

Memorandum

| То: | James Court, MFE | Date: | 30 September 2002 |
|----------|--|--------------|-------------------|
| From: | Chris Hickey – NIWA | Our Ref: | MFE02237 |
| Сору: | Dr Wayne Donovan, Bioresearches; Dr Michael Warne, NSW EPA | , Dr John Cl | hapman, NSW EPA |
| Subject: | Nitrate guideline values in ANZECC 2000 | | |

Background

The issue has been raised as to the certainty associated with the nitrate trigger values as given in Table 3.4.1 of the ANZECC 2000 water quality guidelines. These trigger values indicate that for 95% protection the toxicity of nitrate is higher than for ammonia (by 1.3-times) and for markedly higher for 99% protection (by 19-times).

The basis for the derivation of these numbers was investigated.

ANZECC guidance

The new ANZECC guidelines use acute and chronic laboratory toxicity data for the derivation of "trigger values" for nitrate. The detailed toxicity data for nitrate is provided in Appendix 1 and freshwater toxicity data used for statistical calculation is given in Appendix 2. The guideline summary for freshwaters is: "A freshwater moderate reliability trigger value for nitrate toxicity as NO_3 (nitrate) of 700 µg/L was calculated using the statistical distribution method 95% protection and the default ACR."

The stated guideline value of 700 μ g/L for 95% protection is consistent with the value given in summary table 3.4.1 of the guidelines, but not consistent with the present figure, which indicates a guideline value of approximately 10,000 g/L.

Recalculation procedure

The nitrate database is predominantly acute data, with chronic data for two Australian species (Appendix 2). Based on inspection of the data plot (Appendix 1), it would appear that a mix of acute and chronic data was used for guideline calculation, followed by application of a 10x application factor (AF).

The geometric mean values for the acute toxicity data were converted to chronic values using a 10x AF (Figure 8.3.2, and page 8.3-31, ANZECC 2000). The two chronic values were converted from NO_3 -N to NO_3 prior to this analysis (the values summarised in the database were the NO_3 -N data as reported in Rippon & McBride (1994), Greg Rippon, pers. comm. 11 Sept 2002). The acute and chronic data were then combined prior to guideline calculation using the BurrIII statistical program provided on the Guidelines CD. The recalculated trigger values (rounded) are summarised in the table below together with the values presented in the Guidelines.

| | Chemical | Trigger values for freshwater | | | | | |
|---------------------|-----------|-------------------------------|-----------------|-----------------|--------|--|--|
| | | (μg/L <u>)</u> | | | | | |
| | | | Level of protec | tion (% species | 6) | | |
| | | 99% | 95% | 90% | 80% | | |
| ANZECC 2000 values | Nitrate | 17 | 700 | 3400 | 17000 | | |
| Recalculated values | Nitrate | 21,600 | 31,900 | 38,500 | 52,000 | | |
| Recalculated values | Nitrate-N | 4900 | 7200 | 8700 | 12,000 | | |

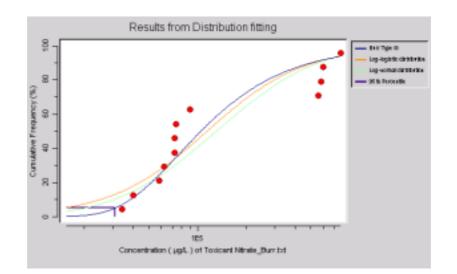


Figure. Distribution of recalculated nitrate toxicity data.

These recalculated nitrate trigger values are markedly higher than those presented in the guidelines. The recalculated values are more consistent with ambient nitrate values (see Table 8.2.6 – but multiply numbers by 4.43x to convert to nitrate as NO₃, ANZECC 2000) and relative to the toxicity trigger values for ammonia.

It appears that the nitrate values given for toxicants are as NO_3 (based on checking against values in one reference, Rubin & Elmaraghy 1977). This differs from the normal way that laboratory results would be presented and how nutrient trigger values are presented in the Guidelines.

I would suggest that the toxicant trigger values should also be presented as NO_3 -N values for consistency of practice.

histopher W. thinky.

Dr Chris Hickey 30 September 2002

References:

- ANZECC & ARMCANZ (2000). Australian and New Zealand guidelines for fresh and marine water quality. National Water Quality Management Strategy Paper No 4, Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia.
- Rippon,G.D and P.McBride (1994). Biological Toxicity Testing of Gadjarrigamarndah Creek Water at Na [sic] Final Report for Project.
- Rubin, A.J. and G.A.Elmaraghy 1977 Studies on the Toxicity of Ammonia, Nitrate and Their Mixtures to Guppy Fry *Water Res.* 11 (10): 927-935

Appendix 1. Nitrate section from ANZECC 2000 guidelines and graphical presentation of data as provided on the guidelines CD

Nitrate

Nitrate is essential for growth of aquatic plants. The main issue with elevated levels of nitrate is its potential to stimulate algal growth and hence to be a factor in nuisance algal blooms and eutrophication of waterways — usually from human wastes or fertilisers. At high enough levels, nitrate can be toxic to aquatic life. Toxicity data were reviewed for both potassium nitrate (KNO₃; CAS 7757-79-1) and sodium nitrate (NaNO₃; CAS 7631-99-4).

Aquatic toxicology

Potassium nitrate was generally more toxic than sodium nitrate (many of the comparative tests were reported in the same publication). Figures are given as mg NO₃/L.

Freshwater fish: (48–96 h LC₅₀): 6 spp, 99–10 000 mg/L (i.e. x 1000 µg/L). Chronic 9-d

NOEC of 14 mg/L to Australian Mogurnda adspersa

Freshwater crustaceans: 48-96 h LC50 to Daphnia magna, 23-4206 mg/L

Freshwater molluscs: Lymnaea sp. 96-h LC50, 664 mg/L

Freshwater insects: 2 spp, 72–96 h LC₅₀, 430–930 mg/L

Freshwater hydra: *Hydra viridissima* 6 d chronic NOEC (population growth) of 9 mg/L (Australian)

Marine fish: 6 spp, 96-h LC50, 2536–13 280 mg/L

Marine mollusc: 1 sp, 96-h LC50, 11 510-27 580 mg/L

Australian and New Zealand data

The only chronic data were for potassium nitrate were on Australian purple-spotted gudgeon *Mogurnda mogurnda* and hydra, *Hydra viridissim*a. There were no overseas chronic data for comparison. Tests with the marine prawn *Penaeus monodon* (Muir et al. 1991), indicated that nitrate had a significant effect on survival of larvae at 1000 μ g/L but no dose-response figures were given.

Guideline

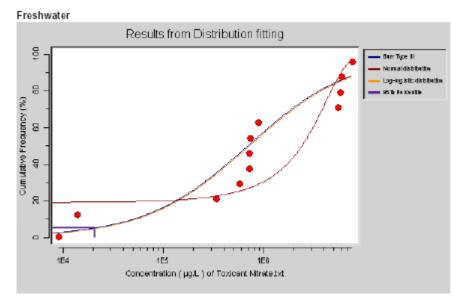
As nitrates are a known stimulant for algal growth at low concentrations, it was considered acceptable to derive trigger values on an adequate number of data without algae. Separate marine figures were derived because of the apparent differences in sensitivity on the limited marine data.

A freshwater moderate reliability trigger value for nitrate toxicity as NO₃ (nitrate) of 700 μ g/L was calculated using the statistical distribution method 95% protection and the default ACR.

Although a marine low reliability figure of 13 000 μ g/L (13 mg/L) could be calculated using an AF of 200 (limited data but a lesser factor due to essentiality), it is preferable to adopt the freshwater figure of 700 μ g/L for nitrate toxicity as NO₃ (nitrate) as a marine low reliability trigger value.

NIWA Taihoro Nukurangi

Nitrate





Appendix 1. Nitrate toxicity data from ANZECC 2000 guidelines database Water Quality Search Results Toxicant nitrate

Date: 2/08/2002

| Toxicant nitrate Latin Name Common | Test Media | Test Type | Duration(h | Endpoin | Effec | Temp pH | Method | Concentratio Code n Used | e Unit | Ref No |
|---|------------|-----------|------------|---------|-------|---------|--------|-----------------------------|--------|-----------|
| | | | | Fish | | | | | | |
| <i>Gambusia holbrooki</i> Eastern mosquitofish | Freshwater | Acute | 48 | LC50 | MORT | | NR | U 1E+07 | ug/L | 200508 |
| <i>Gambusia holbrooki</i> Eastern mosquitofish | Freshwater | Acute | 48 | LC50 | MORT | | NR | U 137000 | ug/L | 200508 |
| <i>Gambusia holbrooki</i> Eastern mosquitofish | Freshwater | Acute | 96 | LC50 | MORT | | NR | U 99000 | ug/L | 200508 |
| Gambusia holbrooki Eastern mosquitofish | Freshwater | Acute | 96 | LC50 | MORT | | NR | U 99000 | ug/L | 200508 |
| Geometric | | | | | | | | 340406.42 U | | |
| Lebistes reticulatus Guppy | Freshwater | Acute | 48 | LC50 | MORT | | NR | 969000 U | ug/L | 207635 |
| <i>Lebistes reticulatus</i> Guppy | Freshwater | Acute | 72 | LC50 | MORT | | NR | 881000 | ug/L | 207635 |
| <i>Lebistes reticulatus</i> Guppy | Freshwater | Acute | 96 | LC50 | MORT | | NR | U 845000 | ug/L | 207635 |
| Geometric | | | | | | | | 896847.91 | | |
| <i>Lepomis macrochirus</i> Bluegill | Freshwater | Acute | 96 | LC50 | MORT | | NR | U 1.4165E | ug/L | 208037 |
| <i>Lepomis macrochirus</i> Bluegill | Freshwater | Acute | 96 | LC50 | MORT | | NR | U 885300 | ug/L | 208037 |
| Friday, 2 August 2002 | | | | | | | | | Pa | ge 1 of 6 |

National Institute of Water & Atmospheric Research Ltd Gate 10, Silverdale Road, Hamilton P O Box 11115, Hamilton, New Zealand www.niwa.co.nz



| , , , , , | En el errer | A | 06 | 1.050 | MODT | ND | U | . /T | 200020 | |
|--|-------------|----------|----|-------|-----------|----|-----------------|------|--------|--|
| <i>Lepomis macrochirus</i> Bluegill | Freshwater | Acute | 96 | LC50 | MORT | NR | 900000 | ug/L | 200930 | |
| <i>Lepomis macrochirus</i> Bluegill | Freshwater | Acute | 96 | LC50 | MORT | NR | U 940000 | ug/L | 200930 | |
| <i>Lepomis macrochirus</i> Bluegill | Freshwater | Acute | 96 | LC50 | MORT | NR | U 186000 | ug/L | 208037 | |
| <i>Lepomis macrochirus</i> Bluegill | Freshwater | Acute | 96 | LC50 | MORT | NR | U 1E+07 | ug/L | 200930 | |
| Geometric | | | | | | | 7630126.27 U | | | |
| Micropterus treculi Guadalupe bass | Freshwater | Acute | 96 | LC50 | MORT | NR | 558200 | ug/L | 211794 | |
| Geometric | | | | | | | 5582000.00 U | | | |
| Oncorhynchus mykiss Rainbow trout | Freshwater | Acute | 96 | LC50 | MORT | NR | 599800 | ug/L | 205115 | |
| Geometric | | | | | | | 5998000.00 U | | | |
| Oncorhynchus Chinook salmon | Freshwater | Acute | 96 | LC50 | MORT | NR | 579900 | ug/L | 205115 | |
| Geometric | | | | | | | 5799000.00 | | | |
| | | | | cr | ustaceans | | U | | | |
| Daphnia magna Water flea | Freshwater | Acute | 48 | LC50 | MORT | NR | 358100 | ug/L | 200915 | |
| Daphnia magna | Freshwater | Acute | 48 | LC50 | MORT | NR | U 358100 | ug/L | 202465 | |
| Water flea | | | | | | | U | | | |
| <i>Daphnia magna</i> Water flea | Freshwater | Acute | 48 | LC50 | MORT | NR | 301000 | ug/L | 200915 | |
| | | | | | | | | | | |

Friday, 2 August 2002

National Institute of Water & Atmospheric Research Ltd Gate 10, Silverdale Road, Hamilton P O Box 11115, Hamilton, New Zealand www.niwa.co.nz Page 2 of 6



| | | | | | | | U | |
|--|------------|-------|----|------|--------|-----------|-------------|-----------|
| <i>Daphnia magna</i> Water flea | Freshwater | Acute | 72 | LC50 | MORT | | 0 ug/L | 200915 |
| <i>Daphnia magna</i> Water flea | Freshwater | Acute | 72 | LC50 | MORT | | U 0 ug/L | 200915 |
| <i>Daphnia magna</i> Water flea | Freshwater | Acute | 96 | LC50 | MORT | | U 0 ug/L | 200915 |
| <i>Daphnia magna</i> Water flea | Freshwater | Acute | 96 | LC50 | MORT | | U 0 ug/L | 200915 |
| <i>Daphnia magna</i> Water flea | Freshwater | Acute | 96 | LC50 | MORT | | U 0 ug/L | 200915 |
| Geometric | | | | | | 720085.68 | ; | |
| | | | | Iı | nsects | | | |
| <i>Cheumatopsyche pettiti</i> Caddisfly | Freshwater | Acute | 72 | EC50 | MORT | | U 0 ug/L | 203879 |
| <i>Cheumatopsyche pettiti</i> Caddisfly | Freshwater | Acute | 72 | EC50 | MORT | | U 0 ug/L | 203879 |
| <i>Cheumatopsyche pettiti</i> Caddisfly | Freshwater | Acute | 96 | EC50 | MORT | | U 0 ug/L | 203879 |
| <i>Cheumatopsyche pettiti</i> Caddisfly | Freshwater | Acute | 96 | EC50 | MORT | | U 0 ug/L | 203879 |
| Geometric | | | | | | 733058.47 | , | |
| <i>Hydropsyche</i> Caddisfly | Freshwater | Acute | 72 | LC50 | MORT | NR 65700 | U 0 ug/L | 203879 |
| <i>Hydropsyche</i> Caddisfly | Freshwater | Acute | 72 | LC50 | MORT | | U 0 ug/L | 203879 |
| Friday, 2 August 2002 | | | | | | | Pa | ge 3 of 6 |

National Institute of Water & Atmospheric Research Ltd Gate 10, Silverdale Road, Hamilton P O Box 11115, Hamilton, New Zealand www.niwa.co.nz Page 7 of 10



| <i>Hydropsyche</i> Caddisfly | Freshwater | Acute | 96 | LC50 | MORT | NR | U 430000 ug/L | 203879 | | |
|---|------------|---------|-----|------|-------------|-------------------------|----------------------------|--------|--|--|
| <i>Hydropsyche</i> Caddisfly | Freshwater | Acute | 96 | LC50 | MORT | NR | U 482000 ug/L | 203879 | | |
| Geometric | | | | | | | 576645.92 | | | |
| Molluscs | | | | | | | | | | |
| <i>Lymnaea sp</i> Pond snail | Freshwater | Acute | 48 | EC50 | HAT | NR | U 914000 ug/L | 200508 | | |
| <i>Lymnaea sp</i> Pond snail | Freshwater | Acute | 72 | EC50 | HAT | NR | U 624000 ug/L | 200508 | | |
| <i>Lymnaea sp</i> Pond snail | Freshwater | Acute | 96 | EC50 | HAT | NR | U 664000 ug/L | 200915 | | |
| Geometric | | | | | | | 723490.70 | | | |
| | | | | Fis | sh | | | | | |
| <i>Mogurnda mogurnda</i> Purple SpottedGudgeon | Freshwater | Chronic | 216 | NOEC | MORT | NR | U 14000 ug/L | 300119 | | |
| Geometric | | | | | | 14000.00 CORRECTED TO N | $O3 = \frac{62020}{62020}$ | | | |
| | | | | Co | oelentrates | | | | | |
| <i>Hydra viridissima</i> Hydra | Freshwater | Chronic | 144 | NOEC | PGR | NR | U 9000 ug/L | 300119 | | |
| Geometric | | | | | | 9000.00 CORRECTED TO N | O3 = <mark>39870</mark> | | | |
| | | | | Fis | sh | | | | | |
| Centropristis striata Black sea bass | Marine | Acute | 96 | LC50 | MORT | NR | U 1.0624E ug/L | 209424 | | |
| Geometric | | | | | | 1 | 0624000.00 | | | |

Friday, 2 August 2002

National Institute of Water & Atmospheric Research Ltd Gate 10, Silverdale Road, Hamilton P O Box 11115, Hamilton, New Zealand www.niwa.co.nz Page 8 of 10

Page 4 of 6



| Monacanthus hispidus | Marine | Acute | 96 | LC50 | MORT | NR | U 253600 ug/L | 209424 |
|---|--------|-------|----|------|---------|----|---------------------------|--------|
| Plane headFilefish Geometric | | | | | | | 2536000.00 U | |
| <i>Oncorhynchus mykiss</i> Rainbow trout Geometric | Marine | Acute | 96 | LC50 | MORT | NR | 465000 ug/L 4650000.00 | 205115 |
| <i>Oncorhynchus</i> Chinook salmon | Marine | Acute | 96 | LC50 | MORT | NR | U 440200 ug/L | 205115 |
| Geometric | | | | | | | 4402000.00 U | |
| Pomacentrus Beaugregory | Marine | Acute | 96 | LC50 | MORT | NR | 1.328E+ ug/L | 209424 |
| Geometric | | | | | | | 13280000.00 | |
| <i>Trachinotus carolinus</i> Florida pompano | Marine | Acute | 96 | LC50 | MORT | NR | U 442600 ug/L | 209424 |
| Geometric | | | | | | | 4426000.00 | |
| | | | | M | olluscs | | U | |
| <i>Crassostrea virginica</i> American or virginia | Marine | Acute | 96 | EC50 | MORT | NR | 1.6821E ug/L | 205098 |
| Crassostrea virginica American or virginia | Marine | Acute | 96 | EC50 | MORT | NR | U 1.1509E ug/L | 205098 |
| Crassostrea virginica American or virginia | Marine | Acute | 96 | EC50 | MORT | NR | U 1.8946E ug/L | 205098 |
| Crassostrea virginica American or virginia | Marine | Acute | 96 | EC50 | MORT | NR | U 2.7578E ug/L | 205098 |
| Geometric | | | | | | | 17833739.78 | |

Friday, 2 August 2002

National Institute of Water & Atmospheric Research Ltd Gate 10, Silverdale Road, Hamilton P O Box 11115, Hamilton, New Zealand www.niwa.co.nz Page 5 of 6



U - Unmodified

- C Converted NOEC
- H Hardness Corrected

HC - Hardness Corrected, Converted NOEC UI - Unmodified Unionized UD - Unmodified Dissociated T - Unmodified Total Tp -Total at pH8.0 TpC -Total at pH8.0, Converted NOEC

Friday, 2 August 2002

National Institute of Water & Atmospheric Research Ltd Gate 10, Silverdale Road, Hamilton P O Box 11115, Hamilton, New Zealand www.niwa.co.nz Page 6 of 6