DERIVATION OF WATER QUALITY GUIDELINE VALUES FOR HEAVY METALS USING A RISK-BASED METHODOLOGY: AN APPROACH FOR NEW ZEALAND

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ABSTRACT

The Australian and New Zealand Environment and Conservation Council (ANZECC) has undertaken a revision of the water quality guidelines for Australia (ANZECC 1992). The revised ANZECC guidelines adopt a statistical approach, which the Ministry for the Environment had proposed for New Zealand before the ANZECC review commenced. In this paper we present the results of the application of the risk-based methodology to guideline calculations for a selected range of priority metals, and discuss their application in relation to the narrative guidelines in the New Zealand Resource Management Act 1991. Guidelines were calculated for freshwater and marine species using chronic (long-term) effects data and 99% level of protection with 50% confidence and 95% level of protection with 50% confidence. The use of the 99% protection guideline values is recommended for waters to be protected from 'adverse effects'. For receiving waters requiring protection from 'significant adverse effects', the statistical approach can be used to vary the level of protection according to the values to be protected. In most cases the 95% protection guideline values are recommended, but in certain circumstances the 90% could be used. All of these guideline values would be implemented on a soluble (ie. $< 0.45\ \mu m$) metals basis.

A number of limitations to the available datasets were identified, including: (i) minimal data available for some contaminants (eg. CrIII and As) which are of concern in the New Zealand environment because of their widespread use in timber treatment; (ii) the datasets used for guideline derivation included very few Australian or New Zealand studies with native species. This largely results from the use of chronic data, whereas the majority of Australasian studies are of acute exposures; (iii) the need to include a range of endpoints (other than the recommended 'no observed effect concentration' (NOEC)) in order to increase the number of species represented; and (iv) the datasets were generally identified as being under-represented in freshwater aquatic insects and marine fish species. We recommend that environmental monitoring data from carefully designed programmes be fed back into the criteria assessment programmes to evaluate the applicability of the guidelines used.

Key words: New Zealand, toxicants, metals, freshwater, marine, water quality guidelines.

INTRODUCTION

New Zealand and Australia share similarities in the approaches being developed to ensure long-term protection of each nation's water resources (RM Act 1991; ANZECC & ARMCANZ 1994). Both countries have adopted an ecosystem-based approach to the protection of water resources and the concept of sustainability. In Australia, the overall purpose is to 'achieve sustainable use of the nation's water resources by protecting and enhancing their quality while maintaining economic and social development'. The purpose of New Zealand's Resource Management Act (RMA) is similar and promotes sustainable management, which is defined to mean (s5 RMA):

Managing the use, development and protection of natural and physical resources in a way or at a rate, which enables people and communities to provide for their health and safety while:

- *Sustaining the potential of natural and physical resources (excluding minerals) to meet the reasonably foreseeable needs of future generations; and*

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- *Safeguarding the life-supporting capacity of air, water, soil, and ecosystems; and*
- *Avoiding, remedying, or mitigating any adverse effects of activities on the environment.*

The national goals of both countries are to be put into effect through state and/or regional powers (regional councils in New Zealand and State Governments in Australia). In New Zealand the Ministry for the Environment has the role of providing guidance on the implementation of the RMA.

The previous Australian and New Zealand Environment and Conservation Council (ANZECC) Guidelines (ANZECC 1992) for toxic chemicals followed the Canadian (CCREM 1987) approach, '... to protect all forms of aquatic life and all aspects of the aquatic life cycle... The intention is to protect all life stages during indefinite exposure to the water', and essentially used the Canadian values. The revised ANZECC Guidelines (ANZECC & ARMCANZ 2000) use the Dutch and OECD risk-based approach for chemical toxicants which was recommended for New Zealand (MfE 1996) and Australia (Warne 1998), based on reviews of the legislative philosophies and methods of guideline derivation.

The framework for the risk-based management procedure incorporates an ecosystem-based approach involving integrating a wide range of potential stressors on biological communities (Hart *et al.* 1999). The New Zealand legislation promotes integrated management, in that all regional councils are required '...to achieve integrated management of the natural and physical resources of the region...' (section 30/1/a, RM Act 1991). For toxicants the proposed approach incorporates using a suite of assessment techniques including: (i) chemical specific guidelines; (ii) direct toxicity assessment (DTA); and (iii) biological monitoring; with guidance provided for deriving site-specific guidelines (ANZECC & ARMCANZ 2000). The relative importance of these components is expected to vary depending on the receiving water characteristics. This approach is in line with approaches adopted and promoted in New Zealand before the revision of the ANZECC Guidelines (Smith *et al.* 1994; MfE 1995).

In this paper, we present the results of the application of the risk-based approach to guideline calculation for a selected range of priority metals and discuss their application in relation to deriving site-specific guidelines relevant to the New Zealand legislation. A core set of priority metals were selected for numeric guideline derivation for fresh and marine waters. The six priority metals were: copper (Cu); chromium (Cr), arsenic (As), cadmium (Cd), zinc (Zn) and lead (Pb). The choice of these metals relates to their widespread use in timber preservation (Cu, Cr, As), their presence in phosphatic fertilisers and batteries (Cd), and as significant components of stormwater runoff (Cu, Zn, Pb). Data for these metals will be used to illustrate the application of this approach using available databases, assess the relative sensitivity of organism groups and the adequacy of the exiting databases for derivation of risk-based guidelines based on chronic data.

New Zealand legislation

The New Zealand Resource Management Act (RM Act 1991) provides narrative standards for environmental protection. Policy and national guidance is provided by the Ministry for the Environment, with implementation by 16 regional councils. Under the RM Act regional councils can prepare statutory regional and coastal plans which specify the values for which waters are to be managed. Many councils have prepared or are preparing regional water management plans. The RMA provides some guidance on the choice of values, such as fish spawning, fisheries or aquatic ecosystem protection. The 'aquatic ecosystem protection' class is stringent and requires that a discharge shall not be allowed if after 'reasonable mixing', there is *any* 'adverse effect' on the aquatic ecosystem.

A general requirement of the RMA is that a discharge does not cause a 'significant adverse effect' after reasonable mixing. A significant adverse effect is not defined in the RMA. MfE is developing a framework for aquatic ecosystem management and this framework will assist with interpreting the concept of a significant adverse effect. The key concept underpinning the framework is defining the values that the community wishes to sustain and that non-achievement of these values is considered to be a significant adverse effect, which is the approach adopted in the Revised ANZECC Water Quality Guidelines. In practice, the monitoring of adverse effects is likely to be undertaken by measuring reduction in species diversity or abundance of aquatic macroinvertebrate and/or fish communities. By comparison, the proposed numerical guideline derivation procedures (ANZECC & ARMCANZ 2000) incorporate the precautionary principle and preferentially use no observed effect concentration (NOEC) data for sub-lethal chronic effects measures (eg. growth, reproduction), which in many cases are likely to result in more conservative guideline values compared with the sensitivity of field monitoring approaches (eg. reduced species diversity).

DERIVATION OF SITE-SPECIFIC TOXIC CONTAMINANT GUIDELINES FOR NEW ZEALAND: METALS

The Ministry for Environment (MfE 1996) suggested the following principles should be included in a methodology for calculating guidelines values:

- incorporate the precautionary principle, as a key component of sustainable management;
- be able to calculate different levels of protection to suit a particular situation and the values that are to be sustained; and
- use a 'transparent' methodology so that the community can understand how a particular guideline value was derived.

Ideally, guidelines would be based on New Zealand native species, such as species that contribute to the 'whitebait' run (whitebaiting is an important activity in New Zealand). In practice, the paucity of suitable chronic data for local species means that the process of guidelines development needed to include species and test data derived largely from the international database. There was, therefore, a limited ability to benchmark the relative sensitivity of local species into the derivation procedure based on the international toxicity database (Hickey and Golding 1997).

Approach

The Dutch and OECD risk-based statistical approach meets the principles listed above. It (i) uses no observed effect concentration (NOEC) data so is inherently precautionary, (ii) can calculate different levels of protection, and (iii) is 'transparent' and easy for the community to understand conceptually.

The Dutch approach is conceptually simple, but mathematically complex, but PC-based software (ETX) has been developed (Aldenberg 1993) to perform the statistical analyses. The approach fits a statistical distribution through the toxicity data for a range of species, in contrast to other methods (eg. US EPA 1986), which concentrate solely on the high sensitivity tail of toxicity data distribution. The approach is best understood diagrammatically (Figure 1).

The key assumptions used in the Dutch approach are as follows:

(i) toxicity data are distributed log-logistically, ie. a logistic distribution is the most appropriate to use. Data can be tested mathematically to see if they fit the logistic distribution (OECD 1995);
(ii) the ecosystem is adequately protected, provided that a certain percentage of species is protected. The Dutch have chosen a level of 95%;
(iii) the test species are randomly selected from the ecosystem;
(iv) there are no interactions between species in the ecosystem;
(v) NOEC data are the most appropriate data to use to set ambient environmental guidelines; and
(vi) NOEC data for five species is a sufficient (minimum) dataset.

Most plans prepared under the RM Act aspire, in broad terms, to ensure that aquatic ecosystems are 'sustained' (ie. 'healthy'). Water managers are therefore interested in small changes to the number of species, because a large change could mean that the ecosystem is 'unhealthy'. Hence water managers are interested in the *tail* of the logistic distribution (see Figure 1). When there are few data, there will be considerable uncertainty in the tail of the distribution, but with an increase in data this uncertainty reduces, as does the confidence interval around the desired effect threshold.

It is possible to attach a distribution to the error associated with a percentile estimation in the tail (see Aldenberg and Slob (1993) for a full mathematical treatment of percentiles). If we know the distribution of the error, it is possible to calculate a certain percentile, such as the 95th percentile with a known level of certainty, ie. we can be sure that the percentile is within a certain band. For example, we can be 50% certain the *true* 95th percentile is less than the *calculated* 95th percentile. The *true* 95th percentile is that which we would calculate if toxicity data were available for *all* the species in an ecosystem. The Dutch chose a 50% certainty level. For these ANZECC

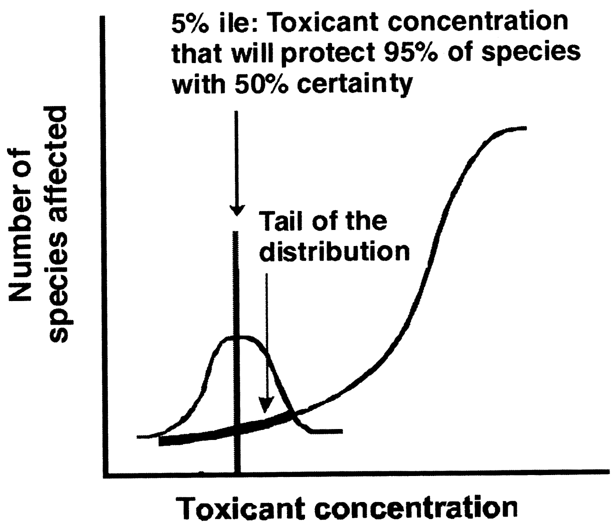

Figure 1. *The Dutch statistical approach, shown in conceptual form. The distribution is assumed to be logistic. The smaller bell-shaped curve shows the confidence interval for the 5th %ile.*

guidelines a 99% level of protection with 50% certainty is chosen for 'no adverse effects' and a 95% protection level with 50% certainty is chosen for the no significant adverse effects, for most cases, with the option of lowering this level in specific situations. These levels of protection and certainty were chosen for the following reasons:

(i) a 1% level of protection should be sufficient to protect the ecosystem provided keystone species are considered and given that the calculated values will be conservative because NOECs data were used,
(ii) a 5% level should protect most species and normal ecosystem functioning, ie. should not result in *significant* adverse effects, provided the keystone species are protected, and
(iii) a higher level of certainty (eg. 95%) cannot be calculated with any accuracy because the statistical inaccuracies become large.

Setting toxicant concentrations for 'no adverse effect' is relatively straight forward, for example, the 99% value which will ensure protection. But setting toxicant concentrations corresponding to 'no significant adverse effect' is more difficult. Ideally, toxicant concentrations would be defined for specific values and locations (ie. by establishing the desired protection level for a given use and using data relevant to the communities present). But the paucity of toxicity data for New Zealand means that there is considerable uncertainty as to what toxicity level corresponds to a certain ecological value. Hence the ANZECC Guidelines recommend the 95% protection guideline value as a starting point. Biomonitoring and Whole Effluent Toxicity (WET) testing (or 'direct toxicity assessment', DTA) are complementary approaches which should be used for assessing whether a discharge has potential to cause a significant adverse effect. DTA is proposed as an integral part of the decision scheme for application of the guidelines (ANZECC & ARMCANZ 2000).

Adequacy of dataset

An adequate dataset for the ETX (Aldenberg and Slob 1993) statistical distribution approach, to protect 95% of species with a predetermined level of confidence, is considered to be chronic NOEC data for at least five species representing four different taxonomic groups (ANZECC & ARMCANZ 2000). This statistical approach uses available data from all tested species and considers these data a subsample of the range (rather than the most sensitive) of concentrations at which effects would occur in all species in the environment. However, it should be realised that the calculated guideline values strongly depend on both the number of data and the variability in the sensitivity of the test species. If the variability is low, five species will give satisfactory results relative to the sensitivity data. However, with a high variability in five species, the extrapolation data will be high, leading to particularly low values (see following sections). Similarly, addition of more toxicity data without changing the variability will result in the statistical model calculating an increased guideline value.

The primary sources of information were: (i) US EPA AQUIRE (AQUatic Information REtrieval) database (US EPA 1994); Australian Ecotox Database (AED); existing Dutch database; published journal reviews; and the Aquatic Sciences and Fisheries Abstracts (ASFA) database. The AQUIRE database was searched in January 1997, at which time it contained 149,417 individual test records for more than 5,900 chemicals and 3,000 freshwater species and marine organisms.

Hardness incorporation

Hardness is a measure of the calcium and/or magnesium concentration in the water. Increasing hardness reduces the toxicity of several metals, including Cd, Cr(III), Cu, Pb, Ni and Zn, to freshwater organisms. Most fresh surface waters in New Zealand are 'soft' with average calcium concentrations 10-fold lower that the world average freshwater value (Smith and Maasdam 1994). Median hardness for 77 rivers and streams in New Zealand's National River Water Quality Network was 26 mg $CaCO_3$/L, and ranged 31-fold from 6.9 to 217 mg CaCO3/L (Hickey 2000). Regression slopes for toxicity response with hardness were summarised from the US EPA criteria derivation US EPA (1985 a,b,c,d, 1987), and these values (Appendix 1) were used to modify the database data to a common hardness value (30 mg/L as $CaCO_3$) prior to calculation of guideline values. Guideline values calculated for a given protection level (eg. 99%, 95%) were then used to derive a hardness-dependent equation (algorithm) for predicting guideline values at different water hardness values (Appendix 1). Notably, some groups of organisms, such as algae, were not included in the hardness based calculations as values are generally not given in algal studies.

Calculation of guideline values

The types of organisms acceptable for inclusion in the Aldenberg and Slob (1993) method are given in Table 1, with the criteria for various guideline levels given in Table 2. The AQUIRE database effect codes are summarised in Appendix 2. The AQUIRE database was searched for freshwater and seawater data for effects on growth and development (GRODEV), reproduction (REPROD) and population and community responses (POPCOM) categories to identify growth and reproduction data. The POPCOM category identified algal data to be included in the chronic dataset.

Appendix 1

Metal	Hardness-dependent algorithm
Cadmium	HMGV = GV $(H/30)^{0.89}$
Chromium (III)	HMGV = GV $(H/30)^{0.82}$
Copper	HMGV = GV $(H/30)^{0.85}$
Lead	HMGV = GV $(H/30)^{1.27}$
Zinc	HMGV = GV $(H/30)^{0.85}$

GV = guideline value (µg/L) at a hardness value of 30 mg/L as $CaCO_3$; HMGV = hardness modified guideline value (µg/L) at specified hardness (H); Slope (coefficient) = values range from 0.82 to 1.27 (from US EPA 1985a,b,c,d, 1987).

Appendix 2. EFFECT CODES BY MAJOR GROUP as used in AQUIRE database

CODE Definition: BEHAVIOUR [BEHAVI] - not used

CODE Definition: BEHAVIOUR [BEHAVI] - not used

CODE Definition: ECOSYSTEM [ECOSYS] - not used

CODE Definition: GROWTH DEVELOPMENT [GRODEV]

ABN Abnormality: Physical malformation due to toxicant exposure (eg. vertebral).

DVP Development: Change in ability to grow to a more mature life stage and in time between separate life stages

GRO Growth: Measurable change in length and/or weight of test organism.

CODE Definition: LETHAL [LETHAL]

IMM Immobilization: Change in the ability to respond or lack of movement after mechanical stimulation.

MOR Mortality: Effect expressed as % death or % survival.

CODE Definition: PHYSIOLOGICAL/BIOLOGICAL [PHYBIO] - not used

CODE Definition: POPULATION COMMUNITY [POCPOM]

PGR Population Growth: Rate of growth. Equivalent to intrinsic rate of increase and maximum possible rate of growth for species. Calculated by relating biomass or abundance to time. Life table data are also included.

PSR Population Size Reduction: Quantifiable reduction in the population size.

CODE Definition: REPRODUCTION [REPROD]

REP Reproduction: Change in male and/or female reproductive ability. Includes vegetation reproductive processes.

Table 1. Types of species which are considered taxonomically different when assessing whether the toxicity data meets the minimum requirements for the Aldenberg and Slob (1993) method (ANZECC & ARMCANZ 2000).

Number	Taxa groups	Taxa code [a]
1.	fish	OS
2.	crustaceans	CR
3	insects	IN
4.	molluscs	ML
5.	annelids	AN
6.	echinoderms	EC
7.	rotifers	RO
8	hydra	CY
9	green algae	AL (CHLO)
10.	blue algae	AL (?)
11.	red algae	AL
12.	macrophytes	MI (ACCO)
13.	blue-green algae (cyanobacteria)	CY
14.	amphibians	AM
15.	bacteria (except *Photobacterium phosphoreum*/*Vibrio fisheri* Microtox)	-
16.	protozoans	PR
17.	coral	CN
18	fungi	FU

[a] Abbreviations from AQUIRE (US EPA 1994)

Mortality and immobilisation responses (LETHAL category) were also searched and survival data for exposures of seven or more days considered for inclusion in the chronic dataset. Each of the data records was then edited to remove 'I' category documents (ie. 'incomplete' data, those with unacceptably low score) together with a range of sublethal effects such as hatching (HAT), photosynthetic rate (PSE), abnormal development (ABN, note: this effect was used for some marine families,Table 2).

The decision criteria used to select data for inclusion in the final guideline calculation are provided in Table 2. Endpoints other than NOECs were included in the dataset, providing the chronic exposure selection criteria were met. This resulted in inclusion of species from a greater number of taxonomic groups and allowed comparison of relative sensitivity of the various groups. Some additional procedures were used in the ANZECC & ARMCANZ (2000) guideline calculation procedures, which included conversion of all endpoints to NOECs. This procedure would have affected the final guideline values calculated.

Only a limited number of data records were excluded from the dataset based on lack of chemical validation of exposure concentrations. Excluded records were only for some freshwater datasets with endpoints at very low concentrations and some high data (low toxicity) which leveraged the distributions. Data exclusions are noted in Tables 3 and 4. Notably, the current input data for these guideline derivations are largely based on ecotoxicological selection criteria, and there is a similar set of selection criteria regarding the chemistry (eg. chemical validation, use of 'clean' techniques, container selection) (see Batley *et al.* 1999). Critical assessment of chemical exposure would be warranted for all data, as the statistical model is influenced by both low concentration data and the spread of the dataset. Such consideration could form a component of site-specific guideline derivation.

REVISED ANZECC APPROACH

Three grades of water quality guidelines (or 'trigger values' (TV), ANZECC & ARMCANZ 2000) are derived, 'Level 1', 'Level 2' and 'Interim' guidelines, depending on the data available (Warne 1998). The levels of guidelines are developed as follows (ANZECC & ARMCANZ 2000, Warne 2001):

Level 1 guidelines, the highest grade, are derived from multiple-species data or chronic NOEC data, provided the minimum requirements for both quantity and quality of data are met ≤5 NOEC values, or appropriate other endpoint, for different taxa groups). The approach for deriving guidelines from chronic NOEC data is to simultaneously apply the Dutch (Aldenberg and Slob 1993) statistical distribution method (ETX: Aldenberg 1993) and the assessment factor approach of OECD (1992). The lowest (most precautionary) of the two would be accepted as the guideline figure (ANZECC 2000, but see Warne 2001 for selection guidance).

No multiple-species (MS) data was used in these derivations. However, Emans *et al.* (1993) reviewed MS experiments for organic compounds and metals in aquatic ecosystems, finding data for 19 organic compounds and 10 metals where one or more NOECs could be derived. They found that many of these MS experiments did not adequately meet their selection criteria for reliable use in guidelines derivation. The MS NOEC values were compared with single-species (SS) guideline data calculated using the Aldenberg and Slob (1993) method. Acknowledging the paucity of

Table 2. Decision criteria summary for data inclusion in these site-specific guideline calculations.

Number	Selection criteria [a]	General comments	ANZECC & ARMCANZ (2000) procedure [b]
1	Database search for chronic endpoints in the following categories: GRODEV, LETHAL, POPCOM, REPROD		
2	'Effect': ABN, DEV, GRO, IMM, MOR, PGR, PSR, REP	ABN & DEV only for marine with EC, CN & ML	Marine ABN & DEV classes not included
3	Duration: ≥7d for GRO & IMM (except for taxa groups Al, CY, EC*, CN*, ML*, & PR = ≥2d)	Short-term chronic data included for microbial species	
4	Initial select all NOEC, LOEC, MATC & ECx for chosen EFFECTS (2 above)		
5	Specific exclusions: marine - No brine ≥40 ppt or low salinity ≤10 ppt; no salt for freshwater ≥5 ppt		
6	Add sensitive species - eg. short-term exposures with high sensitivity		
7	Remove 'NR' (not recorded) endpoint data and 'I' (low reliability) data	A large number of data had 'NR' recorded in the 'Endpoint' column in AQUIRE	
8	Final selection: sort by species then select the most sensitive endpoint for longest exposure duration based on (in ranked order of preference): NOEC >MATC>LOEC> ECx	Multiple effects included (eg. MOR, REP, DEV) for the same species.	1. Endpoints converted to NOECs. Conversion factors are: 5 for EC50 to NOEC; 3 for LOEC to NOEC; and 2 for MATC to NOEC. 2. Geometric mean of all duration and effect measures for a given species
9	Visual inspection of log-data on a normal probability plot to identify outliers.	1. Low outliers (<25th %ile) examined for chemical validation of exposure concentrations. 2. High outliers removed from dataset.	Outlier guidance provided.

[a] Endpoints and effects categories refer to AQUIRE abbreviations summarised in Appendix 2.

[b] Warne (2001)

data, they concluded that SS toxicity data can be used to derive 'safe' guideline values for aquatic ecosystems.

Level 2 guidelines, which reflect a lower confidence in extrapolation methods, are derived either from chronic data with too few taxa groups (eg. 4), or using acute toxicity data, with application of acute-to-chronic ratios (ACR). Minimum requirements for quantity and quality of data (≤5 acute values or 4 chronic values for different taxa groups). The ETX method is applied to acute LC50 data and suitable ACR applied to derive a guideline figure. Again, a figure is also derived by the assessment factor method of OECD (1992) and the lower of the two accepted as the guideline figure.

Interim guidelines can be derived in the absence of a dataset of sufficient quality and quantity. However, no guidelines should be derived on less than the OECD

Table 3. *Guideline values calculated based on values reported in the AQUIRE database for a selection of metals to* ***freshwater*** *organisms following procedures given in Table 2.*

Metal	Initial cases [a]	Final chronic cases [b]	Species No.	Taxa Groups	Lowest chronic (µg/L)	Guideline 99% protection [c] (µg/L)	Guideline 95% protection [c] (µg/L)	Guideline 90% protection [c] (µg/L)	ANZECC (1992) guideline	ANZECC & ARMCANZ (2000) guideline [e]	US EPA [f]
Copper*	573	35 [99]	31	7	0.85	0.25	1.0	2.0	2.0-5.0	1.4	3.3
Cadmium*	612	38 [80]	33	8	0.15	0.008	0.11	0.37	0.2-2.0	0.2	0.96
Zinc*	471	27 [58]	24	6	7.9	0.76	6.4	17	5.0-50	8.0	43
Lead*	165	14 [29]	12	5	0.40	0.30	1.7	3.6	1.0-5.0	3.4	0.68
Arsenic III	277	19	17	7	40	7.6 [d]	60 [d]	148 [d]	50	24	150
Arsenic V	138	12	9	5	10	0.34 [d]	6.2 [d]	23 [d]	-	12	-
ChromiumVI	1164	51	43	9	0.51	0.18	2.8	9.5	10	1.0	11
ChromiumIII*	102	8 [11]	7	3	6.1	2.3	11	21	-	ID	32

ID = Insufficient data
* Metal using hardness calculations. Values calculated for a hardness value of 30 mg /L as $CaCO_3$ using equations given in Appendix 1.
[a] Initial number of cases with acceptable quality scores of 'C' or 'M'.
[b] Values selected from all chronic data with acceptable effects measures and NOECs if multiple endpoints. Metals requiring hardness correction show data with hardness values, with bracketed value indicating the total number of data with acceptable effects. High leverage values removed: Cu 3; Cd 2; Zn 2; Pb 3. Low leverage and chemically unverified: Cu 1.
[c] From ETX software programme based on logistic fit, except AsIII which is based on normal distribution fit.
[d] Poor database. Includes unverified data. 'Interim' guideline recommended.
[e] ANZECC & ARMCANZ (2000) 95% protection trigger value (TV).
[f] US EPA (1996), except Pb (US EPA 1985d), adjusted to a hardness value of 30 mg $CaCO_3$/L.

Table 4. *Guideline values calculated based on values reported in the AQUIRE database for a selection of metals to* ***marine*** *organisms following procedures given in Table 2.*

Metal	Initial cases [a]	Final chronic cases [b]	Species No.	Taxa Groups	Lowest chronic (µg/L)	Guideline 99% protection [c] (µg/L)	Guideline 95% protection [c] (µg/L)	Guideline 90% protection [c] (µg/L)	ANZECC (1992) guideline	ANZECC & ARMCANZ (2000) guideline [e]	US EPA [f]
Copper	754	33	26	5	2	0.49	2.6	5.5	5.0	1.4	2.9
Cadmium	1233	80	70	7	0.9	1.4	11	27	2.0	5.5	9.3
Zinc	641	44	33	7	18	2.4	16	38	50.0	15	86
Lead	184	15	13	5	16	1.4	12	30	5.0	4.4	5.6
Arsenic III	170	9	7	4	60	0.74 [d]	17 [d]	69 [d]	50.0	ID	36
Arsenic V	59	9	8	4	25	0.70 [d]	9.2 [d]	30 [d]	-	ID	-
ChromiumVI	721	39	33	8	0.3	2.9	25	65	50.0	4.4	50
Chromium III	33	5	5	4	469	24	122	256		10	-

[a] Initial number of cases with acceptable quality scores of 'C' or 'M'
[b] values selected from all chronic data with acceptable effects measures and NOECs if multiple endpoints
[c] from ETX software programme based on logistic fit
[d] Poor database. Includes unverified data or minimal references. Too few taxa groups. 'Interim' guideline recommended.
[e] ANZECC & ARMCANZ (2000) 95% protection trigger value (TV)
[f] US EPA (1985a, b, c, d; 1987)

(1981), 'Minimum Pre-marketing Dataset' (fish, crustacean and alga). This is consistent with the Canadian approach (CCREM 1987) and is basically the old 'safety factor' approach.

RESULTS AND DISCUSSION

Guidelines were calculated for 17 metals for freshwater species and 10 metals for saltwater organisms (Hickey and Golding 1997). Results for the six priority metals are summarised for freshwater and marine organisms in Tables 3 and 4 respectively, with ANZECC (1992), ANZECC & ARMCANZ (2000) and US EPA guidelines shown for comparison.

The 99% protection guideline values calculated by the Aldenberg and Slob method were generally markedly lower (1.4x to 70x) than existing ANZECC (1992) and US EPA chronic guideline values (Tables 3 and 4). The 95% guideline values ranged about 3-fold above (eg. marine Cd) and below (eg. freshwater CrVI) the ANZECC (1992) guideline values. Most of the 99% protection guideline values are lower than the lowest chronic test value, indicating that this guideline value would be protective of more than 99% of the species tested. Only the large freshwater Cd and CrVI datasets gave a 99% values higher than the lowest chronic value. Guideline values calculated at the lower 95% protection level exceeded the lowest chronic data for several metals, indicating that site-specific consideration of species sensitivity may be required for these metals. Differences between the 95% guideline levels calculated and the ANZECC & ARMCANZ (2000) values were generally within a factor of 2 and reflect differences in the selection and calculation procedures (Table 2). The 99% protection values are so low for most essential metals (eg. Cu, Cr, Ni, Zn) that they may result in metabolic deficiencies for some species, or in practice, application of guidelines which are below background levels (see later section).

Selected freshwater chronic datasets are shown for the major metals, incorporating the relative sensitivities of the major groups (Figures 2-6). For freshwaters, the sensitivity range was 4.5 to 6 orders of magnitude from the most to the least sensitive species, with a slightly lower sensitivity range for seawater organisms (3 to 5.5 orders of magnitude; data not shown, see Hickey and Golding 1997). Freshwater metals had data from a wide range of representative taxonomic groups (Table 3, eg. Cu, Cd, Zn, Pb and CrVI), while other metals of concern had relatively few data (ie. CrIII, As). However, the seawater organisms were restricted to fewer taxonomic groups (Table 4). The datasets were generally identified as being under-represented in freshwater aquatic insects and marine fish species (Hickey and Golding 1997).

Most of the datasets did not have either highly sensitive, or highly insensitive outliers. The exceptions were freshwater Pb and marine CrVI. The Pb outlier was a crustacean (CR) and the CrVI outlier was an alga. Following hardness standardisation, some datasets showed outliers, for example two high values in the Cd and Zn datasets (Figures 3 and 4), which were removed prior to guideline calculation (Table 3).

Comparison of the relative sensitivity of the various species groups can provide an insight into their ecological susceptibility to that contaminant. For example, in freshwater, comparable sensitivity ranges occurred for algae (AL), crustaceans (CR) and fish (OS) to some metals (eg. Cu, Cd and Zn; Figures 2, 3, and 4 respectively), whereas others such as CrVI show markedly higher sensitivity for crustaceans, lower sensitivity for algae (with one extreme low outlier, Figure 6), and still lower sensitivity of fish. Marine species data was more limited, but generally indicates higher sensitivity for crustaceans with similar sensitivity for molluscs (ML) (Hickey and Golding 1997).

Incorporation of Australian and New Zealand species.

The datasets include very few Australian or New Zealand studies with native species. This largely results from the use of chronic data whereas the majority of Australasian studies are for acute exposure tests. For this reason, derivation of Australasian guidelines based solely on native species, and using the Aldenberg and Slob method, would not be practicable at present. Neither would it be recommended as a goal for the near future, since generally the regional species groups are not expected to be markedly more sensitive than international groups (eg. Hickey 1989; Markich and Camilleri 1997). Rather, there is a need to benchmark the sensitivity of representative native species, in relation to the more widely available acute database, and to undertake appropriate testing with key local species for site-specific situations. For example, some New Zealand freshwater macroinvertebrates have shown high sensitivity to ammonia in acute (Hickey and Vickers 1994) and chronic exposures (Hickey and Martin 1999; Hickey *et al*. 1999), indicating that site-specific guidelines may be required for their protection. A suite of protocols has recently been developed for native New Zealand species (Hall and Golding 1998), which included three acute freshwater tests and two marine tests (2 acute and 1 chronic). Two chronic marine invertebrate tests have also recently been developed (Nipper and Williams 1997; Nipper *et al*. 1997). No data from these native species tests were included in these metals guideline derivations. Future revisions or site-specific applications could utilise data from these species.

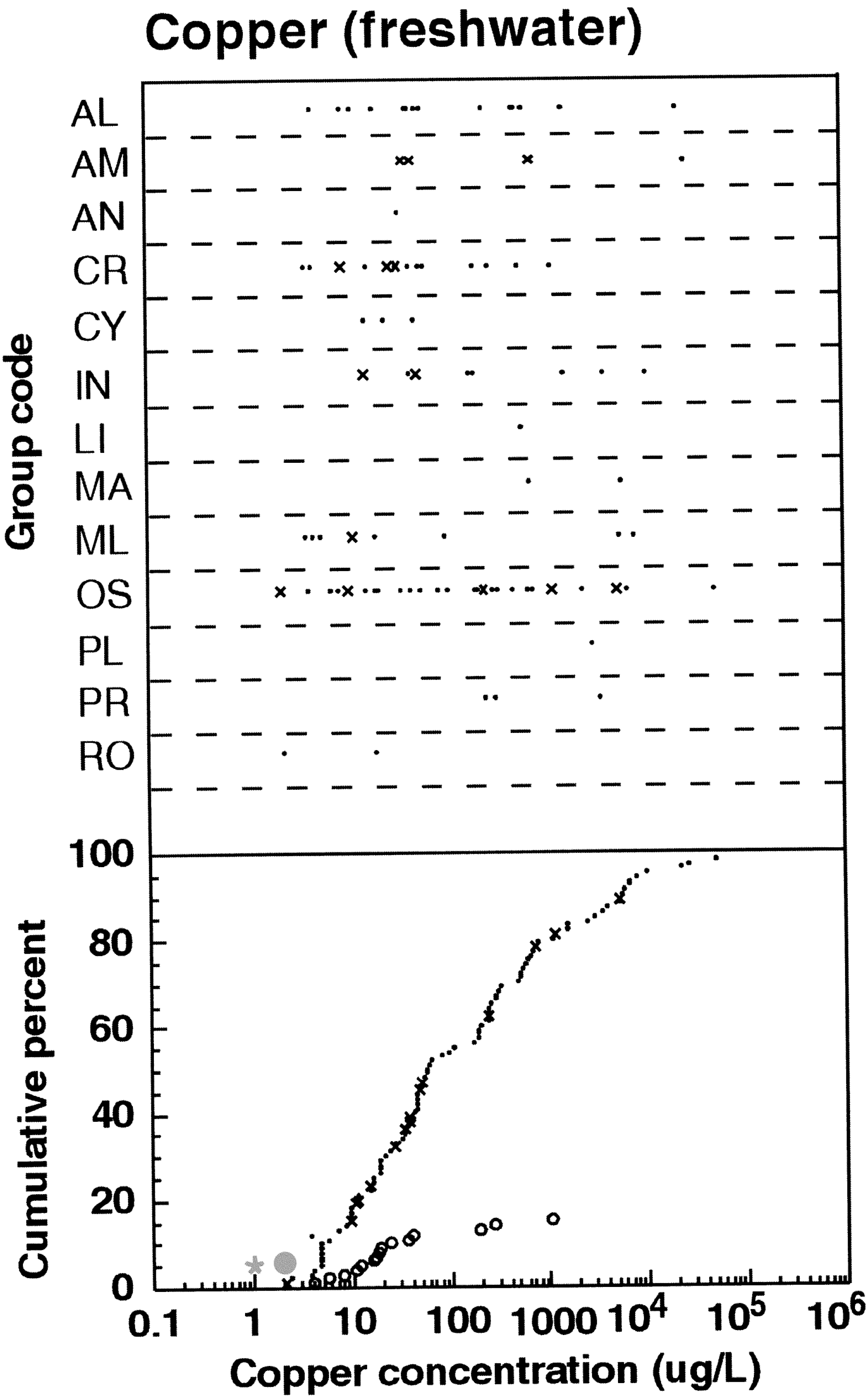

Figure 2. *Summary data for copper in freshwater showing cumulative frequency plot of organism sensitivity and breakdown of organisms sensitivity by taxonomic group. See Table 1 for taxonomic group abbreviations. Abbreviations: + = base data; x = data with hardness values; o = hardness corrected data to 30 mg CaCO3/L; • = ANZECC (1992) guideline; * = 95% protection guideline value (this study).*

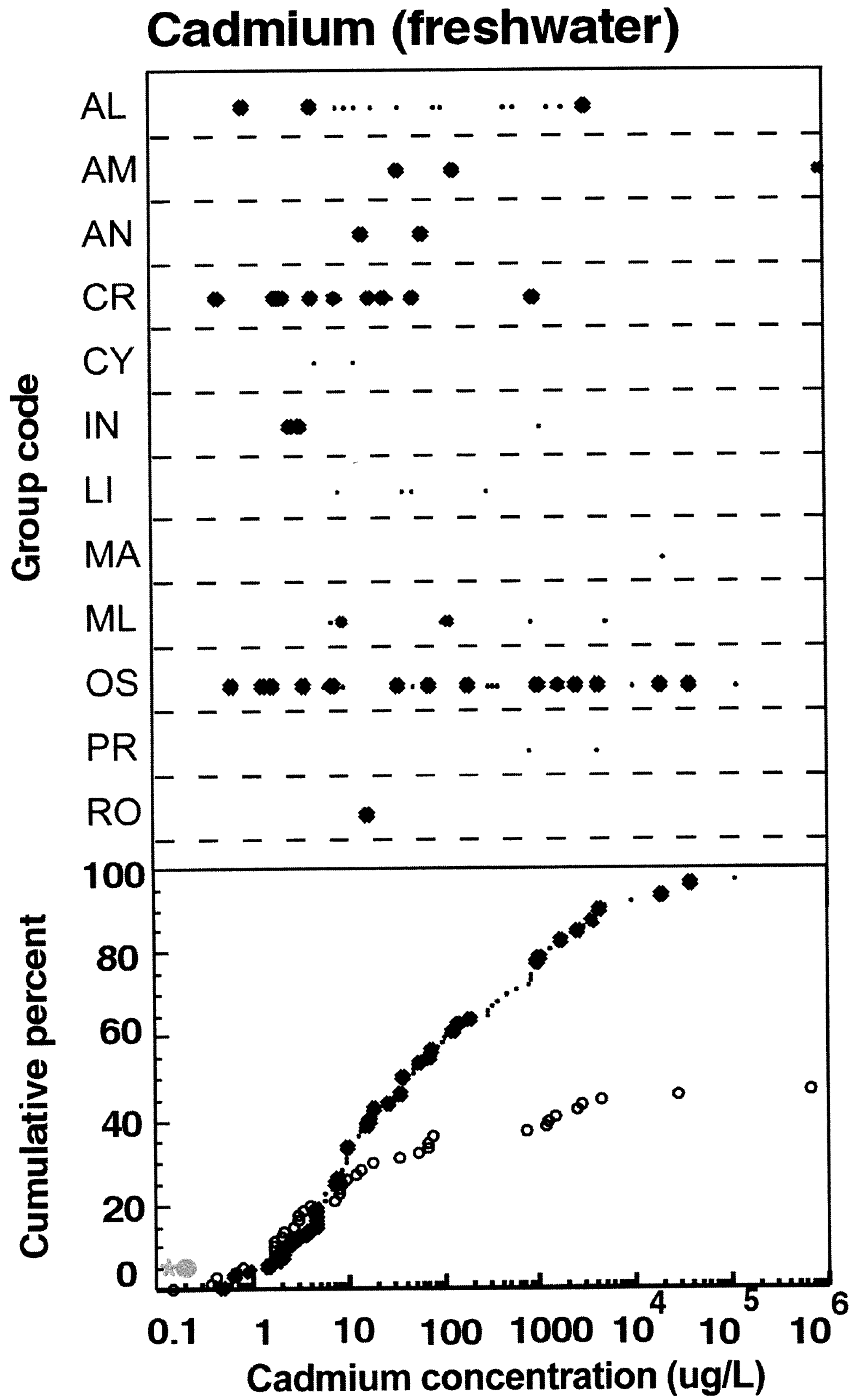

Figure 3. *Summary data for cadmium in freshwater showing cumulative frequency plot of organism sensitivity and breakdown of organisms' sensitivity by group. See Table 1 for taxonomic group abbreviations and Figure 2 for symbol abbreviations.*

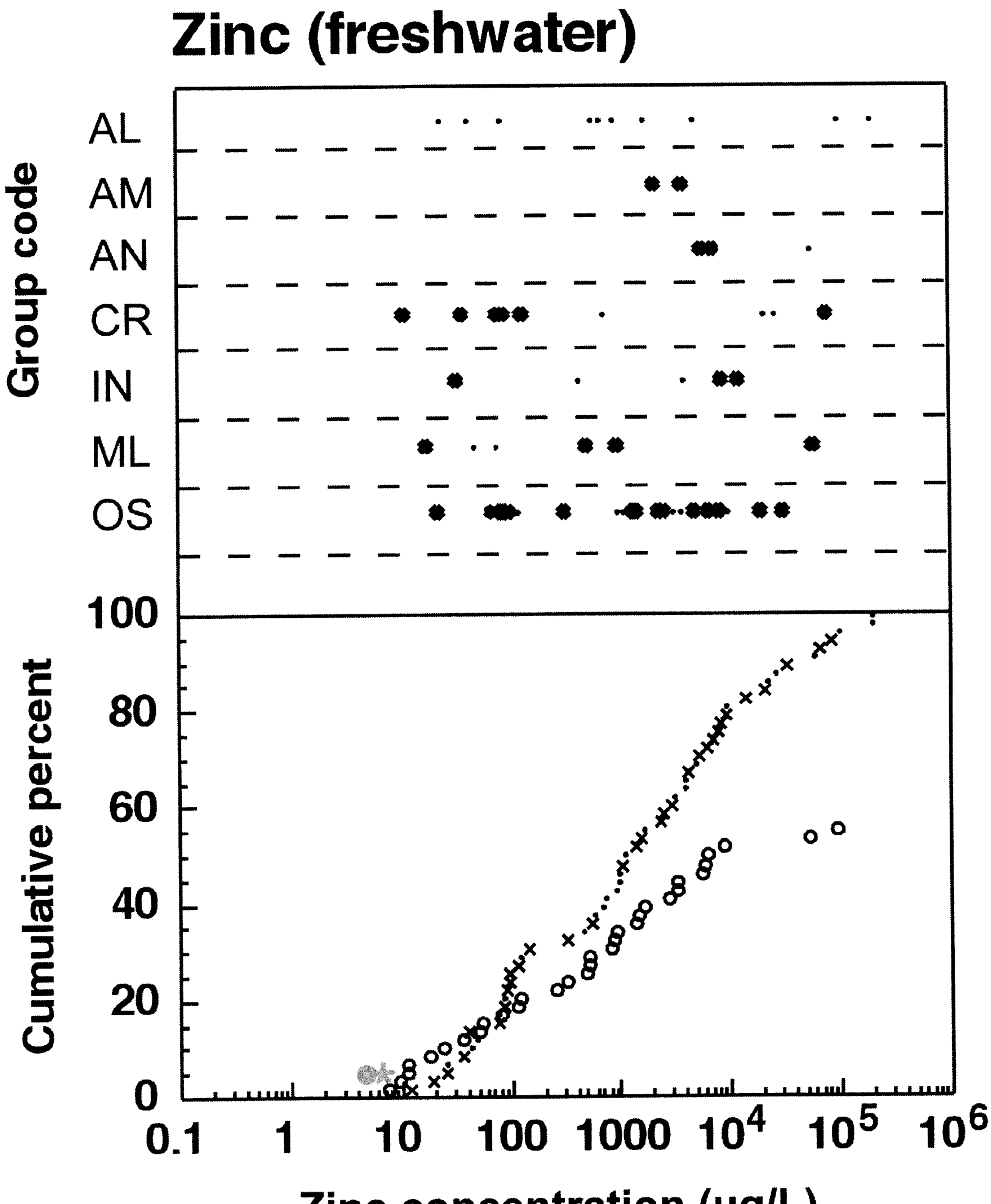

Figure 4. *Summary data for zinc in freshwater showing cumulative frequency plot of organism sensitivity and breakdown of organisms' sensitivity by taxonomic group. See Table 1 for taxonomic group abbreviations and Figure 2 for symbol abbreviations.*

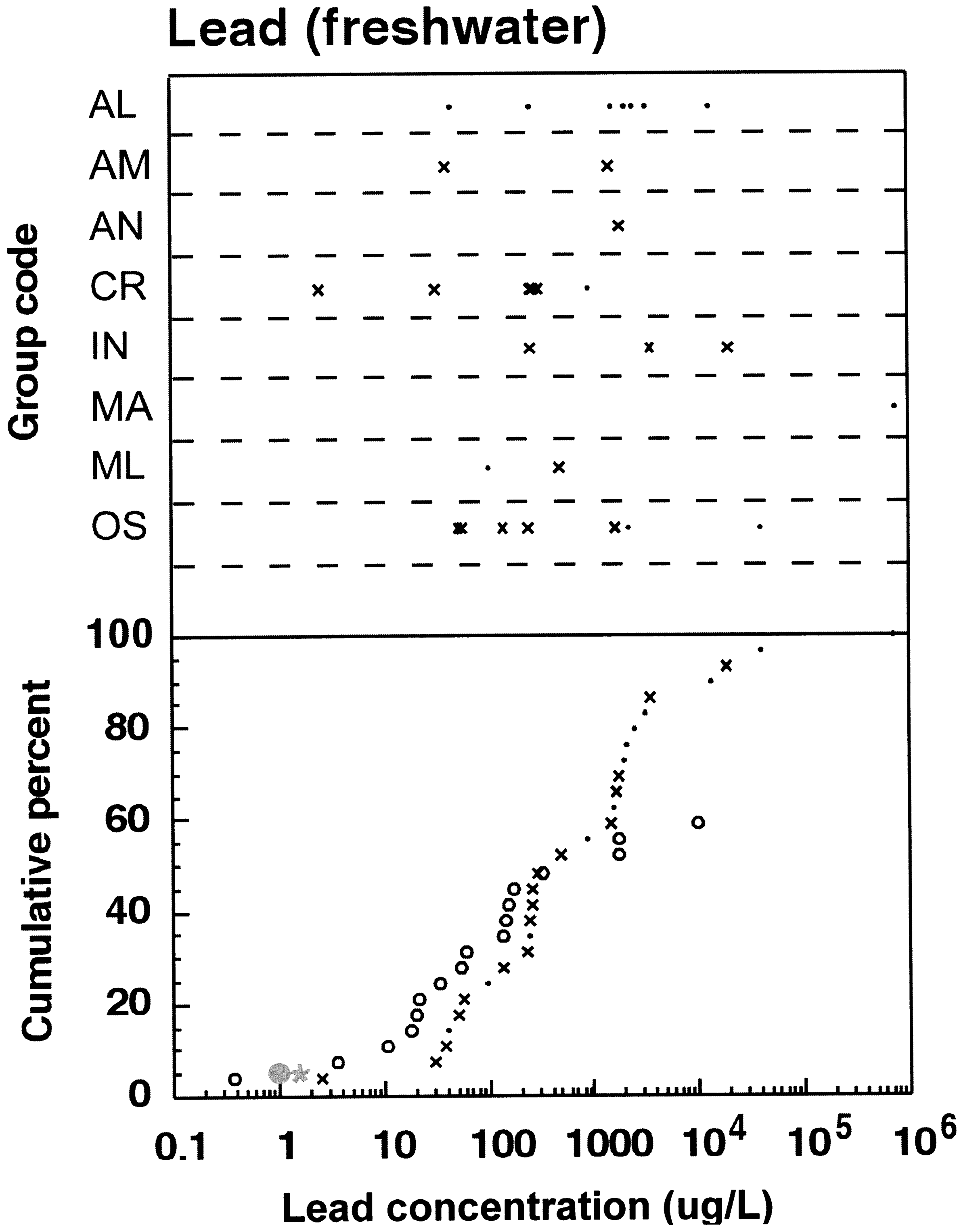

Figure 5. *Summary data for lead in freshwater showing cumulative frequency plot of organism sensitivity and breakdown of organisms' sensitivity by taxonomic group. See Table 1 for taxonomic group abbreviations and Figure 2 for symbol abbreviations.*

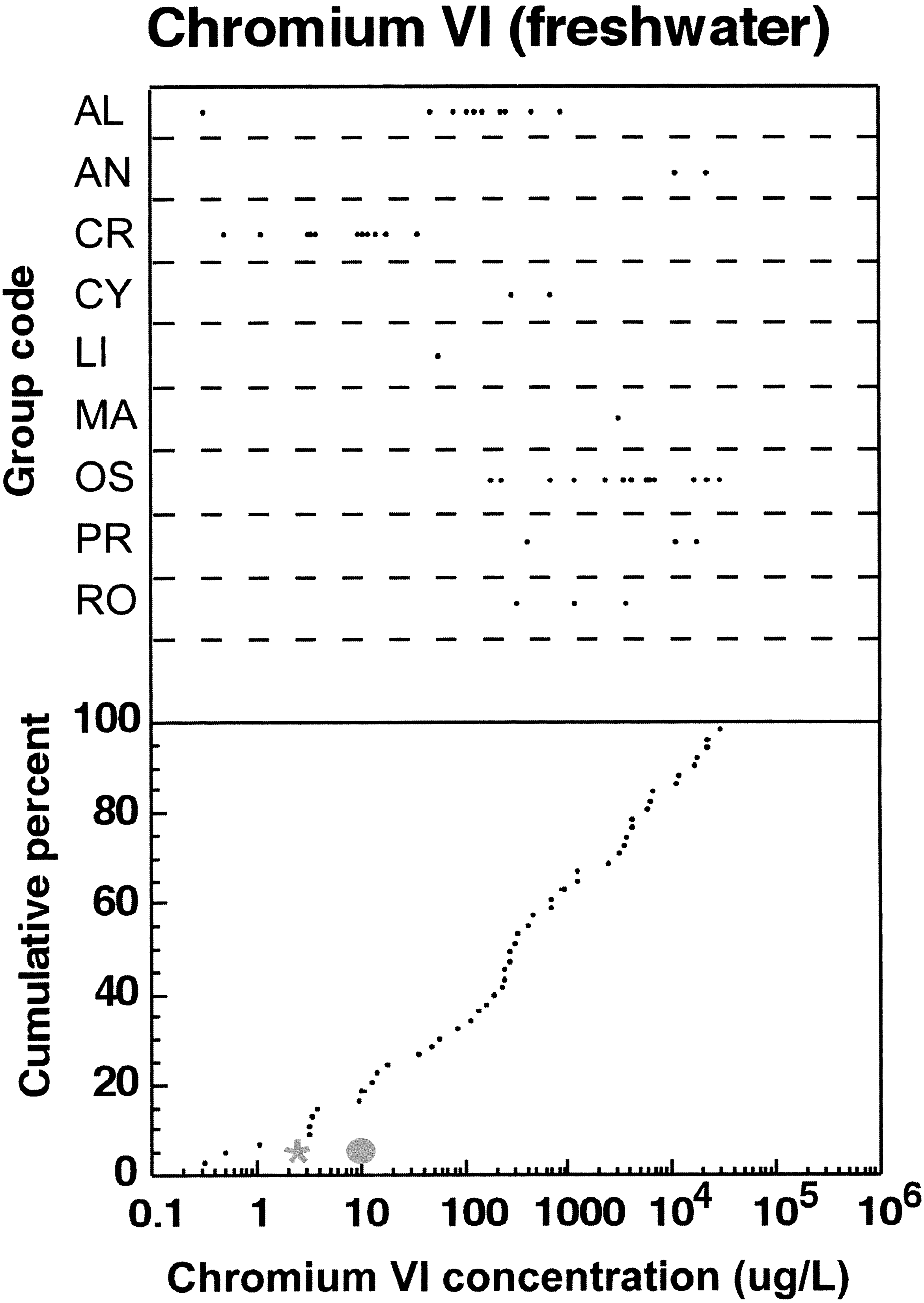

Figure 6. *Summary data for chromium (VI) in freshwater showing cumulative frequency plot of organism sensitivity and breakdown of organisms' sensitivity by taxonomic group. See Table 1 for taxonomic group abbreviations and Figure 2 for symbol abbreviations.*

Table 5. Summary of background metal levels for US, Australian and New Zealand waters using 'clean' techniques

Metal	Salt water (µg/L)	Fresh water (µg/L)	Country
Cadmium	0.01 - 0.2 [a]	0.002 - 0.08 [a]	US
Cadmium	0.002-0.07 [b]	ND	Australia
Cadmium	ND	0.008 [d]	New Zealand
Copper	0.1 – 3 [a]	0.4 – 4 [a]	US
Copper	0.025-0.38 [b]	ND	Australia
Copper	0.1-0.2 [c]	0.15 [d]	New Zealand
Lead	0.01 – 1 [a]	0.01 – 0.19 [a]	US
Lead	<0.006-0.03 [b]	ND	Australia
Lead	ND	0.02-0.03 [d]	New Zealand
Chromium	0.062-0.1 [b]	ND	Australia
Nickel	0.3 – 5 [a]	1 – 2 [a]	US
Nickel	0.13-0.5 [b]	ND	Australia
Nickel	0.33 [c]	0.1-0.15 [d]	New Zealand
Silver	0.005 – 0.2 [a]	ND	US
Silver	<0.0005	ND	Australia
Zinc	0.1 – 15 [a]	0.03 – 5 [a]	US
Zinc	<0.022-0.1 [b]	ND	Australia
Zinc	0.005-0.02 [c]	0.15-0.2 [d]	New Zealand
Arsenic	1.0-1.6 [b]	ND	Australia

ND = No data
References: [a] = Prothro (1993); [b] = Apte *et al.* (1998); [c] = Dickson and Hunter (1981); [d] = Ahlers *et al.* (1991).

There were very few data available for some contaminants (eg. CrIII and As) which are of concern in the New Zealand environment because of their widespread use in timber treatment. Geothermal activity is also a regionally important source of As. Data for these metals were so limited that little information was available on the relative sensitivity of the taxa groups and only Interim guideline values could be derived (Tables 3 and 4).

Background chemical concentrations.

Background metals levels are available for some US, Australian and New Zealand waters (Table 5), away from the immediate influence of discharges and measured using 'clean' techniques. Comparison of these values with those given in Tables 3 and 4 highlights the potential for promulgating guidelines which are below background levels normally experienced by healthy communities. These concerns are greatest for copper and zinc which are common industrial and diffuse source contaminants. The Dutch recommend use of the guidelines as 'add to background' values (Struijs *et al.* 1997). In practice, there will be analytical difficulties with obtaining good data for some metals at the proposed 99% protection guideline levels.

Site-specific applications.

The revised ANZECC guidelines (ANZECC & ARMCANZ 2000) provide guidance for establishing appropriate guideline values (GV), comparing measured concentrations with GVs, dealing with mixtures and selecting appropriate regulatory approaches. All of the proposed GVs would be implemented on a soluble (ie. < 0.45 µm) metals basis, with hardness correction where appropriate. This guidance is consistent with the toxicological measurements having been made on bioavailable metals and with current regulatory advice in the US (Prothro 1993), and would be protective of water-column-dwelling species. There is some uncertainty, however, as to the degree of protection afforded by soluble GVs to filter feeding organisms (eg. mussels) and for protection of sediment dwelling biota, where particle associated contaminants settle and accumulate over time.

The development of site-specific guidelines requires consideration of a range of factors relating to the nature of a chemical discharge and the receiving environment. These include: background concentrations; analytical detection limits; factors modifying bioavailability (eg. pH, hardness, suspended and dissolved organic matter), chemical formulation, mixtures and local species of importance. Factors affecting the dilution and

Table 6. Examples of application of guideline values and assessment approaches relevant to different receiving waters (after ANZECC & ARMCANZ 2000). Bracketed narrative statements relate to the New Zealand Resource Management Act (RM Act 1991).

A. High conservation/ecological value systems (ie. no 'adverse effects')
• use 99% guideline values as planning tool and design criteria
• metals: not exceeding background
• anthropogenic organics: above detection/trace → management
• no detectable change in biological diversity relative to appropriate reference site
• direct toxicity assessment (early option for discharges)
B. Slightly disturbed systems (ie. no 'significant adverse effects')
• compare with 95% protection guideline values (but no lower level of protection)
• apply decision scheme for site-specific guidelines
• direct toxicity assessment
• no detectable change in biological diversity and abundance relative to appropriate reference site
C. Moderately disturbed systems (ie. no 'significant adverse effects')
• compare with 95% protection guideline values
• consider 90% protection guidelines or other values
• apply decision scheme for site-specific guidelines
• direct toxicity assessment
• biological assessment of diversity relative to appropriate reference site
D. Highly disturbed systems (ie. no 'significant adverse effects')
• compare with 95% protection guideline values
• consider other guideline values (eg. 90%, 75%)
• apply decision scheme for site-specific guidelines
• direct toxicity assessment
• biological assessment of diversity relative to best available reference

dispersion of a discharge will also require consideration in relation to the provision of 'reasonable mixing' as required under the RM Act. Thus site-specific application requires an integrated assessment of a wide range of factors influencing the potential impact of a chemical or effluent discharge.

The nature of the effluent and sensitivity of the receiving water will also dictate the relative importance of regulatory approaches, including: chemical-specific guidelines, toxicity measurements (DTA or WET) and field biological assessment. Table 6 illustrates a range of assessment options relevant to ecosystems requiring differing levels of protection.

For receiving waters requiring protection from 'significant adverse effects' either the recommended guidelines for 'adverse effects' could be used, or some lower level of protection could be calculated (eg. 90%) which is more appropriate for the water's designated use. However, this latter approach is fraught with difficulties, because of the present lack of data on New Zealand species and the resulting uncertainty that protection of, for example 90% of species, will ensure that the desired ecological values are sustained.

The application of appropriate guideline values to New Zealand site-specific situations is dependent on the interpretation of the RM Act in relation to 'effect' and the value of the 'precautionary principle'. Deliberation in a recent case has determined that the RM Act is not a "no risk" statute and that the RM Act is precautionary in itself and justifies a precautionary approach (McRae 1999). The Court held that the concept of a wider precautionary 'principle' is not helpful and that references to a precautionary principle are another way of expressing concern about effects of low probability and high potential impact, ie. 'effect' as defined in the RMA. Because such effects must be considered (under s. 104), revisiting these effects under the label of the precautionary principle would amount to duplication of process. This decision supports the in-built precautionary of the revised ANZECC Water Quality Guidelines, such as using NOECs.

The species used in direct toxicity assessment (DTA) or WET testing should be sensitive at concentrations approaching the guideline concentration, based on data supporting the original guideline derivation. Tests would be run at conditions similar to 'critical' (eg. dilution) conditions which could include site-specific exposure factors (eg. temperature, receiving water). This testing may have to be undertaken with surrogate test organisms because of the present lack of suitable chronic test procedures with native species representative of a range of taxonomic groups.

Field biological assessments play an important role in site investigations and monitoring programmes. However, their utility is often limited by the availability of suitable reference sites, particularly in highly disturbed systems (eg. urban streams). In addition, the propensity of biological communities to integrate the multitude of factors which may be influencing their environment (eg. floods, temperature, nutrients) means that they are often poor predictors of cause-effect relationships with chemical toxicants. For this reason, a suite of techniques (ie. chemical-specific, DTA, biological assessment) may be required in disturbed environments to identify factors causing observed effects. Care should be taken to utilise appropriate techniques in order to direct resources to instigating appropriate management to best address environmental problems.

Some site-specific investigations may require reassessment of the data used in the present guideline development. This could involve removal of species of taxonomic groups which are not present in the receiving water or are considered of minor importance (eg. algal primary production). The inclusion of more recent toxicological data may also make a significant difference to some guideline values. Clearly, there are data needs for some metal contaminants which are of importance in the New Zealand environment (eg. CrIII, As) for which only interim guideline values could be calculated.

CONCLUSIONS AND RECOMMENDATIONS

Guidelines were calculated for freshwater and marine organisms using the Aldenberg and Slob (1993) statistical method. The statistical method calculates guideline values with different levels of protection and confidence. The use of the 99% protection guideline value was recommended for waters to be protected from 'adverse effects'. The Dutch recommend use of the guidelines as 'add to background' values (Struijs *et al.* 1997). The 'add to background' approach appears to have merit, and should be considered as a method for applying the numeric guideline values. For receiving waters requiring protection from 'significant adverse effects' either the recommended guidelines for 'adverse effects' could be used, or some lower level of protection could be calculated (eg. 95% or 90%) which are more appropriate for the water's designated use.

To improve the quality and defensibility of the datasets used for guideline derivation, we recommend that:

(i) the sensitivity of the risk-based statistical model (ETX) for effects of the number of chronic data, and of deviations from the logistic model assumptions in the tail regions be determined, in order to better define the optimum model selection, minimum number of species and other dataset requirements (eg. treatment of outliers);
(ii) guidelines be established for data quality for site-specific application in relation to chemical exposure and the use of multiple toxicological endpoints and effects data;
(iii) a review of international and Australasian datasets for background concentrations of essential elements in 'pristine' environments be undertaken, in order to establish minimum values for essential elements;
(iv) a comparison of acute data for native species sensitivity relative to international data be undertaken in order to identify taxonomic groups at risk and prioritise those species for which chronic protocols should be developed;
(v) appropriate representative regional testing species be identified, and chronic methods developed for those species; and
(vi) environmental monitoring data from carefully designed programmes be fed back into the criteria assessment programmes to evaluate the applicability of the guidelines used.

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