

Memorandum

Subject:	Hardness and Nitrate toxicity – site-specific guidelines for sp	ring-fed str	eams in the Waimea and
Copy:			
From:	Chris Hickey – NIWA	Our Ref:	HSJ15201
То:	Joseph Thomas, Tasman District Council	Date:	19 May 2015

Motupipi river catchments and Waikoropupu Springs

Background

Tasman District Council (TDC) engaged NIWA to provide site-specific nitrate toxicity guidelines for spring-fed streams in the Waimea and Motupipi river catchments Waikoropupu ('Pupu') Springs.

Nitrate standards for freshwaters have recently been legislated as part of the National Policy Statement for Freshwater Management (MfE 2014) and are referred to as National Objectives Framework (NOF) standards. The NOF nitrate standards were based on recently updated nitrate water quality guidelines (Hickey 2013a). They have annual median and annual 95th percentile limits which are designed to apply to water management units (WMUs). The two-number system was designed to allow for the known seasonal variation in nitrate concentrations and provide ecosystem protection from elevated concentrations. The more sensitive of the two nitrate standards determines the attribute band for a particular WMU.

The nitrate-N guidelines which formed the basis of the NOF standards were designed to be conservative, being based on long-term (chronic) toxicity tests performed in high water quality and low hardness water – which would be expected to result in the highest nitrate toxicity (Hickey 2013a). Notably, a number of studies have identified water hardness as a factor affecting both acute and chronic toxicity in some species. The results of those studies showed decreasing toxicity as water hardness increased. The mechanism for this effect is presently unknown so no algorithms were included in the recently updated Environment Canada guidelines to adjust for water quality factors (CCME 2012a,b). It is considered that elevated chloride concentrations are a likely moderator of nitrate toxicity – as is known to occur for nitrite toxicity.

Recent toxicity studies with a New Zealand native whitebait (inanga) has shown that this hardness-related response with decreasing toxicity as water hardness increases. The inanga data was included in the guideline derivation (Hickey 2013a) and subsequent NOF standards.

Water hardness provides an indicative measure of the mineral content of water and calculation procedures are available to adjust the nitrate water quality guideline for water hardness based on studies undertaken in Canada (Rescan 2012). This approach was recently used in order to derive site-specific safety factors for nitrate in Hawkes Bay rivers (Hickey 2013b,c).

Hardness adjustment calculation procedures are used here to derive site-specific guidelines for nitrate-N in the springs draining into and the Waimea and Motupipi rivers and for Waikoropupu Springs.



Approach

Monitoring data was supplied by TDC for nitrate and water hardness monitoring at five sites (Borck, Neimann and Pearl creeks draining to the Waimea River; Motupipi River at Reillys Bridge; Waikoropupu Springs). The Waikoropupu Springs nitrate-N data was from Stark (2015; Table 2) as summarised for the period 1970 to 2014, with a water hardness value of 187 mg CaCO₃/L from monitoring on 27 March 2014 (J. Thomas, TDC, pers comm). The location of the Pearl Creek and Neimann Creek sites draining to the lower reaches of the Waimea River are shown in Appendix 1. The water quality data for the sites is provided in Appendix 2, together with median and maximum concentrations. Note that for this assessment the maximum nitrate concentration was used because of the relatively few monitoring occasions at some sites and to provide additional conservatism for comparison with the site-specific guidelines.

The site-specific guidelines were calculated using the following algorithm:

Hardness-specific nitrate-N guideline = $e^{0.9518*Ln(Hardness)}$ - Constant

, where 0.9518 is the slope of the hardness relationship (from Rescan 2012), hardness is the measured median value, and the Constant is a factor to adjust from the NOF nitrate-N reference hardness value of 13 mg CaCO₃/L for annual median and annual 95th percentile standards.

Results

The results of the site-specific nitrate guideline calculations are provided in Table 1 in comparison with the NOF nitrate standards. Calculated river and creek median and maximum nitrate-N concentrations are compared with the site-specific guidelines. Based on this analysis, all sites would fall into an "A" band classification following NOF classification (MfE 2014) with a site-specific hardness adjustment. The calculated 'safety-factors' (i.e., SF = site-specific guideline / measured nitrate-N concentration) are all >1 which indicates a margin of safety for all sites based on both the median and maximum nitrate concentrations.

Toxicity in marine waters as a result of elevated nitrate-N concentrations from freshwater discharges are not a concern. Environment Canada have recently published a chronic nitrate guideline of 45 mg NO₃-N/L for marine waters (CCME 2012b). On this basis, diadromous native fish species such as inanga, would not be expected to be adversely affected in the estuarine environment when migrating from their early life-stage period in marine waters. Management of nitrate-N based on the freshwater NOF standards, or site-specific freshwater guidelines, will provide protection for inanga in their estuarine environment.

Conclusions

Comparison of measured nitrate concentrations with site-specific nitrate guidelines indicates that, based on presently available information, species inhabiting either these spring-fed creeks, or the larger rivers receiving spring-fed discharges, would not experience chronic adverse effects from long-term elevated nitrate-N concentrations.

Management of freshwaters using the NOF nitrate standards will provide a high level of protection for migratory fish species such as inanga. This is because the toxicity of nitrate is markedly lower in seawater than in freshwaters.

The application of the NOF nitrate standards are designed to apply to water management units within an individual catchment or regional context with multiple stream or river systems. As such, the NOF nitrate standards would apply at monitoring stations that include in-stream assimilation and other processes that affect nitrate concentrations. The location of WMUs has not been considered as part of this site-specific assessment.



References

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Table 1: Derived site-specific guidelines for nitrate-N concentrations in Motupipi River, Borck Creek, Pearl Creek, Neimann Creek and Waikoropupu Springs

	NOF Nitrate	e Standards ^a				Hardness-spec	ific guidelines ^b		sured trations		ects safety tor ^c
Attribute State	Annual median	Annual 95th percentile		River	Median hardness	Annual median	Annual 95th percentile	Median	Maximum	Median	Maximu
(ANZECC protection threshold)	Nitrate concentration	Nitrate concentration	Description of Management Class				Nitrate concentration				
	(mg NO ₃ -N /L)	(mg NO ₃ -N /L)			mg CaCO ₃ /L	(mg NO ₃ -N /L)	(mg NO ₃ -N /L)	(mg NO ₃ -N /L)	(mg NO ₃ -N /L)		
A (99%)	1	1.5	Pristine environment with high biodiversity and conservation values.	Motupipi	89	6.3	9.5	1.3	2.7	4.8	3.5
				Borck & Pearl Ck	100	7	10	5.6, 2.9	7.0, 3.9	1.3, 2.4	1.4, 2.6
				Neimann Ck	130	9	13	3.3	8.5	2.7	1.5
				Waikoropupu Springs	190	13	19	0.37	0.51	35	37
B (95%)	2.4	3.5	Environments which are subject to a range of disturbances from human activities, but with minor effects.	Motupipi	89	15	22				
				Borck & Pearl Ck	100	16	24				
				Neimann Ck	130	21	31				
				Waikoropupu Springs	190	31	45				
C (80%)	6.9	9.8	Environment which are measurably degraded and which have seasonally elevated concentrations for significant periods of the year (1-3 months).	Motupipi	89	43	61				
				Borck & Pearl Ck	100	48	68				
				Neimann Ck	130	61	87				
				Waikoropupu Springs	190	89	126				
onitoring statistic:	Annual median	95 th percentile					95 th percentile				

^a National Objectives Framework (NOF) standards were derived for a conservative hardness value of 13 g CaCO₃/L (MfE 2014) ^b Hardness-specific guideline = e^{0.9518}'tn^(Hardness) - Constant, where 0.9518 is the slope of the hardness relationship (from Rescan 2012), hardness is the measured value, and the Constant is a factor to adjust from the "NOF nitrate standards" reference hardness value of 13 mg CaCO₃/L for annual median and 95th percentile concentrations.

[°] Safety factor = Hardness-specific guideline / Measured concentration; based on median and maximum concentrations

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Appendix 1: Site locations for Pearl Creek and Neimann Creek and the Waimea River

Neimann and Pearl Creek Sampling Sites 800

600

400

200

0

1:12,000

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Appendix 2: Monitoring data for nitrate and hardness

T.L.		0						
Waimea River								
Borck @ 400m ds Queen St		Neimann Ck @ 600m us	Neimann Ck @ 600m us Lansdow ne Rd			Pearl Ck @ 200m us tidegate		
From 21-Jan-2009 16	:00:00 to 16-0	Oct-2014 08:55:00	From 27-Jan-2012 13:00:00 to 17-Oct-2014 08:10:00			From 26-Sep-2011 09:50:00 to 17-Oct-2014		
					Hardness			Hardness
	Nitrate-N	Hardness (g/m ³		Nitrate-N	(g/m ³ as		Nitrate-N	(g/m ³ as
Date/Time	(g/m ³)	as CaCO ₃)	Date/Time	(g/m ³)	CaCO ₃)	Date/Time	(g/m ³)	CaCO ₃)
8/04/2013 12:00	4.6	90	27/01/2012 13:00	8.5		26/09/2011 9:50	3.9	
8/07/2013 10:25	5.9		8/07/2013 10:55	2.7		8/04/2013 14:20	3.3	
7/10/2013 10:40	4.7		7/10/2013 9:40	5.8	132	8/07/2013 15:25	2.9	
4/04/2014 8:15	5.9	103	3/04/2014 8:10	3.2	123	7/10/2013 8:10	3.6	92
2/07/2014 11:14	4.9	86	3/07/2014 10:55	1.82	106	3/04/2014 9:15	2.9	93
16/10/2014 8:55	7	120	17/10/2014 8:10	4.1	129	17/04/2014 14:00	2.6	
17/02/2015 13:15	5.6	112	17/02/2015 14:10	3.3	128	3/07/2014 9:46	2.1	97
						17/10/2014 9:20	2.6	99
Medians	5.6	103		3.3	128		2.9	93
Maxima	7			8.5			3.9	

Motupipi River				-00.)		D.,	
Nitrate-N (g/m ³) at RW Motupipi @ Reillys Br From 19-Jun-1992 00:00:00 to 17-Feb-2015 13:25:00			Hardness (g/m ³ as CaCO ₃) at RW Motupipi @ Reillys Br From 13-Feb-2007 10:00:00 to 17-Feb-2015 13:25:00				
19/06/1992 0:00	0.82						
28/04/1998 15:00	0.83						
4/07/2000 0:00	0.84						
18/10/2000 0:00	1.8						
10/01/2001 0:00	0.84						
26/03/2001 0:00	0.74						
10/07/2001 0:00	1.2						
2/10/2001 0:00	1.5						
22/01/2002 0:00	1.6						
9/04/2002 0:00	1.1						
9/07/2002 0:00	1.7						
10/07/2002 14:15	1.7						
31/10/2002 16:15	1.3						
11/02/2003 9:30	0.88						
16/04/2003 0:00	0.82						
22/07/2003 15:30	1.8						
10/12/2003 10:50	1.6						
16/01/2004 13:05	0.78						
22/04/2004 13:55	1.3						
22/07/2004 13:00	1.9						
22/11/2004 10:50	1.2						
14/02/2005 18:50	0.97						
18/04/2005 17:40	0.91						
19/04/2005 16:10	0.93						
27/07/2005 12:15	1.6						
26/10/2005 15:20	1.1						
25/01/2006 8:15	0.69						
26/01/2006 12:05	0.65						
13/02/2006 15:20	0.65						
25/05/2006 10:15	2						
20/07/2006 10:40	2.7						
11/10/2006 9:50	1.6						
13/02/2007 10:00	1.3		13/02/2007 10:00	91			
17/04/2007 9:45	1			5.			
19/07/2007 8:50	2		19/07/2007 8:50	94			
10/10/2007 0:00	0.79			5.			
5/11/2007 11:15	2						



Motupipi River							
Nitrate-N (g/m ³) at RW	Motupipi @ Re	eillys Br	Hardness (g/m ³ as CaCO ₃) at RW Motupipi @ Reillys Br				
From 19-Jun-1992 00:0	0:00 to 17-Fe	b-2015 13:25:00	From 13-Feb-2007 10	:00:00 to 17-F	eb-2015 13:25:00		
Date/Time	Value		Date/Time	Value			
13/02/2008 10:10	0.95						
27/05/2008 17:00	1.9						
20/11/2008 12:30	1.6		20/11/2008 12:30	79			
27/01/2009 15:40	1.6						
21/04/2009 15:30	1.2						
16/07/2009 11:45	1.4						
8/10/2009 11:20	2						
3/02/2010 9:45	0.99						
8/06/2010 12:15	1.9						
28/07/2010 12:20	1.6						
19/10/2010 11:30	1.9						
8/02/2011 13:30	1.4						
23/05/2011 12:45	2.3						
20/07/2011 16:15	2.4						
1/11/2011 8:15	1.9						
8/02/2012 11:00	1.6						
1/05/2012 11:20	1.2						
6/11/2012 10:40	1.55						
18/02/2013 12:05	0.61						
14/04/2013 13:00	0.65		14/04/2013 13:00	87			
9/07/2013 13:50	1.85						
29/10/2013 11:05	1.51						
19/02/2014 14:15	0.66		19/02/2014 14:15	93			
8/04/2014 11:00	0.77		8/04/2014 11:00	85			
8/07/2014 12:20	1.8		8/07/2014 12:20	89			
22/10/2014 9:05	1.27		22/10/2014 9:05	92			
17/02/2015 13:25	0.69		17/02/2015 13:25	89			
Median	1.3		Median hardness	89			
Maximum	2.7						