P A P E R S

THE REVISED AUSTRALIAN AND NEW ZEALAND WATER QUALITY GUIDELINES FOR TOXICANTS: APPROACH TO THEIR DERIVATION AND APPLICATION

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ABSTRACT

The revised Australian and New Zealand water quality guidelines for toxicants present chemical-specific guideline figures for around 200 organic and inorganic (metallic and non-metallic) toxicants covering freshwater and marine systems. These figures are termed "trigger values" because it is intended that, if they are exceeded, further investigations will be triggered. Toxicant guideline trigger values have been derived primarily according to risk assessment principles and recommendations for their use follow a hierarchical decision framework that is also risk-based. This paper discusses the approach and philosophy behind derivation of the revised guideline trigger values, which are estimates of the highest concentration of chemicals that are expected to have no adverse effect. It is intended that, wherever possible, the figures should be applied at specific sites according to a risk-based decision scheme, taking into account the interaction of natural water quality and other parameters with toxic chemicals at the specific site. Such site-specific assessment is therefore an integral part of these guidelines and the detailed decision scheme is intended to assist a catchment manager to arrive at a final guideline value appropriate to the location being studied. A range of approaches may be used to address these interactions depending on the specific issues at hand and the availability of data. The decision-tree framework described in this paper provides catchment managers with practical guidance on how to apply the trigger values to specific sites according to local environmental conditions and also helps to focus future research needs.

Key words: water quality guidelines, toxicants, derivation, site-specific.

INTRODUCTION

It may be considered ideal to eliminate all toxic discharges to the aquatic environment but in many cases this is not feasible. Where discharges are unavoidable, numerical guidelines for toxicants in receiving waters are an essential tool for water management. The revised water quality guidelines for chemical toxicants (ANZECC & ARMCANZ 2000) are designed to protect aquatic ecosystems that are substantially natural ("slightly - moderately disturbed": condition 2) or highly disturbed (condition 3) (see McAlpine and Humphrey 2001). The guidelines provide a framework for setting environmental limits for a range of commonly encountered chemicals, based on available environmental effects data. For aquatic ecosystems considered to be of high ecological value (condition 1), the guidelines recommend a precautionary approach, where anthropogenic chemicals should not be at detectable levels and naturally occurring toxicants should not exceed background concentrations (McAlpine and Humphrey 2001). Relaxation of this approach for high ecological value ecosystems should only occur when there are considerable biological assessment data showing that such a change in water quality would not impact on biological diversity of the ecosystem. Where such data have not yet been gathered, the highest protection level can be applied as a default value.

It is important to remember that the guidelines are only chemical-specific estimates aimed at protecting ambient waters (ie. they are not effluent targets). It is therefore important that the goal of environmental

protection be kept clearly in view for all activities that use these guidelines, so that the water management focus does not shift to merely meeting the numbers. In fact, the guideline figures are termed "trigger values" because it is intended that, if they are exceeded, further investigations, as described below, will be triggered.

APPROACH USED IN DERIVING TRIGGER VALUES FOR TOXICANTS

Extrapolating from laboratory toxicity data to effects in the field (OECD 1992) involves uncertainties and value judgements. All guideline values for individual chemicals are, at best, estimates of maximum concentrations unlikely to cause adverse environmental effects. There are uncertainties associated with what constitutes a significant change in the environment and whether that change is adverse.

It is preferable to calculate trigger values from multiple species toxicity test data, ie. data from tests of appropriate scale that represent the complex interactions of species in the field. However, many of these tests are difficult to interpret and there are few such data available. In most cases it is necessary to rely on data from single-species laboratory toxicity tests, which formed the bulk of the concentration-response information. There were relatively few such data on Australian and New Zealand species and hence it was necessary to derive most trigger values using predominantly overseas data. Although single species tests have their disadvantages (Cairns 1986), there is evidence that they provide some prediction of effects at higher levels of organisation (Sprague 1995; USEPA 1999). Hence they will continue for some time to provide the basis on which to derive water quality guidelines for the large number of chemicals currently in use (Mount 1994; Chapman 1995). As there is no single 'sensitive' test species (Cairns 1986; Pedersen *et al*. 1994), predictions were based on the likely effects of toxicants using a range of test species (OECD 1992).

The previous ANZECC (1992) guidelines for toxicants 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*". This is an admirable long-term objective but it is important to recognise firstly that, in the context of water quality management, almost all human activity causes some degradation of water quality, and possibly some loss of species. Even if all point sources of contaminants were eliminated it would be virtually impossible, given all the diffuse sources of contaminants, to protect all aquatic species. Secondly, limitations in our knowledge of the effects of a toxicant on complex ecosystems may not be adequate to ensure that we will achieve that goal. Furthermore, this goal bore no relationship to the method previously used to derive the values (ANZECC 1992) in which an arbitrary assessment factor (the magnitude of which depends on the data available) is applied to the lowest toxicity value for a particular chemical. Assessment factors have been criticised as a means of deriving water quality guidelines, largely because of their arbitrary nature (Chapman *et al*. 1998; Warne 1998). Nevertheless, factors were still useful for deriving some trigger values, particularly when data did not allow use of alternative methods. The assessment factors used in the revised guidelines accord with OECD (1995).

An alternative approach to using the assessment factors is the use of statistical distribution methods based on a spread of toxicity data (OECD 1995; Roman *et al*. 1999). Warne (1998) reviewed the available methods and recommended using the Aldenberg and Slob (1993) method as a basis for deriving the trigger values, with some modifications. This approach estimates a pre-determined level of protection, usually 95%, using a probability distribution of effects from a range of toxicity data and also attempts to calculate a given confidence level (eg. 50% or 95%) for this value. To overcome statistical limitations of this method (Fox 1999; Warne 2001), modifications were made using CSIRO software based on the Burr (1942) series of distributions (Campbell *et al*. 2000). The expanded distributions provided greater flexibility in the range of shapes to be fitted (Fox (1999). The use of 95% protection does not imply a retreat from high quality environmental protection but provides a more defensible basis for decisions. Warne (1998, 2001) and ANZECC & ARMCANZ (2000) discuss this in more detail.

All methods for deriving trigger values involve degrees of technical and value judgements. However, use of a risk-based approach provides a logically consistent approach that allows informed debate about the level of protection that a community may require and the degree of certainty with which that level of protection can be delivered (NZ Ministry for Environment 1996). Sole reliance on an assessment factor approach prevents any quantitative alteration of protection levels and does not reflect the increase in confidence in the derived trigger value as the dataset becomes more comprehensive. Ecologically sustainable development (ESD) principles imply acceptance of a degree of environmental degradation, as long as the integrity of ecosystems is not threatened. The procedure for deriving guideline trigger values according to a statistically-based risk assessment approach is consistent with ESD. It allows for some estimate of

both the degree of impact and whether a change in protection level for an interim water quality objective would give an acceptable level of protection.

Single species toxicity data, used to derive most water quality guidelines, only account for direct effects of toxicants. However, for some chemicals, the main issue of concern is the indirect risks associated with longer-term bioconcentration, bioaccumulation and biomagnification. There is an absence of formal and specific international guidance on incorporating bioaccumulation into water quality guidelines (Bro-Rasmussen *et al.* 1994). Hence these guideline trigger values have not attempted to take secondary poisoning into consideration (see Connell 2001), except to provide general information for those chemicals likely to bioaccumulate or bioconcentrate for further investigation at specific sites.

APPLICATION OF THE GUIDELINES TO SPECIFIC SITES

The previous guidelines (ANZECC 1992) recommended that the guideline values should be applied so as to take into account the physico-chemical properties of the water at specific sites. At that stage it was not possible to provide detailed guidance on how to undertake this process. The revised guidelines (ANZECC & ARMCANZ 2000) have developed the site-specific approach further, to guide users into a decision scheme that quantitatively, or at least qualitatively, accounts for the effect that these site-specific parameters may exert on the overall toxicity or bioavailability of specific toxicants. It is intended that, if a trigger value is exceeded at a specific site, further investigation would be initiated, although the scheme is optional. Hence, they are termed "trigger values". Use of the trigger values directly would generally result in rather conservative water quality targets.

Wherever possible, the trigger values should also be applied at specific sites according to a risk-based approach, taking into account the interaction between the toxicants and natural water quality and other parameters at the site. Such site-specific assessment is therefore an integral part of these guidelines and the detailed decision scheme is intended to assist a catchment manager to arrive at a final guideline value appropriate to the location being studied. A range of approaches may be used to address these interactions, depending on the specific issues at hand and the availability of data. These include comparisons from literature data, theoretical models (Markich *et al.* 2001) or direct toxicity assessments of biological effects (van Dam and Chapman 2001).

The revised aquatic ecosystem guidelines deal with seven specific ecosystem types - upland rivers, lowland rivers, lakes and reservoirs, wetlands, estuaries, coastal and marine (Hart *et al.* 1998; McAlpine and Humphrey 2001). Chemical-specific trigger values were derived for around 200 organic and inorganic (metallic and non-metallic) toxicants covering freshwater and marine systems, but not specifically for estuaries. Further discussion of estuarine guidelines is given below.

A DESCRIPTION OF THE DECISION SCHEME

The decision scheme for applying the trigger values allows one to consider factors that may affect the toxicity of the chemical at a specific site. Site-specific guideline values may be lower or higher than the recommended trigger values depending on the physico-chemical properties of the water at the site, the sensitivity of local species or other factors.

The site-specific assessment begins by considering the appropriate level of protection arising from the environmental values of the ecosystem (McAlpine and Humphrey 2001). Initial decisions are also made on whether the sample is fresh or saline water, as different trigger values may apply, and whether the chemical is a metal, which includes metalloids such as As or Se, an organic chemical, an inorganic anion such as cyanide or non-metallic chemical such as chlorine. A framework for applying the guidelines to the protection of aquatic ecosystems is illustrated in Figure 1.

The first step (Figure 1) is to measure the total concentration and compare it with the guideline trigger value. This initial measure is intended to reduce costs and make sampling and analysis easier. If the measured concentration is below the trigger value, the chemical is likely to pose a low risk, UNLESS there are factors that increase the toxicity at the particular site. However, if the measured concentration is above the trigger value, there is a possible risk to the environment and the water manager may choose to consider site-specific factors that may modify the trigger value to give a site-specific trigger value. Alternatively, the default trigger values can be used and management action commenced on the basis that the guidelines have been exceeded. If the measured concentration is below the site-specific value that takes into account all of the relevant factors, there is usually no need to proceed further. If it is above the site-specific value, then one may proceed to direct toxicity assessment

Where data are available, the trigger values are modified using mathematical relationships between the parameter and the chemical toxicity. For many

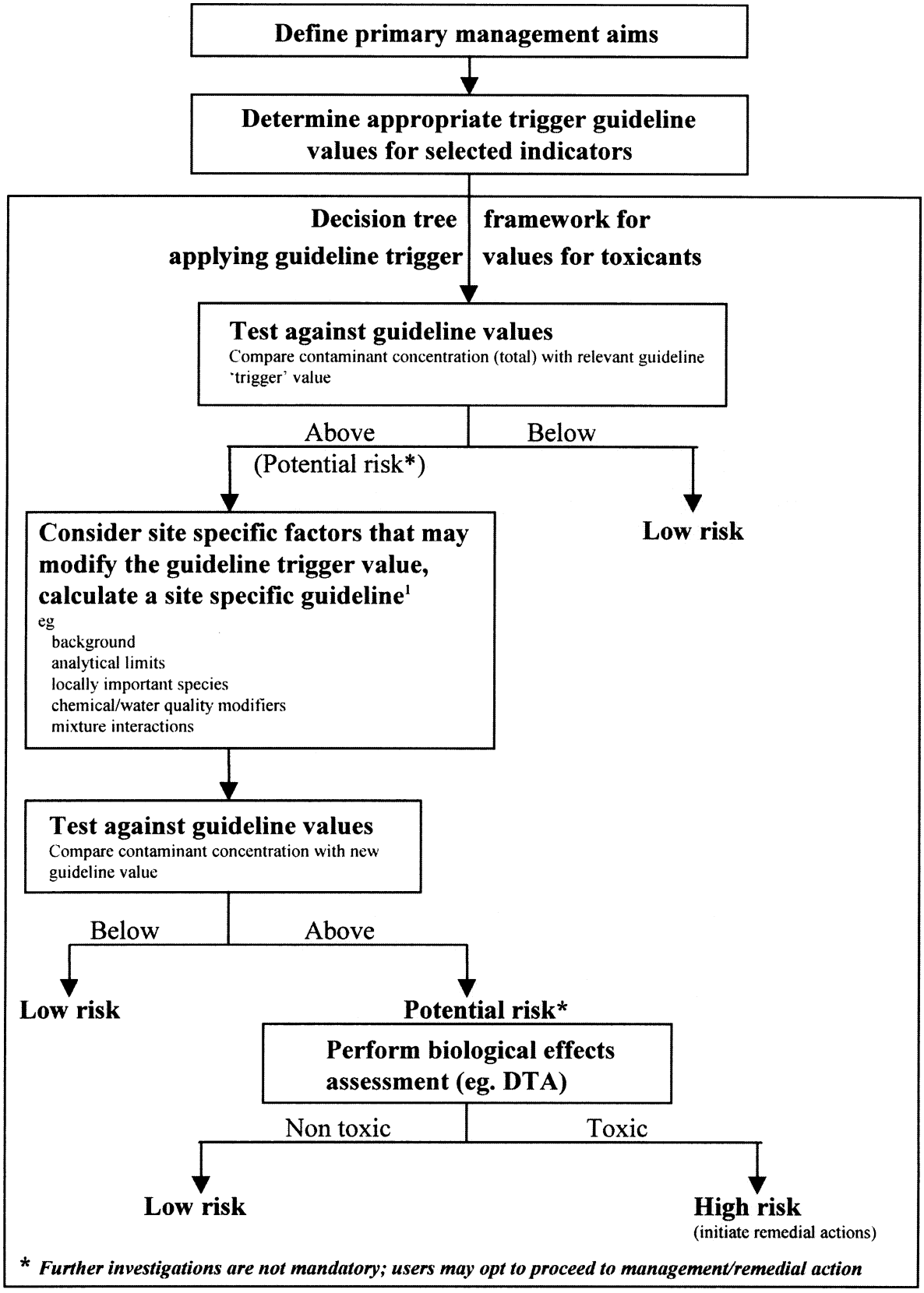

Figure 1. *A generalised outline of the decision scheme for applying toxicant trigger values at specific sites (adapted from ANZECC & ARMCANZ 2000).*

[1] An alternative approach is to undertake more accurate estimates of bioavailable fraction.

chemicals, it may only be possible to make qualitative estimates of these relationships. Typical factors to consider at a specific site are described below, but it may not be appropriate for each chemical to apply all the steps to all groups. Where there is a high degree of confidence in the behaviour of the chemical in the environment, particularly at the specific site, it may be appropriate to skip some steps, with guidance from the regulatory authority or catchment manager. This will largely depend on the type of chemical being examined and the nature of the environment to be protected.

The factors to consider at the specific, and possible responses, are outlined below:

• *The ecosystem condition* (McAlpine and Humphrey 2001) *and the three levels of ecosystem protection*. For more highly disturbed ecosystems (condition 3), it may be possible, if approved by the appropriate catchment management authority, to reduce the level of protection, and hence the guideline value at the specific site would increase. However, the intention should be to continually improve, rather than just maintain, the quality of highly disturbed ecosystems.

• *The background concentration of the chemical.* If it can be confidently demonstrated that the natural background concentration of the chemical is greater than the trigger value at that site, the 80th percentile of the background concentration may become the new site-specific guideline. This assumes that the laboratory is capable of measuring at trace concentrations and that the laboratory quality systems can provide sufficient assurance that the real background concentrations are not overestimated.

• *Analytical practical quantitation limits.* If the guideline trigger value is below the commonly accepted practical quantitation limit (PQL), using best readily-available technology, ANY measurement of that chemical above the PQL demonstrates that the guideline is exceeded, subject to factors discussed below. The PQL does NOT automatically become a *de facto* guideline figure. Also the increased likelihood of errors in measurement at such low levels needs to be included in these considerations. There is common concern that some guideline figures cannot be measured by current analytical techniques. However, it must be remembered that there are chemicals for which significant biological effects may occur at concentrations below the PQL. If the trigger value is below the PQL, one may either accept that any detection implies that the guidelines have been exceeded or proceed to direct toxicity assessment (DTA; van Dam and Chapman 2001), provided that there is confidence that biological effects can be detected at the PQL. PQLs can sometimes be reduced over time with advances in technology.

• *Locally important species.* If there are ecotoxicology data on species occurring at the specific site that were not included in the original guideline derivation, it may be possible to recalculate the guideline using the new data. It is important to adhere to the pre-set rules to ensure that the data are of sufficient quality and do not violate the assumptions of the methods used to calculate the trigger values (Warne 2001). In most cases, species should not be deleted from the selected list for calculation, only added or substituted.

• *Formulation of the chemical.* Some chemicals (eg. pesticides) are used as formulations that, in some cases, may either markedly increase or decrease their toxicity. In such cases, it may be appropriate to apply a factor to the trigger value to account for formulation effects, or else undertake DTA. An example is provided in Chapman *et al.* (2001).

• *Water quality factors that modify the toxicity of the chemical.* These include suspended matter, dissolved organic matter, pH, temperature, hardness, alkalinity and salinity. For many metals, pH, hardness and speciation are particularly important determinants of toxicity and hence affect the magnitude of the trigger value. Some quantitative algorithms and models are available to account for hardness effects on metal bioavailability and Markich *et al.* (2001) describes these in more detail. For each chemical, it is important to refer to the particular detailed chemical description in Chapter 8 of ANZECC & ARMCANZ (2000). In considering these factors, it is important to be aware that bioavailability can change spatially and temporally with changes in water quality. Hence, it is essential to demonstrate a clear understanding of such variations in water quality at the specific site.

• *Effects of mixtures.* Chemicals are often found in the environment as complex mixtures where they may act additively or with synergism or antagonism. If these mixtures contain only a few components, it may be possible to model the toxicity of the mixture using theoretical equations and adjust the combined guideline value accordingly. If the mixture is particularly complex, direct toxicity assessment is more appropriate (see van Dam and Chapman 2001).

If, after adjusting the trigger value to account for these site-specific factors or at any stage, the total chemical concentration still exceeds the new site-specific value, then acceptable methods for measurement of bioavailable chemical levels may be used. For metals,

this is an inherent part of the hardness and speciation calculations. For many organic chemicals, bioavailable measurement may be more problematic due to poor understanding of dynamics in the environment. If the estimated bioavailable concentration is below the site-specific guideline value, then there is low risk to the environment. If the bioavailable concentration is above the site-specific guideline value, there may be an increased risk to the environment. In this case, management action may be required either directly or after assessment of the degree of risk using direct toxicity assessment.

If the estimated ambient bioavailable concentration is still above the site-specific guideline value or if the chemical is just one of a complex mixture of chemicals, the catchment manager still has the option of *Direct Toxicity Assessment (DTA)*. Van Dam and Chapman (2001) discuss this in more detail.

DTA may provide the required link between chemical levels and biological effects or establish concentrations that are unlikely to cause harm. DTA procedures may comprise field, *in situ* and/or laboratory ecotoxicology assessments (Chapman 1995) and further guidance on these is provided (van Dam and Chapman 2001). The section below on "Weight-of-evidence in applying DTA results" also provides some further guidance on applying DTA.

The text below examines in more detail some of these factors that impinge upon site-specific guidelines, while some examples are given in Chapman *et al.* (2001).

ESTUARINE GUIDELINES

Guideline trigger values have been derived for fresh and marine waters, but there are insufficient data to derive similar trigger values for estuarine systems. Although it would be tempting to adopt a mean of the fresh and marine trigger values for estuaries, the data sets used to derive these values for any one chemical are generally quite different. In addition, estuarine organisms face specific environmental stresses from their changing environment, particularly physiological and osmotic stresses from salinity changes due to tidal flushing and floods of freshwater. This can lead to resident fauna that are already naturally stressed. Furthermore, estuaries provide nursery grounds and refuges for particular (sometimes sensitive) life-stages of organisms from both marine and freshwater environments. Hence, it could be argued that estuarine organisms might be more sensitive to chemical stressors than marine or freshwater organisms. However, this theory is untested.

In the absence of specific estuarine toxicity data, users should adopt the lower of the two trigger values (marine or estuarine) and apply whatever salinity corrections are available using the decision tree approach. For metals that are affected by hardness, it is possible to use the freshwater trigger values for salinities up to 2.5 mg/L and apply the hardness algorithms (Markich *et al.* 2001). For higher salinities the marine trigger values for metal should be used. For many chemicals, this remains an area for further research.

REDUCING THE LEVEL OF PROTECTION FOR HIGHLY MODIFIED ECOSYSTEMS

McAlpine and Humphrey (2001) describe the three 'categories of ecosystem condition' used to determine the level of protection for aquatic ecosystems. The statistical distribution method used (Campbell *et al.* 2000) provides a mechanism to develop lower levels of protection, and this can be used by catchment managers for highly disturbed ecosystems (ecosystem condition 3), within the statistical limitations of the method. This is subject to the approval of the appropriate authority and the state of the ecosystem and in many cases the trigger values listed in the guidelines as providing a 95% protection level with 50% confidence would still apply. The overall emphasis should be on ecosystem improvement, not just maintenance of a degraded condition. The Campbell *et al.* (2000) method allows calculation of less stringent or more stringent guideline values, eg. for protection of 99% of species with 50% confidence, 95%, 90% protection or perhaps even 80% protection. For example the 95% protection value for zinc was 8 μg/L (at 30 μg/L $CaCO_3$ hardness, using the screened and hardness-corrected data), the 90% value was 15 μg/L and the 99% value was 2.4 μg/L. The respective values for endosulfan were 0.2 μg/L, 0.6 μg/L and 0.03 μg/L and for phenol, 320 μg/L, 600 μg/L and 85 μg/L. It is necessary to stress that modified values for this lowest level of protection should not approach the acute toxicity levels, which are listed in detail in Section 8 of the guidelines. For example, even the 95% protection figure for endosulfan is uncomfortably close to the lowest LC50 used in deriving the trigger value and is unlikely to be acceptable.

Caution is required whenever changing the level of protection. If the level of protection were to be increased (eg. to 99%, ie. the trigger value decreased), inaccuracies in the tail for the statistical distribution become large. If the level of protection were to be decreased, the reasons should be clear and based on sound ecological principles. For an already degraded ecosystem a lower level of protection may be accepted

as the first interim step toward achieving improved protection in the longer term. This allows the community to make an informed decision on what level of degradation may or may not be tolerated. Catchment managers will need to access the original data to undertake any such recalculations.

If the assessment factor method was used to calculate the trigger value (usually for low reliability trigger values), varying the level of protection is problematic. Assessment factors do not readily fit with a risk-based approach (Warne 1998) and there is no practical and logical procedure to determine the level of protection that an altered assessment factor would provide. A reduction in the size of the factor would need some justification. It is important to consider how close one may go to a no observable effect concentration (NOEC) or an acute LC50 value and what implications this may have on the component of the factors that estimates the acute-to-chronic ratio (see Warne 2001). A preferred approach would be to first re-examine the most sensitive species used to calculate the trigger value, assess whether it, or a related species, is not relevant to a local ecosystem, then to recalculate the guideline with the next most sensitive species.

NATURAL BACKGROUND LEVELS

In some cases, the concentrations needed to maintain or achieve the desired water quality for protection of aquatic ecosystems may not be attainable because of high *natural* background levels, particularly for metals, due to mineralisation from the catchment substrate. It is important to determine whether the background values reflect the natural conditions or an already significantly modified system. It is also important to ensure that the laboratory is capable of accurate measurements at trace levels. Sometimes, background levels can be established from equivalent reference sites with low levels of human impact. In such cases, if established with a high degree of certainty, the 80th percentile of the established background concentration becomes the site-specific guideline for total metal before applying tests for bioavailability or models for metal speciation. It may be preferable to compare filtered concentrations for background determinations. Direct toxicity assessment may help to clarify any lingering uncertainty about the site-specific toxicity of the metal.

Very few organic chemicals would have elevated natural background levels. Some phenols may be an exception, from decaying organic matter, while globally distributed chemicals such as DDT residues may be considered using this approach. Some non-metallic inorganic chemicals such as sulfide, sulfate, ammonia, nitrite and nitrate may occur naturally at elevated levels. Again, the established background level becomes the default value and the hierarchical decision scheme is followed to establish site-specific guideline values that account for natural variations. The chemistry of these ions under the local water conditions needs to be considered.

INCORPORATING LOCAL SPECIES

In most cases, it would only be necessary to examine local species if there is a locally important species (commercially or ecologically) that is not represented by a similar organism in the original dataset used to calculate the trigger value. Generally, data should be added and not substituted. Ideally, when deriving national trigger values it would be preferable to use Australian and New Zealand data under regional conditions. However, there are insufficient regional data for all but a handful of chemicals and new data collection is best targeted towards high priority, high use chemicals with regional or countrywide significance. In general, previous studies with metals (Skidmore and Firth 1983; Markich and Camilleri 1997) and organic chemicals (Johnston *et al.* 1990; Sunderam *et al.* 1992) have indicated that the Australian species tested were within the range of sensitivities of the overseas species to the toxicants tested. This should not be interpreted to mean that toxicity to Australian or New Zealand species could be accurately predicted from overseas data on all chemicals. Some Australian cladocerans and other species were more sensitive to some chemicals (Davies *et al.* 1994; Rose *et al.* 1997).

The scheme for deriving water quality guideline trigger values has drawn upon Australian and New Zealand data whenever quality data were available. It was not considered useful to weight the regional data or discard overseas data unless there was a sufficiently complete set of local data for a particular chemical, and if this dataset indicated a notably different toxicity range. On the broader scale, guideline values could be recalculated using only species native to the country or region of concern or else substituting data from the equivalent representative taxa with data from similar native species, eg. overseas cladoceran data with equivalent native species. It is important to maintain the integrity of the guidelines by adhering to the requirements for data quality and quantity (Warne 1998, 2001) and also to ensure that a comprehensive overseas dataset is not substituted by a native dataset that does not cover the necessary breadth of taxa. Deletion or substitution of data points should not be undertaken without full consideration of the complete dataset.

CHEMICAL FORMULATION

Most pesticides are applied as proprietary formulations, the toxicity of which may vary from the parent technical grade chemical. The exact compositions of the formulations are rarely publicised but they generally contain materials similar to surfactants that act as wetting agents, solubilisers, droplet stabilisers and suspension aids. The formulations are often prepared to facilitate efficient and effective transfer to the target site or pest organism. In some cases, the formulations can be significantly more toxic than the technical grade chemical, whereas in others they may be significantly less toxic. The variations in the toxicity of various commonly used formulations of the herbicide 2,4-dichloro-phenoxyacetic acid (2,4-D), for instance, cover many orders of magnitude. It may not be appropriate to increase the guideline if a less toxic formulation is rapidly broken down to release a more toxic chemical.

CHEMICAL OR WATER QUALITY FACTORS THAT MODIFY TOXICITY

Adsorption/desorption on suspended matter

The guideline trigger values relate to concentrations of toxicants in unfiltered samples but many chemicals may adsorb to suspended material and become unavailable. Many inland waters in Australia are highly turbid and in such waters, the use of unfiltered samples could lead to a possible overestimation of the potentially bioavailable concentration of a toxicant.

The interactions of toxicants with suspended material can be complex, and will vary with concentration of the chemical, concentration of the suspended material and properties of the chemical. Some metals (eg. Cu, Hg, U) adsorb strongly to iron and manganese oxides or organic matter in clay particles, thereby reducing their bioavailability. Filtering of the non-acidified sample (eg. 0.45 μm) and comparison of soluble metal levels in the filtrate with the guideline value will provide an initial estimate of the amount of metal not bound to particles. It is important to recognise that the process of filtering may change the equilibrium between the chemical and suspended material, and alternative processes may be appropriate, eg. centrifuging or direct measurement of chemical species. This process may be best considered jointly with effects of hardness on the metal toxicity (Markich *et al.* 2001).

For organic chemicals, the interactions with suspended material are less well understood and few specific studies have been undertaken. It is assumed that chemicals with log Kow ≤6 would be strongly bound to suspended organic matter and essentially unavailable. Many pyrethroids, PCBs and dioxin fall into this category. For persistent chemicals, such as organochlorine pesticides, it would be preferable to consider only total unfiltered concentrations. For chemicals with log Kow ≤2, or with high water solubility, the presence of suspended material may have little impact on their bioavailability or toxicity and it is not an issue. For intermediate chemicals (log Kow 2-6), caution needs to be exercised whenever considering adsorption of chemicals to suspended matter, as this process is dynamic and reversible, and affected by flocculation of colloids, transfer across biological membranes such as fish gills or through ingestion. Also, the issue of saturation of binding sites for a particular chemical on suspended particles is not clearly understood and can vary from site to site due, for example, to changes in soil chemistry within a catchment.

Incorporating dissolved organic matter

Most interrelationships between chemicals and suspended material also apply to dissolved organic matter (DOM) or total organic carbon (TOC). Again, many metals can strongly adsorb to organic carbon, resulting in a reduction in their toxicity (Markich *et al.* 2001). If the local water conditions are high in DOM or TOC, one is advised to use specialised chemical techniques or speciation modelling (see Markich *et al.* 2001) to estimate potentially bioavailable metal concentrations. Examples are in Chapman *et al.* (2001).

Incorporating pH

Acidity of water affects the availability of many heavy metal ions in solution (Kelly 1988) and hence, their toxicity. At higher pH values, some metals, such as lead and copper, will precipitate out as metal hydroxides or other salts, thus reducing their toxicity. There are conflicting trends of toxicity with pH changes for some other metals. Amphoteric metals, such as aluminium, are more toxic at both low and high pH (CCREM 1987). The effect of pH is at least partially considered in the hardness algorithms (Markich *et al.* 2001).

Changes in pH can alter the rate of degradation of many organic chemicals. For instance, the breakdown rate of the organophosphorus pesticide profenofos is many orders of magnitude slower at pH 9 than at pH 5 (Tomlin 2000). The only organic chemical for which pH algorithms have been reported is pentachlorophenol (USEPA 1986).

The toxicities of several inorganic ions are affected by pH. The most notable of these is *ammonia*, the toxicity of which is governed by the equilibrium between free ammonia and ammonium ion, which is in turn largely a function of pH. Free ammonia is the more toxic form

at high pH and toxicity of ammonia tends to increase with increasing pH. Guideline trigger values were calculated on free ammonia levels at different pH and temperature values and free ammonia can be calculated from total ammonia levels for different pH and temperatures using the table in the guidelines.

Incorporating temperature

Temperature is an important factor to consider in the Australian context as temperature ranges in Australian aquatic ecosystems are often higher and more varied than those in the northern hemisphere ecosystems where much of the toxicity data are derived (Johnston *et al.* 1990). Temperature can have an important effect on the toxicity of chemicals (Cairns *et al.* 1978). A recent Australian study has found that the toxicities of endosulfan, chlorpyrifos and phenol to fish and invertebrates were different at different temperatures (Patra *et al.* 1995, 1996). Toxicity often increased with increasing temperature but not for all chemicals and all species. Some preliminary factors have been developed and examples given in Chapman *et al.* (2001).

Incorporating water hardness

There are few data on the effects of hardness on the toxicity of organic chemicals to aquatic organisms. For metals, speciation changes with varying hardness and alkalinity has a profound effect on their bioavailability, and hence, their toxicity. In the wet-dry tropics of Australia, water hardness varies with season and this becomes a major factor in determining metal ion bioavailability and toxicity on a seasonal basis. Increasing water hardness (calcium and/or magnesium concentration) reduces the uptake and toxicity of several metals, including cadmium, chromium (III), copper, lead, nickel and zinc, to freshwater organisms. Markich *et al.* (2001) contains a detailed review of metal speciation under different hardness conditions.

The current guideline trigger values for metals were derived from data that reported concurrent hardness and pH measurements. Each of these data points was then adjusted to a standard hardness (usually 30 mg/L) and the trigger value calculated at this given level of hardness. This allows calculation of a site-specific figure at a different hardness and assessment of any likely change in toxicity.

Incorporating transient exposure by, and rapid degradation of the chemical

The issue of rapid degradation of chemicals and how guideline values could be modified for such relatively transient chemicals was considered during preparation of the current guidelines. However, there was little international guidance on how to account for such effects in a site-specific scheme. The USEPA (1986) have included averaging periods within their guidelines, which for acute criteria are 1-hour averages and for chronic criteria are 4-day averages, both not to be exceeded more than once every three years on the average. The concepts of kinetic modelling of exposure and species recovery were flagged in the lead up to the next USEPA revision (Delos 1994) but no further developments have been published (C Delos, pers comm. 2000). This is an issue to consider for future revisions. In any event, transience in water may not necessarily mean transience in sediments, and sediment guidelines may need to be assessed separately.

Incorporating toxicant mixtures

These guidelines are chemical-specific and hence do not take into account that other compounds may be present and also exerting toxic effects. Mixtures of most metals and organic chemicals with non-specific mechanisms of action generally have additive toxicity (Hermens *et al.* 1985; Alabaster *et al.* 1994) but certain mixtures can have toxicity greater than the added individual toxicities (synergism) and others a reduced toxicity (antagonism). Warne and Hawker (1995) point out that the extent of deviation from additivity decreases as the number of chemicals in the mixture increases, a phenomenon called the "Funnel Hypothesis". Interactions between chemicals can be either by chemical reactions or by physiological processes such as altering the mechanisms of toxicant uptake, distribution, metabolism and extraction or altering the toxicant-receptor binding affinity and activity (Connell and Miller 1984).

No chemical-specific guidelines, including the ANZECC & ARMCANZ (2000) guidelines, consider the possibility of these effects. If all toxicants were present at close to their guideline values, significant combined effects could be expected (Enserink *et al.* 1991). There are theoretical methods for accounting for the toxicity of mixtures, as described by Warne (1998). Whether or not a mixture exceeds the water quality guideline could be determined using the following formula (modified from Vighi and Calamari 1996) which assumes additivity of toxicity:

$$TTM = \sum(Ci / WQGi)$$

where TTM is the total toxicity of the mixture, Ci is the concentration of the 'i'th component in the mixture and WQGi is the guideline for that component. If TTM exceeds 1, the mixture has exceeded the water quality guideline. Further, if the aqueous concentration of any chemical in the mixture exceeds its guideline figure,

then the water quality guidelines are automatically exceeded. This of course assumes that all of the contaminants contributing to toxicity have been measured.

Incorporating direct toxicity assessment (DTA)

The best method to take into account the toxicity of mixtures is direct toxicity assessment of the effluent or ambient water, which has the potential to integrate toxicity of complex mixtures. Direct toxicity assessment (DTA) or whole effluent toxicity (WET) testing is a complementary approach adopted in many OECD countries (Pedersen *et al.* 1994; Grothe *et al.* 1996) to characterise the toxicity of wastewater and establish discharge criteria. Methods and protocols are currently available for testing a number of Australian and New Zealand species (see van Dam and Chapman 2001).

While analysis of individual chemicals and chemical speciation modelling for metals can predict or detect the forms of chemicals in aquatic systems, they cannot demonstrate that adverse effects on biota are occurring. Bioassays or toxicity tests can measure the direct biological response of whole living organisms to chemicals or complex mixtures, either in the laboratory, *in situ* or in the field. Responses can be assessed at any level of biological organisation, and testing usually includes a range of endpoints and test species from different levels of the food chain. The choice of an ecologically-relevant endpoint is essential if results are to be extrapolated to effects in the field (Chapman 1995). DTA can also be used prior to discharge of any chemical or mixture to set pre-release safe levels.

Toxicity tests include single species tests, *in situ* tests or multispecies and community bioassays and may measure acute or chronic endpoints. The main considerations in establishing a test program using DTA, and selection of endpoints, are discussed in van Dam and Chapman (2001). Normally an assessment factor may be applied to a NOEC or LC50 value from a series of DTA tests, in line with the guideline derivation procedure but there may be argument for treating the data in some other way.

It is anticipated the catchment managers would only resort to DTA in cases where there is a complex mixture of chemicals entering the specific waterbody and where either the resultant toxicity cannot be easily estimated or the prediction needs to be checked.

Weight of evidence in applying DTA results

In many assessments of site-specific guidelines, clear mathematical relationships do not exist but the option is still open to undertake direct toxicity assessment. The original guideline trigger values were derived according to pre-set acceptance criteria (Warne 2001) and it would be preferable to use the same stringency and rigour to derive site-specific guideline values using DTA. However, this may not always be possible due to time and economic constraints. Furthermore, often the site-specific data may have been collected for a different purpose and the design may not neatly fit within these acceptance criteria. It is desirable to use as much of the site-specific information as possible and not to discard useful local data. Hence, it is recommended that a different strategy be used that involves deriving values by all possible means and then weighting the values according to environmental relevance and quality (Menzie *et al.* 1996), as outlined below, to decide upon the site-specific guideline value. This approach is illustrated generally below and specific examples are given in Chapman *et al.* (2001).

The requirements for acceptance of DTA data in such site-specific cases may not need to be as stringent as that for derivation of the original trigger value. For instance the strict categories for determining the five different taxonomic groups necessary for the Aldenberg and Slob (1993) procedure may be broadened to encompass five groups of organisms having different functional positions in the local ecosystem. All data would be considered but higher weightings, sometimes qualitative but weighted according to a pre-determined system (Menzie *et al.* 1996), could be placed on data from organisms that can be demonstrated to be locally dominant or significant. Even if three groups are represented, some progress can be made towards site-specific estimates but the data will constrain the method of calculation. The application of the procedure will vary according to the amount, type and quality of the toxicity data derived by DTA, and will probably differ for each site.

Possible ways to derive site-specific guideline values are listed below:

- data on overseas species used to derive the trigger value can be substituted with equivalent data on sensitive local species and the value recalculated using both the Aldenberg and Slob and Assessment Factor methods, if possible;
- the toxicity data on local species can be added to that used to derive the trigger value and the value recalculated using both the methods if possible;
- any field, microcosm or mesocosm data can be used to derive a value using both the methods if possible.

If only one or two data points can be obtained, these could be included with the above laboratory data, as long as the test endpoint is clearly identified; and/or
- if there are not enough toxicity data for local species of any given type (chronic NOEC and acute EC/LC50) to meet the minimum data requirements, the data can be first converted to chronic NOEC estimates by using conversion factors (EC50 to NOEC 5, LOEC to NOEC 2.5) (Warne 2001) then the figure calculated using both the methods.

Once all possible site-specific values have been derived, the environmental relevance and quality of each value should be weighted, based on each of the following factors (Menzie *et al.* 1996):

- how strongly the measures relate to conditions at the specific site;
- how relevant the species are to the site;
- the quality of design and data production and analysis;
- how closely the experimental conditions and water chemistry reflect those at the site;
- how sensitive the measured endpoint or effect is to the toxicants present at the site;
- how sensitive the species used are compared to those at the site;
- the ecological relevance of the toxicity endpoint or effect measured;
- the duration of the exposure to the toxicant;
- the relevance of the method of toxicant exposure and the form of the toxicant to the site;
- the correlation between exposure and response; and
- the use of standard methods.

For simplicity, it is suggested that only four weightings be used: high relevance, moderate relevance, low relevance and very low relevance. If the process is illustrated graphically, picturing all the derived "guideline" values and their weightings, the ranges of values may be more apparent, as may the most likely values where there is a high degree of supporting evidence. Examples of this are given in Chapman *et al.* (2001).

CONCLUSIONS

The original guideline trigger values for around 200 chemicals in marine and fresh water were derived mostly from single species toxicity data using a combination of the Campbell *et al.* (2000) statistical distribution method and the assessment factors suggested by OECD (1995). The application of both methods was useful as sometimes the lack of certain data precluded use of one or other of the methods.

The trigger values are estimates of concentrations of single chemicals that have no adverse effect on the environment, and their use directly would generally result in rather conservative water quality targets. However, the revised guidelines direct users into a site-specific assessment scheme that takes into account the effects that physico-chemical properties of the water (eg. hardness) and other factors at the specific site. The risk-based decision scheme starts by measuring total concentrations of the chemical, then applies mathematical relationships where available to derive a site-specific guideline value. Considerations include the desired level of ecosystem protection, background concentrations of the chemical, analytical PQLs, locally important species, formulation of the chemical and water quality factors that modify the toxicity of the chemical. The latter include suspended matter, dissolved organic matter, pH, temperature, salinity and hardness. There is also opportunity to consider the effect of mixtures and to measure the direct biological effects using Direct Toxicity Assessment (DTA). The interpretation of different types of DTA data can be assisted by applying a weight-of-evidence approach based on measures of quality and environmental relevance.

Examples of the application of the guidelines at specific sites are given in Chapman *et al.* (2001). It is considered that this scheme, while somewhat complicated, gives a more realistic approach to protecting complex ecosystems than providing a single fixed number. It allows room to move in either direction while maintaining confidence that the environment is being protected. It is likely that site-specific assessments will become easier with practice. This scheme provides a consistent approach to dealing with such assessments and also drives the direction of research to fill significant gaps in knowledge in key areas of guideline application.

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