APPENDIX I

Review of ANZECC (2000) Trigger Values for Zinc

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RECALCULATION OF THE ANZECC TRIGGER VALUES FOR ZINC FOR CHRISTCHURCH CITY COUNCIL

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on behalf of

Christchurch City Council

prepared by

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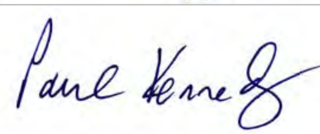
Project Reviewer	**Paul Kennedy**	
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List of Abbreviations

ANZECC	Australian and New Zealand Environment and Conservation Council
CCC	Criteria Continuous Concentration
GRO	Growth
HMTV	Hardness Modified Trigger Value
LOEC	Lowest Observable Effect Concentration
MATC	Maximum Acceptable Toxicant Concentration
MELP	Ministry of Water Land and Air Protection
MORT	Mortality
NRRP	National Resources Regional Plan
NOEC	No Observable Effect Concentration
REP	Reproduction
TV	Trigger Value
USEPA	United States Environmental Protection Agency

1. Introduction

1.1 Background

The purpose of this report is to review the ANZECC trigger values for zinc in support the Christchurch City Council's submission on Chapter Four (Water Quality) of Environment Canterbury's proposed Natural Resources Regional Plan (NRRP).

In July 2004 Environment Canterbury published Chapter Four of its proposed Canterbury Natural Resources Regional Plan (NRRP): Water Quality, which provides the broad planning framework for managing water quality in the Canterbury Region. Chapter Four of the NRPP presents water quality standards for several water classes, including urban rivers managed for amenity and aquatic ecosystems. Christchurch City Council has made submissions on the proposed NRPP. One aspect of their submission is that they consider the water quality standards for urban rivers, as presented in the NRPP, are inappropriate.

The water quality standards for toxicants are provided in Table WQL 19 of the NRPP. Although Chapter Four provides no indication to the source of the water quality standards, a cursory examination is sufficient to suggest they are based on the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC 2000). There are, however, several problems with the manner in which the NRPP seeks to apply ANZECC (2000) trigger values as water quality standards.

Firstly, and most fundamentally, the ANZECC (2000) guidelines do not provide water quality standards in the traditional sense, i.e., fixed standards that should not be exceeded and which are applicable for all national surface waters. Rather, ANZECC state that the uncertainty in the derivation and application of such standards led them to develop trigger values that indicate a potential environmental problem if they are exceeded. The ANZECC (2000) trigger values were never intended be applied in an absolute fashion, rather ANZECC (2000) indicates that if trigger values are exceeded further investigation is required.

Secondly, the NRPP states the toxicants listed in Table WQL 19 are measured as the total fraction; the main relevance of which relates to metals/metalloids. Current science is clear that the best measure of the bioavailable fraction of a metal is its dissolved or soluble fraction (USEPA, 1993; USGS, 1995). ANZECC (2000) also states that analysis of dissolved metal concentrations is more valuable than the total fraction when assessing conformity with trigger values, and that dissolved metals give a better basis for comparison with hardness-modified trigger values. Hence, there is a clear inconsistency with the NRPP using ANZECC total fraction trigger values when they were developed for a dissolved fraction.

Thirdly, there is mounting evidence that the ANZECC (2000) guidelines for metals/metalloids are 'flawed'. This observation does not relate to the fundamental approach to the derivation of trigger values, which is conservative because it is based on the use of no observable effect concentration (NOEC) values. Rather, ANZECC trigger values have been shown to be based on inappropriately selected toxicity data (Kingett Mitchell 2003, 2004, 2005). For example, the ANZECC (2000) 95% trigger value for boron is 370 μg/L, but is based on a toxicity dataset that ignored published NOEC data in preference to estimated NOECs. The trigger value revised by Kingett Mitchell (2004) based on appropriate data is 3,496 μg/L, i.e., almost ten times the ANZECC (2000) value.

Fourthly, it is also noted that Table WQL 19 of NRPP provides no guidance for hardness dependant metals, even though it is well established that the toxicity of certain metals (e.g., copper and zinc) is hardness dependant.

1.2 This Report

In support of the Christchurch City Council submission this report provides evidence on the technical issues associated with the ANZECC trigger values for zinc, which has considerable relevance to urban rivers due to its ubiquitous presence. This document reviews the ANZECC trigger values for zinc, which ANZECC states are based on multiple species NOEC values (ANZECC, 2000). The NOEC-based approach is recognised as being inherently conservative (MELP, 2004) and hence are likely to be over-protective, but this report does not seek to challenge that conservatism. Rather, this report:

- Summarises the ANZECC approach to the derivation of the trigger values.
- Reviews the data used in the development of the ANZECC zinc trigger values.
- Reviews the available toxicological data for zinc.
- Reviews the zinc toxicity-hardness relationship.
- Presents the toxicological data that is appropriate for use in the derivation of zinc trigger values for New Zealand surface waters.
- Re- calculates the zinc trigger values using the methods identified in ANZECC (2000).
- Explains the implications for assessing the water quality of Christchurch waterways with respect to zinc.

2. ANZECC Approach to Derivation of Trigger Values

2.1 ANZECC General Approach to Trigger Value Derivation

The ANZECC trigger values, which have been published for a wide range of chemical contaminants, are generally derived from toxicity tests on single species under laboratory conditions. Most of the published trigger values are moderate reliability because they are based to some degree on acute toxicity data. However, the zinc trigger values are termed 'high reliability' because ANZECC state that they are based solely on chronic (i.e., greater than 96-hour) NOEC data; ANZECC's stated methodology is that NOECs provide the most conservative level of protection.

The toxicity data used by ANZECC (2000) to derive the zinc trigger values was compiled from various sources, including the USEPA AQUIRE database (1994), data from other regulators and data from scientific journals. ANZECC (2000) reports unpublished data which should not be used to derive high reliability trigger values. ANZECC then reviewed the available NOEC data in order to satisfy data quality requirements and inappropriate data was removed.

Once the NOEC data set was established by ANZECC, a Burr-type statistical distribution was fitted to the data. The computer software (BurrliOZ, Campbell et al. 2000) fits Burr Type III statistical distributions to the data and then uses a maximum likelihood method to determine which distribution best fits the data. The software then uses the best fit to calculate the concentration that will protect any specified percentage of species at a confidence level defined by the user. The confidence level used by ANZECC was 50% and is the default level set by the software. The 95% level of protection is the level most commonly applied in the ANZECC (2000) guidelines because it applies to slightly or moderately disturbed ecosystems.

2.2 ANZECC Approach to Trigger Value Derivation of Hardness Dependant Metals

It is generally accepted that the toxicity of certain metals, including zinc, is dependant on water hardness (USEPA, 1976; USEPA, 1986; USEPA, 1987). As well as their published trigger values, which are calculated at a hardness of 30 mg/L as $CaCO_3$, ANZECC has published equations that enable the calculation of a hardness-modified trigger value (HMTV) from their published trigger value, which apply at any hardness concentration (Refer Table 3.4.3 in ANZECC 2000).

The hardness conversion is based on the slope of the regression line that is used to fit the toxicity data versus hardness relationship. ANZECC attribute the slopes to Markich et al. (unpublished, 2000). However, it is apparent the slopes used by ANZECC are those developed previously by USEPA. For zinc the slope factor used by ANZECC is 0.85, whereas that reported by USEPA is 0.8473 (USEPA, 1987).

2.3 ANZECC 2000 Trigger Values for Zinc

The high rehability trigger levels for zinc derived by ANZECC at a hardness of 30 mg/L as $CaCO_3$ are:

Protection of 99% of aquatic species: 2.25 µg/L.
Protection of 95% of aquatic species: 7.99 µg/L.
Protection of 90% of aquatic species: 14.82 µg/L.
Protection of 80% of aquatic species: 31.04 µg/L.

The ANZECC hardness-dependent equation for zinc is:

Zinc HMTV = TV(H/30)0.85

The ANZECC 2000 zinc trigger values are conservative compared with those published by leading regulators. The USEPA Criteria Continuous Concentration (CCC) for zinc (USEPA, 2002) is defined by:

CCC = exp{0.8473[ln(hardness)]+0.884}0.986

Hence, at 30 mg/L hardness the CCC is 43 µg/L.

3. Review of Data Used in the Derivation of the ANZECC Zinc Trigger Values

3.1 Introduction

The toxicity data used by ANZECC (2000) in the development of the zinc trigger value are presented in Table 3.1. The data set comprises 20 species (one amphibian, one annelid, ten fish, four crustaceans, one insect and three molluscs) and contains 67 data points. The 67 data comprise four measured NOECs and 14 converted NOECs. Hence, the vast majority (55 out of 67, 82%) of data used are converted NOECs, an approach that is contrary to ANZECC's statement that high reliability trigger values use only NOEC data.

The use of converted NOEC data from non-NOEC empirical data by ANZECC (2000) is based on simple mathematical relationships (based on Van de Plassche et al. 1993) used to derive NOEC data from either acute (e.g., LC50 or EC50) or chronic (e.g., LOEC or maximum acceptable toxicant concentration, MATC) data, as follows:

NOEC = LC50/5

NOEC = EC50/5

NOEC = LOEC/2.5

NOEC = MATC/2

The practice of using these factors to derive converted NOECs was used extensively by ANZECC in the derivation of the ANZECC (2000) trigger values for boron, often at the expense of measured NOEC data (Kingett Mitchell, 2004). Similarly, the ANZECC 2000 zinc data set also uses converted NOEC data at the expense of measured NOEC data.

Sections 3.2-3.7 review the ANZECC (2000) zinc data-set and discusses any relevant additional zinc toxicity data that was either not selected by ANZECC (2000) or was published after the 2000 guidelines were compiled.

New toxicity data published since the release of ANZECC (2000) was searched for in the USEPA toxicological database (ECOTOX) and from published scientific papers based on extensive database searches; these searches included the following key toxicological journals:

- *Aquatic Toxicology*
- *Archive of Environmental and Contaminant Toxicology*
- *Bulletin of Environmental and Contaminant Toxicology*
- *Chemosphere*
- *Ecotoxicological and Environmental Safety*
- *Environmental Science and Technology*
- *Environmental and Toxicological Chemistry*
- *Environmental Ecology*
- *Environmental Pollution*
- *Journal of Environmental Biology*
- *Journal of Environmental Science and Health*
- *Science and the Total Environment*
- *Toxicological and Environmental Chemistry*
- *Water, Air and Soil Pollution*
- *Water Research*

Table 3.1: Zinc toxicity data used in the derivation of ANZECC 2000 trigger values.

Name	Endpoint	Effect	Zinc µg/L	ANZECC Adjustment	Hardness mg/L $CaCO_3$	Zinc µg/L 30 mg/L $CaCO_3$	Reference
Amphibians							
Ambystoma opacum	LC50	MORT	2,380	LC50/5 = 476.0 µg/L	99	180.4 (173)	Birge et al. (1978)
Annelids							
Limnodrilus hoffmeisteri	TLm	MORT	7,800 (1,773)[a]	TLm/5 = 1,560 µg/L	100	560 (127)	Wurtz & Bridges, (1961)
Crustaceans							
Ceriodaphnia dubia	LC50	MORT	180	LC50/5 = 36.0 µg/L	52	28.0 (28.1)	Carlson et al. (1986)
Ceriodaphnia dubia	LC50	MORT	164	LC50/5 = 32.8 µg/L	36	25.6 (25.5)	Carlson et al. (1986)
Ceriodaphnia dubia	LC50	MORT	149	LC50/5 = 29.8 µg/L	36	22.6	Carlson et al. (1986)
Geometric mean						**25.3**	
Ceriodaphnia reticulata	LC50	MORT	224	LC50/5 = 44.8 µg/L	353	5.52 (5.51)	Carlson & Roush (1985)
Daphnia magna	EC50	REP	102	EC50/5 = 20.4 µg/L	45.3	14.34 (14.4)	Biesinger & Christensen (1972)
Daphnia magna	NOEC	REP	187.5	None	197	32.9 (32.8)	Paulauskis & Winner (1988)
Daphnia magna	NOEC	REP	162.5	None	197	32.8 (37.9)	Paulauskis & Winner (1988)
Daphnia magna	NOEC	REP	87.5	None	101.8	30.6 (31.0)	Paulauskis & Winner (1988)
Daphnia magna	NOEC	REP	37.5	None	51.9	23.5	Paulauskis & Winner (1988)
Daphnia magna	NOEC	REP	12.5	None	51.9	7.80 (7.84)	Paulauskis & Winner (1988)
Geometric mean						**21.04**	
Orconectes virilis	LC50	MORT	84,000	LC50/5 = 16,800 µg/L	26	18,480 (18,973)	Mirenda (1986)
Fish							
Carassius auratus	LC50	MORT	2,540	LC50/5 = 508 µg/L	195	102.4 (103.5)	Birge (1978)
Channa marulius	LC50	MORT	21,090	LC50/5 = 4,218 µg/L	270	650 (652)	Khangarot, (1981)
Ictalurus punctatus	LC50	MORT	6,900	LC50/5 = 1,720 µg/L	313	189.4 (188.0)	Reed et al. (1980)

Name	Endpoint	Effect	Zinc µg/L	ANZECC Adjustment	Hardness mg/L $CaCO_3$	Zinc µg/L 30 mg/L $CaCO_3$	Reference
Lepomis macrochirus	LC50	MORT	12,000[b]	LC50/5 = 2,400 µg/L	370	289.0 (283.7)	Pickering, 1968
Lepomis macrochirus	LC50	MORT	10,700[c]	LC50/5 = 2,140 µg/L	370	258.0 (252.9)	Pickering, 1968
Lepomis macrochirus	LC50	MORT	10,500[c]	LC50/5 = 2,100 µg/L	370	253.0 (248.2)	Pickering, 1968
Lepomis macrochirus	LC50	MORT	7,500[d]	LC50/5 = 1,500 µg/L	370	180.8 (177.3)	Pickering, 1968
Lepomis macrochirus	LC50	MORT	7,200[d]	LC50/5 = 1,440 µg/L	370	173.4 (170.2)	Pickering, 1968
Geometric mean						**226.14**	
Micropterus salmoides	LC50	MORT	5,160	LC50/5 = 1,032 µg/L	99	370.8 (374.1)	Birge et al. 1978
Oncorhynchus mykiss	LC50	MORT	1,060	LC50/5 = 212 µg/L	104	74.4 (73.7)	Birge, 1978
Oncorhynchus mykiss	LC50	MORT	1,060	LC50/5 = 212 µg/L	99	76.0 (76.8)	Birge et al. 1978
Oncorhynchus mykiss	LC50	MORT	555[e]	LC50/5 = 111 µg/L	23	139.2 (139.1)	Chapman, 1978
Oncorhynchus mykiss	LC50	MORT	278[e]	LC50/5 = 55.6 µg/L	23	69.6 (69.7)	Chapman, 1978
Oncorhynchus mykiss	LC50	MORT	120[e]	LC50/5 = 24 µg/L	23	30.0 (30.1)	Chapman, 1978
Oncorhynchus mykiss	LC50	MORT	93[e]	LC50/5 = 18.6 µg/L	23	23.4 (23.3)	Chapman, 1978
Oncorhynchus mykiss	LC50	MORT	66	LC50/5 = 13.2 µg/L	9.2	33.6 (36.1)	Cusimano et al. 1986
Geometric mean						**53.73**	
Oncorhynchus tshawytscha	LC50	MORT	395[e]	LC50/5 = 79.0 µg/L	23	99.0	Chapman, 1978
Oncorhynchus tshawytscha	LC50	MORT	364[e]	LC50/5 = 72.8 µg/L	23	91.2	Chapman, 1978
Oncorhynchus tshawytscha	LC50	MORT	97[e]	LC50/5 = 19.4 µg/L	23	24.4 (24.3)	Chapman, 1978
Geometric mean						**60.4**	
Pimephales promelas	LC50	MORT	700[f]	LC50/5 = 140 µg/L	159.5	14.4 (33.8)	Popken, 1990
Pimephales promelas	LC50	MORT	1350	LC50/5 = 270 µg/L	159.5	140 (65.2)	Popken, 1990
Pimephales promelas	LC50	MORT	140[f]	LC50/5 = 28 µg/L	63.5	14.8	Popken, 1990
Pimephales promelas	LC50	MORT	990	LC50/5 = 198 µg/L	93.9	75.0 (75.1)	Popken, 1990
Pimephales promelas	LC50	MORT	220	LC50/5 = 44 µg/L	63.5	23.2 (23.3)	Popken, 1990
Pimephales promelas	LC50	MORT	190[f]	LC50/5 = 38 µg/L	93.9	14.4	Popken, 1990
Pimephales promelas	LC50	MORT	1630	LC50/5 = 326 µg/L	186	68.0 (69.1)	Pickering & Vigor, 1965
Pimephales promelas	LC50	MORT	1760	LC50/5 = 352 µg/L	186	73.0 (74.6)	Pickering & Vigor, 1965
Pimephales promelas	LC50	MORT	870	LC50/5 = 174 µg/L	186	36.2 (36.9)	Pickering & Vigor, 1965

Name	Endpoint	Effect	Zinc µg/L	ANZECC Adjustment	Hardness mg/L $CaCO_3$	Zinc µg/L 30 mg/L $CaCO_3$	Reference
Pimephales promelas	LC50	MORT	1570	LC50/5 = 314 µg/L	186	65.4 (66.6)	Pickering & Vigor, 1965
Pimephales promelas	LC50	MORT	1620	LC50/5 = 324 µg/L	186	67.6 (68.7)	Pickering & Vigor, 1965
Pimephales promelas	LC50	MORT	1480	LC50/5 = 296 µg/L	186	61.6 (62.8)	Pickering & Vigor, 1965
Pimephales promelas	LC50	MORT	1610	LC50/5 = 322 µg/L	186	67.0 (68.3)	Pickering & Vigor, 1965
Pimephales promelas	LC50	MORT	1780	LC50/5 = 356 µg/L	186	74.0 (75.5)	Pickering & Vigor, 1965
Pimephales promelas	LC50	MORT	1690	LC50/5 = 338 µg/L	186	70.4 (71.7)	Pickering & Vigor, 1965
Pimephales promelas	LOEC	MORT	2720	LOEC/2.5 = µg/L	159.5	262.4 (262.9)	Popken, 1990
Pimephales promelas	LOEC	MORT	910	LOEC/2.5 = µg/L	93.9	138	Popken, 1990
Pimephales promelas	LOEC	MORT	940[f]	LOEC/2.5 = µg/L	159.5	90.8 (90.9)	Popken, 1990
Pimephales promelas	LOEC	MORT	430	LOEC/2.5 = µg/L	63.5	90.8 (90.9)	Popken, 1990
Pimephales promelas	NOEC	MORT	100[f]	None	93.9	37.9	Popken, 1990
Pimephales promelas	NOEC	MORT	150[f]	None	63.5	79.3	Popken, 1990
Pimephales promelas	NOEC	MORT	940	None	159.5	227	Popken, 1990
Pimephales promelas	NOEC	MORT	150	None	63.5	79.3	Popken, 1990
Pimephales promelas	NOEC	MORT	430	None	93.9	163	Popken, 1990
Pimephales promelas	NOEC	MORT	460[f]	None	159.5	111	Popken, 1990
Geometric mean						**71.05**	
Ptychocheilus oregonensis	LC50	MORT	3,650	LC50/5 = 730 µg/L	25	1316 (852)	Andros & Garton, 1980
Ptychocheilus oregonensis	LC50	MORT	2,948	LC50/5 = 589.6 µg/L	25	1063 (688)	Andros & Garton, 1980
Geometric mean						**1182.84**	
Salvelinus fontinalis	LC50	MORT	1,570	LC50/5 = 314 µg/L	186	65.4 (66.6)	Pickering & Vigor, 1965
Salvelinus fontinalis	LC50	MORT	1,550	LC50/5 = 310 µg/L	186	64.6 (65.7)	Pickering & Vigor, 1965
Geometric mean						**65**	
Insects							
Tanytarsus dissimilis	LC50	MORT	36.8[e]	LC50/5 = 7.4 µg/L	46.8	5	Anderson et al. 1980
Molluscs							
Dreissena polymorpha	LC50	MORT	4,293	LC50/5 = 858.6 µg/L	267.7	218.6 (133.6)	Kraak et al. 1994
Dreissena polymorpha	LC50	MORT	1,065	LC50/5 = 213 µg/L	267.7	54.2 (33.1)	Kraak et al. 1994

Name	Endpoint	Effect	Zinc µg/L	ANZECC Adjustment	Hardness mg/L $CaCO_3$	Zinc µg/L 30 mg/L $CaCO_3$	Reference
Geometric mean						**108.85**	
Physa gyrina	LC50	MORT	771	LC50/5 = 154.2 µg/L	36	132	Nebeker et al. 1986
Physa gyrina	NOEC	MORT	570	None	36	487 (488.2)	Nebeker et al. 1986
Geometric mean						**253.16**	
Velesunio ambiguus	LC50	MORT	66,000	LC50/5 = 13,200µg/L	70.1	11,200 (6,420)	Millington & Walker, 1983

Notes: [b] Dissolved oxygen = 5.6 mg/L.
[c] Dissolved oxygen = 3.2 mg/L.
[d] Dissolved oxygen = 1.8 mg/L.
[e]Test media was water that contained other potentially toxic constituents, including trace metals.
\[f] Not based on the whole data set reported.
In cases were ANZECC data is incorrect the correct figures are in parentheses.

3.2 Amphibians

ANZECC (2000) reports zinc toxicity data for one species of amphibian; the marbled salamander, *Ambystoma opacum* (Birge et al. 1978). The reported LC50 (mortality) of 2,380 μg/L was converted to a NOEC of 476.0 μg/L. The reported hardness was 99 mg/L $CaCO_3$; adjustment to 30 mg/L hardness yields a converted NOEC of 172.5 μg/L, although ANZECC state a value of 180.4 μg/L.

Measured zinc NOEC data for amphibians has been reported for several species, namely *Ambystoma jeffersonianum* (Jefferson's salamander), *Rana sylvatica* (wood frog) and *Bufo arenarum* (toad).

Toxicity testing for *Ambystoma jeffersonianum* and *Rana sylvatica* was undertaken at pH 5.5 and lower (Horne & Dunson, 1995). Such data is "generally excluded" by ANZECC because it falls outside it the range of 6.5-9.0. Herkovits & Perez-Coll (1991) have reported a 120 hour NOEC (mortality) of 16,000 μg/L for *Bufo arenarum* at 89.9 mg/L hardness; this data is valid for inclusion in a revised ANZECC data set.

3.3 Annelids

Data for the tubificid worm *Limnodrilus hoffmeisteri* (Wurtz & Bridges, 1961) is included in the ANZECC (2000) data set for zinc. ANZECC cite a TLm (mortality) of 7,800 μg/L at 99 mg/L $CaCO_3$, but this value is for zinc sulfate ($ZnSO_4.7H_2O$). Hence ANZECC's converted NOEC of 560 μg/L at a hardness of 30 mg/L is incorrect. The correct zinc TLm reported by Wurtz & Bridges is 1,773 μg/L and therefore the correct converted NOEC at a hardness of 30 mg/L is 127 μg/L.

3.4 Crustaceans

There are four crustaceans represented in the ANZECC (2000) data set for zinc: *Ceriodaphnia dubia* (water flea), *Ceriodaphnia reticulata* (water flea), *Daphnia magna* (water flea) and the crayfish *Orconectes virilis*.

The toxicity for zinc to *Ceriodaphnia dubia* has been the subject of a USEPA report by Carlson et al. (1986). ANZECC (2000) cites three LOECs (mortality) from that report; after applying conversion factors to the data and adjusting it to a hardness of 30 mg/L they calculate a geometric mean converted NOEC of 25.3 μg/L for the species.

There are two clear problems with ANZECC's use of data from Carlson et al. Firstly, the LC50 data that is cited is based on 48 hour tests, which is too short a period to be considered indicative of chronic toxicity. Secondly, measured NOEC data that is present in the report is ignored. Carlson et al. report a 168 hr NOEC of 94 μg/L for both mortality and reproduction endpoints at 32 mg/L hardness, which is equivalent to 89 μg/L at 30 mg/L hardness using the ANZECC method of hardness adjustment.

Comparison of the 46 hour LC50 data (geometric mean = 126 μg/L at 30 mg/L hardness) with the reported NOEC is useful because it enables the calculation of the LC50/NOEC ratio, which is 1.4. This comparison demonstrates a five-fold LC50-NOEC conversion factor is overly conservative and invalid for *Ceriodaphnia dubia*.

Based on the work of Carlson & Roush (1985), ANZECC report a LC50 of 224 μg/L for *Ceriodaphnia reticulata* at 353 mg/L hardness; hence, ANZECC's converted, hardness adjusted NOEC is 5.52 μg/L. However, ANZECC's approach with respect to *Ceriodaphnia reticulata* is flawed in the same manner as for *Ceriodaphnia dubia*, i.e., the data cited is based on a 48 hour test and measured NOEC data is ignored.

Carlson & Roush (1985) report NOECs for *Ceriodaphnia reticulata* for mortality and reproduction endpoints; the reproduction endpoint is more sensitive and only that specific data is cited here; the 168 hour NOECs are 58 μg/L (hardness = 376 mg/L) and 140 μg/L (hardness = 362 mg/L). The geometric mean of these NOECs adjusted to 30 mg/L hardness using the ANZECC method is 10.7 μg/L. The LC50/NOEC ratio based on the data of Carlson & Roush (1985) is 2.0, and therefore the LC50-NOEC conversion factor of 5.0 is invalid for *Ceriodaphnia reticulata*.

ANZECC (2000) cite two studies on the chronic toxicity of zinc to *Daphnia magna* reproduction (Biesinger & Christensen, 1972; Paulauskis & Winner, 1988), which is a more sensitive endpoint for *Daphnia magna* than mortality or growth. Only the data of Paulauskis & Winner is based on measured NOECs over a hardness range of 51.9-197 mg/L; it is noted that ANZECC only report five out of the six data cited by Paulauskis & Winner (another NOEC of 87.5 μg/L at 101.8 mg/L hardness is reported) and that ANZECC also significantly mis-calculate the hardness adjusted NOEC of one of the data. The true geometric mean of the NOEC data measured by Paulauskis & Winner is 24.57 μg/L at 30 mg/L hardness compared with the converted NOEC of 14.34 μg/L at 30 mg/L hardness calculated from the data of Biesinger & Christensen. Hence, the inappropriate use of using a conversion factor of 5.0 to derive NOECs from LC50s is again demonstrated; in this instance the LOEC/NOEC ratio is 2.9.

Heijerick et al. (2005) have conducted extensive toxicity testing on *Daphnia magna* in order to develop a chronic zinc biotic ligand model for the species and report several 21-day NOECs for reproductive endpoints at various hardness values. This data is too recent to have been used in ANZECC assessment.

Mirenda (1986) has reported a 336 hour LC50 (mortality) of 84,000 μg/L at 26 mg/L hardness for the crayfish *Orconectes virilis*. After application of ANZECC's NOEC conversion factor and hardness adjustment to 30 mg/L a converted NOEC of 18,973 μg/L is obtained; ANZECC report 18,480 μg/L.

There have been several other reports of chronic toxicity of zinc to crustaceans. Zou (1997) has investigated the effects of zinc on the water flea, *Moina iraasa* and found a NOEC (reproduction) of 25 μg/L at 5 mg/L hardness and noted that the effects of zinc at that concentration were beneficial.

3.5 Fish

The ANZECC zinc dataset contains data for ten species of fish: *Carassius auratus* (goldfish), *Channa marulius* (snake-head catfish), *Ictalurus punctatus* (channel catfish), *Lepomis macrochirus* (bluegill), *Micropterus salmoides* (largemouth bass), *Oncorhynchus mykiss* (rainbow trout), *Oncorhynchus tshawytscha* (chinook salmon), *Pimephales promelas* (fathead minnow), *Ptychocheilus oregonensis* (northern squawfish) and *Salvelinus fontinalis* (brook trout).

The majority of the fish data is based on converted LC50 (mortality) data and most is reported accurately by ANZECC. However, there are problems with some of the fish toxicity data that ANZECC cite.

Reed at al. (1980) do not report a LC50 of 6,900 μg/L at a hardness of 313 mg/L for *Ictalurus punctatus*; this figure is actually the reported NOEC and the reported LC50 is 8,200 μg/L. Hence the hardness adjusted NOEC for *Ictalurus punctatus* is 940 μg/L and the LC50/NOEC ratio is 1.2.

Data for *Lepomis macrochirus* is invalid because the toxicity tests were conducted at low dissolved oxygen concentrations (less than or equal to 5.6 mg/L) and data for *Oncorhynchus tshawytscha* should be excluded because the test media contained potentially deleterious concentrations of trace metals, including copper, lead and nickel.

The reference cited by ANZECC for *Salvelinus fontinalis* is incorrect as there are no toxicity data reported by Pikering & Vigor (1965) for brook trout. The LC50s for *Salvelinus fontinalis* cited by ANZECC were attributable to Holcombe & Andrew (1978) but should be excluded because they are acute (96 hour) data.

ANZECC cite seven LC50s for *Oncorhynchus mykiss* but four of the data points from Chapman (1978) are invalid because the test media contained other trace metals. In addition some data has been overlooked. Goettl et al. (1976) have studied the long-term effects of zinc on *Oncorhynchus mykiss* and reports a 1 month NOEC (mortality) of 36 μg/L at 27.7 mg/L hardness and a 27 month NOEC (mortality) of 320 μg/L at 353.3 mg/L hardness. Sinley et al. (1974) have studied the long-term and life-cycle of zinc on mortality and report NOECs of 140 μg/L at 6 mg/L hardness and 320 μg/L at 333 mg/L hardness. Birge et al. (1980) have reported a 28 day LC1 of 216 μg/L, LC10 of 451 μg/L and LC50 of 216 μg/L 1120 at 101 mg/L hardness (mortality).

ANZECC cite two reports on the toxicity of zinc to *Pimephales promelas*. Pickering & Vigor (1965) report LC50 data (mortality) at 186 mg/L hardness whereas Popken (1990) reports LC50, LOEC and NOEC data at low (63.5 mg/L), medium (93.9 mg/L) and high (159.5 mg/L) hardness. Of the data ANZECC used, the only appropriate data for trigger value derivation were the NOECs observed for Popken's complete data set (Popken, 1990).

There have been several other NOECs reported for *Pimephales promelas* that ANZECC did not use:

- Magilette et al. (1995) have reported a seven day NOEC (growth) of 290 μg/L at 190 mg/L hardness.
- Norberg & Mount (1985) have reported a seven day NOEC (mortality) of 85 μg/L at 48 mg/L hardness. The calculated MATC was 125 μg/L.
- Norberg-King Mount (1989) has reported five-day and seven-day NOEC data for both mortality and growth endpoints at a hardness of 43.5 mg/L. The NOECs were 117 μg/L, 277 μg/L and 291 μg/L (mortality) and 117 μg/L, 128 μg/L, 128 μg/L, 129 μg/L, 277 μg/L and 291 μg/L (growth). Five-day and seven-day LC50 data was also reported; the geometric mean LC50 was 264 μg/L at a hardness of 43.5 mg/L.
- Benoit & Holcombe (1978) have reported a seven day NOEC (reproduction) of 78 μg/L at 46 mg/L hardness. The calculated MATC was 125 μg/L.

NOEC data for other fish has been overlooked by ANZECC (2000). Dave et al. (1987) have reported 16-day NOEC data (mortality and reproduction) for *Brachydanio rerio* (zebra danio) of 50,000 μg/L, 25,000 μg/L, 21,875 μg/L, 18,750 μg/L and 18,750 μg/L at 100 mg/L hardness. Meinelt & Stüber (1995) have also reported mortality NOECs for *Brachydanio rerio*; 1,500 μg/L and 20,000 μg/L at hardness values of 62.5 mg/L and 308.8 mg/L respectively.

Nehring & Goettl (1974) have reported 14-day NOECs of 230 μg/L at 54 mg/L hardness (mortality) for *Salmo trutta* (brown trout) and 360 μg/L at 58 mg/L hardness (mortality) for Salmo clarki (cutthroat trout). The 14-day LC50s were 640 μg/L and 670 μg/L respectively.

Bengtsson (1974) has reported a NOEC (reproduction) of 50 μg/L at 28.6 mg/L hardness for the minnow *Phoxinus phoxinus*.

3.6 Insects

ANZECC (2000) has included data for one insect, the midge *Tanytarsus dissimilis*, in its zinc data set. Anderson et al. (1980) report a LC50 (mortality) of 36.8 μg/L at 46.8 mg/L hardness for *Tanytarsus dissimilis*; the converted NOEC is 5.0 at a hardness of 30 mg/L. However it is noted the test media used by Anderson et al. (1980) included detectable concentrations of copper. Hence, the data should be excluded.

3.7 Molluscs

The ANZECC zinc dataset includes three species of mollusc: *Dreissena polymorpha* (zebra mussel), *Physa gyrina* (pouch snail) and *Velesunio ambiguous* (mussel).

Kraak et al. (1994) have reported mortality based on exposure of *Dreissena polymorpha* to zinc, however ANZECC (2000) do not accurately report their findings. Firstly the testing was undertaken at a hardness of 150 mg/L CaO, which is equivalent to 267.7 mg/L $CaCO_3$; ANZECC do not make the hardness correction when they interpret the data. Secondly ANZECC cite two LC50s of 4,293 μg/L (after three weeks) and 1,065 μg/L (after 10 weeks); clearly the former should be dismissed in favour of the latter, which is over a longer timeframe. Thirdly, the data of Kraak et al. (1994) indicates that the ten week LC50 and NOEC with respect to mortality in *Dreissena polymorpha* are 1,065 μg/L and 382 μg/L respectively.

The ANZECC's (2000) use of LC50 data for *Dreissena polymorpha* is invalid and the measured NOEC data should be used in the dataset instead. Making the hardness adjustment according to the ANZECC (2000) method yields a NOEC of 60 μg/L at 30 mg/L hardness; the LC50/NOEC ratio based on ten week data is 2.8.

Nebeker et al. (1986) report LC50 (771 μg/L) and NOEC (570 μg/L) data for *Physa gyrina* at 36 mg/L hardness. The data is correctly cited by ANZECC (2000), however they produce a converted NOEC from the LC50 data and use it in conjunction with the measured NOEC to produce a hardness adjusted geometric mean NOEC of 253.16 μg/L. ANZECC's approach is inappropriate, particularly in view of the fact that the LC50/NOEC ratio is 1.4; only the measured NOEC (488 μg/L at 30 mg/L hardness) should be used.

Millington & Walker (1983) have reported the effects of zinc on the Australian freshwater mussel *Velesunio ambiguous* and calculate a LC50 (mortality) of 66,000 μg/L. The toxicity testing was conducted at a mean hardness of 42 mg/L as the carbonate anion, which is equivalent to 70 mg/L as $CaCO_{3.}$ ANZECC did not make this correction in their hardness adjustment calculation and as a consequence the converted NOEC they report (11,200 μg/L at 30 mg/L hardness) was incorrect.

More importantly, however, ANZECC fail to report the measured NOEC (20,000 μg/L) reported by Millington & Walker (1985); converted to a hardness of 30 mg/L the measured NOEC (mortality) is 9,727 μg/L. It is noted that the ten week LC50/NOEC ratio for *Velesunio ambiguous* is 3.3.

3.8 Discussion

As noted in Section 3.2 to 3.7, the ANZECC (2000) data set for deriving trigger values to zinc contains a number of errors. These include:

- Incorrectly cited data.
- Miscalculated data.
- Use of acute data.
- Inclusion of data not meeting requirements (such as low pH or low DO).
- Use of estimated data in place of real empirical data.

With regard to the last point, it is noted the actual ratios of toxicity endpoints (e.g., the LC50/NOEC ratio) do not compare well with the ANZECC estimates, which are overly conservative.

Hence, the ANZECC (2000) data set for the derivation of zinc trigger values is inappropriate for use. In addition the ANZECC (2000) zinc data set omits data that should be included. A revised ANZECC data set is presented in Table 5.1 of this report.

4. The Zinc Toxicity-Hardness Relationship

4.1 Introduction

The first published report defining the relationship between zinc toxicity and hardness appears to be attributed to Lloyd & Herbert (1962); they described the mathematical relationship between the 48 hour LC50 of zinc and the hardness of the water as:

$$\log[Zn] = -0.9614 + 0.6053 \log[hardness]$$

Subsequently, the zinc toxicity-hardness relationship has been recognised by regulators and employed by USEPA in its ambient water quality criteria for three decades (USEPA, 1976). The first hardness dependant zinc-hardness aquatic criterion developed by the USEPA (USEPA, 1980) was derived based on data from 43 freshwater species, eight of which showed that zinc toxicity decreased as hardness increased. The acute, or criterion maximum concentration (CMC), criterion was given by:

$$CMC = \exp\{0.83[\ln(hardness)]+1.45\}$$

In contrast the 1980 USEPA chronic criterion was 47 μg/L and was not hardness dependant. The first hardness dependent criterion continuous concentration (CCC) or chronic USEPA criterion for zinc was notified, in brief, in the 1986 USEPA criteria update (USEPA, 1986) and had the same slope as the current criterion:

$$CCC = \exp\{0.8473[\ln(hardness)]+0.7614\}$$

More detail into the derivation of the chronic criterion for zinc was provided in the 1987 ambient water quality criteria for zinc (USEPA, 1987).

4.2 Review of the USEPA Derived Toxicity-Hardness Slope

The 1987 USEPA ambient water quality criteria for zinc (USEPA, 1987) provided the derivation of the zinc toxicity-hardness slope. Acute toxicity data for eight species over a range of hardness concentrations were analysed by USEPA and acute *ln*(zinc concentration) versus *ln*(hardness) slopes were derived for each species. The selection conditions for data to be used in the derivation the zinc toxicity-hardness slope were: the highest hardness was at least three times the lowest hardness and the highest was also at least 100 mg/L $CaCO_3$ higher than the lowest. The individual species slopes ranged from 0.56 to 1.65; ultimately USEPA selected a pooled slope of 0.8473 based on all 109 data from the eight species to define the acute toxicity-hardness relationship.

An analogous slope defining the relationship between from chronic zinc toxicity and hardness was not derived by USEPA due to a lack of chronic toxicity data, which totalled just 14 points over ten species. Hence, USEPA simply adopted the acute slope of 0.8473 to define the chronic toxicity-hardness relationship for zinc. In the absence of data this approach was considered legitimate, even though it was clearly a crude estimate.

Almost two decades later, the current USEPA aquatic criteria for zinc still use a slope 0.8473. Likewise, the derivation of the ANZECC (2000) zinc trigger values was reliant on the USEPA slope in order to adjust NOEC data to a common hardness of 30 mg/L $CaCO_3$. However, the continued use of this slope can no longer be supported due to the wealth of chronic zinc toxicity data for freshwater species that is now available. Therefore, it is appropriate to calculate a new chronic zinc toxicity – hardness slope.

4.3 Calculation of a New Chronic Zinc Toxicity-Hardness Slope

4.3.1 Approach

The derivation of a chronic zinc-hardness relationship is not without difficulty because considerable variability exists for those species for which either acute or chronic data is available. For example, Dave et al. (1987) conducted a ring-test on *Danio rerio* at several laboratories and found the reported NOECs (mortality) at 100 mg/L $CaCO_3$ ranged from 12,500 to 50,000 μg/L (mean 26,775 μg/L; standard deviation 13,000 μg/L; n = 20).

Such problems are not unique to zinc. In the 2001 update of the ambient water quality criteria for cadmium USEPA used the same requirements for data selection as in previous hardness dependent criteria, i.e., the highest hardness is at least three times the lowest, and the highest is also at least 100 mg/L greater than the lowest; this reduced the dataset to a mere seven data for three species (USEPA, 2001). Hence, USEPA derived a chronic cadmium versus hardness slope based on *Salmo trutta* (slope = 0.5212, R^2 = 1, n = 2), *Pimephales promelas* (slope = 1.0034, R^2 = 1, n = 2), and *Daphnia magna* (slope = 0.7712, R^2 = 0.962, n = 3); a data point was removed from the *Daphnia magna* dataset due to the poor data fit. The reduced dataset afforded a pooled slope of for these species was 0.7409.

The reality of a chronic cadmium-hardness relationship based on a small dataset and limited precision did not dissuade USEPA from promulgating a chronic criteria. The task of deriving a slope that is valid for all species is qualitative and fraught with uncertainty and yet is one that is required for regulatory purposes.

In this context, a chronic zinc-hardness relationship was calculated according to the USEPA guidelines, however the following conditions were applied:

- datasets for which there were fewer than three data were not used;
- for each species where there was at least three data, the highest hardness was at least three times the lowest, and the highest was also at least 100 mg/L greater than the lowest;
- different endpoints (i.e., LC50/EC50s, LOECs, MATCs and NOECs) and effects (e.g., mortality, reproduction) were analysed separately since it is implausible for a strong toxicity-hardness relationship to exist across different endpoints and/or effects at the same hardness value;
- if toxicity data at the same hardness within a species dataset were present the geometric mean of the effect concentration was used;
- if the R^2 value was poor within each species dataset, data from individual researches was examined to determine if a sub-set of workable data could be found;
- slopes with overtly poor R^2 values were rejected.

4.3.2 Slope calculation

Based on the literature and database review described in Section 3, 265 data were found for chronic zinc toxicity endpoints at stated hardness concentrations; this included LC50, EC50, LOEC, MATC and NOEC endpoints.

LC50/EC50 comprised 40 data, 36 of which from three species met the USEPA hardness requirements. 22 data from two species out of a total of 56 LOEC data and 15 data from two species out of a total of 54 MATC data met the USEPA hardness requirements. Data were most abundant for the NOEC endpoint; all 105 data from four species were suitable for use in deriving a toxicity hardness slope.

Plots of *ln*(zinc concentration) versus *ln*(hardness) slopes were obtained; in cases where more than one endpoint zinc concentration was present for a particular hardness the geometric mean of the zinc concentration was plotted. This approach was used because it effectively removed the data bias from studies that reported multiple toxicity endpoints at the same hardness: in addition it resulted in much stronger toxicity versus hardness correlations. Table 4.1 presents a summary of the *ln*(zinc concentration) versus *ln*(hardness) slopes derived for each species according to endpoint.

Table 4.1: Chronic *ln*(zinc concentration) versus *ln*(hardness) slopes.

Endpoint	Species	Effect	N	Slope	R^2	Comment
LC50/EC50	*Oncorhynchus mykiss*	MORT	12 (8)	1.1273	0.9592	All data used
LC50/EC50	*Pimephales promelas*	MORT	14 (5)	0.8554	0.1111	Researcher specific data did not provide a better fit
LOEC	*Oncorhynchus mykiss*	MORT	5 (3)	0.3536	0.9981	All data used
LOEC	*Pimephales promelas*	GRO	9 (3)	0.4271	0.6105	Researcher specific data did not provide a better fit
LOEC	*Pimephales promelas*	MORT	6 (4)	1.5353	0.9124	All data used
MATC	*Pimephales promelas*	GROT	8 (3)	0.6431	0.6989	Researcher specific data did not provide a better fit
NOEC	*Danio rerio*	MORT	22 (3)	1.2936	0.4678	Researcher specific data did not provide a better fit
NOEC	*Daphnia magna*	REP	7 (3)	1.6559	0.9787	Researcher specific data provided a better fit
NOEC	*Daphnia magna*	MORT	7 (3)	0.6652	1.0000	All data used
NOEC	*Oncorhynchus mykiss*	MORT	4 (4)	0.5840	0.6946	Researcher specific data did not provide a better fit
NOEC	*Pimephales promelas*	GRO	13 (3)	0.8820	0.9202	All data used
NOEC	*Pimephales promelas*	MORT	13 (4)	1.4002	0.8579	All data used

Note: N = unique hardness data points; figure in parentheses represents number of data used to derive the slope i.e., including geometric mean data.

A high degree of correlation was found with LC50/EC50 data for *Oncorhynchus mykiss* (0.9592), LOEC data for *Oncorhynchus mykiss* (0.9981) and *Pimephales promelas* (0.9124), and NOEC data for *Pimephales promelas* (0.9292 for growth and 0.8579 for mortality) and *Daphnia magna* (0.9787 for reproduction and 1.0000 for mortality).

Reasonable correlations were found with LOEC data for *Pimephales promelas* (0.6105), MATC data for *Pimephales promelas* (0.6431) and NOEC data for *Oncorhynchus mykiss* (0.6946). Correlations were poor with LC50/EC50 data for *Pimephales promelas* (0.1111) and with NOEC data for *Danio rerio* (0.4678).

Based on the data presented in Table 4.1, a pooled slope of 0.7143 was selected as the preferred choice for adjusting NOEC data to a common hardness of 30 mg/L $CaCO_3$ prior to recalculation of the ANZECC trigger values. A plot of ln(concentration) versus ln(hardness) data used in the derivation of the pooled slope is presented in Fig. 4.1. It is noted that the pooled slope is based on:

- a sizeable number of data (84);
- ten individual slopes;
- data for a sensitive invertebrate species (*Daphnia magna*);
- data for a sensitive fish species (*Oncorhynchus mykiss*).

As such, although there are qualitative features in the manner in which the slope is derived, the result slope is more robust in terms of data quantity and selection than the current USEPA hardness slope of 0.8473.

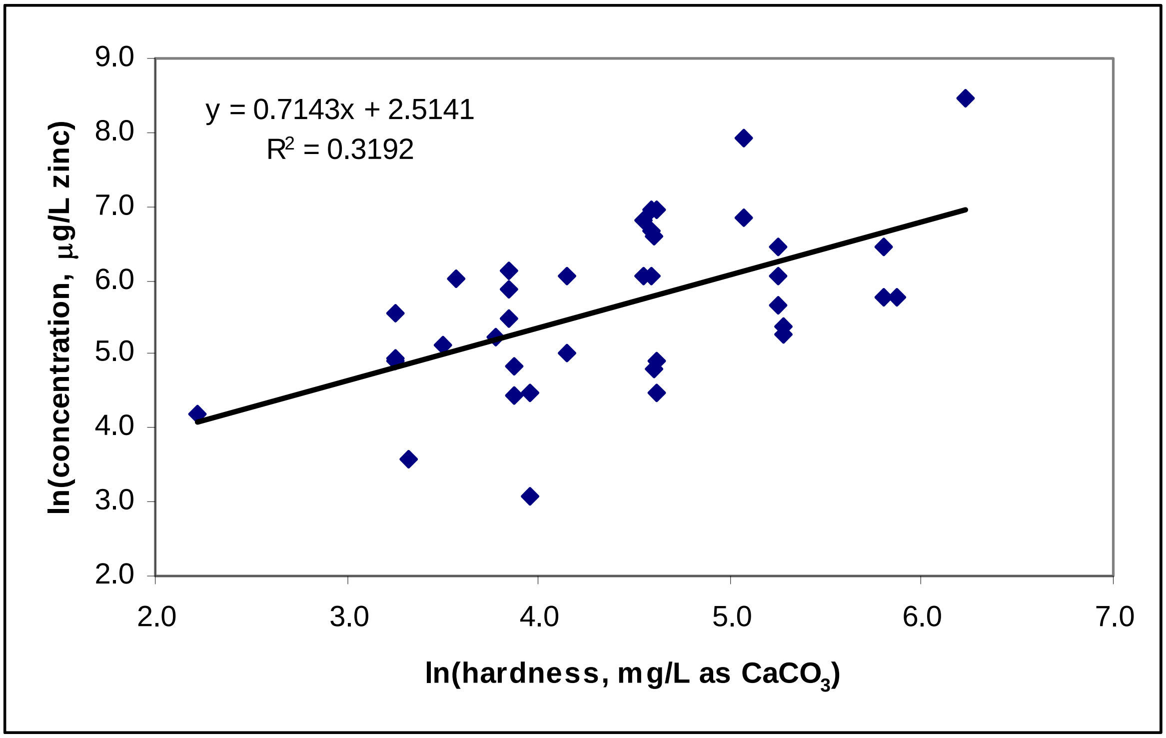

Fig. 4.1: Plot of *ln*(concentration) versus *ln*(hardness) data used in the derivation of the pooled slope.

5. Recalculation of the ANZECC Zinc Trigger Values

5.1 Approach

The approach used in the recalculation of the ANZECC zinc trigger values was as follows:

- construction of an appropriate NOEC dataset (refer sections 3.2-3.7);
- adjustment of NOEC values to a hardness of 30 mg/L $CaCO_3$ using a slope of 0.7143 (refer Section 4.3);
- where appropriate, only the most sensitive NOEC endpoint for a species was used;
- calculation of the geometric mean of the most sensitive NOEC endpoint for each species;
- application of the BurrliOz software.

5.2 Calculation of Trigger Values According to ANZECC Methodology

There is a sufficient number of quality data for the data set to include only measured NOECs, hence the dataset is suitable for use in the derivation of a high reliability trigger values. The revised data set includes one amphibian, four crustaceans, ten fish and three molluscs (a total of 18 species and 78 data), which is considered an appropriate representation of species relevant to New Zealand.

The hardness adjusted (30 mg/L $CaCO_3$) NOECs for these species are presented in Table 5.1.

Fig. 5.1 shows the result of fitting the data using the BurrliOZ software; only the 95th percentile plot is shown. The recalculated high reliability trigger values for zinc at hardness 30 mg/L $CaCO_3$ based upon the BurrliOz outputs are:

- Protection of 99% of aquatic species: 12.4 μg/L.
- Protection of 95% of aquatic species: 22.5 μg/L.
- Protection of 90% of aquatic species: 32.5 μg/L.
- Protection of 80% of aquatic species: 53.6 μg/L.

It should be noted the trigger values relate to the dissolved metals fraction. Also, trigger values at different hardness concentrations can be calculated at according to the following hardness-dependent equation:

Zinc HMTV = TV(H/30)0.7143

5.3 Discussion

The zinc trigger values derived here are high reliability (i.e., based on NOEC data); they will be protective to aquatic biota in New Zealand. The 99th percentile is appropriate for pristine waters, the 95th percentile is generally taken as the default trigger value for New Zealand waters and the 90th percentile is most appropriate for urban surface waters.

As a reality check, the trigger values were compared with those previous published or used by regulators. That data is presented in Table 5.2.

Table 5.1: Summary of zinc aquatic life toxicity data appropriate for use in trigger level development.

Name	Duration hrs	Endpoint	Effect	Zinc µg/L	Hardness	Zinc µg/L 30 mg/L $CaCO_3$	Reference
Amphibians							
Bufo arenarum	120	NOEC	MORT	2,380	89.9	1,087	Herkovits & Perez-Coll (1991)
Crustaceans							
Ceriodaphnia dubia	168	NOEC	REP	94	32	90	Carlson et al. (1986)
Ceriodaphnia reticulata	168	NOEC	REP	58	376	10	Carlson & Roush (1985)
Ceriodaphnia reticulata	168	NOEC	REP	140	362	24	Carlson & Roush (1985)
Geometric mean						**15**	
Daphnia magna	1200	NOEC	REP	12.5	51.9	8.5	Paulauskis & Winner (1988)
Daphnia magna	1200	NOEC	REP	37.5	51.9	25	Paulauskis & Winner (1988)
Daphnia magna	1200	NOEC	REP	87.5	101.8	37	Paulauskis & Winner (1988)
Daphnia magna	1200	NOEC	REP	87.5	101.8	37	Paulauskis & Winner (1988)
Daphnia magna	1200	NOEC	REP	250	197	65	Paulauskis & Winner (1988)
Daphnia magna	1200	NOEC	REP	162.5	197	42	Paulauskis & Winner (1988)
Daphnia magna	504	NOEC	REP	39.2	50	49	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	143	50	27	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	135	50	99	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	143	50	94	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	162	50	99	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	154	50	112	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	133	50	107	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	117	50	92	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	50	75	81	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	48	75	26	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	54	125	25	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	147	125	19	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	92	225	53	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	165	225	22	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	158	325	39	Heijerick et al. (2005)

Name	Duration hrs	Endpoint	Effect	Zinc µg/L	Hardness	Zinc µg/L 30 mg/L $CaCO_3$	Reference
Daphnia magna	504	NOEC	REP	159	325	29	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	98	425	29	Heijerick et al. (2005)
Daphnia magna	504	NOEC	REP	156	425	15	Heijerick et al. (2005)
Geometric mean						**40**	
Moina irrasa	144	NOEC	REP	25	5	90	Zou (1997)
Fish							
Brachydanio rerio	384	NOEC	REP	12500	100	5290	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	780	100	330	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	3130	100	1325	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	780	100	330	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	780	100	330	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	780	100	330	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	12500	100	5290	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	3130	100	1325	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	12500	100	5290	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	6250	100	2645	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	6250	100	2645	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	780	100	330	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	3130	100	1325	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	3130	100	1325	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	780	100	330	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	780	100	330	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	12500	100	5290	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	3130	100	1325	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	12500	100	5290	Dave et al. (1987)
Brachydanio rerio	384	NOEC	REP	3130	100	1325	Dave et al. (1987)
Geometric mean						**1234**	
Ictalurus punctatus	336	NOEC	MORT	6,900	313	1,292	Reed et al. (1980)

Name	Duration hrs	Endpoint	Effect	Zinc µg/L	Hardness	Zinc µg/L 30 mg/L $CaCO_3$	Reference
Jordanella floridae	2,400	NOEC	GRO	26	44	20	Spehar (1976)
Jordanella floridae	2,400	NOEC	GRO	85	44	65	Spehar (1976)
Geometric mean						**36**	
Lepomis macrochirus	336	NOEC	MORT	8,200	313	1,536	Reed et al. (1980)
Micropterus salmoides	336	NOEC	MORT	6,000	313	1,124	Reed et al. (1980)
Oncorhynchus mykiss	720	NOEC	MORT	36	27.7	38	Goettl et al. (1976)
Oncorhynchus mykiss	19,440	NOEC	MORT	320	353.2	55	Goettl et al. (1976)
Oncorhynchus mykiss	> 96	NOEC	MORT	140	26	155	Sinley et al. (1974)
Oncorhynchus mykiss	15,120	NOEC	MORT	320	333	57	Sinley et al. (1974)
Geometric mean						**66**	
Pimephales promelas	168	NOEC	GRO	290	190	78	Magliette et al. (1995)
Pimephales promelas	144	NOEC	GRO	120	100	51	Dawson et al. (1988)
Pimephales promelas	120	NOEC	GRO	128	43.5	98	Norberg-King (1989)
Pimephales promelas	168	NOEC	GRO	128	43.5	98	Norberg-King (1989)
Pimephales promelas	168	NOEC	GRO	117	43.5	90	Norberg-King (1989)
Pimephales promelas	168	NOEC	GRO	129	43.5	99	Norberg-King (1989)
Pimephales promelas	168	NOEC	GRO	277	43.5	212	Norberg-King (1989)
Pimephales promelas	168	NOEC	GRO	291	43.5	223	Norberg-King (1989)
Pimephales promelas	768	NOEC	GRO	275	43.5	211	Norberg-King (1989)
Pimephales promelas	768	NOEC	GRO	275	43.5	211	Norberg-King (1989)
Pimephales promelas	768	NOEC	GRO	275	43.5	211	Norberg-King (1989)
Pimephales promelas	120	NOEC	GRO	285	43.5	219	Norberg-King (1989)
Geometric mean						**134**	
Phoxinus phoxinus	>3,228	NOEC	REP	50	28.6	52	Bengtsson (1974)
Salmo clarki	336	NOEC	MORT	360	58	225	Nehring & Goettl (1974)

Name	Duration hrs	Endpoint	Effect	Zinc µg/L	Hardness	Zinc µg/L 30 mg/L $CaCO_3$	Reference
Salmo trutta	336	NOEC	MORT	230	54	151	Nehring & Goettl (1974)
Molluscs							
Dreissena polymorpha	1,680	NOEC	MORT	382	267.7	80	Kraak et al. (1994)
Physa gyrina	720	NOEC	MORT	570	36	500	Nebeker et al. (1986)
Velesunio ambiguous		NOEC	MORT	20,000	70	10,919	Millington & Walker (1983)

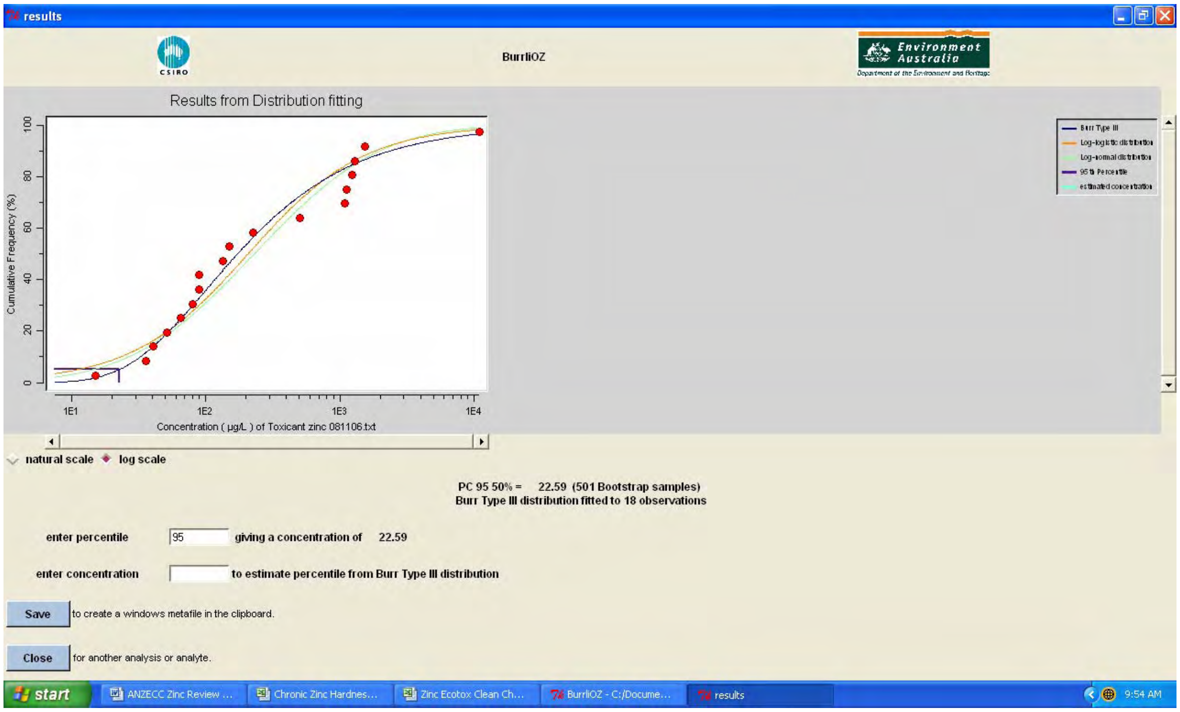

Fig. 5.1: Burr Type III fit of NOEC data for zinc; 95 percentile output shown.

Table 5.2: Comparison of recalculated trigger values compared with other published guidelines at hardness 30 mg/L $CaCO_3$.

	Zinc (µg/L)
USEPA (1987)	43.2
Golden Cross site-specific (KMA, 1988)	19.3
Black Hills site specific (TIMES, 1996)	55.8
Golden Cross site-specific revision (KMA, 1998)	22.9
ANZECC (2000, 95% trigger value)	8.0
Coeur d'Alene site-specifc (Windward, 2002)	87.9
ANZECC recalculated (95% trigger value, this work)	22.5

The trigger values developed here are less stringent than the ANZECC (2000) trigger values for zinc, which are inappropriate due to a combination of poor data selection and omission of relevant data. It is noted the ANZECC (2000) 95th percentile trigger does not correspond with other zinc criteria developed either in New Zealand or in the United States. However, the 95th percentile trigger value developed here is consistent with the site specific criteria developed for use at the Golden Cross mine (KMA, 1988; KMA, 1998).

In contrast, with the exception of the 80th percentile trigger value, the trigger values developed are more stringent than the current USEPA chronic criterion; this is due in large part to the fact that the ANZECC approach is conservative in its use of NOEC data. Given that the USEPA criteria has enjoyed almost 20 years of successful use, there is a high degree of confidence that the more conservative re-calculated trigger values will afford the high level of protection required for New Zealand aquatic species.

This confidence is further enhanced when noting that the recalculated trigger values are 1.9 to 3.9 times more conservative compared with site-specific criteria (Black Hills and Coeur d'Alene) developed in the United States.

6. Summary and Conclusions

This report has reviewed the ANZECC (2000) trigger values for zinc. Specifically it has:

- Reviewed the ANZECC (2000) approach to the derivation of the trigger values.
- Reviewed the data used in the development of the ANZECC (2000) zinc trigger values.
- Reviewed the available toxicological data for zinc from a range of sources, including ECOTOX.
- Reviewed the zinc toxicity-hardness relationship and recalculated a zinc-hardness slope using the USEPA approach.
- Derived toxicological data that is appropriate for use in the derivation of zinc trigger values for New Zealand surface waters.
- Re- calculated the zinc trigger values using the methods identified in ANZECC (2000).

This report has found the ANZECC (2000) data set for deriving trigger values to zinc contains a number of errors; hence the ANZECC (2000) data set for the derivation of zinc trigger values is inappropriate for use. In addition the ANZECC (2000) zinc data set omits data that should be included.

The revised data set coupled with a revised zinc-hardness slope resulted in the calculation of the following trigger values for zinc at a hardness of **30 mg/L $CaCO_3$**:

- Protection of 99% of aquatic species: 12.4 μg/L
- Protection of 95% of aquatic species: 22.5 μg/L
- Protection of 90% of aquatic species: 32.5 μg/L
- Protection of 80% of aquatic species: 53.6 μg/L

The re-calculated HMTV for zinc is:

Zinc HMTV = TV(H/30)0.7143

The re-calculated zinc trigger values are less stringent than the ANZECC (2000) trigger values but more stringent than the current USEPA chronic criterion. A high level of protection for New Zealand aquatic species can be expected from the recalculated trigger values.

The implications of using the ANZECC (2000) trigger values for zinc for assessing water quality of Christchurch waterways is that regular exceedance of trigger values will be identified and the cost of unnecessary additional investigations and monitoring to determine if an actual effect has occurred. The revised ANZECC trigger value for protection of 90% of aquatic species is 2.2 times the ANZECC (2000) trigger value.

7. References

Anderson, R. L.; Walbridge, C. T.; Fiandt, J. T. 1980: Survival and Growth of Tanytarsus dissimilis (Chironomidae) Exposed to Copper, Cadmium, Zinc, and Lead Arch. Environ. Contam. Toxicol. 9 (3) 329-335.

Andros, J. D.; Garton, R. R. 1980: Acute Lethality of Copper, Cadmium, and Zinc to Northern Squawfish Trans. Am. Fish. Soc. 109 (2) 235-238.

ANZECC, 2000: Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000. Australian and New Zealand Environment and Conservation Council, Agriculture and Resource Management Council of Australia and New Zealand.

AQUIRE, 1994: EPA ERL-Duluth's Aquatic Ecotoxicology Data Systems. USEPA.

Bengtsson, B. E. 1974: The effects of zinc on mortality and reproduction of the minnow, Phoxinus phoxinus. Arch. Environ. Contam. Toxicol., 2: 342-355.

Benoit, D. A.; Holcombe, G. W. 1978: Toxic Effects of Zinc on Fathead Minnows (Pimephales promelas) in Soft Water J. Fish Biol. 13(6):701-708.

Biesinger, K. E.; Christensen, G .M. 1972: Effects of Various Metals on Survival, Growth, Reproduction, and Metabolism of Daphnia magna J. Fish. Res. Board Can. 29 (12) 1691-1700.

Birge, W. J. 1978: Aquatic Toxicology of Trace Elements of Coal and Fly Ash IN: J.H.Thorp and J. W. Gibbons (Eds.), Dep. Energy Symp. Ser., Energy and Environmental Stress in Aquatic Systems, Augusta, GA 48 219-240.

Birge, W. J.; Hudson, J. E.; Black, J. A.; Westerman, A. G. 1978: Embryo-Larval Bioassays on Inorganic Coal Elements and in Situ Biomonitoring of Coal-Waste Effluents In: Symp. U.S. Fish Wildl. Serv., Surface Mining Fish Wildl. Needs in Eastern U.S., W.VA 97-104.

Birge, W. J.; Black, J. A; Westerman, A. G.; Hudson, J. E. 1980: Aquatic toxicity tests on inorganic elements occurring in oil shale. In: Oil shale symposium: Sampling, analysis and quality assurance. Gale, C. (Ed.). EPA-600/9-80-022. National Technical Information Service, Springfield, VA. pp. 519-534.

Campbell, E.; Palmer, M. J.; Shao, Q.; Warne, M. St J.; Wilson, D. 2000: BurrliOZ: A computer program for calculating toxicant trigger values for the ANZECC and ARMCANZ water quality guidelines. Perth WA.

Carlson, A. R.; Nelson, H.; Hammermeister, D. 1986: Evaluation of Site-Specific Criteria for Copper and Zinc: An Integration of Metal Addition Toxicity, Effluent and Receiving Water Toxicity, and EPA 600/3-86-026, U.S. EPA, Duluth, MN 68 p.

Carlson, A. R.; Roush, T. H. 1985: Site-Specific Water Quality Studies of the Straight River, Minnesota: Complex Effluent Toxicity, Zinc Toxicity, and Biological Survey Relationships EPA 600/3-85-005, U.S. EPA, Duluth, MN. (U.S. NTIS PB85-160703) 59 p.

Chapman, G. A. 1978: Toxicities of Cadmium, Copper, and Zinc to Four Juvenile Stages of Chinook Salmon and Steelheads Trans. Am. Fish. Soc. 107 (6) 841-847.

Cusimano, R. F.; Brakke, D. F.; Chapman, G. A. 1986: Effects of pH on the Toxicities of Cadmium, Copper, and Zinc to Steelhead Trout (Salmo gairdneri) Can. J. Fish. Aquat. Sci. 43 (8) 1497-1503.

Dave, G.; Damgaard, B.; Grande, M.; Martelin, J. E.; Rosander, B.; Viktor, T. 1987: Ring Test of an Embryo-Larval Toxicity Test with Zebrafish (Brachydanio rerio) Using Chromium and Zinc As Toxicants Environ. Toxicol. Chem. 6(1):61-71.

Dawson, D. A.; Stebler, E. F.; Burks, S. L.; Bantle, J. A. 1988: Evaluation of the Developmental Toxicity of Metal-Contaminated Sediments Using Short-Term Fathead Minnow and Frog Embryo-Larval Assays Environ. Toxicol. Chem. 7(1):27-34.

ECOTOX. USEPA: ecotoxicology database, http://www.epa.gov/ecotox. Accessed September 2006.

Goettl, J. P. Jr.; Davies, P. H.; Sinley, J. R. 1976: In: D. B. Cope (Ed.), Colorado Fish.Res.Rev.1972-1975, DOW-R-R-F72-75, Colorado Div.of Wildl., Boulder, CO :68-75.

Heijerick, D. G.; De Schamphelaere, K. A. C.; Van Sprang, P. A.; Janssen, C. R. 2005: Development of a chronic zinc bioitic ligand model for Daphnia magna Ecotox. Environ. Saf. 62:1-10.

Herkovits, J.; Perez-Coll, C. S. 1991: Antagonism and Synergism Between Lead and Zinc in Amphibian Larvae. Environ. Pollut. 69:217-221.

Holcombe, G. W.; Andrew, R. W. 1978: The Acute Toxicity of Zinc to Rainbow and Brook Trout: Comparison in Hard and Soft Water. EPA-600/3-78-094. National Technical Information Service, Springfield, VA.

Horne, M. T.; Dunson, W. A. 1995: Effects of Low pH, Metals, and Water Hardness on Larval Amphibians Arch. Environ. Contam. Toxicol. 29(4):500-505.

Khangarot, B. S. 1981: Effect of Zinc, Copper and Mercury on Channa marulius (Hamilton) Acta Hydrochim. Hydrobiol. 9 (6) 639-649.

Kingett Mitchell, 1988: Golden Cross water right applications: Appendix I Derivation of proposed Waitekauri Criteria. Report prepared for Cyprus Gold, May 1988.

Kingett Mitchell 1998: Updated toxicology data for the Golden Cross Mine. Report prepared by Kingett Mitchell Ltd for Coeur Gold New Zealand Ltd, June 1999.

Kingett Mitchell, 2003: In-stream boron criteria for the protection of aquatic life: re-evaluating the ANZECC trigger values. Report prepared by Kingett Mitchell Ltd for Solid Energy International, May 2003.

Kingett Mitchell, 2004: Ash Disposal at Rotowaro Assessment of Environmental Effects. Appendix 8, boron ecology. Report prepared by Kingett Mitchell Ltd for Solid Energy Ltd.

Kraak, M. H. S.; Wink, Y. A.; Stuijfzand, S. C.; Buckert-De Jong, M. C.; De Groot, C. J.; Admiraal, W. 1994: Chronic Ecotoxicity of Zn and Pb to the Zebra Mussel Dreissena polymorpha. Aquat. Toxicol. 30 (1) 77-89.

Lloyd, E.; Herbert, D. W. M. 1962: J. Inst. Public Health Eng. 61, 132.

Magliette, R. J.; Doherty, F. G.; McKinney, D.; Venkataramani, E. S. 1995: Need for Environmental Quality Guidelines based on Ambient Freshwater Quality Criteria in Natural Waters-Case Study "Zinc" Bull. Environ. Contam. Toxicol. 54(4):626-632.

Meinelt, T.; Stüber, A. 1995: Subchronic Fish Toxicity of Copper and Zinc Dependent upon Water Hardness. Fortschr. Fisch. Wiss. 12:129-136.

MELP 2004: Water Protection Section Ministry of Water, Land and Protection. Ambient water quality guidelines for boron.

Millington, P. J.; Walker, K. F. 1983: Australian Freshwater Mussel Velesunio ambiguus (Philippi) As a Biological Monitor for Zinc, Iron and Manganese Aust. J. Mar. Freshwater Res. 34 (6) 873-892.

Mirenda, R. J. 1986: Acute Toxicity and Accumulation of Zinc in the Crayfish, Orconectes virilis (Hagen) Bull. Environ. Contam. Toxicol. 37 (3) 387-394.

Nebeker, A. V.; Stinchfield, A.; Savonen, C.; Chapman, G. A. 1986: Effects of Copper, Nickel and Zinc on Three Species of Oregon Freshwater Snails. Environ. Toxicol. Chem. 5 (9) 807-811.

Nehring, R. B. Jr. 1974: Acute Toxicity of a Zinc-Polluted Stream to Four Species of Salmonids. Bull. Environ. Contam. Toxicol. 12(4):464-469.

Norberg, T. J.; Mount, D. I. 1985: A New Fathead Minnow (Pimephales promelas) Subchronic Toxicity Test Environ.Toxicol.Chem. 4(5):711-718.

Norberg-King, T. J. 1989: An Evaluation of the Fathead Minnow Seven-Day Subchronic Test For Estimating Chronic Toxicity Environ.Toxicol.Chem. 8(11):1075-1089.

Paulauskis, J. D.; Winner, R. W. 1988: Effects of Water Hardness and Humic Acid on Zinc Toxicity to Daphnia magna Straus. Aquat. Toxicol. 12 (3) 273-290.

Pickering, Q. H. 1968: Some Effects of Dissolved Oxygen Concentrations upon the Toxicity of Zinc to the Bluegill, Lepomis macrochirus. Raf. Water Res. 2 187-194.

Pickering, Q. H.; Vigor, W. N. 1965: The Acute Toxicity of Zinc to Eggs and Fry of the Fathea d Minnow. Prog. Fish-Cult. 27 (3) 153-157.

Popken, G. J. 1990: Effects of Calcium on the Toxicity of Zinc to Embryos and Larvae of the Fathead Minnow (Pimephales promelas), M.S. Thesis, Eastern Kentucky University, Richmond, KY: 0 64 p.

Reed, P.; Richey, D.; Roseboom, D. 1980: Acute Toxicity of Zinc to Some Fishes in High Alkalinity Water Ill. State Water Surv. Circ. 142 1-21.

Sinley, J. R.; Goettl, Jr. J. P.; Davies, P. H. 1974: The Effects of Zinc on Rainbow Trout (Salmo gairdneri) in Hard and Soft Water, Bull. Environ. Contam. Toxicol. 12(2):193-201.

USEPA, 1976: Quality criteria for water. US Environmental Protection Agency.

USEPA, 1986: Quality criteria for water 1986. US Environmental Protection Agency. EPA 440/5-86-001.

USEPA, 1987: Ambient water quality criteria for zinc. US Environmental Protection Agency.

USEPA, 1993: Office of water policy and technical guidance on interpretation and implementation of aquatic life metals criteria. US Environmental Protection Agency.

USEPA 2001: 2001 update of ambient water quality criteria for cadmium. US Environmental Protection Agency. EPA-822-R-01-001.

USEPA, 2002: National recommended water quality criteria: 2002. US Environmental Protection Agency. EPA-822-R-02-D47.

USGS, 1995: Preliminary compilation of descriptive geoenvironmental mineral deposit metals. US Geological Survey.

Van de Plassche, E. J.; Polder, M. D.; Canton, J. H. 1993: Derivation of maximum permissible concentrations for several volatile compounds for water and soil. National Institute for Public Health and Environmental Protection, Report 679101 008, Bilthoven, The Netherlands.

Windward 2002: Development of site-specific water quality criteria for the South Fork Coeur d'Alene River, Idaho: Derivation of acute and chronic criteria for lead and zinc. Report prepared for Idaho Department of Environmental Quality, May 2002.

Wurtz, C. B.; Bridges, C. H. 1961: Preliminary Results From Macro-Invertebrate Bioassays Proc. Pa. Acad. Sci. 35 51-56.

Zou, E. 1997: Effects of Sublethal Exposure to Zinc Chloride on the Reproduction of the Water Flea, Moina irrasa (Cladocera) Bull. Environ. Contam. Toxicol. 58(3):437-441.

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