaiSAC) and, because of the extremely high natural, ecological, biodiversity, spiritual, cultural and economic values associated with this remarkable feature, work towards ensuring that their values are sustained has commenced. This initiative seeks a Water Conservation Order to sustainably manage the springs themselves, plus the surface and ground waters that supply and sustain them.

NIWA was requested to recommend numerical water quality limits for water in these aquifers, based on a desk-top evaluation of available information on groundwater ecosystem responses to key water quality variables.

1.2 Scope and limitations

This report provides recommendations based on a preliminary analysis of scant data and available information, and its recommendations must be regarded as tentative. A more rigorous water quality guideline and limit setting process, ideally backed by a more substantial body of research information, is essential to review and revise these recommendations as soon as practical.

The approach taken here was to review the limited available information on stygofauna tolerances to a few key water quality variables and compare this toxicity information with the relevant concentrations in New Zealand's surface water quality guidelines (i.e., the ANZECC guidelines ((ANZECC & ARMCANZ 2000)). Effects of water quality on aquifer microbes, notably those comprising biofilms, are not considered here, despite their importance in aquifer ecological functioning and the established relationships between water quality and both suspended and attached (i.e., non-biofilm and biofilm, respectively) bacterial community composition (Flynn et al. 2013; Sirisena et al. 2014).

Two key variables, organic carbon and dissolved oxygen, are not covered by the ANZECC guidelines, but are essential for most groundwater ecosystems. Their concentrations vary naturally in groundwaters, as well as being influenced indirectly via human activities.

2 Groundwater quality

Water quality generally is a measure of the extent to which water and the substances that it contains is fit for purpose, either for human purposes and/or for natural ecosystem functioning. Several categories of substances may be involved in water quality, such as toxicants (e.g., metals and other chemicals that are toxic in low concentrations), others that are resources at low concentrations but toxic at high concentrations (e.g., nitrate and other nutrients), and other resources which are essential for life and may interact with each other (e.g., dissolved oxygen and dissolved organic carbon).

The quality of New Zealand's surface freshwaters is managed in large part using the ANZECC guidelines (ANZECC & ARMCANZ 2000). These guidelines were intended "to achieve the sustainable use of Australia's and New Zealand's water resources by protecting and enhancing their quality while

[1] Te Waikoropupu Springs water is considered to originate from at least three aquifers, the Arthur Marble, Takaka Limestone and Takaka Valley Unconfined Gravel aquifers (Stewart & Williams 1983). This has significant implications for managing the springs' water, but these complexities are beyond the scope of this report.

maintaining economic and social development" (ANZECC & ARMCANZ 2000: xii), indicating that any guideline concentrations or limits for protecting a high conservation value surface water body should be more stringent than the ANZECC guideline values. The guidelines are, however, the only available and comprehensive set of research-based and ecologically meaningful concentrations of several important potential toxicants for surface freshwaters.

The water quality requirements for sustaining groundwater ecosystems and their biodiversity components are poorly researched and poorly understood internationally and in New Zealand. This applies even for the small set of key variables discussed here: organic carbon, dissolved oxygen, nitrate and ammonia. Water quality within the WaiSAC is poorly defined, and few relevant data are available. Thus, any limits for water quality variables to sustain the WaiSAC and its ecosystem must be very tentative, and regarded as very preliminary until: (a) more comprehensive monitoring data on of all relevant water quality parameters are available, (b) a rigorous limits setting exercise can be completed, and (c) there is a much better understanding of the water quality requirements for sustaining groundwater ecosystems generally and for the WaiSAC in particular.

In the absence of the underpinning science outlined above, water quality guidelines for the proposed Water Conservation Order must be linked to the WCO's objective of sustaining the diverse values of Te Waikoropupu Springs. This means that any water quality guidelines or limits for the springs and associated aquifers should be based on historical and present water quality of the springs and of the contributing aquifers, tempered by any additional relevant scientific information. The 99% protection level concentrations provided within the ANZECC guidelines (see ANZECC & ARMCANZ 2000; Table 3.4.1) could provide interim default guidelines concentrations for groundwater in the absence of any other relevant information, but the numerous limitations of these guidelines identified within that report, and their uncertain applicability to groundwater ecosystems, must be considered.

The following discusses preliminary guidelines concentrations of four key attributes for the WaiSAC water, including some not included in the ANZEEC guidelines.

2.1 Organic carbon (no ANZEEC guideline concentration)

Organic carbon, as the primary food source for most groundwater organisms, varies seasonally and generally determines groundwater community composition and abundance (e.g., Baker 2000, Sinton 1984, Fenwick et al. 2004, Datry et al. 2005, Hancock & Boulton 2008). In dissolved or very fine particle forms (including in bacteria cells), it may be carried into the aquifer with inflowing water in the upper catchment or at any point along a catchment (Baker 2000; Jones 1995; Scarsbrook 2003). Most importantly, organic carbon also enters groundwater from overlying land use activities where it is incorporated into biofilms (Fenwick et al. 2004, Boulton et al. 2008, Hartland et al. 2011).

Biological activity in groundwater ecosystems is frequently limited by organic carbon availability (Baker 2000; Jones 1995). Many stygobitic[2] taxa are adapted to living in aquifers where food is scarce, with their metabolic (and reproductive) rates and oxygen requirements generally appreciably lower than equivalent epigean[3] or stygophilic[4] species (e.g., Spicer, 1998; Wilhelm et al. 2006). Increased organic carbon and food availability potentially cancels the competitive advantages of this stygobitic physiological adaptation, enabling stygophilic species with higher metabolic rates (and faster generation times) to displace the natural stygobitic community (assuming dissolved oxygen is

[2] Stygobite or stygobitic species: obligate or strictly subterranean aquatic inhabitants for the entire lives. Taxa: generally used here to mean a species, at times means some other taxonomic unit or grouping of organisms.
[3] Epigean: inhabiting surface waters.
[4] Stygophilic species or stygophile: inhabit both surface and subterranean aquatic environments, not constrained to either.

not limiting)(Wilhelm et al. 2006). Thus, while increased organic carbon supply increases abundances of some species, it may lead to other strictly stygobitic species and communities being displaced or even eliminated through competition by non-obligate stygophilic species, especially if other environmental factors (e.g., dissolved oxygen) change to suit the stygophiles (Datry et al. 2005). Such a shift in community composition occurred within a large coastal aquifer contaminated by treated wastewater (increased nitrate, biochemical oxidation demand, dissolved organic carbon) over 45 years, with one omnivorous species becoming the dominant, displacing others (including apparent extinction of one endemic stygobitic species)(Marsciopinto et al. 2006).

Community density increased with organic carbon enrichment in a New Zealand alluvial aquifer some 5 km from the nearest surface waters (Sinton 1984), but taxonomic resolution was insufficient to observe any associated changes in species richness. That study did report repeated significant kills of stygofauna at the most contaminated wells, apparently due to excessive organic carbon from effluent leading to anoxic conditions (Sinton 1984).

Stygofauna within karst cave systems appears similarly affected by organic carbon enrichment. For example, massive organic enrichment resulting from dumping sawdust into a cave exterminated the previously abundant and diverse stygofauna, biofilms >1 cm thick coated the gravel substrate, and huge populations of opportunistic species (tubificid worms and chironomid flies) developed (Culver 1992). Similar shifts in community composition in response to organic carbon enrichment are noted for several other SGDEs (e.g., Illife 1984).

Organic carbon concentrations tend to be higher closer to upper catchment recharge areas, than lower in the catchment (see Table 1) and some decrease in concentration with increasing depth in the aquifer seems likely. Some organic carbon hotspots associated with buried ancient wood or other organic material seem likely at any depth within many alluvial aquifers. Organic carbon concentrations also may vary over quite small distances and quite short time spans within alluvial aquifers. For example, dissolved organic carbon (DOC) varied from 1.5 to 24 mg/L seasonally over an eight-month period in an Austrian aquifer (2-6 m depth) (Gunatilaka 1994).

Some of the variability reported in these studies may be natural, and some does result from human activities. To date, there is no clear understanding of organic carbon concentrations or its natural variation in groundwaters completely unaffected by human activities. Organic carbon was optically undetectable in water emerging from the springs when measured twice (February 1993 and March 1995) (Davies-Colley & Smith 1995). There are no data on organic carbon concentrations elsewhere within the catchment and aquifer, but it must be generally very low for the organic carbon to be entirely consumed during the water's transit to the springs.

Table 1 lists reported organic carbon concentrations available from New Zealand research on aquifers. These values come from diverse measurements, some gathered over several years, others a single measurements. Perhaps the most relevant values are those from groundwater adjacent to the upper reaches of the Selwyn River, at a point where the river leaves less intensively farmed foothills to disappear into the aquifer that flows seaward under more intensively farmed plains. In our experience, organic carbon concentrations of up to 3-4 mg/L, in combination with moderate concentrations of dissolved oxygen (e.g., >4 mg/L) are associated with apparently healthy, functional alluvial groundwater ecosystems.

Clearly, organic carbon concentrations within the WaiSAC require urgent measurement to provide a meaningful background for guiding management of water quality at the springs. On-going

monitoring, especially to determine any seasonal variations and changes to these, are essential. This measurement and monitoring is likely to find different organic carbon concentrations at different points within each of the contributing aquifers and at different seasons at each point. Thus, it is inappropriate to suggest any initial guideline or limit concentrations for this variable, other than for at the springs water itself, where concentrations of dissolved organic carbon must remain undetectable to maintain the water's extreme clarity.

Table 1: Concentrations of organic carbon reported for New Zealand aquifers.

Organic carbon (mg/L)	Location	Contamination	Aquifer details	Source
undetectable	Te Waikoropupu Springs	Low; probably uncontaminated	Karst & alluvial (3 aquifers contribute)	Davies-Colley & Smith 1995
1.1-3.4	Templeton, Canterbury	Moderate	Alluvial aquifer c. 18 m to water table; control well	Fenwick & Wilson 1999
1.5-5.6	Templeton, Canterbury	Highly	Alluvial aquifer c. 18 m to water table; wastewater	Fenwick & Wilson 1999
8.1	Leeston, Canterbury	Moderate	Fine-grained alluvial aquifer, contaminated	Hartland et al. 2011
9.0-18.2	Leeston, Canterbury	Highly	Fine-grained alluvial aquifer, wastewater contaminated	Hartland et al. 2011
1.2 (n=4)	Selwyn River, Canterbury	Low (headwaters)	Alluvial aquifer riverine recharge zone	Williamson et al. 2012
0.7 (n=4)	Selwyn River, Canterbury	Moderate (lower reach)	Alluvial aquifer close to lowland river	Williamson et al. 2012
0.4 (n=4)	Lincoln, Canterbury	Moderate	Alluvial aquifer	Williamson et al. 2012
0.6-3.4 (n>20)	Selwyn River, Canterbury	Low (headwaters)	Alluvial aquifer riverine recharge zone	Larned et al. 2014
0.4-2.1 (n>20)	Selwyn River, Canterbury	Moderate (lower reach)	Alluvial aquifer close to lowland river	Larned et al. 2014

2.2 Dissolved oxygen (no ANZEEC guideline concentration)

Normally, unpolluted, gravel-bed stream water is close to 100% saturated with oxygen (i.e., c. 10 mg/L, depending on temperature (Davies-Colley & Wilcock 2004)), although natural processes and human impacts can deplete oxygen, especially where higher temperatures and/or organic carbon enrichment increase chemical and biological demand for oxygen beyond its replenishment rate. In aquifers, water flowing through the aquifer matrix often has minimal or no oxygenation from contact with air for long periods (weeks, months, years, decades). Consequently, alluvial aquifer waters tend

to contain less oxygen with increasing distance from their recharge zones and typically are 5-45% saturated (e.g., Danielopol et al. 2001; Hancock et al. 2005).

Oxygen is fundamental to aerobic organisms, including most stygofaunal invertebrates and especially crustaceans (Malard & Hervant 1999), and its availability can be the dominant, direct effect on stygofunal community composition and abundance (Mosslacher, Pospisil et al. 1996). Aerobic organisms take up and use oxygen for respiration, even at rest, although taxa differ in their oxygen consumption rates and ability to withstand reductions in dissolved oxygen availability. True stygobitic species consume less oxygen than their stygophilic and epigean counterparts (Spicer 1998; Mosslacher 2000; Wilheim, Taylor et al. 2006), frequently enabling survival at the lower (<3 mg/L) dissolved oxygen concentrations common in subterranean interstitial habitats (Malard & Hervant 1999). Under such hypoxic conditions (oxygen concentrations typically < 2-3 mg/L), some stygobites switch to anaerobic metabolism to fuel their energy needs (Hervant et al. 1996), although there is no clear evidence that any normally aerobic stygobitic species survives anoxia indefinitely. Others, such as some hyporheic amphipods, actively move towards and into higher dissolved oxygen concentrations, independent of flow direction (Henry and Danielopol 1999).

Any food or organic carbon enrichment that stimulates microbial activity may use much or all of the available dissolved oxygen (e.g., Baker et al. 2000). Stygofaunal communities increase in density in response to increased food (i.e., organic carbon) only if there is sufficient dissolved oxygen (Mösslacher & Notenboom 1999). Enrichment and bacterial stimulation without sufficient dissolved oxygen (perhaps due to reduced water flows or increased temperature) can lead to anoxia that kills much of the stygofauna (Sinton 1984; Boulton et al. 2008).

Field evidence of the effect of dissolved oxygen on community compositions and species abundances are generally confounded by other interacting environmental variables. For example, the stygofauna inhabiting wells generally closer to a river differed from that at more distant wells where the aquifer was shallower, contained less dissolved oxygen and transmissivity was lower (Dumas et al. 2001).

As with organic carbon, therefore, setting any limits for dissolved oxygen concentrations is complicated and requires a substantial body of research information, much of this specific to the WaiSAC. A cursory survey of readily available information on dissolved oxygen in New Zealand alluvial aquifers (Table 2) provides little guidance, except that Te Waikoropupu's water contains c. 6.5 mg/L of oxygen (at least in 1976). The only appropriate guideline is that the WaiSAC should be managed to ensure that water discharging from the springs contains at least 6.0 mg/L of dissolved oxygen. It is inappropriate to suggest any guideline levels for dissolved oxygen concentrations elsewhere within the WaiSAC in the absence of specific information on current dissolved oxygen concentrations within different parts of the aquifer and their relationships to spring water.

We note that dissolved oxygen is replenished primarily via recharge water and that as recharge declines, so too do water levels (depths below ground)(i.e., hydraulic head decreases) and dissolved oxygen concentrations. In particular, dissolved oxygen appears to become a critical factor at low aquifer levels when the hydraulic gradient is reduced and the rate of water replacement (containing more dissolved oxygen) is slowed. Thus, managing, water levels to ensure near natural velocities/flows through the aquifer matrix, in tandem with managing organic carbon concentrations within groundwater, seems likely to sustain higher dissolved oxygen concentrations within most aquifers.

Table 2: Dissolved oxygen concentrations for various New Zealand aquifers.

Dissolved oxygen mg/L	Location	Contamination	Aquifer details	Source
6.5	Te Waikoropupu Springs	None; natural?	Discharge from Arthur Marble Aquifer of	Michaelis 1976
6.4-8.1	Templeton, Canterbury	Moderate	Alluvial aquifer c. 18 m to water table; control well	Fenwick & Wilson 1999; Scarsbrook & Fenwick 2003
3.7-8.4	Templeton, Canterbury	Highly	Alluvial aquifer c. 18 m to water table; wastewater	Fenwick & Wilson 1999; Scarsbrook & Fenwick 2003
6.3-9.6	Waimakariri R, Canterbury	Low	Alluvial aquifer riverine recharge zone	Scarsbrook & Fenwick 2003
3.3-8.5	Hawkes Bay: Ngaruroro R.	Moderate	Riverine alluvial aquifer	Scarsbrook & Fenwick 2003
6.0-7.8	Hawkes Bay: Waipaua R.	Moderate	Riverine alluvial aquifer	Scarsbrook & Fenwick 2003
2.1–8.6 (n=3)	Selwyn River, Canterbury	Low (headwaters)	Alluvial aquifer riverine recharge zone	Williamson et al. 2012
1.52–4.73 (n=3)	Selwyn River, Canterbury	Moderate (lower reach)	Alluvial aquifer close to lowland river	Williamson et al. 2012
7.4 (n=4)	Lincoln, Canterbury	Moderate	Alluvial aquifer	Williamson et al. 2012
0.3-7.1	Selwyn River, Canterbury	Low (headwaters)	Alluvial aquifer riverine recharge zone	Larned et al. 2014
0.7-7.2	Selwyn River, Canterbury	Moderate (lower reach)	Alluvial aquifer close to lowland river	Larned et al. 2014

2.3 Nitrate

The nitrate[5] ion (NO_3^-) occurs naturally in the environment along with ammonium (NH_4^+) and nitrite (NO_2^-) in ionic form as the most common inorganic forms of nitrogen. Ammonium is usually converted (oxidised) to nitrite and nitrate by common aerobic bacteria when oxygen is present, even at low (1 mg/L) oxygen concentrations, so that nitrate predominates in aerobic aquatic environments (e.g., Camargo et al. 2005). Nitrate is removed from aquatic environments when taken up as an essential nutrient by plants or converted to nitrogen gas (N_2) by bacteria in anaerobic situations (and

[5] It is the concentration of nitrate ions (NO_3^-) that determines toxicity. However, toxic concentrations frequently are reported in terms of nitrate-nitrogen (NO_3-N), which can be converted to nitrate ion equivalent by multiplying by 4.43 (and the converse by multiplying by 0.23 to derive mg NO_3-/L)(after Hickey 2013: 8). Here, we follow the common approach of reporting toxicities as mg NO_3-N /L, but the difference in reporting unit makes no difference to toxicity (Hickey 2013: 8).

at anaerobic micro-sites within more generally aerobic environments). However, substantial additional nitrate enters many surface and groundwaters from human sources (e.g., agricultural runoff, municipal and industrial wastewaters, urban runoff), frequently increasing total dissolved nitrate concentrations substantially (e.g., Tidswell et al. 2012).

The primary concern over nitrate in the environment is due to its toxicity to humans, farm and domestic stock, and to aquatic invertebrates. In all cases, nitrate binds to the oxygen-carrying blood pigments (haemoglobin in humans and mammals, haemocyanin in many invertebrates), preventing these pigments from transporting oxygen to body tissues (Camargo et al. 2005). Nitrates also are implicated as potential carcinogens for humans, adding to concern about drinking nitrate contaminated water. Thus, nitrate is a high priority for resource management, especially for managing freshwaters.

Although there are few useful data on nitrate toxicities for groundwater invertebrates, equivalent information for surface water faunas provide useful guidelines. Nitrate increases in toxicity to aquatic animals with increasing concentrations and with exposure times, and may decrease with increasing body size, water salinity, and environmental adaptation (Camargo et al. 2005). Based several experiments and other results, a maximum nitrate (as nitrogen) concentration of 2.0 mg NO_3-N/L (or 8.86 mg NO_3^-/L) was recommended to protect sensitive surface water species during longer-term exposures (Kincheloe et al. 1979; Camargo et al. 2005).

The effects of nitrate on groundwater biofilms and stygofauna in situ are less clear. Amphipod crustaceans appear to be among the more sensitive of invertebrates and are especially relevant here because they dominate many groundwater communities.

In a detailed, expert review of all available data on nitrate toxicology for freshwaters and using the ANZECC (2000) and Environment Canada's methodology, Hickey & Martin (2009) recommended specific NO_3-N concentrations for high conservation/ecological value surface water ecosystems, slightly to moderately disturbed systems and for highly disturbed systems for Canterbury's freshwater environments. They noted, however, that the "datasets are particularly lacking in species which are known to be of high sensitivity to contaminants", especially "amphipods, mayflies and some native fish species that are more sensitive to some chemical contaminants than the standard international test species" (Hickey & Martin 2009: 19). A subsequent update of that review for New Zealand lakes and rivers (not groundwaters) included several new acute and chronic data (including for a native mayfly and juveniles of an endemic fish), partially addressing the earlier information gaps (Hickey 2013). It recommended average long-term exposure concentrations of 1.0 mg NO_3-N/L to protect high conservation value ecosystems (concentrations at which no effect was observed; termed Grading) and threshold effect (termed Surveillance) concentrations of 1.5 mg NO_3-N/L for managing seasonal (up to three months) maximum concentrations (Table 3).

Table 3: Guideline concentrations for nitrate (reported as NO_3-N concentrations) to protect surface water species. Grading guidelines are based on species' no observed effect concentrations, and Surveillance guidelines based on threshold effect concentrations. From Hickey (2013): 16 (Table 5.1).

Guideline Type	Grading Nitrate concentration (mg NO_3-N /L)	Surveillance Nitrate concentration (mg NO_3-N /L)	Description of Management Class
Chronic – high conservation value systems (99% protection)	1.0	1.5	Pristine environment with high biodiversity and conservation values.
Chronic – slightly to moderately disturbed systems (95% protection)	**2.4**	**3.5**	**Environments which are subject to a range of disturbances from human activities, but with minor effects.**
Chronic – highly disturbed systems (90% protection)	3.8	5.6	Environments which have naturally seasonally elevated concentrations for significant periods of the year (1-3 months).
Chronic – highly disturbed systems (80% protection)	6.9	9.8	Environment which are measurably degraded and which have seasonally elevated concentrations for significant periods of the year (1-3 months).
Acute	20	30	Environments which are significantly degraded. Probable chronic effects on multiple species.
Method of comparison	Annual median	Annual 95th percentile	

This is the best available compilation of relevant toxicity data for freshwater and groundwater organisms. However, it noted continuing significant knowledge gaps in:"(i) the adequacy of native fish and invertebrate [nitrate toxicity] data for surface waters; (ii) absence of [data on] hyporheic species; and (iii) [nitrate] toxicity modification in relation to water mineral content (measured by hardness)" (Hickey 2013: 25). Hickey (2013) also noted the need for field validation of these results and the potential ameliorating effects of water hardness and chloride ion concentrations. Further important information gaps are (i) the sensitivities of stygobitic fauna and biofilms to nitrate, (ii) how these sensitivities change with other human-induced stresses, especially dissolved oxygen, and (iii) nitrate concentrations for sublethal effects that interfere with biodiversity and ecosystem functioning are poorly understood, particularly for stygobites.

Recent reports indicate concentrations of NO_3-N[6] mostly within 0.0-2.0 mg/L closer to the springs, concentrations between 2.1 and 4.0 mg NO_3-N /L further up the catchment and values exceeding 4.1 mg NO_3-N /L at 3-4 monitoring points upstream of the springs (Stevens 2010). Water in the springs was reported to contain 0.31-0.32 mg/L (0.31-0.32 g/m^3) of NO_3-N in 1976 (Michaelis 1976), with

[6] Stevens (2010) reported nitrate concentrations in units of mg/L-N. We assume that these units are mg NO_3-N/L.

recent nitrate concentrations reported as “typically <0.4 mg/L-N” (median 0.36 mg/L; Stevens 2010: 31).

Based simply on Hickey’s (2013) recommendations, his chronic-high conservation value of 1.0 mg NO_3-N/L could be regarded as an upper limit, as an interim measure. However, because present concentrations are less than half this value and historical data indicate significant increases since the 1970s, the aquifers and catchments should be managed to ensure that NO_3-N concentrations in spring water do not exceed 0.4 mg NO_3-N/L in order to protect the springs’ high conservation values.

2.4 Ammonia

Under anaerobic conditions, nitrate is reduced to ammonium (NH_4^+), which persists in equilibrium with unionised ammonia (NH_3) (Close et al. 2001). Ammonia is an important and highly toxic contaminant, whereas ammonium (NH_4^+) is largely inert (Russo 1985; Prenter et al. 2004), however the two forms exist in a dynamic equilibrium influenced by temperature and pH (Emerson, Lund et al. 1975). At lowest water levels and/or with excessive organic carbon loadings when dissolved oxygen concentrations are very low (i.e., hypoxic conditions) and especially at higher pH (>9.2) and temperature, ammonia concentrations in groundwater can threaten groundwater ecosystems.

Ammonia (NH_3) is toxic to freshwater invertebrates at low concentrations. For example, 50% of individuals of three freshwater amphipod species died after exposure to 0.36, 1.16 and 1.54 mg NH_3/L, with sublethal effects (disruption of mating) occurring at concentrations as low as 0.12 and 1.23 mg/L (Prenter et al. 2004). Another investigation of amphipods reported that 50% of individuals died after 96 h exposed to 0.71 mg NH_3/L and after 21 hours for a concentration of 6 mg NH_3/L (McCahon, Poulton et al. 1991), comparable to 50% mortality after 27 h exposure to 3 mg NH_3/L from another study (Williams, Green et al. 1986).

Ammonia concentrations reported for Te Waikoropupu Springs (as NH_3-N) were 0.00026 mg/L in the 1970s (estimated from Michaelis’s (1976) 0.04 mg/L NH_4-N using an on-line calculator) and more recently reported to be 0.0-0.05 mg/L, with higher concentrations in nearby groundwater (Stevens 2010). These values and available information on toxicities of ammonia indicate that WaiSAC water should be managed to maintain ammonia concentrations below 0.05 mg/L and perhaps substantially lower. Certainly, the ANZECC trigger value of 0.32 mg/L NH_3 for protecting 99% of species seems inappropriate for Te Waikoropupu springs water and the WaiSAC generally.

3 Conclusions

The guideline concentrations for the four substances discussed here must be regarded as tentative because they are based on a review of a very small body of empirical information. A more rigorous and comprehensive approach is highly desirable, but there is scant information on toxicities, tolerances and sublethal effects for groundwater ecosystems, including biofilms, and specifically for New Zealand or WaiSAC stygofauna. For these reasons, refining these suggested limits will require significant time and other resources.

4 Acknowledgements

Sincere thanks to Scott Larned and Clive Howard-Williams for their critical reviews of this report and for their several suggestions that improved the report’s rigour and helped to clarify some key issues. Thanks also to Roger Young (Cawthron Institute) for identifying my error in reporting nitrate-nitrogen concentrations from Michaelis (1976)(now corrected on p. 12).

5 References

Australian and New Zealand Environment and Conservation Council, Agriculture and Resource Management Council of Australia and New Zealand. 2000. Australian and New Zealand guidelines for fresh and marine water quality. Volume 2, Aquatic ecosystems. 678 pp. http://www.environment.gov.au/water/quality/publications/australian-and-new-zealand-guidelines-fresh-marine-water-quality-volume-2

Baker, M.A., H.M. Valett, and C.N. Dahm. (2000). Organic carbon supply and metabolism in a shallow groundwater ecosystem. Ecology 81(11): p. 3133-3148.

Boulton, A.J., Fenwick, G.D., Hancock, P.J., Harvey, M.S. (2008). Biodiversity, functional roles and ecosystem services of groundwater invertebrates. Invertebrate Systematics, 22(2): 103-116. 10.1071/is07024

Camargo, J.A., A. Alonso, and A. Salamanca. (2005). Nitrate toxicity to aquatic animals: a review with new data for freshwater invertebrates. Chemosphere 58(9): p. 1255–1267.

Close, M.E., Rosen, M.R., Smith, V.R. (2001). Fate and transport of nitrate and pesticides in New Zealand's aquifers. In: M.R. Rosen & P.A. White (Eds). Groundwaters of New Zealand. New Zealand Hydrological Society, Wellington, New Zealand: 185-220.

Culver, D.C., W.K. Jones, J.R. Holsinger. (1992). Biological and hydrological investigation of the Cedars, Lee County, Virginia, an ecologically significant ad threatened karst area, in Proceedings of the first international conference on groundwater ecology, J.A. Stanford and J.J. Simons, Editors. American Water Resources Association: Bethesda, Maryland. p. 281-290.

Danielopol, D., P. Pospisil, J. Dreher. (2001). Structure and functioning of ghroundwater ecosystems in a Danube wetland at Vienna, in Groundwater ecology: a tool for management of water resources, C. Griebler, et al., Editors. Office for Official Publications of the European Communities: Luxembourg. p. 121-141.

Datry, T., F. Malard, J. Gibert. (2005). Response of invertebrate assemblages to increased groudnwater recharge rates in a phreatic aquifer. Journal of the North American Benthological Society 24(3): p. 461-477.

Davies-Colley, R.J.; Smith, D.G. (1995). Optically pure waters in Waikoropupu ('Pupu') Springs, Nelson, New Zealand. New Zealand Journal of Marine and Freshwater Research 29(2): 251-256, DOI: 10.1080/00288330.1995.9516658

Davies-Colley, R., B. Wilcock. (2004). Water quality and chemistry in running waters, in Freshwaters of New Zealand, J. Harding, et al., Editors. New Zealand Hydrological Society Inc. New Zealand Limnological Society Inc.: Christchurch, New Zealand. p. 11.1-11.17.

Di Lorenzo, T., Galassi, D.M.P. (2013). Agricultural impact on Mediterranean alluvial aquifers: do groundwater communities respond? Fundamental and Applied Limnology, 182(4): 271-282. 10.1127/1863-9135/2013/0398

Dumas, P., Bou, C., Gibert, J. (2001). Groundwater macrocrustaceans as natural indicators of the Ariege alluvial aquifer. International Review of Hydrobiology, 86(6): 619-633.

Dumas, P., Lescher-Moutoue, F. (2001). Cyclopoid distribution in an agricuturally impacted alluvial aquifer. Archiv Fur Hydrobiologie, 150(3): 511-528.

Emerson, K., Lund, R.E., Thurston, R.V., Russo, R.C. (1975). Aqueous ammonia equilibrium calculations: effect of pH and temperature. Journal of the Fisheries Research Board of Canada, 32: 2379-2383.

Fenwick, G.D., Thorpe, H., White, P.A. (2004). Groundwater systems. In: J. Harding, C. Pearson & B. Sorrell (Eds). Freshwaters of New Zealand. New Zealand Hydrological Society Inc & New Zealand Limnological Society Inc, Christchurch: 29.21-29.18.

Flynn, T.M., Sanford, R.A., Ryu, H., Bethke, C.M., Levine, A.D., Ashbolt, N.J., Domingo, J.W.S. (2013) Functional microbial diversity explains groundwater chemistry in a pristine aquifer. Bmc Microbiology, 13.

Griebler, C. and T. Lueders. (2009). Microbial biodiversity in groundwater ecosystems. Freshwater Biology 54(4): p. 649-677.

Gunatilaka, A., J. Dreher, A. Richter. (1994). Dissolved organic carbon dynamics in a groundwater environment. Internationale Vereinigung fur Theoretische und Angewandte Limnologie Verhandlungen 25(3): p. 1420-1425.

Hancock, P.J., A.J. Boulton. (2008). Stygofauna biodiversity and endemism in four alluvial aquifers in eastern Australia. Invertebrate Systematics 22(2): p. 117-126.

Hancock, P.J., A.J. Boulton, W.F. Humphreys. (2005). Aquifers and hyporheic zones: Towards an ecological understanding of groundwater. Hydrogeology Journal 13(1): p. 98-111.

Hartland, A., Fenwick, G.D., Bury, S.J. (2011). Tracing sewage-derived organic matter into a shallow groundwater food web using stable isotope and fluorescence signatures. Marine and Freshwater Research, 62(2): 119-129. 10.1071/mf10110

Henry, K.S., Danielopol, D.L. (1999). Oxygen dependent habitat selection in surface and hyporheic environments by Gammarus roeseli Gervais (Crustacea, Amphipoda): experimental evidence. Hydrobiologia, 390: 51-60.
http://download.springer.com/static/pdf/602/art%253A10.1023%252FA%253A1003541300460.pdf?auth66=1409447271_351828c78ffc85ff52abb8f717ffc960&ext=.pdf

Hervant, F., et al. (1996). Behavioral, ventilatory, and metabolic responses of the hypogean amphipod Niphargus virei and the epigean isopod Asellus aquaticus to severe hypoxia and subsequent recovery. Physiological Zoology 11(1): p. 1277-1300.

Hickey, C.W. (2013). Updating nitrate toxicity effects on freshwater aquatic species, in NIWA Client Report National Institute of Water & Atmospheric Research: Hamilton, New Zealand. p. 1-39.

Hickey, C.W., M.L. Martin. (2009). A review of nitrate toxicity to freshwater aquatic species. Environment Canterbury. p. 1-46.

Illife, T.M. and T.D. Jickells. (1984). Organic pollution of an inland marine cave from Bermuda. Marine Environmental Research 12: p. 173-189.

Jones Jr, J.B. (1995). Factors controlling hyporheic respiration in a desert stream. Freshwater Biology 34: p. 91-99.

Kincheloe, J.W., G.A. Wedemeyer, D.L. Koch. (1979). Tolerance of developing salmonid eggs and fry to nitrate exposure. Bulletin of Environmental Contamination and Toxicology 23(1): p. 575-578.

Larned, S.T., M.J. Unwin, and N.C. Boustead. (2014). Ecological dynamics in the riverine aquifers of a gaining and losing river. Freshwater Science 34(1): p. 1-19.

Malard, F., F. Hervant. (1999). Oxygen supply and the adaptations of animals in groundwater. Freshwater Biology 41(1): p. 1-30.

Masciopinto, C., et al. (2006). Stygofauna abundance and distribution in the fissures and caves of the Nardo (southern Italy) fractured aquifer subject to reclaimed water injections. Geomicrobiology Journal 23(5): p. 267-278.

McCahon, C.P., Poulton, M.J., Thomas, P.C., Xu, Q., Pascoe, D., Turner, C. (1991). Lethal and sub-lethal toxicity of field simulated farm waste epeisodes to several freshwater invertebrate species. Water Research, 25(6): 661-667. http://ac.els-cdn.com/004313549190041N/1-s2.0-004313549190041N-main.pdf?_tid=840db6ce-28df-11e4-9b6c-00000aacb35e&acdnat=1408590298_abb77e1b9aab5799cf3dfd92e4fe6ce9

Michaelis, F.B. (1976). Physico-chemical features of Pupu Springs. New Zealand Journal of Marine and Freshwater Research 10(4): 613-628.

Ministry for the Environment. 2007. Proposed National Environmental Standard for Sources of Human Drinking-water Resource Management Act Section 32 Analysis of the costs and benefits. Report ME number: 798, 49 pp. http://www.mfe.govt.nz/sites/default/files/nes-drinking-water-section-32-mar07.pdf

Mosslacher, F. (2000). Sensitivity of goundwater and surface water crustaceans to chemical pollutants and hypoxia: implications for pollution management. Archiv fur Hydrobiologie 149(1): p. 51-66.

Mösslacher, F., J. Notenboom. (1999). Groundwater biomonitoring. Environmental Science Forum 96: p. 119-140.

Mosslacher, F., Pospisil, P., Dreher, J. (1996). A groundwater ecosystem study in the "Lobau" wetland (Vienna), reflecting the interactions between surface water and groundwater. Archiv fuer Hydrobiologie Supplement, 113(1-4): 451-455.

Prenter, J., MacNeil, C., Dick, J.T.A., Riddell, G.E., Dunn, A.M. (2004). Lethal and sublethal toxicity of ammonia to native, invasive, and parasitised freshwater amphipods. Water Research, 38(12): 2847-2850. http://dx.doi.org/10.1016/j.watres.2004.03.042

Russo, R.C. (1985). Ammonia, nitrite and nitrate. In: G.M. Rand & S.R. Petrocelli (Eds). Fundamentals of aquatic toxicology: methods and applications. Hemisphere publishing Corporation, London: 455-471.

Scarsbrook, M.R. and G.D. Fenwick. (2003). Preliminary assessment of crustacean distribution patterns in New Zealand groundwater aquifers. New Zealand Journal of Marine and Freshwater Research 37(2): p. 405-413.

Sinton, L.W. (1984). The macroinvertebrates in a sewage-polluted aquifer. Hydrobiologia, 119(3): 161-169. 10.1007/BF00015207

Sirisena, K.A.; Daughney, C.J., Moreau, M., Ryan, K.G., Chambers, G.K. (2014). Relationships between molecular bacterial diversity and chemistry of groundwater in the Wairarapa Valley, New Zealand, New Zealand Journal of Marine and Freshwater Research, DOI: 10.1080/00288330.2014.923921

Spicer, J.I. (1998). Is the reduced metabolism of hypogean amphipods solely a result of reduced food? Hydrobiologia 377: 201-204.

Stevens, G. (2010). Groundwater quality in Tasman District: State of the Environment Report. Tasman District Council Ref: R10003. 53 pp.

Stewart, M.K., Williams, P.W. (1981). Environmental isotopes in New Zealand hydrology 3 Isotope hydrology of the Waikoropupu Springs and Takaka River, northwest Nelson. New Zealand Journal of Science 24: 323-337.

Tidswell, S., Conwell, C., Milne, J.R. (2012). Groundwater quality in the Wellington region: state and trends. Greater Wellington Regional Council, GW/EMI-T-12/140: 1-122. http://www.gw.govt.nz/assets/Our-Environment/Environmental-monitoring/Environmental-Reporting/Groundwater-Quality-SoE-report.pdf

Wilheim, F.M., Taylor, S.J., Adams, G.L. (2006). Comparison of routine metabolic rates of the stygobite, Gammarus acherondytes (Amphipoda: Gammaridae) and the stygophile, Gammarus trogolphilus. Freshwater Biology, 51: 1162-1174. 10.1111/j.1365-2427.2006.01564.x

Williams, K.A., Green, D.W.J., Passcoe, D. (1986). Studies on the acute toxicity of pollutants to freshwater macroinvertebrates. III: Ammoni. Archiv Fur Hydrobiologie, 106(1): 61-70.

Williamson, W.M., et al. (2012). Groundwater biofilm dynamics grown in situ along a nutrient gradient. Ground Water 50(5): p. 690-703.

Wilson, G.D.F. and G.D. Fenwick. (1999). Taxonomy and ecology of Phreatoicus typicus Chilton, 1883 (Crustacea, Isopoda, Phreatoicidae). Journal of the Royal Society of New Zealand 29(1): p. 41-64.