Memorandum

To:	Ms Vera Power, MfE	Date:	7 March 2014
From:	Chris Hickey – NIWA	Our Ref:	MFE13504
Copy:	John Phillips, MfE		
Subject:	**Derivation of indicative ammoniacal nitrogen guidelines for the National Objectives Framework**		

Background

The National Policy Statement for Freshwater Management (NPS-FM) requires regional councils to set water quality objectives and limits to manage values of our aquatic ecosystems. As part of this process the Ministry for the Environment is developing a National Objectives Framework (NOF) for freshwaters, which includes an attribute table of ammoniacal-nitrogen (NH_4-N, or total ammoniacal nitrogen (TAN)) toxicity values applicable to lakes and riverine environments [1]. The NOF values include a national "bottom line", which is the minimum water quality level that all water bodies must achieve, and a range of higher water quality "attribute states". NIWA has undertaken a review to provide updated indicative ammoniacal-N guidelines to contribute to the NOF attribute table.

The proposed numeric ammoniacal-N guideline values for the NOF framework are based on the statistically-derived 'no observed effect concentration' (NOEC) and 'threshold effect concentration' (TEC)[1] values for 19 species. This update is considered "indicative" in that the derivation is based on the ANZECC (2000) dataset [2] which has been updated with sensitive North American freshwater mussel data that was incorporated into the recently updated U.S. EPA ammonia guidelines [3], and includes consideration of sensitivity data for the New Zealand freshwater mussel glochidia [4]. A thorough literature review and updating of the ANZECC (2000) freshwater data database has not been undertaken as part of this review.

Derivation

The approach used is comparable with that used for the nitrate-N guidelines as proposed for the NOF [1, 5]. The two-number guideline and management framework is based on, and is consistent with, the ANZECC (2000) guidelines risk-based methodology to provide various levels of ecosystem protection. The compliance monitoring basis provides species protection for both average long-term exposure and daily/seasonal maximum concentrations and pH/temperature condition. This approach provides species protection for ammonia toxicity, where the proportion of unionised ammonia-N and associated toxicity increases with increasing pH and temperature. The guidelines are summarised together with narrative descriptors in Table 1. The terms "Grading" and "Surveillance" are derived from the compliance descriptors applied to microbiological standards. The Grading values are derived from the species

[1] The threshold effect concentration (TEC) is the geometric mean of the no observed effect concentration (NOEC) and the lowest observed effect concentration (LOEC). The TEC value is below the lowest statistically significant effect concentration.

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NOEC values and recommended for compliance assessment based on the annual median concentrations and physico-chemical conditions. The Grading values are equivalent to trigger values as derived using the ANZECC (2000) procedure. The Surveillance values are derived from the species TEC values and recommended for compliance assessment based on the 95th percentile of the monitoring data to include daily and seasonal variability in concentration and physico-chemical conditions. The most sensitive guideline would establish the regulatory assessment value.

Table 1: Freshwater ammoniacal-N toxicity guidelines:

Guideline Type [a]	Grading Ammoniacal-N concentration (mg NH_4-N /L)	Surveillance Ammoniacal-N concentration (mg NH_4-N /L)	Description of Management Class
NOF attribute state A	<0.03	<0.05	Pristine environment with high biodiversity and conservation values. Based on statistical 99% species protection level.
NOF attribute state B	0.03-0.24	0.05-0.40	Environments which are subject to a range of disturbances from human activities, but with minor effects. Based on statistical 95% species protection level.
NOF attribute state C [b]	0.24-0.54	0.40-0.92	Environments which are measurably degraded and which have elevated concentrations from point source discharges or diffuse organic inputs. Potential for marked diurnal temperature and pH variability associated with excessive macrophyte, river periphyton and lake phytoplankton growths. Based on statistical 80% species protection level.
Acute	3.9	7.8	Environments which are significantly degraded. Probable chronic effects on multiple species.
Method of comparison [c]	Annual median	Annual 95th percentile	

Note: Based on pH 8.0 and 20^{0}C. Compliance with the numeric attribute states would be after pH adjustment.
[a] MfE proposed NOF band classification [1]. Technical basis provided in Description of Management Class. "Acute" values are from U.S. EPA (2013) [3].
[b] Note this bottom line threshold differs from that proposed in MfE (2013). Values are based on the 90th percentile threshold (Appendix 2).
[c] Significant daily or seasonal variation in physico-chemical conditions (primarily pH) may require incorporation of short-term monitoring data into the NOF guideline assessment for chronic exposures.

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Methodology

The guideline derivation is based on the ANZECC (2000) ammoniacal-N dataset which has been updated for the recent chronic freshwater mussel data which has been included in the revised U.S. EPA guidelines [3]. No other data has been included in the updated database, but recent freshwater mussel glochidial sensitivity [4] has been included to benchmark the sensitivity of this early life-stage. The toxicity data used is summarised in Appendix 1 for a standardised pH of 8.0.

The statistical guideline derivation used the ANZECC (2000) BUR Type III distribution model based on the statistically-derived NOEC values for the dataset. The average value of the TEC values for the most sensitive freshwater mussel and sphaeriid species was used to calculate a NOEC/TEC ratio which was then applied to estimate the TEC-based guideline values for the dataset. The results of the guideline derivation for various levels of protection are summarised in Appendix 2, together with the species sensitivity distribution for the NOEC data.

Both temperature and pH affect the ionisation of ammonia and the associated toxicity to aquatic species. The ANZECC (2000) incorporates the U.S. EPA pH algorithm [6] to adjust the species chronic toxicity, as is used in the latest EPA guidelines [3]. A temperature adjustment is also incorporated into the EPA guidelines but not the ANZECC (2000) guidelines. The ANZECC guidelines relationship with pH are shown in Appendix 3, together with the adjustment ratios to correct values to a standard pH of 8.0. Conversion to standard pH involves dividing the measured ammoniacal-N concentration by the ratio for the pH appropriate to the measurement conditions (see Compliance monitoring below).

Comparative acute guidelines for pH 8 and 20°C (Table 1) are from U.S. EPA [3].

Limitations and risks

The toxicity thresholds are weighted relative to the most sensitive taxa (mussels and fingernail clams, Appendix 1 & 2). The guideline derivation is based on 19 species, which include five native or resident New Zealand species (two mayflies, a sphaeriid clam, a water flea and rainbow trout). The sensitivity of these species is markedly lower than the 95% protection guideline (mayfly, *Deleatidium* sp. 7.5-fold; mayfly *Coloburiscus*, 18-fold; rainbow trout, 26-fold; water-flea, *Ceriodaphnia* 54-fold). Only the NZ finger-nail clam (*Sphaerium novaezelandiae*) has a NOEC and TEC values which fall within the 80th percentile guidelines.

Recent data for NZ freshwater mussel glochidia sensitivity to ammoniacal-N shows that their sensitivity is markedly lower than guideline values (Appendices 1 & 2). Use of an acute to chronic conversion factor for glochidia to estimate juvenile mussel sensitivity indicates that their sensitivity would be comparable to those measured for the North American species included in this dataset [4], indicating that inclusion of these species should provide suitable surrogates for protection of native NZ mussel (kakahi) species.

The dataset is lacking in chronic NZ-specific data for native fish species. However, acute data for native fish is available for 8 species and indicated that invertebrates are generally more sensitive, with the most sensitive native fish species at the 15th percentile of the dataset [7]. These data indicate that fish should be protected based on use of data from sensitive invertebrate species.

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The use of the chronic 80th percentile guideline value was originally proposed as a "bottom line" threshold (MfE 2013 [1]). However, the 80th is greater than all of the mussel species and the NZ fingernail clam measuring chronic survival and growth endpoints, while being less than mayfly and other native or resident species (Appendices 1 & 2). The use of the 90th percentile guideline values as a bottom line is recommended (Table 1). These values are protective of the native fingernail clam, though some effects are indicated for the North American juvenile mussels, which are not resident in New Zealand.

Assessment monitoring

The guidelines are applicable to stream, river and lake environments. Assessment monitoring should be based on the more sensitive of the grading or surveillance guidelines.

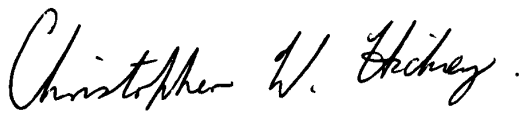
The following assessment approach should be applied:

(i) Monthly monitoring data over an annual period would generally be used to establish Management Classification based on exceedance of the most sensitive guideline value (i.e., median or 95th percentile). However, where significant daily diurnal variation in temperature and pH occurs, such as when periphyton or macrophytes are present, then additional monitoring and statistical analysis may be required to establish the physico-chemical conditions;

(ii) The guideline values are provided for a standard pH 8.0 and nominally 20^0C. The compliance should be assessed after conversion of the compliance band boundary values to the pH-adjusted value based on the median and 95th percentile pH for the site. The conversion table is provided in ANZECC (2000, Table 8.3.7) for calculation relative to the pH 8 value (see Appendix 3).

(iii) Percentile compliance monitoring should be used for classification. For example, monthly monitoring 12 monitoring data with 2 exceedances over an annual monitoring period are permitted, each of which should be less than 20% above the band boundary; see look-up Table 13.2 from Bell et al. (2002) [8], Appendix 4, based on McBride & Ellis (2001) [9]). Compliance should not be assessed on the basis of rolling-means calculated for longer monitoring periods. Note: the monitoring frequency and compliance confidence relationships in this table have not been reviewed and optimised for application to the NOF monitoring requirements.

It is anticipated that in many lowland streams and rivers the elevated temperatures and diel pH variation will result in the surveillance guideline being the more limiting for those sites. Eutrophic lakes which stratify and deoxygenate their hypolimnion may experience highest ammoniacal-N, temperature and pH conditions during autumn destratification when lake mixing occurs.



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Appendix 1: Summary data used for derivation of NOF ammoniacal-N guidelines

Species: Scientific name	Species: Common name	Effect	Endpoint	NOEC NH_4-N (mg/L) [b]	TEC NH_4-N (mg/L) [b]	Ratio of NOEC/TEC	Notes
Ceriodaphnia acanthina	Water flea	REP	NOEC [a]	19.77			
Oncorhynchus clarki	Cutthroat trout	MORT	NOEC [a]	19.72			
Daphnia magna	Water flea	REP	NOEC [a]	17.14			
Ceriodaphnia dubia	Water flea	REP	NOEC [a]	13.03			
Pimephales promelas	Fathead minnow	MORT	NOEC [a]	8.81			
Oncorhynchus mykiss	Rainbow trout	MORT	NOEC [a]	6.15			
Echridella menziesii	Mussel glochidia (NZ)	MORT		6.05	7.5	0.81	[c]
Lepomis cyanellus	Green sunfish	BIOMA	NOEC [a]	4.88			
Catastomus commersoni	White sucker	BIOMA	NOEC [a]	4.79			
Micropterus dolomieui	Smallmouth bass	BIOMA	NOEC [a]	4.56			
Coloburiscus humeralis	Mayfly (NZ)	MORT	NOEC	4.4			
Oncorhynchus nerka	Sockeye salmon	HAT	NOEC [a]	4.16			
Ictalurus punctatus	Channel catfish	GRO	NOEC [a]	3.27			
Sphaerium transversum	Long fingernail clam	MORT	NOEC [a]	2.62			
Deleatidium sp.	Mayfly (NZ)	MORT	NOEC	1.79			
Lepomis macrochirus	Bluegill	BIOMA	NOEC [a]	1.35			
Lampsilis fasciola	Wavy-rayed lampmussel	MORT		0.59	0.90	1.5	[d]
Sphaerium novaezelandiae	Fingernail clam (NZ)	MORT	NOEC	0.54	1.28	2.4	
Lampsilis siliquoidea	Fatmucket mussel	MORT		0.38	0.50	1.3	[d]
Villosa iris	Rainbow mussel	GRO(length)		0.24	0.54	-	[d]
						1.7	**Average ratio** [e]

Abbreviations: MORT = mortality; BIOMA = biomass; HAT = hatching; GRO = growth; REP =reproduction; NOEC = no observed effect concentration; TEC threshold effect concentration (geometric mean of NOEC and lowest observed effect concentration); ChV = chronic value, which is equivalent to the TEC.

Shading indicates new freshwater mussel data added to ANZECC (2000) data [2]

[a] Note: These endpoints designated "NOEC" in ANZECC (2000) database but US EPA (1991) EC_{20} or LC_{20} values (either single data or geometric mean values) used in guideline calculations

[b] All endpoint concentrations adjusted to pH 8.0

[c] Clearwater et al (2014) [4] (from Table 1 using average of 48 h data for pH 8 from lakes Rotoiti and Taupo glochidia. Indicative value for New Zealand mussel glochidia and not included in revised guideline calculation.)

[d] Wang et al (2007) [10] (from Table 8 with conversion from pH 8.2 to pH 8.0 using a factor of 1.35. Rainbow mussel NOEC concentration estimated based on geometric mean of Control and LOEC concentrations, so NOEC/TEC not calculated for this species)

[e] Average ratio of NOEC/TEC for three species shown used to adjust guideline values for short-term effects

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Appendix 2: Statistical derivations of ammoniacal-N guidelines

Table A2: Statistical derivations of ammoniacal-N thresholds

	NOEC [a]	TEC estimate [b]
Nominal Protection	NH_4-N(mg/L)	
99%	0.03	0.05
95%	0.24	0.39
90%	0.54	0.92
80%	1.2	2.1

See Appendix 1 for abbreviation definitions
[a] NOEC threshold using ANZECC (2000) BUR model and data from Appendix 1
[b] TEC estimates based on: NOEC-derived thresholds x (NOEC/TEC ratio). NOEC/TEC ratio = 1.7 (from Appendix 1)

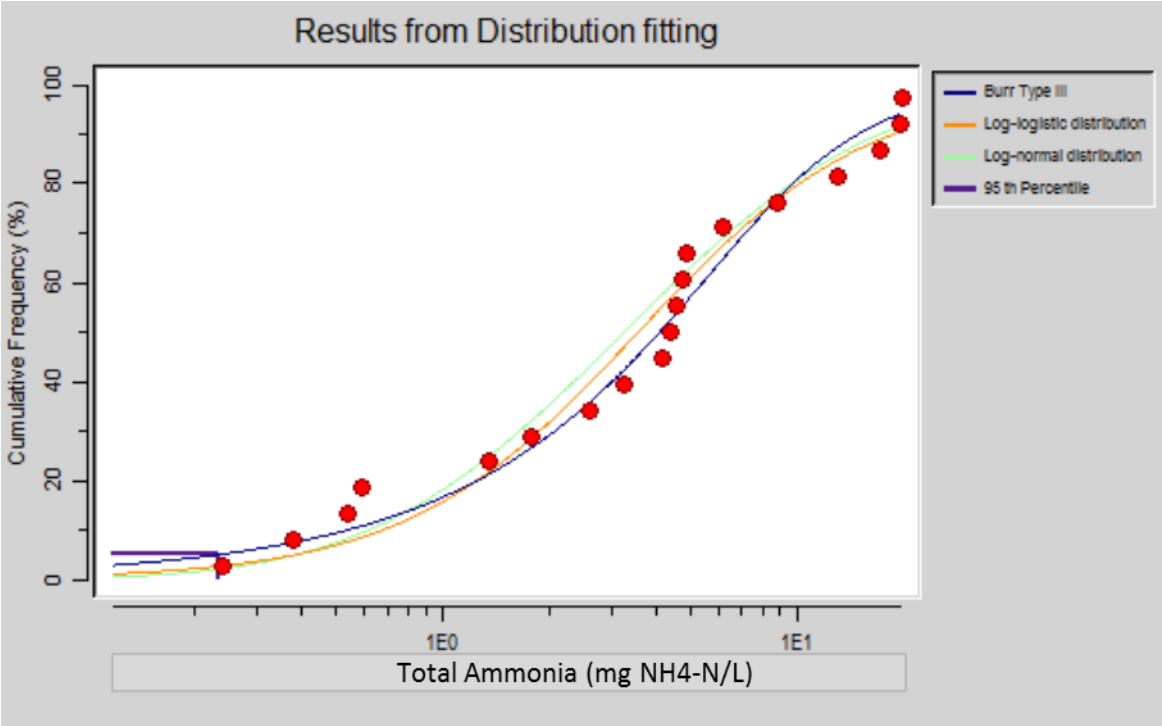

Figure A2: Species sensitivity distribution for updated ammoniacal-N dataset (Appendix 1) using ANZECC (2000) BUR model.

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Appendix 3: ANZECC (2000) total ammoniacal nitrogen guidelines in relation to pH

pH	Freshwater trigger value (mg/L) [a]	Ratio relative to pH 8
6	2.57	2.86
6.1	2.56	2.84
6.2	2.54	2.82
6.3	2.52	2.80
6.4	2.49	2.77
6.5	2.46	2.73
6.6	2.43	2.70
6.7	2.38	2.64
6.8	2.33	2.59
6.9	2.26	2.51
7	2.18	2.42
7.1	2.08	2.31
7.2	1.99	2.21
7.3	1.88	2.09
7.4	1.75	1.94
7.5	1.61	1.79
7.6	1.47	1.63
7.7	1.32	1.47
7.8	1.18	1.31
7.9	1.03	1.14
8	**0.9**	**1.00**
8.1	0.78	0.87
8.2	0.66	0.73
8.3	0.56	0.62
8.4	0.48	0.53
8.5	0.4	0.44
8.6	0.34	0.38
8.7	0.29	0.32
8.8	0.24	0.27
8.9	0.21	0.23
9	0.18	0.20

[a] Table 8.3.7 from ANZECC (2000) with trigger values converted to mg/L.
[b] Ratios calculated from trigger values with pH response relationship from US EPA (1999) [6] (temperature not taken into consideration).
Conversion to standard pH: Measured concentration / pH ratio for measured average or 95 percentile pH value
Note: for pH values greater than 9.0 a maximum ratio from pH 9 should be used.

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Appendix 4: Percentile compliance and sample numbers from New Zealand Municipal Wastewater Monitoring Guidelines (from Bell et al 2002, [8] based on McBride & Ellis (2001) [9]).)

Table 13.2: Number of exceedances (e) out of n samples permitted to meet percentile discharge compliance standards based on a discharger's risk of no more than 10%.

Number of samples taken in monitoring period (*n*)	Number of permitted exceedances (*e*) for a 10% discharger's risk to meet the performance standards listed.			
	Median (50%ile)	80%ile	90%ile	95%ile
5	4	2	1	1
6	5	2	2	1
7	5	3	2	1
8	6	3	2	1
9	6	3	2	1
10	7	4	2	1
11	8	4	2	2
12	8	4	3	2
13	9	4	3	2
14	9	5	3	2
15	10	5	3	2
16	11	5	3	2
17	11	6	3	2
18	12	6	3	2
19	12	6	4	2
20	13	6	4	2
21	13	7	4	2
22	14	7	4	2
23	15	7	4	3
24	15	7	4	3
25	16	8	4	3
26	16	8	5	3
27	17	8	5	3
28	17	8	5	3
29	18	9	5	3
30	19	9	5	3
31	19	9	5	3
32	20	9	5	3
33	20	10	6	3
34	21	10	6	3
35	21	10	6	3
36	22	10	6	4
40	24	11	6	4
50	30	14	8	5
100	56	25	14	8

Note: the monitoring frequency and compliance confidence relationships in this table have not been reviewed and optimised for application to the NOF monitoring requirements.

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