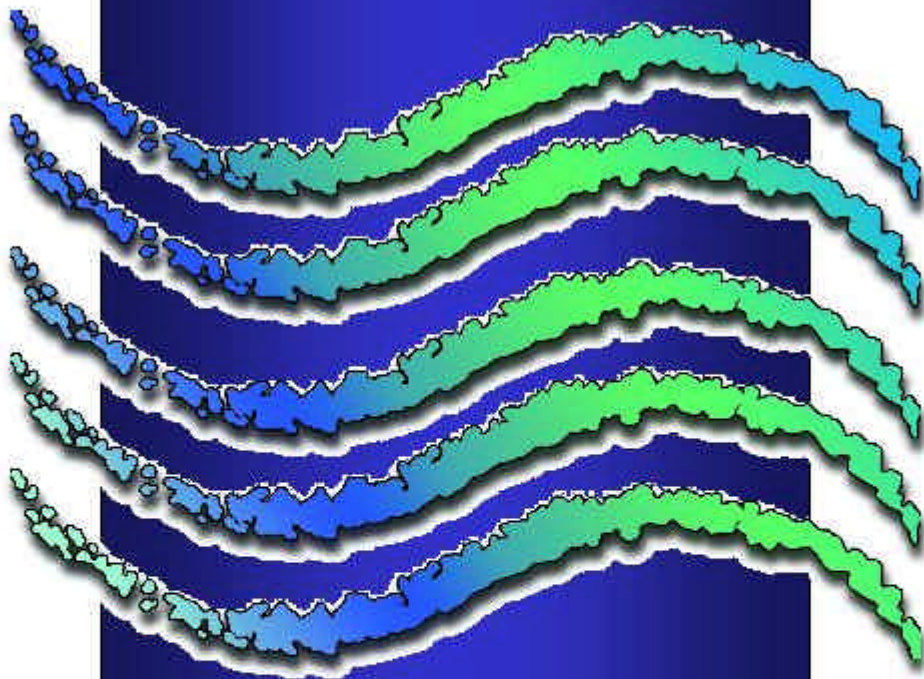


**SOUTH AFRICAN  
WATER QUALITY  
GUIDELINES**

**VOLUME 7  
AQUATIC  
ECOSYSTEMS**



Department of Water Affairs and Forestry



Second Edition 1996



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Water Quality  
Guidelines**

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Ecosystems**

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This volume is the seventh in a series of eight volumes comprising the South African Water Quality Guidelines.

- Volume 1: South African Water Quality Guidelines -  
Domestic Water Use
- Volume 2: South African Water Quality Guidelines -  
Recreational Water Use
- Volume 3: South African Water Quality Guidelines -  
Industrial Water Use
- Volume 4: South African Water Quality Guidelines -  
Agricultural Water Use: Irrigation
- Volume 5: South African Water Quality Guidelines -  
Agricultural Water Use: Livestock Watering
- Volume 6: South African Water Quality Guidelines -  
Agricultural Water Use: Aquaculture
- Volume 7: *South African Water Quality Guidelines -  
Aquatic Ecosystems***
- Volume 8: South African Water Quality Guidelines -  
Field Guide
-

# Foreword

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The Department of Water Affairs and Forestry is the custodian of South Africa's water resources. Part of its mission is to ensure that the quality of water resources remains fit for recognised water uses and that the viability of aquatic ecosystems are maintained and protected. These goals are achieved through complex water quality management systems which involve role players from several tiers of government, from the private sector and from civil society.

A common basis from which to derive water quality objectives is an essential requirement that enables all role players involved in such a complex system to act in harmony in order to achieve the overarching goal of maintaining the fitness of water for specific uses and to protect the health of aquatic ecosystems. For these reasons the Department initiated the development of the *South African Water Quality Guidelines*, of which this is the second edition. The *South African Water Quality Guidelines* serve as the primary source of information for determining the water quality requirements of different water uses and for the protection and maintenance of the health of aquatic ecosystems.

The process that followed and the wide variety of organizations and individuals involved in the development of these guidelines ensured the acceptance and use of these guidelines by all significant role players, as the *South African Water Quality Guidelines*. These guidelines are technical documents aimed at users with a basic level of expertise concerning water quality management. However, the role players involved in the different water use sectors are expected to use these guidelines as a basis for developing material to inform water users in specific sectors about water quality and to empower them to effectively participate in processes aimed at determining and meeting their water quality requirements.

The Department recognises that water quality guidelines are not static and will therefore update and modify the guidelines on a regular basis, as determined by ongoing research and review of local and international information on the effects of water quality on water uses and aquatic ecosystems. The process of developing water quality guidelines, and the involvement of key role players, is a continuing one. The second edition is published in a loose leaf, ring binder format to facilitate the regular updating of the guidelines. All those who want to comment on and make suggestions concerning the *South African Water Quality Guidelines* are invited to do so at any time by contacting the Director: Water Quality Management, Department of Water Affairs and Forestry, Private Bag X313, Pretoria 0001.

Finally I wish to express my sincere appreciation to all those who have been involved in the development of these guidelines. I also look forward to their continued involvement in maintaining one of the corner-stones of the water quality management system in South Africa.



Professor Kader Asmal MP  
Minister Of Water Affairs and Forestry

May 1996

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# **Chapter 1**

## **Introduction**

# Introduction

## Scope and Purpose of the Water Quality Guidelines

**Introduction** The process of deriving quality criteria and associated management guidelines for freshwater ecosystems has a long history in South Africa. Over the past decade, several different approaches have been proposed and evaluated. The lack of a generally accepted set of quality criteria for local (South Africa) application led to the initiation of this project by the Department of Water Affairs and Forestry (DWAF).

The aim of the project has been to develop procedures and to derive a set of water quality criteria for safeguarding freshwater ecosystems in South Africa. An indepth process of consultation with a large number of water quality specialists, stimulated and improved the understanding of criteria development among aquatic scientists and resource managers. This process established the basis for that development of the water quality guidelines contained in this volume. The publication of this first edition of the *South African Water Quality Guidelines for Aquatic Ecosystems* is part of an ongoing effort to improve the decision support tools required for the management of the country's water resources.

The list of water quality constituents addressed in this volume is by no means complete, especially in the case of organic compounds. The constituents were selected on the basis of current priorities experienced by DWAF, and according to the availability of the required cause-effect data and/or local knowledge.

Further actions which address the limitations associated with chemical-specific criteria for certain constituents, and which are envisaged for future development by DWAF, include in-stream biological monitoring, direct assessment of whole-effluent-toxicity and biotoxicological assessment of sediment quality. The additional need for whole-effluent criteria and biological criteria is highlighted in this chapter.

**Scope** The *South African Water Quality Guidelines for Aquatic Ecosystems* is essentially a specification of:

- ! The surface water quality required to protect fresh water aquatic ecosystems (the guidelines do not deal with marine and estuarine ecosystems);
- ! Quantitative and qualitative criteria for chronic and acute toxic effects for toxic constituents ;
- ! Quantitative and qualitative criteria to protect ecosystem structure and functioning, for non-toxic constituents and system variables;
- ! Quantitative and qualitative criteria to protect aquatic ecosystems against changes in trophic status in the case of nutrients;
- ! Modifications that can be made to water quality criteria on a site-specific basis, whilst still providing the same level of protection as the original criteria.

**Purpose** The *South African Water Quality Guidelines for Aquatic Ecosystems* are used by the Department of Water Affairs and Forestry in water quality management as the primary source of reference information and decision support required for the management and protection of aquatic ecosystems.

The *South African Water Quality Guidelines* contains information similar to that which is available in the international literature. However, the information provided is more detailed, and not only provides information on the water quality requirements for the management and protection of aquatic ecosystems but in addition provides background information to help users of the guidelines make informed judgements on the likely impacts of water quality on the health and integrity of aquatic ecosystems.

**Users of the guidelines** The *South African Water Quality Guidelines for Aquatic Ecosystems* have been designed primarily for use by water quality managers. Educators and other interested members of the general public will also find them a valuable source of information. The *South African Water Quality Guidelines for Aquatic Ecosystems* are intended to serve as a primary source of information as far as is reasonably possible. Although the guidelines are primarily aimed at supporting water resource managers, they would also be of interest to those impacting on water quality and other interested persons.

**Ongoing Review** The *South African Water Quality Guidelines* will be periodically reviewed. The purpose of the reviews is to:

- ! Add guidelines for constituents not yet included in the guidelines;
- ! Update the guidelines for constituents currently included as relevant new information from international and local sources becomes available on the water quality or support information for a particular constituent.

The loose leaf/ring binder format of the guidelines, as well as the footnotes at the bottom of each page which clearly indicate the exact version of a guideline, have been designed to facilitate regular updating of the guidelines.

**Overview** The *South African Water Quality Guidelines for Aquatic Ecosystems* is divided into seven chapters:

- ! Chapters 1 - 5 provide an introduction to the guidelines, define important water quality concepts, explain how aquatic ecosystems are characterised, describe how the guidelines were developed and, provide guidance on how the guidelines should be used.
- ! Chapter 6 provides the actual guidelines for each of the different water quality constituents.
- ! Chapter 7 consists of Appendices and Glossaries which provide additional supporting information.

## Water Quality

**Introduction** To be able to correctly use the *South African Water Quality Guidelines* it is important for users of the guidelines to understand how water quality and some related concepts were defined for the purpose of developing the guidelines.

**Definition of Water Quality** The term *water quality* is used to describe the physical, chemical, biological and aesthetic properties of water that determine its fitness for a variety of uses and for the protection of the health and integrity of aquatic ecosystems. Many of these properties are controlled or influenced by constituents that are either dissolved or suspended in water.

**Water Quality Constituent** The term *constituent* is used generically in this edition of the *South African Water Quality Guidelines* for any of the properties of water and/or the substances suspended or dissolved in it. In the international and local literature, several other terms are also used to define the properties of water or for the substances dissolved or suspended in it, for example water quality variable, characteristic or determinand.

Examples of constituents that are used to describe water quality, and the context in which they are used, are:

- ! The **temperature** of the water is 20 EC.
- ! The **colour** of the water is green.
- ! The concentration of **calcium** is 60 mg/R.
- ! 30 % of the surface of the water body is covered with **water hyacinth**.

The statements that describe water quality constituents in these examples provide no information as to how desirable or acceptable it is for water to have the properties listed. The acceptability of levels or concentrations of specific water quality constituents, and the protection afforded to aquatic ecosystems, can be assessed against the water quality criteria given in the guidelines.

**Water Quality Criteria** *Water quality criteria* are scientific and technical information provided for a particular water quality constituent, in the form of numerical and qualitative that describe its potential effects on the health of aquatic ecosystems and the fitness of water for other uses.

The derivation of criteria was based on the best available information, using the species representative of major trophic groups occurring in aquatic ecosystems. The rationale for this is that if the most sensitive species within representative trophic groups are protected, then other species within the trophic group will also be protected.

The criteria used in the *South African Water Quality Guidelines* were derived by assuming continuous and long term exposure to water of a given quality.

**Types of Criteria** Three broad classes of water quality criteria can be identified for aquatic ecosystems. These are:

- ! **constituent-specific criteria**, where a numerical value or range for each constituent of concern represents a level of ecological risk associated with the presence of that constituent in the water;

- ! **criteria for complex mixtures**, in which the whole-effluent toxicity testing approach is followed to evaluate the toxicity of complex mixtures containing several constituents, where the individual effects of each constituent cannot be resolved, and where synergistic and antagonistic effects may occur;
- ! **biological criteria**, which may be either quantitative or qualitative data that describe the biological status of aquatic systems. These are usually site- or region-specific and are based on the reference (least impacted) condition of the biological communities inhabiting a specific geographical region or a specific site.

Biological guidelines and criteria for complex mixtures still need to be developed and are the subjects of current initiatives by the Department. This edition deals only with constituent-specific water quality criteria.

**Constituent-specific criteria**

The constituent-specific criteria have been divided into four categories based on the effects that the constituents may have on aquatic biota, and on the methodologies of derivation used in the criteria. The constituents were chosen on the basis of problems currently experienced in South African aquatic ecosystems. The four categories are:

- ! **Toxic constituents**, which seldom occur in high concentrations in unimpacted systems. Criteria are given as single numerical values associated with a specific level of risk, or a value below which no adverse effect is expected. Examples of typically toxic constituents are:
  - Inorganic constituents, e.g. Al, As, Cd, Cu, F, Hg, Mn, NH<sub>4</sub><sup>+</sup>
  - Organic constituents, e.g. phenol, atrazine
- ! **System variables**, which regulate essential ecosystem processes such as spawning and migration. The biotas of aquatic ecosystems are usually adapted to the natural seasonal cycles of changing water quality which characterize these systems. Changes in the amplitude, frequency and duration of these cycles may cause severe disruptions to the ecological and physiological functions of aquatic organisms and hence the ecology of the system. Criteria are given as numerical ranges for constituents such as temperature, pH and dissolved oxygen.
- ! **Non-toxic inorganic constituents**, which may cause toxic effects at extreme concentrations, but which are generally "system characteristics", in that their natural concentrations depend on localised geochemical, physical and hydrological processes. Criteria are given as numerical ranges or as proportional changes from local background conditions for constituents such as total dissolved solids (TDS) and total suspended solids (TSS).
- ! **Nutrients**, which are generally not toxic, but which stimulate eutrophication if present in excess. Criteria are given as narrative or numerical, site-specific values or ranges for constituents such as inorganic nitrogen (nitrate, nitrite, ammonium) and inorganic phosphorus (ortho-phosphates).

**Target Water Quality Range**

The Target Water Quality Range (TWQR), is not a water quality criterion but is rather a management objective which has been derived from quantitative and qualitative criteria. This is the range of concentrations or levels within which no measurable adverse effects are expected on the health of aquatic ecosystems, and should therefore ensure their protection.

These ranges assume life-long exposure. As a matter of policy the DWAF will strive to protect South Africa's water resources by maintaining water quality within the TWQR.

**Chronic Effect Value**

The Chronic Effect Value (CEV), is defined as that concentration or level of a constituent at which there is expected to be a significant probability of measurable chronic effects to up to 5 % of the species in the aquatic community. If such chronic effects persist for some time and/or occur frequently, they can lead to the eventual death of individuals and disappearance of sensitive species from aquatic ecosystems. This can have considerable negative consequences for the health of aquatic ecosystems, since all components of aquatic ecosystems are interdependent.

It is important to note that:

- ! Even if the concentration of a constituent is always below the CEV there is still a significant risk of chronic effects to a small percentage of the most sensitive organisms;
- ! If the CEV is exceeded the chronic effects will be more widespread, and the likelihood of possible acute effects will increase with increasing concentration, frequency and duration of exceedance of the CEV.

**Acute Effect Value**

The Acute Effect Value (AEV) is defined as that concentration or level of a constituent above which there is expected to be a significant probability of acute toxic effects to up to 5 % of the species in the aquatic community. If such acute effects persist for even a short while, or occur at too high a frequency, they can quickly cause the death and disappearance of sensitive species or communities from aquatic ecosystems. This can have considerable negative consequences for the health of aquatic ecosystems, even over a short period.

**Water Quality Guidelines**

A water quality guideline is a set of information provided for a specific water quality constituent. It consists of the TWQR and water quality criteria, the CEV and the AEV together with the support information which includes the occurrence of the constituent in the aquatic environment, the norms used to assess its effects on water uses, and the conditions for case-, site- and region-specific modifications.

The volumes entitled the *South African Water Quality Guidelines* consist of the guidelines for domestic, recreational, industrial, agricultural (irrigation, livestock watering and aquaculture) uses, as well as guidelines for the protection of the health and integrity of aquatic ecosystems and guidelines for the protection of the marine environment.



## **Chapter 2**

### **Approach to Guideline Development**

# Approach to Guideline Development

## Approach and Methodology

**Approach** The approach used to develop the *South African Water Quality Guidelines for Aquatic Ecosystems* was as follows:

- ! To describe water quality-related problems or issues, typically experienced in South Africa, and which affect the protection of aquatic ecosystems;
- ! To ascertain the key water quality constituents in South Africa which are associated with these problems or issues;
- ! To ascertain, for each category of the water quality constituents, appropriate norms for assessing the effects of water quality on the protection of the aquatic environment;
- ! To identify major trophic groups of organisms in order to derive criteria that afford protection to the most sensitive species within each trophic level, (see Appendices for detailed discussion of the derivation procedures);
- ! To use international and local sources of information and expertise to develop draft guidelines for each constituent selected;
- ! Through a process of technical review and stakeholder participation, reach consensus on the *South African Water Quality Guidelines*.

**Norms** Norms are the "yardsticks" used to evaluate the effects of a water quality constituent for a particular use. At a species or organism level, the following norms were used to derive water quality criteria:

- ! For the category of toxic substances, the norms used were acute and chronic toxic effects on aquatic organisms;
- ! For the category of system variables, the norms used were acute and chronic toxic effects, and changes from local natural cycles that affect ecosystem structure and functioning;
- ! For the category of non-toxic inorganic constituents, the norm used was changes from local natural cycles which affect ecosystem structure and functioning;
- ! For the category of nutrients, the norm used was change of trophic status from local natural conditions.

**Tentative Guidelines** The information available on the effects of some constituents on aquatic ecosystems is either very limited, or else there may be unresolved differences in opinion as to the effects that these constituents might have. In these cases, guidelines have been included in the *South African Water Quality Guidelines for Aquatic Ecosystems* as Tentative Guidelines, and are clearly indicated as such.

During the ongoing review of the guidelines, it is intended that the status of Tentative Guidelines will be confirmed, either when sufficient information becomes available or when sufficient consensus is reached concerning the effects of these constituents on aquatic ecosystems. It is expected that periodic reviews will allow all water quality guidelines to be revised where appropriate.

## Sources of Information

### Sources

The guidelines for aquatic ecosystems were developed to be representative of South African conditions. However, very few data are available with which to assess the water quality requirements of local species. Hence, data published in the international literature, and in international toxicological databases, provided the major part of the information used in guideline development. Where available, local information was used to supplement other sources.

South African experts were consulted during the development of water quality guidelines. The following key documents published in the international literature were also used as background and supplementary information in the development of the South African Water Quality Guidelines for aquatic ecosystems:

- ! USA Quality Criteria (USEPA, 1986);
- ! Canadian Water Quality Guidelines (CCREM, 1987);
- ! Australian Water Quality Guidelines (ANZECC, 1992).

In addition, the following South African summaries of water quality criteria for the protection of aquatic ecosystems were also used:

- ! Department of Water Affairs and Forestry Publication which provided Comparisons with International Criteria (Kempster, Hattingh & Van Vliet, 1982);
- ! Water Research Commission Report on Water Quality Criteria for Aquatic Ecosystem Health (Dallas & Day, 1993).

For the derivation of numerical criteria for toxic substances, the USEPA databases ASTER and AQUIRE were used extensively. These data bases contain data obtained from peer-reviewed publications with sufficient support information to indicate that acceptable test procedures were employed and that the results are reliable. These data bases are being maintained by the USEPA.

## **Chapter 3**

# **Aquatic Ecosystems in the Context of Water Quality Management**

# Aquatic Ecosystems in the Context of Water Quality Management

**Resource Base** The Department of Water Affairs and Forestry considers fresh water aquatic ecosystems to be "the base from which the [water] resource is derived" (White Paper, on Water Supply and Sanitation, 1994). Man depends on many "services" provided by healthy aquatic ecosystems, namely:

- ! Maintaining the assimilative capacity of water bodies for certain wastes through self purification;
- ! Providing an aesthetically pleasing environment;
- ! Serving as a resource used for recreation;
- ! Providing a livelihood to communities dependent on water bodies for food; and
- ! Maintaining biodiversity and providing habitats to those biota dependent on aquatic ecosystems.

Aquatic ecosystems, as the resource base, must therefore be effectively protected and managed to ensure that South Africa's water resources remain fit for agricultural, domestic, recreational and industrial uses on a sustained basis.

**Definition of Aquatic Ecosystems** For the purposes of developing water quality guidelines, aquatic ecosystems are defined as the abiotic (physical and chemical) and biotic components, habitats and ecological processes contained within rivers and their riparian zones, reservoirs lakes and wetlands and their fringing vegetation. Terrestrial biota, other than humans dependent on aquatic ecosystems for survival are included in this definition. For the purposes of these guidelines, the scope has been restricted to inland surface waters, separate sets of guidelines have been developed for marine and estuarine systems. Water quality requirements for human-centred uses are covered in the other water quality guidelines documents contained in this series.

The definition of aquatic ecosystems includes three primary abiotic and biotic components, namely, sediments (bottom or suspended), water and the riparian zone. However, for the purposes of this first edition of the guidelines, only the water component will be considered; excluded from this component are ground water, sub-surface water and water in bank storage.

**South African Context** South Africa is a semi-arid country, with annual rainfall below the world average, and high evaporation rates. Seasonal rainfall often occurs as high-intensity storms of short duration; the resulting runoff washes silt, and organic and inorganic material accumulated in the catchment, into water bodies. There are marked climatic gradients across the country and these have resulted in a wide variety of different types of aquatic ecosystems with biotas adapted to different water quality regimes and flow patterns.

In many rivers, flow is strongly seasonal, and there is considerable year to year variability in flow rates. Many streams and rivers may dry up completely outside the rainy season, and reservoirs are prone to considerable changes in water level. An additional factor in South Africa is the regulation of, and abstraction of water from, many rivers and streams for water

supply purposes. Such regulation may lead to unnatural flow conditions, which cause stresses on aquatic ecosystems. The biotas of ecosystems which are already stressed, for example due to flow regulation, are likely to be more susceptible to changes in water quality than those of unimpacted systems.

## Important Characteristics of Aquatic Ecosystems

**Introduction** As a result of the characteristics of aquatic ecosystems, there are important differences between the approaches used to determine the water quality requirements for protecting and maintaining the health of aquatic ecosystems compared to the approach used to determine the requirements of other water uses. Some of these characteristics of aquatic ecosystems, and the implications these have for the approach used to develop guidelines, are described below.

**Complex Systems** Aquatic ecosystems include numerous species, habitats and processes, all of which are interlinked and interdependent, and which require protection if healthy ecosystem structure and functioning are to be maintained. As a consequence of the complex and interlinked nature of aquatic ecosystems, the effects of changes in water quality on specific components of ecosystems are often indirect. A simple example of such indirect effects might be that a certain species of fish might disappear as a result of a change in water quality, not because the fish species itself cannot tolerate the change in water quality, but because the organisms that are its primary food source might be eliminated by that particular change in water quality.

The complexity of determining the effects of changes in water quality on aquatic ecosystems is compounded by the fact that many of the cause-effect relationships are poorly understood or completely unknown. It is therefore often difficult to separate the effects of changes in water quality from other effects such as changes in flow regime or climatic changes. Hence water quality criteria for aquatic ecosystems have to be derived indirectly through extrapolation of the known effects of water quality on a very limited number of aquatic organisms. This often results in significant uncertainty being associated with the derived criteria.

In comparison to aquatic ecosystems, the effects of water quality on water uses such as domestic supply and irrigation, are usually much more direct. Even in those cases where the effects may be indirect, the cause-effect relationships are usually well understood. Consequently, water quality requirements for such water uses can be derived with a reasonable degree of accuracy by means of direct observation or experimentation to determine the effects of changes in water quality on a particular use.

**Aquatic Habitat** The aquatic environment is the habitat of aquatic organisms. It is seldom possible to mitigate the effects of poor water quality to the same degree as for domestic, agricultural and industrial water uses, these being predominantly off stream. It is often possible to abstract and treat water of poor quality before it is used off stream, but in the case of aquatic ecosystems it is seldom possible to mitigate the effects of poor water quality to the same degree. Hence, for the purpose of protecting and maintaining aquatic ecosystems, prevention, rather than mitigation, of the effects of poor water quality has to be given even greater emphasis than would be the case for other water uses. For this reason, the criteria for aquatic ecosystems provide different levels of protection. This is in contrast to the criteria for other water uses, which show the effects of changes in water quality for a particular water use sector.

## Policy Concerning Water Quality and Aquatic Ecosystems

### **Role of the Department**

Although aquatic ecosystems are not considered to be "users" of water, (in competition with other users), water, within certain quality ranges, is required to protect and maintain their health. As the custodian of South Africa's water resources, the policy of the Department of Water Affairs and Forestry (DWAF) is to ensure that aquatic ecosystems are healthy, and that they are utilized on a sustainable basis.

The different components of aquatic ecosystems which form the resource base may be utilised by humans in several ways, for example for recreation, irrigation and as a source of potable water. The DWAF recognises that such utilization of South Africa's water resources will inevitably result in some impact on, and modification of, aquatic ecosystems. However, utilization has to be managed and regulated in such a way that these impacts do not reduce the capacity of aquatic ecosystems to maintain their integrity.

Aquatic ecosystems often appear to have certain thresholds, beyond which it is difficult to recover or regain their functional capacity without mitigation. Each aquatic ecosystem possesses natural limits or thresholds to the extent and frequency of change it can tolerate without being irreversibly altered. The DWAF accepts its responsibility to ascertain what these limits or thresholds are in order to ensure that utilization does not exceed these limits.

The department has a special role in safe-guarding aquatic ecosystems, compared to its role with respect to other water-use sectors. Water users in the main water use sectors either are, or can be, organised to collectively look after the sector's interests. This places them in a position to state their water quality requirements and to defend these in situations where conflicts in water quality requirements between different interest groups have to be resolved. Currently it is the responsibility of DWAF, and all other provincial and local authorities to safe-guard the health of aquatic ecosystems. This means that they determine the water quality requirements for ecosystems, and look after the interests of aquatic ecosystems in cases where conflicts over utilization of water resources need to be resolved.

### **Effluent Disposal**

The department's policy requires that all effluent is treated and returned to natural water courses in order to obtain maximum utilization of scarce water resources. While this augments the quantity of water available further downstream, it affects the quality of the water, as pollutants contained in effluents are returned to the receiving waters. An important purpose of developing water quality guidelines for aquatic ecosystems is to provide information that can be used to determine the degree to which water quality may be altered through the return of effluent, and other impacts, without compromising the health of aquatic ecosystems.

### **Precautionary Approach**

As a result of the vulnerability of aquatic ecosystems to changes in water quality, the uncertainty about changes which they can tolerate, and the fact that there are very few options for mitigating the effects of poor water quality, a precautionary approach is required to protect the health of aquatic ecosystems. This approach means that active measures are taken to avert or minimise potential risks of undesirable impacts on the environment. Part of the precautionary approach is to minimize risk to the environment in all the decision-making steps involved in water quality management. This precautionary approach has been followed in the development of these guidelines.

## **Chapter 4**

**Information  
contained in the  
Guidelines**



# Information contained in the Guidelines

## Structure of the guidelines

- Presentation of Information** The information contained in a guideline for a particular constituent is organized into three sections, namely:
- ! Background information, containing the supporting information required to evaluate the occurrence and significance of the constituent;
  - ! For each constituent, information on the effects of the constituent on in stream aquatic biota and on the criteria for the constituent is provided; and
  - ! Additional sources of information for further reference.

The information in each section of the guideline for a constituent is organised under a series of labels in the left hand margin that identify the type of information and can assist users of the guidelines to quickly locate the information they require. The contents of the different sections of a guideline are explained briefly, below.

## Information Provided

- Background Information**
- Introduction.** The introduction to the guideline for each constituent includes a short description of the constituent as well as a brief statement of its significance for aquatic ecosystems.
- Occurrence.** Information on the fate and occurrence of a constituent in the aquatic environment, as well as on its natural and man-made sources, is provided as background to help the user understand the form and circumstances under which, the constituent is likely to occur.
- Interactions.** The effects of a water quality constituent on aquatic ecosystems can sometimes be modified significantly by interactions with other constituents in the water, e.g. antagonistic or synergistic effects. These effects, where known, are described in the guideline and should be considered when making judgements as to whether or not the aquatic environment will be protected at specific concentrations of the constituents in question.
- Measurement.** The effects of many constituents depend on the state (dissolved or particulate) and the chemical species (such as oxidised or reduced; inorganic or organic) in which the constituents occur. It is important to understand how concentrations of a specific constituent are measured in water, and which methodologies are appropriate for measurement.
- Data interpretation.** Guidance is provided on how data should be interpreted for the assessment of water quality.
- Effects and Criteria**
- Norms.** A brief description is given of the norms used to derive criteria for a particular constituent.

**Effects.** Where the information is available, the effects of a water quality constituent on different components of aquatic ecosystems are summarized. These effects can vary widely, and include lethality, interference with breeding, feeding, behavioural or migratory patterns, and stimulation of eutrophication.

The severity and reversibility of effects often depends on the extent, frequency and duration of excursions outside the given protective criteria. These factors are not discussed in this edition.

**Criteria.** In the guidelines for aquatic ecosystems, the water quality criteria provided for most of the constituents are given as numerical values associated with a level of risk of acute or chronic toxicity effects. The Target Water Quality Range is highlighted as the water quality that ensures adequate protection of aquatic ecosystems.

**Modifications.** Several site- and case-specific factors modify the effects of water quality on aquatic ecosystems. The information on modification provided in the guidelines is of a very general nature and merely indicates whether or not the criteria for a constituent can be modified and, if so, the circumstances under which such modification should occur. *Where criteria are to be modified for a specific site or region, expert advice should be obtained, and the Department should be consulted regarding specific requirements.*

## **Sources of Information**

It was not possible to include in this edition of the guidelines all the water quality constituents which might affect aquatic ecosystems, or to include all the relevant information on the constituents for which criteria were derived.

Additional sources of information are therefore provided on each constituent. These sources also provide information on constituents which are not yet included in the *South African Water Quality Guidelines for Aquatic Ecosystems*.

If additional information is required, over and above that contained in these guidelines, a wealth of unpublished information is available from a number of organizations and individuals in South Africa. Access to some of this information can be obtained through the list of people and organizations who are acknowledged for their participation in the development of these guidelines.

# **Chapter 5**

## **Management Applications**

# Management Applications

## Application of Water Quality Guidelines in Management

**Use of Criteria** It is often possible to describe the likely effects of specific water quality constituents on individual species or components of the system. However, the complex interrelationships between different components of aquatic ecosystems usually make it impossible to extrapolate these effects to the system as a whole. Despite uncertainties inherent in the approach used, protection of a few species within each trophic level is assumed to offer protection to all organisms.

It is important to follow a precautionary approach when setting water quality objectives on the basis of the water quality criteria. This implies that water quality objectives should not necessarily be set at a level which might adversely affect the resilience of aquatic ecosystems, since loss of this resilience might well limit options for future development of water resources.

In keeping with the goal of assuring the health and integrity of aquatic ecosystems, the different water quality criteria and objectives provided in these guidelines are typically used in the following ways:

- ! The Target Water Quality Range (TWQR) is a management objective that is used to specify the desired or ideal concentration range and/or water quality requirements for a particular constituent.
- ! The Chronic Effect Value (CEV) is a criterion that is used, in certain special cases where the TWQR is exceeded. The setting of water quality requirements or objectives at the CEV protects aquatic ecosystems from acute toxicity effects. Examples of where it would be appropriate for water quality requirements for aquatic ecosystems to be set at the CEV would be:
  - Within the mixing zone of an effluent discharge.
  - As interim water quality objectives in those situations where remediation is required, but water quality cannot immediately, or in one step, be restored to the TWQR.
- ! The Acute Effect Value (AEV) is a criterion used to identify those cases requiring urgent management attention because the aquatic environment is threatened, even if the situation persists only for a brief period. The AEV may also be used to identify those cases in need of urgent mitigatory action. **However, the AEV should not be used for setting water quality requirements for aquatic ecosystems.**

**Independence of Criteria** The Chronic Effect Value and Acute Effect Value are independently derived values. There is no linear incremental change in the degree of protection afforded to aquatic ecosystems as the concentration of a constituent increases in the range covered by these criteria. Users of these guidelines should therefore be aware that *they cannot derive, through interpolation between the criteria, the potential effects of constituent concentrations which fall between these criteria.*

## **Limitations of Criteria**

The derivation procedure for criteria represents an integrated approach which is intended to provide broad protection. The criteria are based largely on the physiological effects of substances on aquatic organisms. Secondary effects, such as changes in ecosystem structure, composition and functioning, may arise from direct chronic or acute toxic effects, or from changes in behaviour of aquatic organisms. The limitations associated with the use of the constituent-specific criteria presented in this volume include the following:

- ! the criteria address the water column only, which forms but one compartment of aquatic ecosystems;
- ! the criteria ignore interactions between constituents which could result in additive, synergistic or antagonistic effects;
- ! the criteria do not fully account for environmental partitioning under various chemical and physical water conditions, which may induce change in the bio-availability of a constituent;
- ! the procedure for deriving criteria makes use of data from a limited number of species, often determined by their ease of laboratory culturing; and
- ! the criteria often rely on single-species dose-response data, rather than multi-species or community response data.

*Assessment of potentially adverse secondary effects should be referred to a specialist in aquatic ecology.*

## **Modification of Criteria**

### **Introduction**

The potential effects of a given water quality, for example, of a given concentration of a toxic constituent, on the health and integrity of aquatic ecosystems, depend on certain system characteristics. For example aquatic organisms found in cold-water systems are generally more sensitive to certain water quality constituents than those typically found in warm-water systems. Similarly, the potential effects on aquatic organisms of a given concentration of a toxic metal, such as mercury, may be less severe in hard-water systems than in soft-water systems.

Therefore, DWAF recognizes that it is both possible and necessary to modify the criteria provided in these guidelines for case- and site-specific situations. However, the requirement for any such modification is that the modified criteria must afford the same level of protection to aquatic ecosystem in question as was intended to be provided by the unmodified criteria.

### **Modification Procedure**

Modification to water quality criteria must be carried out according to very specific procedures laid down by the Department. The information on modification provided in these guidelines is very general and, alone, is insufficient for decision-taking. *Where criteria are to be modified for a specific site or region, DWAF will require that expert advice be obtained.*

**Conditions for Modification**

The following conditions should be met before the water quality criteria for a constituent are modified:

- ! adequate site-specific data for the constituent of concern, covering at least one hydrological cycle, are available;
- ! site-specific studies demonstrate that modified criteria can afford the same level of protection to organisms inhabiting the aquatic ecosystem as that specified by the original criteria.

The information on modification in these guidelines is generic and locally important factors may dictate that other information be considered for the derivation of site-specific criteria. The detailed procedure to be followed when criteria are to be modified is given in **Appendix 3**. *In addition, expert advice should always be sought when water quality criteria are to be modified.*

**Constituents for Which no Criteria or only Tentative Criteria are Provided**

There are many water quality constituents for which criteria have not been derived, or for which only tentative guideline values could be calculated on the basis of available data.

If criteria are required for water quality constituents which are not included in this edition of the guidelines, such information will have to be developed for specific cases or sites. The development of the required information will involve the following steps:

For toxic substances in such cases, it will be necessary to:

- ! refer to relevant water quality criteria published elsewhere;
- ! conduct toxicity tests using local species to generate the necessary data; and
- ! refer the matter to a specialist in ecotoxicology.

For the non-toxic inorganic substances, system variables and nutrients, the following is necessary:

- ! establish local background conditions at impacted and unimpacted (reference) sites;
- ! refer to relevant water quality criteria published elsewhere; and
- ! refer the matter to a specialist in aquatic ecology who has knowledge of the local system in question.

**Rationale**

Many different water quality criteria and guidelines have been published in the international and local literature. Different approaches and methodologies have often been used to derive criteria and guidelines, for example, some criteria specify maximum concentrations for constituents fit for use, whereas others attempt to define the ideal concentration of a constituent, often with the inclusion of safety factors. Therefore, depending on the guideline or criteria used to establish water quality requirements, one can arrive at answers which sometimes differ by a factor of a hundred or more.

The rationale for developing the South African Water Quality Guidelines was to:

- ! Develop a single set of guidelines and criteria that is appropriate for South Africa, based on a consensus of South African expertise and other role players in water quality and fitness for use. The intention of this approach is to limit the confusion that often arises from the use of different criteria and guidelines to establish the water quality requirements for a particular water use by the stakeholders of water supply and utilization in South Africa;
  
- ! Modify international guidelines in the light of local research and experience.

# **Chapter 6**

## **Water Quality Constituents**



# Aluminium

## Tentative guideline

### Background Information

**Introduction** Aluminium is the third most abundant element in the earth's crust. It occurs primarily as aluminosilicate minerals which are too insoluble to participate readily in bio-geochemical reactions. Aluminium is a strongly hydrolysing metal and is relatively insoluble in the neutral pH range. Under acidic (pH < 6.0) or alkaline (pH > 8.0) conditions, or in the presence of complexing ligands, elevated concentrations may be mobilised to the aquatic environment.

The solubility of aluminium in water is strongly pH dependent. Under acid conditions, it occurs as soluble, available and toxic hexahydrate (aquo) species. At intermediate pH values, it is partially soluble and probably occurs as hydroxy- and polyhydroxo- complexes. At alkaline pH values, aluminium is present as soluble but biologically unavailable hydroxide complexes or as colloids and flocculants.

Aluminium is described as a *non-critical* element, though there is growing concern over the effects of elevated concentrations of aluminium in the environment, primarily that mobilized as a result of acid mine drainage and acid precipitation. Studies of the environmental chemistry and toxicity of aluminium provide a limited understanding of the processes regulating the aqueous concentration, speciation and bio-availability of this element. Clearly, the toxicity of aluminium depends on the chemical species involved.

**Occurrence** Aluminium can be mobilised from soils and sediments by both natural weathering and accelerated acidification processes, resulting in detectable concentrations in surface waters. Although aluminium is found in waters made naturally acidic by humic and fulvic acids, it usually adsorbs onto these and is therefore not available in soluble form in such waters, even at low pH.

Aluminium is found in soluble forms mainly in acid mine drainage waters and is also of concern in natural waters affected by acid rain. Aluminium is one of the principal particulates emitted from the combustion of coal, and aluminium fluoride is emitted from aluminium smelters. Industries using aluminium in their processes or in their products include the following:

- ! the paper industry,
- ! the metal construction industry,
- ! the leather industry, and
- ! the textile industry.

In addition to liquid effluents that may be generated from the above industries, alum or aluminium sulphate is used in most water treatment processes as a flocculating agent for suspended solids, including colloidal materials, micro-organisms and "humic rich" dissolved organics.

**Interactions** The speciation (and hence solubility and bio-availability) of aluminium is strongly pH-dependent. Aluminium is least soluble in the neutral pH range (6.5 - 7.5), in the absence of complexing agents. At low pH values (pH < 4.0), aluminium is largely in the aqua form (Al<sup>3+</sup>), which is both soluble and very toxic. As pH values increase (pH 4.5 - 6.5),

aluminium undergoes hydrolysis, resulting in a series of OH<sup>-</sup> complexes, and decreases in solubility. Above pH 6.5, aluminium exists primarily as the more insoluble aluminium hydroxide (Al(OH)<sub>3</sub>).

At low pH values, aluminium may form complexes with ions (e.g., F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), Si and a variety of organic solutes, particularly humic substances. In complex form aluminium becomes unavailable and hence non-toxic, although even slight changes in pH may cause it to revert to a toxic form.

Various species of aluminium and their salts and complexes act as buffers in very acid waters in which the carbonate/bicarbonate buffering system is no longer operational. It has also been suggested that the lower limit of pH observed in acidic waters may be regulated by the dissolution of aluminium, which forms an important component of acidity in these waters.

Through adsorption and coagulation reactions, aluminium may alter the cycling and availability of important elements such as phosphorus, organic carbon and certain trace metals.

**Measurement** Aluminium criteria for aquatic ecosystems are based on the **acid-soluble aluminium concentration**. The samples need to be acidified in the field before analysis. The reference methods for the determination of the acid-soluble aluminium concentration are the catechol violet colorimetric method, atomic absorption flame spectrometry (AAFS), and inductively coupled plasma optical emission spectrometry (ICPOES).

As with all trace metal determinations, care must be taken to prevent contamination of water samples. Polyethylene bottles which have been suitably pre-cleaned to remove metal contaminants should be used.

**Data Interpretation** Ninety percent (90 %) of all acid-soluble aluminium measurements for a site in question should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxic effects will occur if aluminium measurements exceed the Acute Effect Value (AEV). The potential effects of aluminium on the aquatic environment are modified by the chemical species present, the relative proportions of each form, and other factors such as water pH and hardness.

## Effects and Criteria

**Norms** The norms for assessing the effects of dissolved aluminium on aquatic ecosystems are chronic and acute toxic effects of aluminium on aquatic organisms.

**Effects** Elevated concentrations of bio-available aluminium in water are toxic to a wide variety of organisms. There is, however, uncertainty as to the form(s) of bio-available aluminium as well as to the mechanism(s) of toxicity. The toxic effects are dependent on the species and life stage of the organism, the concentration of calcium in the water, and pH. The pH may not only affect the chemistry of aluminium but may also determine how the organism responds to dissolved aluminium. In acidic waters, aluminium is generally more toxic over the pH range of 4.4 - 5.4, with maximum toxicity occurring about pH 5.0 - 5.2.

The mechanism of toxicity in fish seems to be related to interference with ionic and osmotic balance and with respiratory problems resulting from coagulation of mucus on the gills. It has also been suggested that aluminium interferes with calcium metabolism, thereby altering the functioning of the calcium regulating protein, calmodulin. Aluminium has been shown to interfere with ion exchange sites, in particular those involved in sodium homeostasis. This in turn may lead to neuromuscular dysfunction.

## Criteria

The TWQR and criteria for acid-soluble aluminium in aquatic ecosystems are:

TWQR and Criteria	Aluminium concentration ( $\mu\text{g/l}$ )	
	pH < 6.5	pH > 6.5
<i>Target Water Quality Range (TWQR)</i>	# 5	# 10
Chronic Effect Value (CEV)	10	20
Acute Effect Value (AEV)	100	150

### Note:

- C Even though the data available satisfied the minimum chronic and acute database requirements, the TWQR and criteria are given as TENTATIVE, because the toxicity and bio-availability of aluminium is governed by complex interactions with other water quality variables, which have not been fully accounted for in the derivations.

## Sources of Information

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# Ammonia

## Background Information

**Introduction** Un-ionized ammonia ( $\text{NH}_3$ ) is a colourless, acrid-smelling gas at ambient temperature and pressure. It is produced naturally by the biological degradation of nitrogenous matter and provides an essential link in the nitrogen cycle.

Ammonia may be present in the free, un-ionized form ( $\text{NH}_3$ ) or in the ionized form as the ammonium ion ( $\text{NH}_4^+$ ). Both are reduced forms of inorganic nitrogen derived mostly from aerobic and anaerobic decomposition of organic material. They exist either as ions, or can be adsorbed onto suspended organic and inorganic material.

The toxicity of ammonia is directly related to the concentration of the un-ionized form ( $\text{NH}_3$ ), the ammonium ion ( $\text{NH}_4^+$ ) having little or no toxicity to aquatic biota. The ammonium ion does, however, contribute to eutrophication. Modifying factors may alter the acute toxicity by altering the concentration of un-ionized ammonia in the water through changes in the ammonia-ammonium ion equilibrium, or may increase the toxicity of the un-ionized ammonia to organisms.

**Occurrence** Ammonia is present in small amounts in air, soil and water, and in large amounts in decomposing organic matter. Natural sources of ammonia include gas exchange with the atmosphere; the chemical and biochemical transformation of nitrogenous organic and inorganic matter in the soil and water; the excretion of ammonia by living organisms; the nitrogen fixation processes whereby dissolved nitrogen gas enters the water and ground water. Ammonia, associated with clay minerals enters the aquatic environment through soil erosion. Bacteria in root nodules of legumes fix large amounts of nitrogen in the soil and this may be leached into surrounding waters.

Ammonia is a common pollutant and is one of the nutrients contributing to eutrophication. Commercial fertilizers contain highly soluble ammonia and ammonium salts. Following application of fertilizer, if the concentration of such compounds exceeds the immediate requirements of the plant, transport *via* the atmosphere or irrigation waters can carry these nitrogen compounds into aquatic systems. Other sources of ammonia include:

- ! fish-farm effluent (un-ionized ammonia);
- ! sewage discharge;
- ! discharge from industries that use ammonia or ammonium salts in their cleaning operations;
- ! manufacture of explosives and use of explosives in mining and construction; and
- ! atmospheric deposition of ammonia from distillation and combustion of coal, and the biological degradation of manure.

**Interactions** The most significant factors that affect the proportion and toxicity of un-ionized ammonia in aquatic ecosystems are water temperature and pH. An increase in either results in an increase in the relative proportion of un-ionized ammonia in solution, and hence an increase in toxicity to aquatic organisms, as given in Table 1.

**Table 1: Contribution of un-ionised NH<sub>3</sub> to Total Ammonia (expressed as a percentage), as a Function of pH Value and Water Temperature**

pH	Water Temperature (°C)							
	0	5	10	15	20	25	30	35
6.0	0.0083	0.012	0.019	0.027	0.039	0.056	0.079	0.11
6.5	0.026	0.039	0.059	0.086	0.12	0.18	0.25	0.35
7.0	0.083	0.12	0.18	0.27	0.39	0.56	0.79	1.1
7.5	0.26	0.39	0.58	0.85	1.2	1.7	2.4	3.4
8.0	0.82	1.2	1.8	2.6	3.8	5.3	7.3	9.9
8.5	2.6	3.8	5.5	7.9	11	15	20	26
9.0	7.6	11	16	21	28	36	44	52
9.5	21	28	37	46	55	64	71	78

Ammonia toxicity is also affected by the concentrations of dissolved oxygen, carbon dioxide and total dissolved solids, and the presence of other toxicants, such as metal ions. The acute toxicity of ammonia to fish increases as dissolved oxygen decreases. Ammonia is oxidized to nitrate in well oxygenated waters. Ammonia may also be adsorbed onto suspended and bed sediments and to colloidal particles.

### Measurement

Ammonia criteria for aquatic ecosystems are calculated from the total ammonia concentration, that is, the sum of the NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations. The reference method for the determination of total ammonia is the phenate hypochlorite method, followed by spectrophotometry or colorimetry. The concentration of free ammonia is estimated from Table 1. The most reliable results are obtained on fresh samples. However, if prompt analysis is not possible, samples should be preserved with H<sub>2</sub>SO<sub>4</sub>, stored at 4 EC, and neutralised with NaOH or KOH prior to analysis.

As with all determinations of nutrients, care must be taken to prevent contamination of water samples. Glass bottles/vials, suitably pre-cleaned to remove nitrogenous contaminants, are required. Samples should not be preserved with nitric acid and no head space in the bottle should be allowed.

### Data Interpretation

Single measurements of ammonia are of limited use. Preferably, weekly ammonia concentrations, averaged over a period of at least 4 weeks, with the minimum and maximum values reported, should be compared with the Target Water Quality Range (TWQR).

Interpretation of the ammonia criteria is based on the free ammonia concentrations. The potential effect of ammonia on the aquatic environment is modified by the chemical species present, the relative proportions of each, and other factors such as pH, temperature and dissolved oxygen concentration.

Ninety percent (90 %) of all free ammonia estimates should be within the TWQR. All free ammonia estimates should be below the chronic effect value (CEV). In the case of accidental spills, chronic and acute toxicity effects will occur if ammonia estimates exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of free ammonia on aquatic ecosystems are chronic and acute toxic effects of ammonia on aquatic organisms.

**Effects** The toxicity of ammonia and ammonium salts to aquatic organisms is directly related to the amount of free ammonia in solution. At low to medium pH values, the ammonium ion dominates, but as pH increases ammonia is formed, the latter being considerably more toxic to aquatic organisms. Prior exposure or acclimation to ammonia increases the tolerance of fish to ammonia and enables them to withstand concentrations that would otherwise be acutely lethal.

Un-ionized ammonia affects the respiratory systems of many animals, either by inhibiting cellular metabolism or by decreasing oxygen permeability of cell membranes. Acute toxicity to fish may cause a loss of equilibrium, hyper-excitability, an increased breathing rate, an increased cardiac output and oxygen intake, and in extreme cases convulsions, coma and death.

Chronic effects include a reduction in hatching success, reduction in growth rate and morphological development, and pathological changes in tissue of gills, liver and kidneys. An increased ventilation of the gills following exposure to ammonia indicating a respiratory effect has been observed in mayfly larvae *Ecdyonurus dispar*.

**Criteria** The TWQR and criteria for un-ionised ammonia in aquatic ecosystems are :

TWQR and Criteria	Un-ionised Ammonia Concentration (Fg N/l)
<i>Target Water Quality Range (TWQR)</i>	# 7
Chronic Effect Value (CEV)	15
Acute Effect Value (AEV)	100

**Note:**

C The data available satisfied the minimum database requirements, therefore no safety factors were applied.

**Modifications** In certain areas, or at certain sites, it may be necessary to modify the ammonia criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to ammonia;
- ! Where aquatic organisms may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background ammonia concentrations are higher than the TWQR.

#### *Conditions for Modification*

The following conditions should be satisfied before criteria for ammonia are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in ammonia concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Arsenic

## Background Information

**Introduction** Arsenic is a metalloid element which is toxic to marine and freshwater aquatic life and is a known carcinogen. Elemental arsenic is insoluble in water, but many of its compounds are highly soluble. Arsenic occurs in several oxidation states, namely, III, IV, V and III, depending on the pH and redox potential of the water. The two most common forms are arsenic (III) and arsenic (V), both of which form stable compounds with carbon, resulting in numerous organo-arsenical compounds. Elemental arsenic also combines readily with many metals to form arsenide salts, which are toxic to organisms.

Most forms of arsenic, including the arsenical gases arsine ( $\text{AsH}_3$ ) and trimethyl arsine, are very toxic. The USEPA has classified arsenic as "very toxic and relatively accessible" to aquatic organisms.

**Occurrence** Elemental arsenic is found to a limited extent in nature, mostly as a result of weathering of arsenic-containing rocks and of volcanic activity. Arsenic most commonly occurs as arsenides of metals or as arsenopyrite. Inorganic arsenic occurs in aquatic ecosystems primarily as arsenic (III) and as arsenic (V), depending on pH and redox potential. Arsenic readily adsorbs onto sediments and suspended solids, and is lipid-soluble.

Arsenic may occur at high concentrations in water bodies subject to industrial pollution, or in the vicinity of industrial activities utilising or discharging arsenic or arsenal compounds.

Manufacturers that use arsenic in their processes, or in their products, include:

- ! the mining industry,
- ! the metal processing industry,
- ! producers of pesticides and fertilizers,
- ! producers of glass and ceramics,
- ! tanneries,
- ! dye manufacturers,
- ! producers of wood preservation products,
- ! the chemical industry,
- ! producers of detergents.

**Interactions** The aquatic chemistry of arsenic is complex. Redox values and pH levels play a major role in determining the form of arsenic in freshwater, and thus its toxic effects. The presence of dissolved and particulate organic matter, suspended solids and sediments are also important, since arsenic adsorbs readily to suspended material and combines with dissolved organic carbon.

Existing data do not indicate that water hardness has any effect on the toxicity of arsenic. Water temperature influences arsenic toxicity to estuarine invertebrates, with higher water temperatures increasing the toxicity of arsenic. There is no known relationship between arsenic toxicity and salinity.

Inorganic and organic arsenical salts have been shown to counteract the toxicity of selenium to aquatic organisms though the mechanisms involved are unknown.

**Measurement** The derivation of the arsenic criteria is based on toxicity data for dissolved arsenic. Due to the extreme toxicity of arsenic, a precautionary approach adopted, and, it is recommended that the methods used measure total arsenic, i.e. the **dissolved** and the **particulate (acid soluble)** forms of arsenic. The reference method for the determination of arsenic is atomic absorption spectrometry with hydride generation. The various forms of arsenic are converted to As(V) in an acid digestion and then reduced to As(III), prior to the generation of arsenine gas with borohydride. **Where the detection limit is above the criteria given, standard sample concentration procedures need to be used.**

As with all trace metal determinations, care must be taken to prevent contamination of water samples. Polyethylene bottles which have been suitably pre-cleaned to remove metal contaminants are required.

**Data Interpretation** Ninety percent (90 %) of all dissolved arsenic measurements for the site in question should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if arsenic measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of arsenic on aquatic ecosystems are the chronic and acute toxic effects of arsenic and its compounds on aquatic organisms.

**Effects** Arsenic has been reported to have a variety of adverse effects on both vertebrate and invertebrate aquatic organisms; the type and severity of adverse effects being dependent on the life stages of the organisms concerned. Exposure to arsenic results in reduced growth and reproduction in both fish and invertebrate populations. Arsenic also causes behavioural changes such as reduced migration in fish.

Organic arsenal compounds have been shown to be less toxic than inorganic forms of arsenic to fish. In fresh water, there is little evidence to suggest that different inorganic forms of arsenic vary significantly in their toxicity to aquatic biota. Arsenic (V) is more toxic to plants than arsenic (III). Arsenates, although not particularly toxic, interfere with energy metabolism, whereas arsenites inhibit the activity of a variety of essential enzymes.

Increased duration of exposure to arsenic at a given concentration leads to a reduction in adverse effects experienced by aquatic organisms, and they have been shown to develop tolerance. The response of organisms to arsenic is reduced by pre-exposure, and organisms may become gradually acclimated to high concentrations of arsenic in aquatic ecosystems.

Although inorganic arsenic does not accumulate in aquatic organisms, various forms of arsenic are lipid-soluble and therefore accumulate, in fatty tissue. Arsenic accumulation is usually higher in algae and invertebrates than in fish, though bottom-feeding fish are most likely to accumulate arsenic. Humans are more sensitive to arsenic than are aquatic organisms; therefore, consumption of contaminated products can pose a health risk to humans. Arsenic can be bio-concentrated in aquatic organisms because it has a high affinity for organic substances.

Many of the toxic effects of arsenic on aquatic organisms can be reversed if arsenic concentrations are reduced and maintained at very low levels.

**Criteria**

The TWQR and criteria for the total arsenic concentration in aquatic ecosystems are:

TWQR and Criteria	Arsenic concentration (µg/l)
<i>Target Water Quality Range (TWQR)</i>	<b># 10</b>
Chronic Effect Value (CEV)	20
Acute Effect Value (AEV)	130

**Note:**

- C The data available satisfied the minimum database requirements, therefore no safety factors were applied.

**Modifications**

In certain areas, or at certain sites, it may be necessary to modify the arsenic criteria provided in this guideline. *Where any modification is anticipated, the user of the guidelines must obtain expert advice.* All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require the derivation of case- and site-specific criteria:

- ! Where untested locally important species may be very sensitive to arsenic;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background arsenic concentrations are higher than the TWQR.

*Conditions for Modification*

The following conditions should be satisfied before criteria for arsenic are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in arsenic concentrations.

If information on the local fate and effects of arsenic is not available, *expert opinion should be sought before the arsenic criteria are modified.*

*All modifications that result in criteria values that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Atrazine

## Background Information

**Introduction** Atrazine (6-chloro-N<sup>2</sup>-ethyl-N<sup>4</sup>-isopropyl-1,3,5-triazine-2,4-diamine) is a systemic herbicide which inhibits photosynthesis and interferes with other enzymic processes.

Otherwise known as 1,3,5-triazine, atrazine is used for the control of weeds in crops such as maize, sorghum, sugar cane and pineapple.

**Occurrence** Entry of atrazine into aquatic ecosystems occurs during production, spillage, use and disposal.

Atrazine concentrations in the aquatic environment have been reported as 1 % of agriculturally applied quantities. However, the timing of runoff is very important, high runoff events within two weeks of application of atrazine leads to elevated levels in aquatic ecosystems.

Atrazine is reversibly adsorbed onto soil particles and does not readily leach. Adsorption and desorption depend on factors such as soil composition, temperature, moisture and pH. Atrazine is not normally found deeper than 30 cm into the soil in detectable quantities.

Microbial activity possibly accounts for the decomposition of a significant proportion of atrazine in the soil. The atrazine half-life in soil is 60 - 150 days, as a result of microbiological degradation.

Atrazine hydrolyses slowly at neutral pH, but much more rapidly at alkaline or acid pH.

**Interactions** The presence of organic solvents and surfactants increases the toxicity of atrazine considerably.

**Measurement** The reference method for the determination of atrazine in water is gas chromatography after solvent extraction and clarification.

**Data Interpretation** Ninety percent (90 %) of all atrazine measurements for the site in question should be within the Target Water Quality Range (TWQR). All measurements must be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. Where only sparse or sporadic data are available, interpretation should take into account the fact that the data may not be representative. In the case of accidental spills, chronic and acute toxicity effects will occur if atrazine measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of atrazine on aquatic ecosystems are the chronic and acute toxic effects of atrazine on aquatic organisms.

## Effects

In tolerant plants, atrazine is readily metabolised. In sensitive plants, unaltered atrazine accumulates and results in chlorosis and death. Mutagenic qualities of atrazine have been noted in certain terrestrial plants.

Decreased growth and reproduction have been observed in invertebrates exposed to atrazine, whilst atrazine is a mild skin irritant in mammals. The lipophilic nature of atrazine results in its concentration in fat reserves of organisms, though it is usually eliminated rapidly from the body. In mammalian toxicity tests, more than 50 % of the dose was eliminated rapidly from the body in the urine and in the faeces.

Due to its effects on phytoplankton and other primary producers which form the basis of the food chain, atrazine may lead to imbalances in aquatic food-webs.

## Criteria

The TWQR and criteria for atrazine in aquatic ecosystems are:

TWQR and Criteria	Atrazine concentration (µg/l)
<i>Target Water Quality Range (TWQR)</i>	<i># 10</i>
Chronic Effect Value (CEV)	19
Acute Effect Value (AEV)	100 *20

### Note:

C The data available **did not** satisfy the minimum acute database requirement. A safety factor of 100 was used for the derivation of the AEV.

\* AEV for the protection of aquatic plants

## Modifications

Normally, no modifications to the atrazine criteria for aquatic ecosystems should be allowed. However, where modifications to the criteria are anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to the aquatic ecosystems as stipulated by the criteria given in this guideline.

The following conditions should be satisfied before the atrazine criteria are modified:

- ! Adequate, site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in atrazine concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

## Sources of Information

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# Cadmium

## Background Information

**Introduction** Cadmium is a metal element which is highly toxic to marine and fresh water aquatic life. Elemental cadmium is insoluble in water though many of its organic and inorganic salts are highly soluble. Cadmium occurs primarily in fresh waters as divalent forms including free cadmium (II) ion, cadmium chloride and cadmium carbonate, as well as a variety of other inorganic and organic compounds.

Cadmium is defined by the United States Environmental Protection Agency as potentially hazardous to most forms of life, and is considered to be toxic and relatively accessible to aquatic organisms.

**Occurrence** Cadmium is present in the earth's crust at an average concentration of 0.2 mg/kg, usually in association with zinc, lead and copper sulphide ore bodies.

Due to its abundance, large quantities of cadmium enter the global environment annually as a result of natural weathering processes. Cadmium is found at trace concentrations in fresh waters and mostly a result of industrial activity.

The main sources of cadmium in the environment are due to:

- ! emissions to air and water from mining, metal (zinc, lead and copper) smelters, and industries involved in manufacturing alloys, paints, batteries and plastics;
- ! agricultural use of sludges, fertilizers and pesticides containing cadmium;
- ! burning of fossil fuels (very limited effect); and
- ! the deterioration of galvanized materials and cadmium-plated containers.

**Interactions** The chemistry of cadmium in water is similar to that of zinc, and to a lesser extent, copper. The toxicity of cadmium in water is dependent upon its hardness and chemical speciation, which is influenced by pH, water temperature, ligands and coexisting metal cations present in the water. Redox potential has little effect on cadmium speciation. All these factors influence uptake and bio-concentration of cadmium by aquatic organisms. Salinity also affects cadmium toxicity, as acute toxicity effects generally increase as salinity decreases. Temperature effects seem to be mostly organism-specific.

Most of the cadmium found in waters up to pH 9.0 is in the divalent cation form ( $\text{Cd}^{2+}$ ), while solubility decreases above pH 9.0 due to the formation of cadmium hydroxide. Cadmium has a low solubility at neutral or alkaline pH values and is highly soluble under acidic conditions. Cadmium is removed from the water column by adsorption onto humic substances and organic complexing agents in waters of high organic content. The presence of dissolved organic substances substantially lowers the cadmium toxicity to cladocerans, but not to fish.

In water, co-precipitation of cadmium with hydrous iron, aluminium and manganese oxide occurs.

The presence of other metals may result in either synergistic or antagonistic interactions. The presence of cadmium and mercury may result in reduced toxic effects of both metals, while the interaction of copper and cadmium leads to a fivefold increase in the toxicity of



each metal. The sulphates of cadmium and zinc have an additive toxic effect on fish. The presence of zinc accentuates the toxicity of cadmium to some aquatic plants, while selenium provides a protective effect against cadmium toxicity to aquatic animals and plants. The toxic effects of cadmium and cyanide ions are also additive.

The level of uptake and bio-accumulation of cadmium in aquatic ecosystems is dependent on water quality conditions. Bio-accumulation generally increases with increasing water temperature; a reduction in pH leads to greater cadmium uptake in bacteria and algae. Tissue concentrations of cadmium decrease as water hardness increases.

#### Measurement

The derivation of the cadmium criteria is based on toxicity data for dissolved cadmium. Due to the extreme toxicity of cadmium, a precautionary approach is adopted, and, it is recommended that the methods used measure total cadmium, i.e., the **dissolved** and the **particulate (acid soluble)** forms of cadmium. The reference method for the determination of total cadmium is electrothermal atomic absorption spectrometry. **Where the detection limit is higher than the values given in the criteria, standard procedures for concentrating the sample should be used.**

As with all trace metal determinations, care must be taken to prevent contamination of water samples. Polyethylene bottles which have been suitably pre-cleaned to remove metal contaminants are required.

#### Data Interpretation

Ninety percent (90 %) of all **total** cadmium measurements for the site in question should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if cadmium measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

#### Norms

The norms for assessing the effects of cadmium on aquatic ecosystems are chronic and acute toxic effects of cadmium on aquatic organisms.

#### Effects

Cadmium is easily absorbed by mammals, where it is concentrated by binding with the protein metallothionein. Many plant and animal tissues contain cadmium, but there is no evidence that cadmium is biologically essential or beneficial. Cadmium is chemically similar to zinc, and its physiological effects are often due to its replacement of zinc in some enzymes, thereby impairing enzyme activity. Cadmium is known to inhibit bone repair mechanisms, and is teratogenic, mutagenic and carcinogenic.

Bioavailable cadmium may be accumulated by macrophytes, phytoplankton, zooplankton, invertebrates and fish. Bioavailability is dependent on cadmium speciation; for example, the free ion,  $Cd^{2+}$ , is readily taken up by aquatic plants, whereas organo-cadmium complexes are not absorbed. Lethal concentrations of cadmium also vary depending on the test animal, water hardness and temperature, and time of exposure. The level of bio-accumulation is dependent on the species and age of the organism. Cadmium bio-accumulates in the food chain due to its tendency to bind strongly to sulphhydryl groups.

Bio-concentration factors range from  $10^2$  to  $10^5$  for both invertebrates and fish. However, there is no evidence for cadmium bio-magnification through the aquatic food web.

**Criteria**

The TWQR and criteria for total cadmium at different water hardness (mg CaCO<sub>3</sub>/ℓ) in aquatic ecosystems are:

TWQR and Criteria	Cadmium concentration (µg/ℓ)			
	< 60 (Soft)	60-119 (Medium)	120-180 (Hard)	> 180 (Very hard)
<b>Target Water Quality Range (TWQR)</b>	<b># 0.15</b>	<b># 0.25</b>	<b>#0.35</b>	<b># 0.40</b>
Chronic Effect Value (CEV)	0.3	0.5	0.7	0.8
Acute Effect Value (AEV)	3	6	10	13

**Table of Recommended Cadmium Criteria and TWQR (Fg/ℓ) for Cold-water adapted Fish Species**

TWQR and Criteria	Water Hardness (mg CaCO <sub>3</sub> /ℓ)			
	< 60 (Soft)	60-119 (Medium)	120-180 (Hard)	> 180 (Very hard)
<b>Target Water Quality Range (TWQR)</b>	<b># 0.07</b>	<b># 0.1</b>	<b># 0.15</b>	<b># 0.17</b>
Chronic Effect Value (CEV)	0.15	0.19	0.29	0.34
Acute Effect Value (AEV)	1.8	2.8	5.1	6.2

**Note:**

! The data available satisfied the minimum database requirements, therefore no safety factors were applied.

**Modifications**

In certain areas, or at certain sites, it may be necessary to modify the cadmium criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to cadmium;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature;
- ! Where natural background cadmium concentrations are higher than the TWQR;
- ! Where water hardness and alkalinity have profound effects on the chronic and acute toxic effects of cadmium; and
- ! Where cold-water adapted species require protection.

*Conditions for Modification*

The following conditions should be satisfied before criteria for cadmium are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in cadmium concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

## Sources of Information

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# Chlorine

## Background Information

**Introduction** Elemental chlorine ( $\text{Cl}_2$ ) is a greenish-yellow gas that dissolves readily in water. It is not normally a constituent of natural waters since chlorine is too reactive to persist in the aquatic environment.

**Occurrence** Free forms of chlorine such as  $\text{HOCl}$  and  $\text{OCl}^-$ , or combined available chlorine (chloramines), occurs in aquatic ecosystems as a result of:

- ! chlorination of drinking water (to remove unwanted tastes and odours, and for the purposes of disinfection);
- ! the textile industry (bleaching, slimicide);
- ! the pulp and paper industry (bleaching, slimicide);
- ! sewage treatment (reduce odour, algicide, bactericide);
- ! cooling waters (slimicide); and
- ! swimming pools (disinfection).

Effluents containing ammonia, organic matter or cyanides convert chlorine into substances such as chloramines, which may be less toxic but more persistent than chlorine, thereby posing a long-term threat to aquatic life.

**Interactions** Chlorine can be described either being available, or *residual*. When present as chloramine it is referred to as *combined*.

Available chlorine is present as an equilibrium mixture of chlorite ions ( $\text{OCl}^-$ ) and hypochlorous acid ( $\text{HOCl}$ ). Combined available chlorine is in the form of chloramines or other compounds with a N-Cl bond.

When chlorine is added to water containing ammonia it will, in the absence of stronger reducing agents initially form chloramine, then chlorimine ( $\text{NHCl}_2$ ), and finally nitrogen trichloride.

Chloramines slowly reach an equilibrium with a small concentration of hypochlorous acid which accounts for their toxicity to fish. Since sewage effluents always contain ammonia the effects of chlorine must not be considered without taking into account the effects of chloramine, which though less toxic than chlorine are more persistent. Hypochlorous acid and hypochlorite ions slowly decompose forming chloride ion and oxygen.

Toxicity of chlorine to fish is increased by a reduction in dissolved oxygen concentration. Organic carbon and ammonia also affect chlorine toxicity, whereas alkalinity does not affect toxicity. Salinity does not appear to greatly affect chlorine toxicity to aquatic biota.

Chlorine can react with a variety of organic substances to form stable chloro-organic compounds, some of which are harmful to fish even at low concentrations.

**Measurement** The criteria are given in terms of the **total residual** chlorine concentration, in units of  $\text{Fg Cl}_2/\text{R}$ . The reference method for the determination of chlorine and chloramine concentrations is amperometric titration.

**Data Interpretation** Ninety percent (90 %) of all chlorine measurements for the site in question should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if chlorine measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of chlorine on aquatic ecosystems are the chronic and acute toxic effects of chlorine on aquatic organisms.

**Effects** The toxic effects of chlorine are usually irreversible. Free chlorine is more toxic but less persistent than combined chlorine. Diatoms are more sensitive to chlorine than are green algae, which, in turn, are more sensitive than blue-green algae. Newly hatched fish larvae are more sensitive to chlorine than are fish eggs.

Avoidance behaviour, adverse changes in the blood chemistry, damage to gills, decreased growth rate, restlessness preceding loss of equilibrium and death have been observed for fish exposed to chlorine. Invertebrates become immobile, and exhibit reduced reproduction and reduced survival on exposure to chlorine. Aquatic plants may become chlorotic, whilst reduced rates of photosynthesis and respiration are observed for phytoplankton.

Acclimation to sublethal chlorine concentrations leads to increased resistance. Chlorine itself does not accumulate, but chlorinated organic substances may bio-concentrate in aquatic organisms.

**Criteria** The TWQR and criteria for the total residual chlorine concentration in aquatic ecosystems are:

TWQR and Criteria	Chlorine concentration ( $\mu\text{g}/\text{R}$ )
<i>Target Water Quality Range (TWQR)</i>	<b># 0.2</b>
Chronic Effect Value (CEV)	0.35
Acute Effect Value (AEV)	5

**Note:**

C The data available **did not** satisfy the minimum acute database requirement . A safety factor of 6 was used for the derivation of the AEV.

**Modifications** In certain areas, or at certain sites, it may be necessary to modify the chlorine criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to chlorine; and
- ! Where aquatic organisms may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background chlorine concentrations are higher than the TWQR.

*Conditions for Modification*

The following conditions should be satisfied before criteria for chlorine are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available;
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in chlorine concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

## Sources of Information

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USEPA 1986. *Quality Criteria for Water*. USEPA Office of Water Regulations and Standards, Washington DC, 20460. Report No. EPA 440/5-86-001.



# Chromium

## Background Information

**Introduction** Chromium is a relatively scarce metal, and the occurrence and amounts thereof in aquatic ecosystems are usually very low. Chromium ions occur in a variety of forms:

- ! chromium (II) - chromous ion ( $\text{Cr}^{2+}$ ),
- ! chromium (III) - chromic ion ( $\text{Cr}^{3+}$ , trivalent),
- ! chromium (III) - chromite ion ( $\text{CrO}_3^{3-}$ , trivalent),
- ! chromium (VI) - chromate ion ( $\text{CrO}_4^{2-}$ , hexavalent),
- ! chromium (VI) - dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ , hexavalent).

Chromium(VI) is a highly oxidized state and occurs as the yellow dichromate salt in neutral or alkaline media, and as the orange chromate salt in acid medium. Both of these chromium(VI) salts are highly soluble at all pH values. The reduced forms, chromium(II) and chromium(III) are reported as being less toxic and therefore less hazardous than chromium(VI).

**Occurrence** The most common ore of the metal chromium is chromite, in which chromium occurs in the trivalent state. Other minerals containing chromium do occur, but are not common. Most elevated levels of chromium in aquatic ecosystems are a consequence of industrial activity.

In the aquatic environment chromous compounds tend to be oxidized to chromic forms, whilst the chromium(VI) form can be reduced to chromium(III) by heat, in the presence of organic matter and by reducing agents.

Of the trivalent chromium salts, the chloride, nitrate and sulphate salts are readily soluble, whereas the hydroxide and carbonate salts are relatively insoluble. Of the hexavalent chromate salts only the sodium, potassium, and ammonium chromates and dichromates are soluble.

Hexavalent chromium salts are used extensively:

- ! in metal pickling and plating;
- ! in the leather industry as tanning agents; and
- ! in the manufacture of paints, dyes, explosives, ceramics and paper.

Trivalent chromium salts are used much less frequently, but are important as:

- ! fixatives in textile dye manufacture;
- ! in the ceramic and glass industry; and
- ! in photography.

Chromium compounds may also be discharged in chromium-treated cooling waters where chromium has been used as a corrosion inhibitor.

**Interactions** In natural waters chromium exists in three oxidation states. However, these are difficult to distinguish because of inter-conversion reactions and contamination during sample collection, storage and processing.

The equilibrium between the chromium(VI) and chromium(III) is strongly influenced by pH and redox potential. The presence of oxidizable organic matter and iron (II) salts encourages reduction to lower, less toxic oxidation states.

Water hardness and pH affect the toxicity of both chromium(III) and chromium(VI). Limited data available indicate that acute toxicity decreases as water hardness and pH increase. There are reports that sodium chromate is more toxic in water with low concentrations of dissolved oxygen.

**Measurement** Chromium criteria for aquatic ecosystems are based on the **dissolved concentration of chromium(III) and chromium(VI)**. The reference method for the determination of chromium(VI) is the diphenyl carbizide spectrophotometry. The concentration of chromium(III) is calculated by difference. **Where the detection limit is above the values given in the criteria, standard sample concentration procedures need to be used.**

As with all trace metal determinations, care must be taken to prevent contamination of water samples. Polyethylene bottles, which have been suitably pre-cleaned to remove metal contaminants, are required.

**Data Interpretation** Ninety percent (90 %) of all the dissolved chromium measurements should be within the Target Water Quality Range (TWQR). All concentrations should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if chromium measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of chromium(III) and chromium(VI) on aquatic ecosystems are based on chronic and acute toxic effects of chromium(III) and chromium(VI) on aquatic organisms.

**Effects** Chromium exerts a toxic effect at different concentrations in different groups of aquatic organisms. Fish are the most resistant, and in some cases the toxicity of chromium(VI) is no greater than for chromium(III). A temporarily reduced growth phase has been reported for young fish at low chromium concentrations. Invertebrates are usually at least an order of magnitude more sensitive, with daphniids showing the greatest sensitivity to chromium. Green algae are also more sensitive than fish, whilst bacterial responses to chromium are variable.

**Criteria**

The TWQR and criteria for dissolved chromium(VI) in aquatic ecosystems are:

<b>TWQR and Criteria</b>	<b>Chromium(VI) concentration (µg/l)</b>
<b><i>Target Water Quality Range (TWQR)</i></b>	<b># 7</b>
Chronic Effect Value (CEV)	14
Acute Effect Value (AEV)	200

The TWQR and criteria for dissolved chromium(III) in aquatic ecosystems are:

<b>TWQR and Criteria</b>	<b>Chromium(III) concentration (µg/l)</b>
<b><i>Target Water Quality Range (TWQR)</i></b>	<b># 12</b>
Chronic Effect Value (CEV)	24
Acute Effect Value (AEV)	340

**Notes:**

- C The data available **did not** satisfy the minimum chronic and acute database requirements for chromium(III) . A safety factor of 3 was used for the derivation of the AEV and the CEV for chromium(III).
- C No safety factors were used for the derivation of the AEV or the CEV for chromium(VI), since the databases satisfied the minimum requirements.

**Modifications**

In certain areas, or at certain sites, it may be necessary to modify the chromium criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to chromium;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background chromium concentrations are higher than the TWQR.

*Conditions for Modification*

The following conditions should be satisfied before the criteria for chromium are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available;
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in chromium concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Copper

## Background Information

**Introduction** Copper is one of the world's most widely used metals. Although copper occurs naturally in most waters, it is regarded as potentially hazardous by the USEPA.

Copper occurs in four oxidation states, namely, 0, I, II and III. The two most common forms are cuprous copper(I) and cupric copper(II). Cuprous copper is unstable in aerated aqueous solutions and will normally be oxidized to cupric copper.

**Occurrence** Copper is a common metallic element in the rocks and minerals of the earth's crust, and is commonly found as an impurity in mineral ores. Chalcopyrite ( $\text{CuFeS}_2$ ) is the most abundant of the copper minerals. Crustal (igneous) rocks contain more copper (23 - 55 mg/kg) than sedimentary rocks (4 - 45 mg/kg).

The occurrence of natural sources of copper in the aquatic environment is due to weathering processes or from the dissolution of copper minerals and native copper. Metallic copper is insoluble in water, but many copper salts are highly soluble as cupric or cuprous ions. Anthropogenic sources account for 33 - 60 % of the total annual global input of copper to the aquatic environment.

The main anthropogenic sources of copper in the aquatic environment are:

- ! corrosion of brass and copper pipes by acidic waters;
- ! sewage treatment plant effluents;
- ! copper compounds used as aquatic algicides;
- ! runoff and ground water contamination from the use of copper as fungicides and pesticides in the treatment of soils; and
- ! liquid effluents and atmospheric fallout from industrial sources such as mining, smelting and refining industries, coal-burning, and iron- and steel-producing industries.

**Interactions** Copper exhibits complex behaviour in aquatic ecosystems, and may be present in the following forms:

- ! a solution of cupric ions;
- ! complexed with inorganic or organic ligands;
- ! associated with suspended or bed sediments; and
- ! as precipitates of hydroxides, phosphates and sulphides.

The proportion of various copper species depends on pH and on the presence of ligands such as sulphate, chloride and nitrate in the water. Copper is generally more soluble in acidic waters, and precipitates as copper hydroxides ( $\text{Cu}(\text{OH})_2$ ) at pH values above 6.5. Divalent copper salts are mostly very soluble in water. Copper (II) carbonate, hydroxide and sulphide are insoluble in water, while copper sulphate and nitrate are soluble. Cupric chloride is highly soluble, while cuprous chloride is almost insoluble in water. Ammonium complexes of copper are also soluble in water.

The toxicity of copper is dependent on local water quality conditions. Copper toxicity increases:

- ! with a decrease in water hardness;
- ! with a decrease in dissolved oxygen; and
- ! when present in combination with other metals.

Copper toxicity decreases:

- ! in the presence of chelating agents such as, humic acids, amino acids and suspended solids;
- ! with an increase in alkalinity; and
- ! in the presence of zinc, molybdenum, sulphate, calcium or magnesium. Sodium nitrite and sodium nitrate decrease the toxicity of copper sulphate to fish.

The toxicity of copper in natural waters containing organic matter is usually less than that predicted from laboratory tests, due to the ameliorative effect of suspended matter in the water column.

Copper is easily adsorbed and precipitated in sediments at alkaline pH. Less than 1 % of total copper exists in the free ionic form in natural waters. At pH levels and inorganic carbon concentrations characteristic of natural fresh waters, most of the soluble copper is present as complexes of cupric carbonate. Adsorption and precipitation are therefore important in determining the abiotic fate of copper in the aquatic environment. In reducing acidic environments, remobilization of sorbed or co-precipitated copper can occur. In the presence of soluble organic matter, adsorption of copper onto particles may be ineffective, resulting in an increase in soluble copper forms (complexed with the dissolved organic carbon) in the water column.

### Measurement

The derivation of the copper criteria is based on toxicity data for **dissolved copper**. Because of the extreme toxicity of dissolved copper, a precautionary approach is adopted, and, it is recommended that the methods used measure total copper, i.e. the **dissolved** and the **particulate (acid soluble)** forms of copper. The reference method for the determination of copper is electrothermal atomic absorption spectrometry. **Where the detection limit is above the values given in the criteria, standard sample concentration procedures need to be used.**

As with all trace metal determinations, care must be taken to prevent contamination of water samples. Polyethylene bottles, which have been suitably pre-cleaned to remove metal contaminants, are required.

### Data Interpretation

Ninety percent (90 %) of all dissolved copper measurements for the site in question should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if copper measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of copper on aquatic ecosystems are the chronic and acute toxic effects of copper on aquatic organisms.

**Effects** Copper is a micronutrient and an essential component of enzymes involved in redox reactions and is rapidly accumulated by plants and animals. It is toxic at low concentrations in water and is known to cause brain damage in mammals. Copper exerts its effect by forming stable co-ordinate bonds in proteins, where it functions as a catalyst in redox reactions. Metabolically, copper interacts with zinc, molybdenum, arsenic and selenium.

The effect of elevated copper concentrations on aquatic organisms is also related to factors such as the duration of exposure and life stage of the organism. Studies have shown that species richness and species composition of invertebrate communities and changed as copper concentrations increased. Early life stages of organisms appear to be more sensitive than adults to copper pollution.

Nitrogen fixation by blue-green algae is reduced by the addition of trace amounts of copper. Although bio-concentration factors range from 100 - 26 000, there is no evidence to suggest that copper is bio-magnified.

**Criteria** The TWQR and criteria for dissolved copper at different water hardness (mg CaCO<sub>3</sub>/ℓ) in aquatic ecosystems are:

TWQR and Criteria	Copper concentration (µg/ℓ)			
	< 60 (Soft)	60-119 (Medium)	120-180 (Hard)	> 180 (Very hard)
<b>Target Water Quality Range (TWQR)</b>	<b># 0.3</b>	<b># 0.8</b>	<b>#1.2</b>	<b>#1.4</b>
Chronic Effect Value (CEV)	0.53	1.5	2.4	2.8
Acute Effect Value (AEV)	1.6	4.6	7.5	12

**Note:**

C The data available satisfied the minimum database requirements, therefore no safety factors were applied.

**Modifications** In certain areas, or at certain sites, it may be necessary to modify the copper criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to copper;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background copper concentrations are higher than the TWQR.

*Conditions for Modification*

The following conditions should be satisfied before criteria for copper are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available;
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in copper concentrations.

*All modifications that result in criteria that are higher than those specified in the above table are subject to approval by the Department of Water Affairs and Forestry.*



## Sources of Information

ANZECC 1992. *Australian Water Quality Guidelines*. Australian and New Zealand Environment & Conservation Council, Melbourne, Australia.

APHA 1992. *Standard Methods for the Examination of Water and Waste Water*. American Public Health Association, American Water Works Association & American Pollution Control Federation Joint Publication, 18th Edition, Washington DC.

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USEPA 1986. *Quality Criteria for Water - 1986*. United States Environmental Protection Agency Office of Water Regulations and Standards, Washington DC 20460. Report No. 440/5-86-001.

# Cyanide

## Background Information

**Introduction** Hydrocyanic acid (HCN) which is the most toxic form of cyanide reacts with water to release cyanide ions (CN<sup>-</sup>).

**Occurrence** Most of the cyanide in water is in the hydrocyanic acid form which is largely undissociated at pH values of 8 or less. Cyanide in the environment is usually found complexed with metals. Cyanides are present in effluents from gas works and coke ovens, scrubbing of gases at steel plants, metal cleaning, electroplating and chemical industries. Cyanide is a common reagent in gold extraction processes and large quantities of cyanide are found in gold mine tailing dams. Cyanide is sometimes present in phenolic wastes.

**Interactions** Cyanide toxicity in water varies markedly with pH and temperature, dissolved oxygen concentration, salinity and the presence of other ions in solution. Sub-lethal concentrations of cyanide, in the presence of other contaminants, may elicit antagonistic, additive or synergistic effects. For example, nickel may complex with cyanide, and reduce the toxicity of cyanide, especially under conditions of high pH. Conversely, zinc and cadmium cyanide complexes are more toxic than either of the metals alone.

The effect of water temperature on the toxicity of cyanide is dependent on its concentration. At low concentrations, cyanide is more toxic at lower temperatures. At higher concentrations, cyanide is more toxic at higher temperatures. Aquatic organisms may become acclimatized to cyanide and their tolerances to cyanide increase with increasing acclimation temperature. Cyanide toxicity also increases with low dissolved oxygen concentrations. Cyanide decomposes under ultra-violet radiation.

**Measurement** The cyanide criteria for aquatic ecosystems are based on the **free** cyanide concentration. The reference method for the determination of cyanide is acid distillation followed by colorimetry. **Where concentrations are below the detection limit standard sample concentration procedures should be used.**

Care must be taken to prevent contamination of water samples. Polyethylene bottles which have been suitably pre-cleaned to remove contaminants should be used.

**Data Interpretation** Ninety percent (90 %) of all cyanide measurements should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if cyanide measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of cyanide on aquatic ecosystems are chronic and acute toxic effects of cyanide on aquatic organisms.

**Effects** Cyanide interferes with aerobic respiration and is therefore toxic only to aerobic organisms. Cyanide is thus not as toxic to "lower" organisms (invertebrates) as it is to fish and other vertebrates. There is a greater variability in sensitivities of invertebrates than there is in fish species. Embryos, sac larvae and warm-water-adapted species of fish are more resistant to cyanide than are other life stages or species of fish. The gills of fish suffering from cyanide poisoning are bright red in colour.

**Criteria** The TWQR and criteria for free cyanide in aquatic ecosystems are:

<b>TWQR and Criteria</b>	<b>Free Cyanide concentration (µg/l)</b>
<i>Target Water Quality Range (TWQR)</i>	<i># 1</i>
Chronic Effect Value (CEV)	4
Acute Effect Value (AEV)	110

**Note:**

C The data available satisfied the minimum database requirements, therefore no safety factors were used.

**Modifications** In certain areas, or at certain sites, it may be necessary to modify the cyanide criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to cyanide;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where the protection of cold-water adapted species is required.

*Conditions for Modification*

The following conditions should be satisfied before criteria for cyanide are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available;
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in cyanide concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

## Sources of Information

CCREM 1987. *Canadian Water Quality Guidelines*. Prepared by the Task Force on Water Quality Guidelines of the Canadian Council of Resource and Environmental Ministers. Canada.

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# Dissolved Oxygen

## Background Information

**Introduction** Gaseous oxygen (O<sub>2</sub>) from the atmosphere dissolves in water and is also generated during photosynthesis by aquatic plants and phytoplankton. Oxygen is moderately soluble in water. Equilibrium solubility, termed the saturation solubility, varies non-linearly with temperature, salinity and atmospheric pressure, and with other site-specific chemical and physical factors.

The maintenance of adequate dissolved oxygen (DO) concentrations is critical for the survival and functioning of the aquatic biota because it is required for the respiration of all aerobic organisms. Therefore, the DO concentration provides a useful measure of the health of an aquatic ecosystem. Measurement of the biochemical oxygen demand (BOD) or the chemical oxygen demand (COD) are inappropriate for aquatic ecosystems, but are useful for determining water quality requirements of effluents discharged into aquatic systems, in order to limit their impact.

**Occurrence** In unpolluted surface waters, dissolved oxygen concentrations are usually close to saturation. Typical saturation concentrations at sea level, and at TDS values below 3 000 mg/R, are: 12.77 mg/R at 5 EC; 10.08 mg/R at 15 EC; 9.09 mg/R at 20 EC.

There is a natural diel variation (24 hour cycle) in dissolved oxygen associated with the 24-hour cycle of photosynthesis and respiration by aquatic biota. Concentrations decline through the night to a minimum near dawn, then rise to a maximum by mid afternoon. Seasonal variations arise from changes in temperature and biological productivity.

Reduction in the concentration of dissolved oxygen can be caused by several factors:

- ! Resuspension of anoxic sediments, as a result of river floods or dredging activities.
- ! Turnover or release of anoxic bottom water from a deep lake or reservoir.
- ! The presence of oxidizable organic matter, either of natural origin (detritus) or originating in waste discharges, can lead to reduction in the concentration of dissolved oxygen in surface waters. The potential for organic wastes to deplete oxygen is commonly measured as biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The COD is used as a routine measurement for effluents, and is measure of the amount of oxygen likely to be used in the degradation of organic waste. However, in aquatic ecosystems it is unlikely that all organic matter will be fully oxidised.
- ! The amount of suspended material in the water affects the saturation concentration of dissolved oxygen, either chemically, through the oxygen-scavenging attributes of the suspended particles, or physically through reduction of the volume of water available for solution.

Dissolved oxygen concentrations can be increased by natural diffusion of gaseous oxygen from the atmosphere into water. Diffusion continues until the saturation concentration is reached. The rate of increase of dissolution of oxygen can be accelerated if turbulence of the water increases, causing entrainment of air from the atmosphere.

**Interactions** Under anoxic conditions (in the absence of free and bound oxygen) in the water column or in sediments, heavy metals such as iron and manganese can appear in solution, as ferrous (Fe<sup>2+</sup>) and manganous (Mn<sup>2+</sup>) species, and toxic sulphides (S<sup>-</sup>) may also be released.

High water temperatures combined with low dissolved oxygen levels can compound stress effects on aquatic organisms. The depletion of dissolved oxygen in conjunction with the presence of toxic substances can also lead to a compounded stress response in aquatic organisms. Under such conditions increased toxicity of zinc, lead, copper, cyanide, sulphide and ammonia have been observed.

### Measurement

The dissolved oxygen concentration must be measured as the lowest instantaneous concentration recorded in a 24-hour period, or as the instantaneous concentration at 06h00. Saturation concentration must be calculated for the time and place of sampling. If dissolved oxygen is measured at some other time of day or night, then interpretation of the result will require knowledge and understanding of the chemical and biological conditions at the sampling site over the 24-hour cycle.

The dissolved oxygen concentration in water is measured in the laboratory or *in situ*:

- ! The Winkler titration is a commonly used laboratory technique, suitable for fresh waters with low alkalinity.
- ! The *in situ* use of an oxygen-sensitive electrode is useful for waters with salinity levels up to those of sea water.
- ! Care must be taken to prevent oxygenation of the sample during collection and samples must be fixed if transported.

In shallow or fast-flowing water, a grab sample should be taken immediately below the water surface. In lakes, reservoirs and deep rivers where dissolved oxygen concentrations are known to vary with depth, a depth profile must be measured.

### Data Interpretation

Dissolved oxygen measurements are reported either as milligrams per litre (mg/l) or as a percentage of the saturation concentration at the time of sampling. Saturation concentration at the time and place of sampling must be calculated and reported, in order to assess the severity of the possible effects of oxygen depletion on biota.

Concentrations of less than 100 % saturation indicate that dissolved oxygen has been depleted from the theoretical equilibrium concentration. Results in excess of saturation (super-saturation of oxygen) usually indicate eutrophication in a water body.

The significance to aquatic biota of dissolved oxygen depletion depends on the frequency, timing and duration of such depletion. Continuous exposure to concentrations of less than 80 % of saturation can be harmful, and could have acute effects; repeated exposure to reduced concentrations may lead to physiological and behavioural stress. Occasional short-lived depletion of oxygen is less important. In all cases, if the rate of change in dissolved oxygen concentration is rapid, adverse effects on aquatic organisms will be increased significantly.

Useful measures of the impact of dissolved oxygen depletion are the 7-day mean minimum concentration and the 1-day minimum concentration. These are defined in the table below.

Minimum Value	Definition
7-day mean minimum concentration	The arithmetic mean of the daily (24-hour) minimum instantaneous concentrations measured at hourly intervals over seven consecutive days
1-day minimum concentration	The lowest instantaneous concentration recorded in a 24-hour cycle, or the instantaneous concentration at sunrise

## Effects and Criteria

**Norms** The norms for assessing the effects of dissolved oxygen depletion in aquatic ecosystems are chronic and acute physiological effects of dissolved oxygen on aquatic biota, and behavioural effects.

**Effects** Aerobic organisms are dependent for respiration on the presence of dissolved oxygen in water. Anoxic or hypoxic conditions may be lethal within short time scales (minutes to hours).

The sensitivity of many species, especially fish and invertebrates, to changes in dissolved oxygen concentrations depends on the species and the life stages (eggs, larvae or adult) and behavioural changes (feeding and reproduction). Juveniles of many aquatic organisms are more sensitive to physiological stress arising from oxygen depletion, and in particular to secondary effects such as increased vulnerability to predation and disease. Where possible, many species will avoid anoxic or oxygen-depleted zones.

Cold-water-adapted species such as salmonids (e.g., trout) are especially sensitive to depletion of dissolved oxygen. Reproduction and growth in these species is reduced under continuous exposure to oxygen concentrations less than 100 % saturation.

Oxygen concentrations above saturation may cause gas bubble disease in fish. Super-saturated conditions also tend to inhibit photosynthesis in green algae, favouring instead blue-green algae, which are more tolerant of super-saturation, but which may become a nuisance to other water users.

The reversibility of toxic effects on organisms depends on the duration, frequency and timing of the occurrence of oxygen depletion. Physiological stress effects in adult or less sensitive life stages may be rapidly reversed if oxygen depletion is short-lived. Prolonged exposure of aquatic communities to dissolved oxygen concentrations less than 50 % of saturation can cause significant changes in community composition, as more tolerant species are favoured.

**Criteria** Criteria for dissolved oxygen concentrations (in terms of percentage saturation) are given in terms of the Minimum Allowable Values (MAV), in the table below. These concentrations provide limits which will ensure protection of aquatic biota from the adverse effects of oxygen depletion.

The MAV will protect sensitive life stages which may last for only a few days, and take into account the resilience of aquatic organisms to short-duration oxygen depletion (see *Data Interpretation*).

<b>TWQR and Criteria</b>	<b>Concentration</b>	<b>Condition</b>	<b>Application</b>
<i>Target Water Quality Range</i>	<i>80 % - 120 % of saturation</i>	<i>06h00 sample or lowest instantaneous concentration recorded in a 24-hour period</i>	<i>Will protect all life stages of most southern African aquatic biota endemic to, or adapted to, aerobic warm water habitats. Always applicable to aquatic ecosystems of high conservation value.</i>
Minimum Allowable Values	> 60 % (Sub-lethal)	7-day mean minimum (see <i>Data Interpretation</i> )	The 7-day mean minimum <i>and</i> the 1-day minimum should apply together. Violation of these minimum values is likely to cause acute toxic effects on aquatic biota.
	> 40 % (Lethal)	1-day minimum (see <i>Data Interpretation</i> )	

### **Modifications**

Modifications may be considered on a site-specific basis where measurement of natural or unimpacted conditions indicates the TWQR to be too stringent or not appropriate. In particular, site-specific derivation of dissolved oxygen criteria which are different from the TWQR and the MAV should be considered:

- ! in naturally eutrophic systems;
- ! in deep reservoirs where oxygen depletion or anoxia of the hypolimnion is a regular, usually seasonal, occurrence;
- ! where endemic or introduced organisms may have more stringent dissolved oxygen requirements, for example, in cold-water habitats; and
- ! where key aquatic species of recreational, commercial or conservation importance are identified; site-specific criteria should be derived according to the needs of these species.

Strict control should be applied to the frequency, duration and extent of oxygen depletion to less than 80 % of saturation, because of its rapid effect on aquatic biota.

The following specific conditions should be applied:

- ! The expected range in dissolved oxygen must be determined by measurement at a site over several consecutive 24-hour cycles, repeated in each season to take account of climatic influences.



- ! Where natural physical, chemical or ecological processes lead to dissolved oxygen concentrations which fall below the MAV range, then the minimum acceptable site-specific concentration should be set at a level which is related to the measured natural minimum concentration.

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# Endosulfan

## Background Information

<b>Introduction</b>	Endosulfan is a chlorinated hydrocarbon insecticide and one of the pesticides most toxic to fish. Endosulfan poses an acute environmental risk because of its chemical and biological stability, its mobility in the environment and its effects on non-target organisms.
<b>Occurrence</b>	Agricultural and urban runoff are the main routes whereby endosulfan enters aquatic ecosystems. Accidental and uncontrolled releases also occur from manufacturers, transporters and end-users, as well as from incorrect waste disposal practices.
<b>Interactions</b>	Water hardness has no significant effect on the toxicity of endosulfan to many fish species.
<b>Measurement</b>	The reference method for the determination of endosulfan concentrations in water is by gas chromatography, after extraction and concentration of the organic compounds from the sample. Samples are collected in pre-washed glass containers, acidified, and must be extracted within 5 days and analysed within 30 days. No head space is allowed in the sample bottles. <b>Where the detection limit is above that of the criteria given, standard sample concentration procedures need to be used.</b>
<b>Data Interpretation</b>	Ninety percent (90 %) of all endosulfan measurements should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic biota. In the case of accidental spills, chronic and acute toxicity effects will occur if endosulfan measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

<b>Norms</b>	The norms for assessing the effects of endosulfan on aquatic ecosystems are the chronic and acute toxic effects of endosulfan on aquatic organisms.
<b>Effects</b>	<p>Endosulfan is a highly toxic insecticide. Toxic effects may include mortality, birth defects, tumours and genetic changes and altered behaviour. Indirect impacts include reduction of food sources or reduction in rates of photosynthesis, decomposition or mineralisation. Some organisms accumulate endosulfan from the water or sediments and this is then passed on through the food chain; the effects of endosulfan in fish are transitory, due to rapid elimination thereof.</p> <p><b>Toxicity data suggest that the degradation products of endosulfan, may be more toxic than the parent compound, endosulfan.</b></p>

**Criteria**

The TWQR and criteria for endosulfan in aquatic ecosystems are:

<b>TWQR and Criteria</b>	<b>Endosulfan concentration (µg/R)</b>
<i>Target Water Quality Range (TWQR)</i>	<b># 0.01</b>
Chronic Effect Value (CEV)	0.02
Acute Effect Value (AEV)	0.2

**Note:**

- C The data available **did not** satisfy the minimum chronic database requirement. A safety factor of 3 was applied for the derivation of the CEV.

**Modifications**

In certain areas, or at certain sites, it may be necessary to modify the endosulfan criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to endosulfan; and
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background endosulfan concentrations are higher than the TWQR.

*Conditions for Modification*

The following conditions should be satisfied before criteria for endosulfan are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in endosulfan concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

## Sources of Information

CCREM 1987. *Canadian Water Quality Guidelines*. Prepared by the Task Force on Water Quality Guidelines of the Canadian Council of Resource and Environmental Ministers. Canada.

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# Fluoride

## Background Information

**Introduction** Fluoride is a halogen gas which is highly reactive with a variety of substances. It is seldom found as free fluorine gas in nature, but occurs either as the fluoride ion or in combination with calcium, potassium and phosphates.

**Occurrence** Fluoride occurs in the earth's crust at an average concentration of 0.3 g/kg, most often as a constituent of fluorite ( $\text{CaF}_2$ ), often known as fluorspar or calcium fluoride, in sedimentary rocks. Other important occurrences of fluoride are cryolite and fluorapatite in igneous rocks. Traces of fluoride ( $< 1 \text{ mg/R}$ ) occur in many aquatic ecosystems, whilst higher concentrations (often  $> 10 \text{ mg/R}$ ) can be found in ground waters derived from igneous rocks.

Fluoride is used in:

- ! the manufacture and use of insecticides;
- ! disinfecting brewery apparatus;
- ! fluxes used in the manufacture of steel;
- ! wood preservatives;
- ! glass and enamel manufacture;
- ! chemical industries;
- ! water treatment, where fluoride may be added for dental purposes; and
- ! other minor uses.

**Interactions** Fluoride reacts rapidly with calcium and phosphate ions to form insoluble complexes, which tends to settle out of the water column. Fluoride reacts readily with magnesium and aluminium at alkaline pH values to form complexes which are not easily absorbed by aquatic biota. Fluoride also reacts with, and solubilizes, beryllium, scandium, niobium, tantalum and tin in aquatic systems. Increasing water temperature increases the toxic effects of fluoride, whilst increasing water hardness reduces toxic effects.

**Measurement** Fluoride criteria for aquatic ecosystems are based on **dissolved fluoride concentrations**. The reference method for the determination of fluoride is by inverse colorimetry. Filtered, (prewashed 0.45  $\mu\text{m}$  membrane filter) unpreserved samples are distilled to separate out the fluoride and tested with SPADNS reagent. **Where the detection limit is above that of the values given in the criteria, standard concentration procedures need to be used.**

Care must be taken to prevent contamination of water samples and glass sample bottles should be avoided. All water samples should be collected in pre-cleaned polyethylene bottles.

**Data Interpretation** Ninety percent (90 %) of all dissolved fluoride measurements should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if fluoride concentrations exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of fluoride on aquatic ecosystems are the chronic and acute toxic effects of fluoride on aquatic organisms.

**Effects** Low concentrations of fluoride (< 1 000 Fg/R) strengthen tooth enamel and bones in mammals. Skeletal fluorosis may occur if exposure to intermediate fluoride concentrations occurs over long periods. Isolated observations in the Kruger National Park have shown that Hippopotamus exposed to fluoride concentrations of greater than 4 000 Fg/R have developed distinct signs of bone and tooth enamel fluorosis.

**Criteria** The TWQR and criteria for dissolved fluoride in aquatic ecosystems are:

<b>TWQR and Criteria</b>	<b>Fluoride concentration (µg/R)</b>
<i>Target Water Quality Range (TWQR)</i>	<b># 750</b>
Chronic Effect Value (CEV)	1 500
Acute Effect Value (AEV)	2 540

**Modifications** In certain areas, or at certain sites, it may be necessary to modify the fluoride criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to fluoride;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background concentrations are higher than the TWQR.

### *Conditions for Modification*

The following conditions should be satisfied before criteria for fluoride are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in fluoride concentrations.

*All modifications that result in criteria values that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Iron

## Tentative Guideline

### Background Information

**Introduction** Iron is the fourth most abundant element in the earth's crust and may be present in natural waters in varying quantities depending on the geology of the area and other chemical properties of the water body. The two common states of iron in water are the reduced (ferrous, Fe<sup>2+</sup>) and the oxidised (ferric, Fe<sup>3+</sup>) states. Most iron in oxygenated waters occurs as ferric hydroxide in particulate and colloidal form and as complexes with organic, especially humic, compounds. Ferric salts are insoluble in oxygenated waters, and hence iron concentrations are usually low in the water column. In reducing waters, the ferrous form, which is more soluble, may persist and, in the absence of sulphide and carbonate anions, high concentrations of ferrous iron may be found.

The toxicity of iron depends on whether it is in the ferrous or ferric state, and in suspension or solution. Although iron has toxic properties at high concentrations, inhibiting various enzymes, it is not easily absorbed through the gastro-intestinal tract of vertebrates. On the basis of iron's limited toxicity and bio-availability, it is classified as a non-critical element.

Iron is an essential micronutrient for all organisms, and is required in the enzymatic pathways of chlorophyll and protein synthesis, and in the respiratory enzymes of all organisms. It also forms a basic component of haeme-containing respiratory pigments (for example, haemoglobin), catalyses, cytochromes and peroxidases. Under certain conditions of restricted availability of iron, photosynthetic productivity may be limited.

**Occurrence** Iron is naturally released into the environment from weathering of sulphide ores (pyrite, FeS<sub>2</sub>) and igneous, sedimentary and metamorphic rocks. Leaching from sandstones releases iron oxides and iron hydroxides to the environment. Iron is also released into the environment by human activities, mainly from the burning of coke and coal, acid mine drainage, mineral processing, sewage, landfill leachates and the corrosion of iron and steel. Various industries that also use iron in their processes, or in their products, include:

- ! the chlor-alkali industry,
- ! the household chemical industry,
- ! the fungicide industry,
- ! the petro-chemical industry.

South Africa has extensive gold, uranium and coal mines, drainage from which potentially affects many of our water bodies. Streams may be negatively impacted by high levels of iron in acid mine drainage. Pyrite, iron sulphide, is often found in close association with coal deposits. Upon exposure to moisture and atmospheric oxygen, the ferrous iron is oxidised to the ferric state, a reaction which is frequently accelerated by bacteria of the *Thiobacillus-Ferrobacillus* group. If the mine drainage results in acid conditions in the stream, the rate of oxidation will be slow. If, however, the acid is neutralized (the rate of neutralization depends on the surface geology) and pH rises to between 7 and 8, the rate of oxidation will increase and ferric hydroxide will precipitate. A layer of ferric hydroxide precipitate, so-called "yellowboy", on stream bottoms and structures is a common sight in areas affected by acid mine drainage. The receiving water is often also oxygen deficient.



**Interactions** The chemical behaviour of iron in the aquatic environment is determined by oxidation-reduction reactions, pH and the presence of coexisting inorganic and organic complexing agents. It has been predicted that, at a low pH, ferrous iron will predominate in the absence of oxygen, whilst ferric iron will predominate in oxygenated water. At alkaline pH values, ferrous hydroxy complexes will be present in the absence of oxygen, whilst ferric hydroxide complexes will be present in oxygenated water. The most common form of ferric iron in natural waters is colloidal suspensions of ferric hydroxide [Fe(OH)<sub>3</sub>] particles. These gels or flocs may remain suspended in the water or form flocculent materials that settle in the stream bed. Hardness also affects the concentration of the iron and "soft" waters, with very low concentrations of bicarbonate, usually contain higher concentrations of iron, most of which is oxidised to ferric iron.

The amount of iron in solution may be affected by biological interactions. Micro-organisms and fungi in subsurface environments may mobilise the flocculent materials and bring iron into solution. In anaerobic sediments, ferric oxide and hydroxides may be reduced when certain strains of micro-organisms and an organic food source are present. The growth cycles of freshwater algae may influence the concentrations of iron in surface waters, in particular the demand for iron during algal blooms can significantly reduce iron concentrations. Iron taken up during growth may be released back into the water column upon death and decay of the plants.

**Measurement** Iron criteria for the natural aquatic environment are based on **dissolved iron concentrations**. Because iron may occur in different forms in water, for example, in the oxidised or reduced states, in the dissolved state, as suspended particles, and as complexes with other substances, analyses need to take account of the relative proportions of each of these states. The generally accepted approach is to determine the total inorganic iron and ferrous (Fe<sup>2+</sup>) component, and to obtain ferric iron<sup>3</sup>(Fe<sup>3+</sup>) by difference. Total iron, including organic Fe, may be estimated after a wet digestion. The most common methods for measuring total and ferrous iron are colorimetrically, or via atomic absorption flame spectrometry (AAFS) or inductively coupled plasma optical emission spectrometry (ICPOES).

To obtain reliable environmental data it is important that the proper measures be taken at all stages of sample collection, sample storage, laboratory analysis and data interpretation.

**Data Interpretation** Ninety percent (90 %) of all dissolved iron measurements should be within the Target Water Quality Range (TWQR).

## Effects and Criteria

**Norms** The norms for assessing the effects of iron on aquatic ecosystems are the chronic and acute toxic effects of iron on aquatic organisms.

**Effects** Data on the acute and chronic toxicity of iron to both invertebrates and vertebrates are rather limited, and therefore only a tentative guideline is given.

**Criteria**

The TWQR for iron in aquatic ecosystems is:

<b>Target Water Quality Range (TWQR)</b>
The iron concentration should not be allowed to vary by more than 10 % of the background dissolved iron concentration for a particular site or case, at a specific time.

**Note: There is insufficient data to derive a CEV or an AEV.**

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# Lead

## Background Information

**Introduction** Lead exists in several oxidation states, that is, 0, I, II and IV, all of which are of environmental importance. Lead occurs as metallic lead, inorganic compounds, and organometallic compounds. The divalent form, lead (II), is the stable ionic species present in the environment and is thought to be the form in which most lead is bio-accumulated by aquatic organisms. In fresh waters lead is generally present as  $\text{PbCO}_3$  and as lead-organic complexes, with a small proportion in the form of free lead ions. Lead may also be complexed with organic ligands, yielding soluble, colloidal and particulate compounds.

Lead is defined by the USEPA as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms.

**Occurrence** Lead is principally released into the aquatic environment through the weathering of sulphide ores, especially galena. Since metallic lead and common lead minerals such as sulphides, sulphates, oxides, carbonates and hydroxides are almost insoluble, levels of dissolved lead (acetate and chloride salts) in aquatic ecosystems are generally low. Most of the lead entering aquatic ecosystems is associated with suspended sediments, while lead in the dissolved phase is usually complexed by organic ligands.

The photolysis of lead compounds is an important process in the removal of lead from the atmosphere. The products of this photo-degradation are lead oxides and halides, which enter the aquatic ecosystems via direct deposition or surface runoff.

The major sources of lead in the aquatic environment are anthropogenic, these include:

- ! precipitation, fallout of lead dust and street runoff (associated with lead emissions from gasoline-powered motor vehicles);
- ! industrial and municipal wastewater discharge;
- ! mining, milling and smelting of lead and metals associated with lead, e.g. zinc, copper, silver, arsenic and antimony; and
- ! combustion of fossil fuels.

**Interactions** Decreasing pH increases the bioavailability of divalent lead, which is accumulated by aquatic biota. At a constant pH, solubility decreases with increasing alkalinity. Soluble lead is removed from solution by association with sediments and suspended particulates of inorganic and organic material, such as hydrous oxides and clays and humic acids, respectively.

Adsorption is the primary factor responsible for low lead concentrations in the aquatic environment. In the presence of clay suspensions at pH 5 - 7, lead is precipitated and adsorbed, mostly as relatively insoluble hydroxides. Below pH 5 - 6 the formation of stable cationic species may prevent the formation of hydroxides.

Lead uptake by aquatic organisms is dependent on the action of calcium; therefore, hardness is an important factor determining the toxicity of lead in aquatic systems.

Calcium, at a concentration of 50 mg/R, is able to prevent the toxic effects of lead at 1.0 mg/R. Therefore, in soft waters, lead is potentially more toxic than in hard waters. Chronic toxicity also decreases with increasing water hardness. Lead toxicity has been shown to increase with decreasing concentrations of dissolved oxygen.

**Measurement** Lead criteria for aquatic ecosystems are based on the **dissolved lead concentration**. The reference methods for the determination of lead are flame atomic absorption spectrometry (requires an extraction procedure for low concentrations) and electrothermal atomic absorption spectrometry (more sensitive for low concentrations and does not require extraction). **Where the detection limit is higher than the concentrations given in the criteria, standard sample concentration procedures need to be used.**

As with all trace metal determinations, care must be taken to prevent contamination of water samples. Polyethylene bottles, which have been suitably pre-cleaned to remove metal contaminants, are required.

**Data Interpretation** Ninety percent (90 %) of all dissolved lead measurements should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if lead measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of lead on aquatic ecosystems are the chronic and acute toxic effects of lead on aquatic organisms.

**Effects** Lead is a common and toxic trace metal which readily accumulates in living tissue. Metabolically, lead interacts with iron and therefore interferes with haemoglobin synthesis. It also affects membrane permeability by displacing calcium at functional sites, and inhibits some of the enzymes involved in energy metabolism. Lead that has been absorbed by vertebrate organisms is largely deposited in the bony skeleton, where it does not usually exhibit toxic effects. If stress results in decalcification or deossification, lead deposits may result in toxic effects. It has been shown that rainbow trout develop spinal deformities after exposure to lead in soft water, while no deformities were evident in hard water.

Low concentrations of lead affect fish by causing the formation of a film of coagulated mucous over the gills and subsequently over the entire body. This has been attributed to a reaction between lead and an organic constituent of the mucous. Death of fish is due to suffocation brought about by the mucous layer since insoluble lead is apparently not toxic to fish.

Lead is bio-accumulated by benthic bacteria, freshwater plants, invertebrates and fish. Bio-concentration factors for four species of invertebrates and two species of fish ranged from 42 - 1 700, though lead does not appear to bio-magnify through the aquatic food web.

**Criteria**

The TWQR and criteria for dissolved lead at different water hardness (mg CaCO<sub>3</sub>/ℓ) in aquatic ecosystems are:

TWQR and Criteria	Lead concentration (µg/ℓ)			
	< 60 (Soft)	60-119 (Medium)	120-180 (Hard)	> 180 (Very hard)
<i>Target Water Quality Range (TWQR)</i>	<b># 0.2</b>	<b># 0.5</b>	<b># 1.0</b>	<b># 1.2</b>
Chronic Effect Value (CEV)	0.5	1.0	2.0	2.4
Acute Effect Value (AEV)	4	7.0	13	16

**Note:**

- C The data available **did not** satisfy the minimum chronic database requirement. A safety factor of 6 was used for the derivation of the CEV.

**Modifications**

In certain areas, or at certain sites, it may be necessary to modify the lead criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to lead;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature;
- ! Where natural background lead concentrations are higher than the TWQR;
- ! Where water hardness affects the solubility of lead and hence its toxicity; and
- ! Where low dissolved oxygen concentrations are of concern.

*Conditions for Modification*

The following conditions should be satisfied before criteria for lead are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in lead concentrations.

Water hardness and alkalinity have profound effects on the chronic and acute toxic effects of lead. As toxicity data for very soft waters are not readily available, there is the possibility that the criteria derived may be under-protective.

Because lead toxicity increases with decreasing dissolved oxygen concentrations in water, a factor is applied to correct for ambient dissolved oxygen concentrations.

**The table below gives the factors by which the threshold concentration of lead must be multiplied to determine concentrations of equal toxicity at progressively lower dissolved oxygen concentrations**

<b>Dissolved oxygen (% of saturation)</b>	100	80	60	40
<b>Factor</b>	1.0	0.95	0.85	0.71

*All other modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Manganese

## Background Information

**Introduction** Manganese is an essential micronutrient for plants and animals. It is a functional component of nitrate assimilation and an essential catalyst of numerous enzyme systems in animals, plants and bacteria. When manganese is not present in sufficient quantities, photosynthetic productivity may be limited and plants may exhibit chlorosis (a yellowing of the leaves) or failure of leaves to develop properly. A deficiency in manganese in vertebrates leads to skeletal deformities and reduced reproductive capabilities.

High concentrations of manganese are toxic, and may lead to disturbances in various metabolic pathways, in particular disturbances of the central nervous system caused by the inhibition of the formation of dopamine (a neurotransmitter).

**Occurrence** Manganese is the eighth most abundant metal in nature, and occurs in a number of ores. In aquatic ecosystems, manganese does not occur naturally as a metal but is found in various salts and minerals, frequently in association with iron compounds. It may exist in the soluble manganous ( $Mn^{2+}$ ) form, but is readily oxidised to the insoluble manganic ( $Mn^{4+}$ ) form. The  $Mn^{2+}$  ion occurs at low redox potentials and low pH. Permanganates ( $Mn^{7+}$ ) do not persist in the environment. They rapidly oxidise organic materials and are therefore reduced. Nitrate, sulphate and chloride salts of manganese are fairly soluble in water, whereas oxides, carbonates, phosphates, sulphides and hydroxides are less soluble.

Soils, sediments and metamorphic and sedimentary rocks are significant natural sources of manganese. Industrial discharges also account for elevated concentrations of manganese in receiving waters. Various industries use manganese, its alloys and manganese compounds in their processes, or in their products, examples of which are given below:

- ! the steel industry, in the manufacture of dry cell batteries;
- ! the fertilizer industry (manganese is used as a micro-nutrient fertilizer additive); and
- ! the chemical industry in paints, dyes, glass, ceramics, matches and fireworks.

Acid mine drainage also releases a large amount of the manganese. Iron and steel foundries release manganese into the atmosphere, where it is then redistributed through atmospheric deposition.

**Interactions** Manganese is similar to iron in its chemical behaviour, and is frequently found in association with iron. The concentration of dissolved manganese is influenced by changes in redox potential, dissolved oxygen, pH and organic matter.

In natural waters, a large proportion of manganese is present in suspended and adsorbed forms. In surface waters, divalent manganese is rapidly oxidised to insoluble manganese dioxide, which settles out of the water column. The presence of complex-forming organic and inorganic compounds stabilises the manganese oxides, via the formation of complex ions. Under anaerobic conditions with low pH, soluble manganese forms may persist. Increased carbonate activity decreases manganese solubility and, at high concentrations, carbonate has been shown to reduce the oxidation rate of manganese.

**Measurement** Manganese criteria for aquatic ecosystems are based on the **dissolved manganese concentration**. Manganese will normally be present as soluble  $Mn^{2+}$  or in suspension in the form of hydrated oxides. The reference methods for the determination of dissolved manganese are atomic absorption flame spectrometry (AAFS) or inductively coupled plasma optical emission spectrometry (ICP-OES).

To obtain reliable environmental data it is important that the proper measures be taken at all stages of sample collection, sample storage, laboratory analysis and data interpretation.

**Data Interpretation** Ninety percent (90 %) of all the dissolved manganese measurements should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if manganese measurements exceed the Acute Effect Value (AEV). Because the toxicity of manganese depends on the form of the metal, the proportion of each of the states will modify the potential effect on the aquatic environment.

## Effects and Criteria

**Norms** The norms for assessing the effects of manganese on aquatic ecosystems are the chronic and acute toxic effects of manganese on aquatic organisms.

**Effects** Information on the acute and chronic toxicity effects of manganese to algae, invertebrates and vertebrates are very limited.

**Criteria** The TWQR and criteria for dissolved manganese in aquatic ecosystems are:

TWQR and Criteria	Manganese concentration ( $\mu\text{g/l}$ )
<i>Target Water Quality Range (TWQR)</i>	<i># 180</i>
Chronic Effect Value (CEV)	370
Acute Effect Value (AEV)	1 300

**Note:**

- C The data available **did not** satisfy the chronic and acute minimum database requirements. A safety factor of 3 was used for the derivation of the CEV and the AEV.

## **Modifications**

In certain areas, or at certain sites, it may be necessary to modify the manganese criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to manganese;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background manganese concentrations are higher than the TWQR.

### *Conditions for Modification*

The following conditions should be satisfied before criteria for manganese are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in manganese concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Mercury

## Background Information

**Introduction** Mercury is a heavy metal that is of quite rare geological occurrence, and its concentration in the environment is normally very low. Mercury occurs in three oxidation states in the natural aquatic environment, namely: as the metal, as mercury(I), and as mercury(II). The dissolved forms of mercury and those adsorbed onto particulate material are included in the guideline since they are both available for uptake by aquatic organisms. Mercury is also found as organo-mercurial salts, the most important of which is methyl mercury.

Mercury and mercury-organic complexes are of concern in the natural aquatic environment because of their extreme toxicity to aquatic organisms and the potential to bio-accumulate in the food chain. Intake of mercury can occur via air, food and water.

**Occurrence** Mercury may occur at high concentrations in water bodies subject to industrial pollution, or in the vicinity of industrial activities utilising or discharging mercury or compounds thereof. Important industries that use mercury in their processes, or in their products, include:

- ! the chlor-alkali industry,
- ! the paint industry,
- ! the fungicide industry,
- ! the paper and pulp industry,
- ! medical and dental industries, and
- ! the electrical equipment industry.

Mercury has a strong affinity for sediments and suspended solids. Under anaerobic conditions, bacteria readily transform inorganic mercury into methyl mercury. Dissolved mercury salts are also easily absorbed by aquatic organisms and can be bio-accumulated.

Methyl mercury, the most common form of mercury found in aquatic organisms, is lipid soluble (readily passes through plant and animal membranes) and is stored within the bodies of organisms. In aquatic animals, bio-accumulated mercury is stored in fatty tissues, whilst in aquatic plants, mercury is usually stored in roots and stems.

**Interactions** Alkylated mercury compounds, such as mono- and di-methyl mercury, are of serious concern in the aquatic environment because they are much more toxic to man and animals than are the inorganic forms of mercury. As alkylation is bacteriologically mediated, factors such as pH, oxygen level and the organic carbon level influence the degree of methylation and the type of organo-mercurial salts formed, and hence the degree of toxicity.

The derivation of the Target Water Quality Range (TWQR) assumes that 10 % of the total mercury present in a sample is in the form of organo-mercury compounds.

**Measurement** The derivation of the mercury criteria is based on toxicity data for **dissolved mercury**. Due to the extreme toxicity of mercury, a precautionary approach is adopted, and, it is recommended that the methods used measure **total mercury**, i.e. the **dissolved** and the **particulate (acid soluble)** forms of mercury. The reference type method for the determination of the dissolved mercury concentration is by flameless atomic absorption. **Where values are below the detection limit, standard sample concentration procedures need to be used.** Suitable preservation techniques should be used, such as acidification, and/or the use of an oxidant.

Because mercury can occur in different forms in water, namely, in the dissolved state, as suspended particles, and as complexes with other substances, both the method of analysis selected and the treatment of water samples before analysis, will determine how much of the mercury in each of these categories will be included in the analysis. It is crucial that analysts should state whether their method measures only one or more forms of the mercury, or total mercury.

**Data Interpretation** Ninety percent (90 %) of all total mercury measurements for the site in question should be within the TWQR. All measurements must be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxic effects will occur if mercury measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of total mercury and its compounds on aquatic ecosystems are the chronic and acute toxic effects of mercury and its compounds on aquatic organisms.

**Effects** Because of its neuro- and renal toxicity, mercury is severely poisonous to mammals. Poisoning by mercury takes the form of neurological disturbances, particularly in the case of organo-mercurial salts such as methyl mercury, and of renal dysfunction in the case of inorganic mercury. The kidneys are the main route of excretion of inorganic mercury. De-methylation is a slow process, and methyl mercury is only excreted over a long period.

Methyl mercury accumulated in fatty tissue or storage organs can be mobilized rapidly into the nervous and reproductive systems. This bio-accumulated mercury increases the risk of mercury toxicity to aquatic and terrestrial organisms in the food chain.

Organic forms of mercury are approximately ten times more toxic than inorganic forms because they pass rapidly through biological membranes. Solid inorganic forms of mercury have relatively low toxicity to vertebrates since solids are not easily absorbed by the gastrointestinal tract. In contrast, dissolved mercury salts are easily absorbed by aquatic organisms and can be bio-accumulated.

**The toxic effects of mercury on aquatic organisms cannot be reversed.**

## Criteria

The TWQR and criteria for total mercury in aquatic ecosystems:

TWQR and Criteria	Mercury concentration (Fg/R)
<i>Target Water Quality Range (TWQR)</i>	<i># 0.04</i>
Chronic Effect Value (CEV)	0.08
Acute Effect Value (AEV)	1.7

### Note:

- C The South African criteria for mercury have been derived on the assumption that a maximum of 10 % of the total mercury in a water sample is present as methyl mercury. This assumption is justified for all well-aerated waters where reducing conditions, which favour the occurrence of methyl mercury, are absent. However, in poorly-aerated waters, a greater proportion of the total mercury will be present as methyl mercury;
- C The data available **did not** satisfy the minimum chronic database requirement. A safety factor of 6 was used for the derivation of the CEV; and
- C The effects of both inorganic and organic compounds were treated as being linearly related to their respective concentrations as well as being additive.

## Modifications

In certain areas, or at certain sites, it may be necessary to modify the mercury criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to the aquatic ecosystem as stipulated by the criteria given in this guideline.

The following circumstances may require the derivation of case- and site-specific criteria:

- ! Where untested, locally important species may be very sensitive to mercury;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature;
- ! Where natural background concentrations of mercury are higher than the guideline range;
- ! Where the oxygen saturation level of the local sediment may have a crucial influence on the form and fate of mercury in the aquatic environment. Where stable anoxic (no free or bound oxygen) or anaerobic (no free oxygen) conditions occur in sediments, mercury is quickly transformed to the more toxic-methyl and di-methyl mercury forms; and
- ! Where acid volatile sulphide is present in sediments.

The following conditions should be satisfied before the mercury criteria are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in mercury concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Nitrogen (Inorganic)

## Background Information

**Introduction** The term inorganic nitrogen includes all the major inorganic nitrogen components ( $\text{NH}_3 + \text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$ ) present in water. Both the dissolved forms of inorganic nitrogen and those adsorbed onto suspended inorganic and organic material are included, since they are all available for uptake by algae and higher plants.

Ammonia ( $\text{NH}_3$ ) and ammonium ( $\text{NH}_4^+$ ) are reduced forms of inorganic nitrogen and their relative proportions are controlled by water temperature and pH. Both forms can exist as dissolved ions, or can be adsorbed onto suspended material.

Nitrite ( $\text{NO}_2^-$ ) is the inorganic intermediate, and nitrate ( $\text{NO}_3^-$ ) the end product, of the oxidation of organic nitrogen and ammonia. Nitrate is the more stable of the two forms and is usually far more abundant in the aquatic environment. In view of their co-occurrence and rapid inter-conversion, nitrite and nitrate are usually measured and considered together. Inter-conversions between the different forms of inorganic nitrogen are part of the nitrogen cycle in aquatic ecosystems.

Inorganic nitrogen is primarily of concern due to its stimulatory effect on aquatic plant growth and algae. Most aquatic organisms are sensitive to the toxic effects of ammonia. See guideline for ammonia.

**Occurrence** Surface runoff from the surrounding catchment area, the discharge of effluent streams containing human and animal excrement, agricultural fertilizers and organic industrial wastes are the major sources of inorganic nitrogen which enters aquatic systems. In highly impacted catchments, the inorganic nitrogen arising from human activities can greatly exceed "natural" sources. In addition, many groups of bacteria are able to transform organic nitrogen to inorganic nitrogen during the decomposition of organic material.

Inorganic nitrogen is seldom present in high concentrations in unimpacted surface waters. This is because inorganic nitrogen is rapidly taken up by aquatic plants and converted into proteins and other organic forms of nitrogen in plant cells. In South Africa, inorganic nitrogen concentrations in unimpacted, aerobic surface waters are usually below 0.5 mg N/R but may increase to above 5 - 10 mg N/R in highly enriched waters.

Oxidized forms of inorganic nitrogen (usually nitrate) can sometimes be present in very high concentrations ( $> 150 \text{ mg NO}_3\text{-N/R}$ ) in ground water. Such high concentrations can occur under natural conditions (e.g., mineral salts derived from rocks and soil, not due to man's activity), or due to seepage from sewage systems and leaching of organic and inorganic fertilizers from soil.

**Interactions** The processes of ammonification, nitrification, denitrification, and the active uptake of nitrate by algae and higher plants, are regulated by water temperature, oxygen availability and pH. Changes to water temperature and pH affect the rates at which these processes occur and the concentration of inorganic nitrogen present in water.

Nitrite can be transformed rapidly to nitrate, and vice versa, by bacterial processes. Under aerobic conditions, nitrite is oxidized to nitrate by nitrifying bacteria. Conversely, under

anaerobic conditions, nitrate is reduced to nitrite (and then to molecular nitrogen) by denitrifying bacteria. Denitrification is the most important process whereby nitrate is lost from aquatic systems.

Enrichment of waters with dissolved organic carbon (e.g., through the discharge of treated sewage effluent) can increase rates of nitrogen loss via denitrification by providing an energy source for denitrifying bacteria.

Several chemical bonding processes, as well as the forces which control the charge on the surface of sediment particles, regulate the amount of inorganic nitrogen which may be adsorbed to, or desorbed from, suspended particulate material. Typically, these reactions are strongly influenced by water temperature and pH, as well as by bacterial activity.

When particulate material settles out of the water onto the sediments, bound inorganic nitrogen becomes trapped in the sediments. Some of the bound inorganic nitrogen can be released by diffusion into the overlying water; nitrate present in anaerobic sediments can be lost from the system via denitrification.

### **Measurement**

The concentration of inorganic nitrogen species in water is obtained by adding together the individual concentrations of ammonia ( $\text{NH}_3 + \text{NH}_4^+$ ), plus nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ). No single analytical technique will provide a measure of inorganic nitrogen.

Nitrite plus nitrate is determined by the cadmium reduction method followed by diazotisation and spectrophotometry. Nitrite alone is determined by diazotisation without prior reduction of the nitrate present to nitrite. Total ammonia, the sum of the  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations, is determined by the phenate hypochlorite method, followed by spectrophotometry or colorimetry.

Where other analytical methods are used, their characteristics relative to the reference type methods should be known. Concentrations are usually expressed as milligrams of inorganic nitrogen per litre of water sample (mg N/l).

Prior filtration may be required where water samples are turbid. Considerable difficulty is experienced in the analysis of any inorganic nitrogen that is adsorbed onto the surface of suspended material or associated with bottom sediments.

Analysis of inorganic nitrogen in the laboratory should be started as soon as possible after sample collection to minimize the effects of bacterial transformation and pH changes. Water samples should preferably not be preserved with acid before analysis; rather, the samples should be kept at low temperature (< 4 °C).

### **Data Interpretation**

Occasional increases in the inorganic nitrogen concentration above the Target Water Quality Range (TWQR) are less important than continuously high concentrations. Single measurements of inorganic nitrogen are a poor basis for assessment. Average summer inorganic nitrogen concentrations provide the best basis from which to estimate the likely biological consequences of inorganic nitrogen.

Weekly inorganic nitrogen concentrations, averaged over a period of at least 4 weeks, should be compared with the TWQR.

Any assessment of the influence of inorganic nitrogen concentrations should be coupled to an evaluation of the inorganic nitrogen to inorganic phosphorus ratio. Unimpacted systems

typically have an N:P ratio greater than 25-40 : 1, whilst most impacted (i.e., eutrophic or hypertrophic) systems have an N:P ratio of less than 10:1. At such low N:P ratios, nitrogen fixation is likely to occur; this will provide additional inorganic nitrogen to the system.

In unimpacted, well-oxygenated (dissolved oxygen concentration 80-120 % saturation) waters, most (> 80 %) of the inorganic nitrogen should be present as nitrate; typically, ammonia concentrations will be below 0.1 mg N/R, or less than 20 % of the inorganic nitrogen present.

Where effluent discharges containing high ammonia or nitrate concentrations have impacted on aerobic waters, background inorganic nitrogen concentrations rise. This will usually be accompanied by a decrease in the dissolved oxygen concentration and an increase in the BOD, COD and pH.

## Effects and Criteria

**Norms** Changes in the trophic status accompanied by the growth of algae and other aquatic plants in rivers, lakes and reservoirs, is the norm used to assess the effects of inorganic nitrogen on aquatic ecosystems.

**Effects** Site-specific conditions, especially the availability of phosphorus, are critically important in modifying the influence of inorganic nitrogen on eutrophication. Inorganic nitrogen toxicity is not considered to be important for setting inorganic nitrogen water quality guidelines for protection of aquatic ecosystems.

Inorganic nitrogen concentrations below 0.5 mg N/R are considered to be sufficiently low that they can limit eutrophication and reduce the likelihood of nuisance growths of blue-green algae and other plants. However, in the presence of sufficient available phosphorus, nitrogen-fixing organisms will be able to fix atmospheric nitrogen, thereby compensating for any deficit caused by low inorganic nitrogen concentrations.

The information given in the table below illustrates typical symptoms associated with selected ranges of inorganic nitrogen concentrations, if all other nutrients and environmental conditions are within favourable ranges for the organisms concerned.

Average Summer Inorganic Nitrogen Concentration (mg/l)	Effects
< 0.5	Oligotrophic conditions; usually moderate levels of species diversity; usually low productivity systems with rapid nutrient cycling; no nuisance growth of aquatic plants or the presence of blue-green algal blooms.
0.5 - 2.5	Mesotrophic conditions; usually high levels of species diversity; usually productive systems; nuisance growth of aquatic plants and blooms of blue-green algae; algal blooms seldom toxic.
2.5 - 10	Eutrophic conditions; usually low levels of species diversity; usually highly productive systems, nuisance growth of aquatic plants and blooms of blue-green algae; algal blooms may include species which are toxic to man, livestock and wildlife.
> 10	Hypertrophic conditions; usually very low levels of species diversity; usually very highly productive systems; nuisance growth of aquatic plants and blooms of blue-green algae, often including species which are toxic to man, livestock and wildlife.

### Criteria

The inorganic nitrogen concentration for a specific system must be based on the existing trophic status of the system. It is undesirable to allow inorganic nitrogen concentrations to rise to a level which will change the trophic status of the system. A Target Water Quality Range should be derived only after case- and site-specific studies.

Water Resource	Target Water Quality Range
All surface waters	<p><b>C</b> <i>Inorganic nitrogen concentrations should not be changed by more than 15 % from that of the water body under local unimpacted conditions at any time of the year; and</i></p> <p><b>C</b> <i>The trophic status of the water body should not increase above its present level, though a decrease in trophic status is permissible (see Effects); and</i></p> <p><b>C</b> <i>The amplitude and frequency of natural cycles in inorganic nitrogen concentrations should not be changed.</i></p>

### Modifications

The inorganic nitrogen criteria given in the above table should only be modified in the case of turbid systems. Limited light penetration or increased turbulence will reduce the extent of nuisance algal growths at a given inorganic nitrogen concentration. Nuisance growths of free-floating aquatic macrophytes (e.g. Water Hyacinth) will not be reduced in such cases.

The following conditions should be satisfied before a decision is taken to modify the TWQR for inorganic nitrogen:

- ! Adequate data, covering at least one summer season, are available;
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in inorganic nitrogen concentration in trophic status; and
- ! Account for other contributory factors, such as low inorganic phosphorus concentrations, high turbidity and turbulence, which will reduce the effects of increased inorganic nitrogen.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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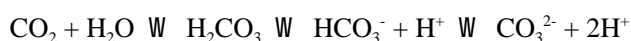
# pH (Acidity and Alkalinity)

## Background Information

**Introduction** The pH value is a measure of the hydrogen ion activity in a water sample. It is mathematically related to hydrogen ion activity according to the expression:  $\text{pH} = -\log_{10} [\text{H}^+]$ , where  $[\text{H}^+]$  is the hydrogen ion activity. The pH of pure water (that is, water containing no solutes) at a temperature of 24 EC is 7.0, the number of  $\text{H}^+$  and  $\text{OH}^-$  ions are equal and the water is therefore electrochemically neutral. As the concentration of hydrogen ions  $[\text{H}^+]$  increases, pH decreases and the solution becomes more acid. As  $[\text{H}^+]$  decreases, pH increases and the solution becomes more basic.

The equilibrium between  $\text{H}^+$  and  $\text{OH}^-$  ions is influenced by reactions with acids and bases introduced into the aqueous system. In general, acidity is the number of  $\text{OH}^-$  ions that have reacted over a given pH range during a base titration, that is, a measure of the water's ability to neutralise base. Similarly, alkalinity is a measure of the number of  $\text{H}^+$  ions that have reacted over a given pH range during an acid titration, that is, a measure of the water's ability to neutralise acid.

Alkalinity is primarily controlled by carbonate species and is therefore usually expressed in terms of equivalence to calcium carbonate ( $\text{CaCO}_3$ ). Briefly, carbon dioxide dissolves in water to form carbonic acid ( $\text{H}_2\text{CO}_3$ ) which, depending on pH, dissociates to form carbonate, bicarbonate and hydrogen ions:



At a pH value of less than 4.0, carbonate species are mostly in the form of  $\text{H}_2\text{CO}_3$ , whilst between pH values of 6.4 and 8.6 they are in the form  $\text{HCO}_3^-$ . As the pH increases to greater than 8.6, so the proportion of  $\text{CO}_3^{2-}$  increases, and above pH 10.3  $\text{CO}_3^{2-}$  predominates.

The rate of change of pH, on addition of a given quantity of an acid or base, depends on the buffering capacity of the water. The most important buffering system in fresh waters is the carbonate-bicarbonate one, and between pH values of 6.4 - 10.3 the hydrogen carbonate ion predominates. In naturally acid waters, complex polyphenolic organics and their salts may form the major buffering system, while aluminium and its salts become effective buffering agents in waters subject to acid precipitation.

**Occurrence** For surface water, pH values typically range between 4 and 11. The relative proportions of the major ions, and in consequence the pH, of natural waters, are determined by geological and atmospheric influences. Most fresh waters, in South Africa, are relatively well buffered and more or less neutral, with pH ranges between 6 and 8. Very dilute sodium-chloride-dominated waters are poorly buffered because they contain virtually no bicarbonate or carbonate. If they drain catchments containing certain types of vegetation (for example, fynbos), the pH may drop as low as 3.9 owing to the influence of organic acids (for example, humic and fulvic acids). In South Africa such conditions are found in parts of the south-western and southern Cape and in the coastal swamp forests of Natal.

The pH may also vary both diurnally and seasonally. Diurnal fluctuations occur in productive systems where the relative rates of photosynthesis and respiration vary over a 24-hour period, because photosynthesis alters the carbonate/bicarbonate equilibrium by removing CO<sub>2</sub> from the water. Seasonal variability is largely related to the hydrological cycle, particularly in rivers draining catchments with vegetation such as fynbos, where the concentration of organic acids is consistently lower during the rainy season.

Industrial activities generally cause acidification rather than alkalization of rivers. Acidification is normally the result of three different types of pollution, namely:

- ! low-pH point-source effluents from industries, such as pulp and paper and tanning and leather industries;
- ! mine drainage, which is nearly always acid, leading to the pH of receiving streams dropping to below 2; and
- ! acid precipitation resulting largely from atmospheric pollution caused by the burning of coal (and subsequent production of sulphur dioxide (SO<sub>2</sub>)) and the exhausts of combustion engines (nitrogen oxides). Both sulphur oxides (SO<sub>x</sub>) and nitrogen oxides (NO<sub>x</sub>) form strong mineral acids when dissolved in water. When acid rain falls on a catchment, the strong acids leach calcium and magnesium from the soil and also interfere with nutrient availability.

Elevated pH values can be caused by increased biological activity in eutrophic systems. The pH values may fluctuate widely from below 6 - above 10 over a 24-hour period as a result of changing rates of photosynthesis and respiration.

## Interactions

The pH is affected by factors such as temperature, the concentrations of inorganic and organic ions, and biological activity. The pH may also affect the availability and toxicity of constituents such as trace metals, non-metallic ions such as ammonium, and essential elements such as selenium.

The pH of fresh water decreases by 0.1 of a unit for a temperature increase of 20 EC, and changes in temperature are therefore unlikely to be of any significance in the measure of pH in aquatic ecosystems.

The toxic effects of acid pH values on fish increase as the concentrations of calcium, chloride and sodium decrease.

Extreme rates photosynthesis, whether natural or as a result of eutrophication, commonly result in very high pH values in standing waters. High rates of consumption of CO<sub>2</sub> during photosynthesis drive the carbonate species equilibrium toward carbonic acid and hence to extremely high pH values (> 10). This process occurs only in the light. At night, the major biotic processes of respiration and decomposition release CO<sub>2</sub>, resulting in a decrease in pH. Very eutrophic systems may, therefore, exhibit significant diel fluctuations in pH. Extreme eutrophication, however, is not common in rivers, where large fluctuations in pH are rare.

In relation to this, high concentrations of dissolved oxygen may decrease the effect of high pH values on fish, particularly if alkaline conditions are the result of intense photosynthetic activity of aquatic plants, which is normally accompanied by high levels of dissolved oxygen.

The buffering capacity affects the rate of change of pH in aquatic systems. In poorly buffered waters, pH can change rapidly, which in turn may have severe effects on the aquatic biota.

The degree of dissociation of weak acids and bases is affected by changes in pH. Thus, pH determines the chemical species of many metals, and thereby alters the availability and toxicity of metals in the aquatic environment. The metals most likely to have increased detrimental environmental effects as a result of lowered pH are silver, aluminium, cadmium, cobalt, copper, mercury, manganese, nickel, lead and zinc.

Non-metallic ions can be similarly affected by changes in pH. Ammonium ions ( $\text{NH}_4^+$ ), which are not toxic, are the main form in which nitrogen is assimilated by aquatic plants. However, at pH values greater than 8, the  $\text{NH}_4^+$  ions are converted to the highly toxic un-ionized ammonia ( $\text{NH}_3$ ).

A decrease in pH can also decrease the solubility of certain essential elements such as selenium. Human populations from areas polluted by acid rain are at risk of being subject to selenium deficiencies.

Since the adsorptive properties of large molecules (such as polyphenolics) and of particulate matter in water depend on their surface charges, altering the pH can also alter the degree to which nutrients such as  $\text{PO}_4^{3-}$ , trace metals and biocides adsorb to these materials. This is of particular significance where lowered pH levels can lead to the release of toxic metals from sediments.

#### **Measurement**

The mean pH is calculated from the mean hydrogen ion ( $[\text{H}^+]$ ) concentration. The accuracy is normally  $\pm 0.1$  of a pH unit. The pH may also be measured by storing water in bottles and using a laboratory pH meter. Such meters have a greater accuracy ( $\pm 0.02$  of a pH unit). Where possible laboratory pH metres should not be used for poorly buffered systems, because the pH can increase by greater than 2 units in stored water samples. Ideally, pH should be measured over a 24-hour period so that diel variations are determined, although "spot" or instantaneous measurements are more often taken. In systems with significant biological activity, however, these measurements are almost valueless unless taken under comparable conditions of ambient light and temperature, preferably at night.

By definition, pH values are calculated arithmetically, and mean values are estimated from the logarithms of the reciprocals. Reporting the range of pH values, in addition to the mean value, is recommended.

#### **Data Interpretation**

Background pH values, in addition to diel and seasonal variability, need to be established if deviation from natural pH values for a particular water body at a particular time is to be assessed. The significance of pH changes to aquatic biota depends on the extent, duration and timing of the changes. Small changes in pH often cause large changes in the concentration of available metallic complexes and can lead to significant increases in the availability and toxicity of most metals.

All pH measurements for the site in question should be within the Target Water Quality Range (TWQR).



## Effects and Criteria

**Norms** The norms for assessing the effects of pH on aquatic ecosystems are:

- ! acute and chronic physiological effects on aquatic organisms;
- ! changes in background site-specific pH values, which result in changes to ecosystem structure and function.

**Effects** A change in pH from that normally encountered in unimpacted streams may have severe effects upon the biota. The extent of acidification or alkalization is important in determining the severity of the effects, which do not vary linearly either with pH or over time. When assessing the potential effect of a change in pH, it is important to note that some streams are naturally more acidic than others and their biotas are often adapted to these conditions.

Direct effects of pH changes consist of alterations in the ionic and osmotic balance of individual organisms, in particular changes in the rate and type of ion exchange across body surfaces. This requires greater energy expenditure, with subsequent effects such as slow growth and reduced fecundity becoming apparent. Aquatic organisms, however, generally have well developed mechanisms for maintaining ionic and osmotic balance. Impacts of indirect pH changes include changes in the availability of toxic substances such as aluminium and ammonia.

### **Acidic pH**

Gradual reductions in pH may result in a change in community structure, with acid-tolerant organisms replacing less tolerant organisms.

Streams with acidic pH values have different periphyton (micro flora and fauna living on solid surfaces) communities and lower overall production compared with less acidic streams.

The discharge of acid wastes into water containing bicarbonate alkalinity results in the formation of free carbon dioxide. If the water is alkaline, free CO<sub>2</sub> may be liberated and be toxic to fish even though the pH does not drop to a level normally considered toxic.

### **Alkaline pH**

Limited information is available on the effects of elevated pH.

**Criteria**

The criteria for pH in aquatic ecosystems are:

Water Resource	Target Water Quality Range
All aquatic ecosystems	C pH values should not be allowed to vary from the range of the background pH values for a specific site and time of day, by > 0.5 of a pH unit, <b>or</b> by > 5 %, <b>and should be assessed by whichever estimate is the more conservative.</b>

The TWQR for pH should be stated in terms of the background site-specific pH regime. In all cases, local background conditions should be determined (including diel and seasonal variability where appropriate) before a water quality objective for a particular aquatic ecosystem is set.

Both spatial and temporal variability in pH need to be determined on a case- and site-specific basis.

Spatial variability includes:

- ! geographic differences; and
- ! longitudinal differences (upper, middle and lower reaches of rivers and streams).  
differences in pH at various depths of water

Temporal variability includes:

- ! diel differences; and
- ! seasonal differences.

**Modifications**

In certain areas, or at certain sites, it may be necessary to modify the pH criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific pH criteria be derived:

- ! Where untested locally important species may be very sensitive to changes in pH;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow and water quality; and
- ! Where background pH values have a range of variation which is greater than that specified by the TWQR.

*Conditions for Modification*

The following conditions should be satisfied before criteria for pH are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, and diel cycles are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in pH range.

All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.

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# Phenol

## Background Information

**Introduction** Phenol is an organic compound consisting of a hydroxyl group attached to a benzene ring.

**Occurrence** In unimpacted water systems phenol is only found in very low concentrations, usually in the Fg/R range or less. Phenol is produced as byproducts in many industrial processes where organic chemicals are used. Phenol is also used as a disinfectant, and as a starting material for a wide variety of synthetic organic processes. Phenolic wastes arise from the distillation of wood and coal, from oil refineries, chemical plants, pulp and paper industries, livestock dips and human and animal wastes. Phenol is often present in sewage at levels between 0.07 - 0.1 mg/R. Phenol is generally biodegraded in water.

**Interactions** Phenol undergoes a wide variety of reactions and transformations. Phenol tends to be very reactive because the hydroxyl group is highly electrophilic. Apart from reacting with other organic compounds in reactions typical of organic alcohols, it may also form organo-metallic complexes. Phenol may also undergo hydrogen displacement reactions with a wide range of organic and inorganic substances, which account for the extensive range of phenol interactions.

The following factors influence the lethal concentration of phenol:

- ! Increase in temperature, increase the resistance of fish to phenol;
- ! Low concentrations of dissolved oxygen increase the lethality of phenol;
- ! The toxicity of phenol decreases with increasing concentrations of total hardness.
- ! The sensitivity to phenols increases with increases in salinity.

**Measurement** The reference method for the determination of phenol is by gas chromatography.

Samples must be collected in prewashed glass containers, pH adjusted to less than 2 (using concentrated sulphuric acid) and dichloromethane added. No head space should be allowed in the bottle and samples can be stored at 4 EC until analysis. Samples must be extracted within seven days and analysed within 30 days of collection.

**Data Interpretation** Ninety percent (90 %) of all phenol measurements for the site in question should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if phenol measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of phenol on aquatic ecosystems are chronic and acute toxic effects of phenol on aquatic organisms.

## Effects

Phenol is thought to be a nerve poison which gives rise to an increased blood supply to the gills and heart cavities. Fish exposed to phenol become excited, swim more rapidly, become more sensitive to stimuli and show increased respiratory rates, colour changes and increased secretion of mucus. Death may occur quickly or follow a period of depressed activity and loss of equilibrium, with occasional convulsions. Fish surviving long-term exposure to low phenol concentrations show general inflammation and necrosis of tissues. This is possibly due to irreversible changes in protein structure. Histopathological changes in the blood, liver, heart, skin and spleen may also occur. Reduction in growth and sexual activity and a loss of balance and co-ordination have been observed in some fish species. Phenol affects some aquatic organisms directly by increasing their demand for oxygen.

Reduction in oxygen consumption occurs in some invertebrates. Avoidance behaviour has been observed in leeches. Phenols have also been shown to reduce rates of photosynthesis in aquatic plants.

## Criteria

The TWQR and criteria for phenol in aquatic ecosystems are:

<b>TWQR and Criteria</b>	<b>Total phenol concentration (µg/l)</b>
<i>Target Water Quality Range (TWQR)</i>	<b># 30</b>
Chronic Effect Value (CEV)	60
Acute Effect Value (AEV)	500

### Note:

- C The data available satisfied the minimum database requirements, therefore no safety factors were applied.

## Modifications

In certain areas, or at certain sites, it may be necessary to modify the phenol criteria provided in this guideline. Where any modification is anticipated, the user of the guidelines must obtain expert advice. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to phenol;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow and water quality; and
- ! Where natural background concentrations may be higher than the TWQR.

### *Conditions for Modification*

The following conditions should be satisfied before criteria for phenols are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in phenol concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

## **Sources of Information**

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# Phosphorus (Inorganic)

## Background Information

**Introduction** Phosphorus can occur in numerous organic and inorganic forms, and may be present in waters as dissolved and particulate species. Elemental phosphorus does not occur in the natural environment. Orthophosphates, polyphosphates, metaphosphates, pyrophosphates and organically bound phosphates are found in natural waters. Of these, orthophosphate species  $\text{H}_2\text{PO}_4$  and  $\text{HPO}_4^{2-}$  are the only forms of soluble inorganic phosphorus directly utilizable by aquatic biota. Soluble Reactive Phosphate (SRP), or orthophosphate, is that phosphorus which is immediately available to aquatic biota which can be transformed into an available form by naturally occurring processes.

The forms of phosphorus in water are continually changing because of processes of decomposition and synthesis between organically bound forms and oxidised inorganic forms. The phosphorus cycle is influenced by the exchange of phosphorus between sedimentary and aqueous compartments. In turn this is affected by various physical, chemical and biological modifying factors such as mineral-water equilibria, water pH values, sorption processes, oxygen-dependent redox interactions, and the activities of living organisms.

Phosphorus is an essential macronutrient, and is accumulated by a variety of living organisms. It has a major role in the building of nucleic acids and in the storage and use of energy in cells. In unimpacted waters it is readily utilized by plants and converted into cell structures by photosynthetic action. Phosphorus is considered to be the principle nutrient controlling the degree of eutrophication in aquatic ecosystems.

**Occurrence** Natural sources of phosphorus include the weathering of rocks and the subsequent leaching of phosphate salts into surface waters, in addition to the decomposition of organic matter. Spatial variation is high and is related to the characteristics of regional geology. Phosphorus levels are generally lowest in mountainous regions of crystalline rocks and levels increase in lowland waters derived from sedimentary deposits.

In South Africa, phosphorus is seldom present in high concentrations in unimpacted surface waters because it is actively taken up by plants. Concentrations between 10 and 50 Fg/R are commonly found, although concentrations as low as 1 Fg/R of soluble inorganic phosphorus may be found in "pristine" waters and as high as 200 mg/R of total phosphorus in some enclosed saline waters.

Elevated levels of phosphorus may result from point-source discharges such as domestic and industrial effluents, and from diffuse sources (non-point sources) in which the phosphorus load is generated by surface and subsurface drainage. Non-point sources include atmospheric precipitation, urban runoff, and drainage from agricultural land, in particular from land on which fertilizers have been applied.

**Interactions** Phosphate is extremely reactive under oxidizing conditions, and interacts with many cations (e.g. Al, Fe, Ca) to form relatively insoluble compounds that precipitate out of water. Availability is also reduced by adsorption of phosphate to inorganic colloids, organic compounds such as humics and particulate material (e.g. clays, carbonates, hydroxides).

The flow regime is a major factor in the mobility, availability and spatial distribution of phosphorus within a river. Settlement of particulate matter and biotic uptake result in the removal of phosphorus from the water column to the sediments, and during periods of low discharge, stream bed sediments act as a sink for phosphorus. During rainfall events, phosphorus levels may be elevated by runoff from the land, and by re-suspension and flushing of deposited material from the river bed to the water column.

Several chemical bonding processes regulate the amount of inorganic phosphorus which is bonded to iron, aluminium, calcium or organic polyphenols and adsorbed onto suspended particulate material. Adsorbed phosphorus may be released from the sediments under conditions of high flow and under anoxic conditions from both sediments and water. The form of phosphorus in natural surface waters and the equilibrium of the different forms, is influenced by pH.

### **Measurement**

Phosphorus concentrations are usually determined as orthophosphates, total inorganic phosphate or total dissolved phosphorus (which includes organically bound phosphorus and all phosphates). The dissolved forms are measured after filtering the sample through a pre-washed 0.45 µm filter. Concentrations of particulate phosphorus can be calculated from the difference between the concentrations of the total and dissolved fractions.

Chemical analysis of phosphorus usually centres around the reactivity of phosphates with molybdate ions. During enzymatic and acidic hydrolysis complexes of phosphorus are converted to phosphate species, which are then measured colorimetrically. Four operational categories of phosphates result; these are soluble reactive P, soluble unreactive P, particulate reactive P, and particulate unreactive P. The most commonly measured is Soluble Reactive Phosphate (SRP).

Analysis of phosphorus in the laboratory should be started as soon as possible after sample collection to minimize the possible effects of bacterial transformation and pH changes. Water samples should preferably not be preserved with acid before analysis; rather, the samples should be kept at low temperature (< 4 °C).

### **Data Interpretation**

Occasional increases in the inorganic phosphorus concentration above the Target Water Quality Range (TWQR) are less important than continuously high concentrations. Single measurements of phosphorus are a poor basis for assessment. Average summer inorganic phosphorus concentrations provide the best basis from which to estimate the likely biological consequences of phosphorus. Weekly inorganic phosphorus concentrations, averaged over a period of at least 4 weeks, should be compared with the TWQR.

Any assessment of the influence of the inorganic phosphorus concentrations should be coupled with an evaluation of the ratio of inorganic nitrogen to inorganic phosphorus. Unimpacted streams typically have an N:P ratio greater than 25 - 40:1, whilst most impacted (i.e., eutrophic or hypertrophic) systems have an N:P ratio of less than 10:1.



## Effects and Criteria

**Norms** Changes in trophic status accompanied by the growth of algae and other aquatic plants in rivers, lakes and reservoirs, are the norms used to assess the effects of inorganic phosphorus on aquatic ecosystems.

**Effects** The most significant effect of elevated phosphorus concentrations is its stimulation of the growth of aquatic plants. Both phosphorus and nitrogen limit plant growth, and of these, phosphorus is likely to be more limiting in fresh water. The effect is dependent on the form of phosphorus present in the water, since not all forms are available for uptake by plants. Other factors, such as water temperature, light and the availability of other nutrients, also play an important role in limiting plant growth.

Inorganic phosphorus concentrations of less than 5 Fg P/R are considered to be sufficiently low to reduce the likelihood of algal and other plant growth.

The information given in the table below illustrates typical symptoms associated with selected ranges of inorganic phosphorus concentrations, if all other nutrients and environmental conditions are within favourable ranges for the organisms concerned.

<b>Average Summer Inorganic Phosphorus Concentration (Fg/R)</b>	<b>Effects</b>
< 5	Oligotrophic conditions; usually moderate levels of species diversity; usually low productivity systems with rapid nutrient cycling; no nuisance growth of aquatic plants or blue-green algae.
5 - 25	Mesotrophic conditions; usually high levels of species diversity; usually productive systems; nuisance growth of aquatic plants and blooms of blue-green algae; algal blooms seldom toxic.
25 - 250	Eutrophic conditions; usually low levels of species diversity; usually highly productive systems, with nuisance growth of aquatic plants and blooms of blue-green algae; algal blooms may include species which are toxic to man, livestock and wildlife.
> 250	Hypertrophic conditions; usually very low levels of species diversity; usually very highly productive systems; nuisance growth of aquatic plants and blooms of blue-green algae, often including species which are toxic to man, livestock and wildlife.

**Criteria** The inorganic phosphorus concentration for a specific system must be based on the existing trophic status of the system. It is undesirable to allow inorganic phosphorus concentrations to rise to a level which will change the trophic status of the system. A Target Water Quality Range should be derived only after case- or site-specific studies.

Water Resource	Target Water Quality Range
All surface waters	<p>C Inorganic phosphorus concentrations should not be changed by &gt; 15 % from that of the water body under local, unimpacted conditions at any time of the year; <b>and</b></p> <p>C The trophic status of the water body should not increase above its present level, though a <i>decrease</i> in trophic status is permissible (see <i>Effects</i>); <b>and</b></p> <p>C The amplitude and frequency of natural cycles in inorganic phosphorus concentrations should not be changed.</p>

### Modifications

The inorganic phosphorus criteria given in the above table may be modified upwards in the case of turbid systems. Limited light penetration or increased turbulence will reduce the extent and density of algal growths at a given inorganic phosphorus concentration. Growth of free-floating aquatic macrophytes (e.g. Water Hyacinth) will not be reduced in such cases.

The following conditions should be satisfied before a decision is taken to modify the Target Water Quality Range for inorganic phosphorus:

- ! Adequate data (covering at least one summer season) are available;
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in inorganic phosphorus concentration in trophic status; and
- ! Other contributory factors, such as low inorganic nitrogen concentrations, high turbidity and turbulence, will reduce the effects of increased inorganic phosphorus.

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# Selenium

## Background Information

**Introduction** Selenium is a non-metallic element similar to sulphur. Selenium occurs in five oxidation states, namely, -II, 0, II, IV and VI, of which the tetravalent state is the most common. Small quantities of selenium are essential to animals and bacteria, where it is important in certain enzyme systems, but selenium is apparently not essential for plants.

**Occurrence** Selenium occurs naturally as ferric selenite, calcium selenate, as elemental selenium and in organic compounds derived from decayed plant tissue. Although selenium occurs in some natural waters, it is usually in nanogram quantities.

Selenium may occur at increased concentrations in water bodies subject to industrial pollution, or in the vicinity of industrial activities utilising or discharging selenium or selenium compounds. Industries that use selenium in their processes, or in their products, include:

- ! the paint industry;
- ! the food processing industry;
- ! the steel industry;
- ! vehicle and aircraft plating industries;
- ! the pesticide industry;
- ! the glass and ceramics industries;
- ! the dye manufacturing industry;
- ! the rubber industry; and
- ! the metal alloy and electrical apparatus industries.

**Interactions** The toxicity of selenium to some fish species is directly related to water temperature. A decrease in water pH decreases the solubility of selenium and hence, decreases in pH have very little impact on the toxicity of selenium. Selenium is antagonistic to the toxic effects caused by mercury, thallium and silver. Selenium is also antagonistic to cadmium toxicity in green algae.

**Measurement** The derivation of the selenium criteria is based on toxicity data for **dissolved selenium**. Because of the extreme toxicity of selenium, a precautionary approach is adopted, and, it is recommended that the methods used measure total selenium, i.e. the **dissolved** and the **particulate (acid soluble)** forms of selenium. The reference method for the determination of selenium is by atomic absorption spectrometry. Prior to analysis, digestion of the sample followed by reduction of Se(VI) to Se(IV) with hydrochloric acid and the formation of selenium hydride using borohydride, is required.

Ideally, samples should be filtered at the time of collection through a 0.45 Fm membrane filter and thereafter preserved with nitric acid: (1:100 (v:v)) sample. Samples that cannot be adequately filtered should not be preserved with acid. **Where the detection limit is above the values given in the criteria, standard sample concentration procedures need to be used.**

As with all trace metal determinations, care must be taken to prevent contamination of water samples. Polyethylene bottles which have been suitably pre-cleaned to remove metal contaminants are required.

**Data Interpretation** Ninety percent (90 %) of all total selenium measurements for a site in question should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if selenium measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of total selenium on aquatic ecosystems are chronic and acute toxic effects of selenium on aquatic organisms.

**Effects** Because these are chemical similarities between selenium and sulphur, selenium can replace sulphur in some biologically important substances and thereby cause toxic effects. The toxic effects are similar in cold- and warm-water adapted fish.

Selenium toxicity effects observed in fish include changes in feeding behaviour and equilibrium, pathological changes, deformities, haematological (blood) changes and death. Fish are generally less sensitive to selenium than are invertebrates. Toxic effects of selenium that have been recorded in invertebrates include immobilisation, reduced survival and reduced reproduction.

Selenium is passed up through the aquatic food chain and accumulates in the liver of mammals and fish; it may therefore pose a threat to predators. Selenium undergoes biological methylation in sediments, a process similar to mercury methylation. Selenomethionine is ten times more toxic than inorganic selenium.

**Criteria** The TWQR and criteria for total selenium in aquatic ecosystems are:

TWQR and Criteria	Selenium concentration (µg/l)
<i>Target Water Quality Range (TWQR)</i>	# 2
Chronic Effect Value (CEV)	5
Acute Effect Value (AEV)	30

**Note:**

C The data available **did not** satisfy the minimum acute database requirement. A safety factor of 3 was used for the derivation of the AEV.

**Modifications** In certain areas, or at certain sites, it may be necessary to modify the selenium criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to selenium;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow, water quality and temperature; and
- ! Where natural background selenium concentrations are higher than the TWQR.

#### *Conditions for Modification*

The following conditions should be satisfied before criteria for selenium are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in selenium concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Temperature

## Background Information

**Introduction** Temperature may be defined as the condition of a body that determines the transfer of heat to, or from, other bodies. As temperature increases viscosity, surface tension, compressibility, specific heat, the ionization constant and the latent heat of vaporization decrease, whereas thermal conductivity and vapour pressure increase. The solubilities of the following gasses, H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and O<sub>2</sub> decrease with increasing temperature.

Temperature plays an important role in water by affecting the rates of chemical reactions and therefore also the metabolic rates of organisms. Temperature is therefore one of the major factors controlling the distribution of aquatic organisms. Natural variations in water temperature occur in response to seasonal and diel cycles and organisms use these changes as cues for activities such as migration, emergence and spawning. Artificially-induced changes in water temperature can thus impact on individual organisms and on entire aquatic communities.

**Occurrence** The temperatures of inland waters in South Africa generally range from 5 - 30 EC. Thermal characteristics of running waters are dependent on various features of the region and catchment area, including:

- ! the latitude and altitude of the river;
- ! hydrological factors such as the source of water, the relative contribution of ground water, and the rate of flow or discharge;
- ! climatic factors such as air temperature, cloud cover, wind speed, vapour pressure and precipitation events; and
- ! structural characteristics of the river and catchment area, including topographic features, vegetation cover, channel form, water volume, depth and turbidity.

Surface waters exhibit daily and annual periodicity patterns, in addition to longitudinal changes along a river course, and vertical stratification in deeper waters. The minimum and maximum temperatures, and temperature ranges vary depending on the factors mentioned above.

Anthropogenic sources which result in changes in water temperature include:

- ! discharge of heated industrial effluents;
- ! discharge of heated effluents below power stations;
- ! heated return-flows of irrigation water;
- ! removal of riparian vegetation cover, and thereby an increase in the amount of solar radiation reaching the water;
- ! inter-basin water transfers; and
- ! discharge of water from impoundments.

**Interactions** Higher temperatures reduce the solubility of dissolved oxygen in water, decreasing its concentration and thus its availability to aquatic organisms.

If the organic load into a water body is high, oxygen depletion accelerates microbial activity which takes place at higher water temperatures.

Elevated water temperatures increase metabolic rates, including respiration and thus oxygen demand, of aquatic organisms. Oxygen demand therefore increases leading to a decrease in dissolved oxygen supply.

Unnaturally low temperatures, such as those induced by bottom releases of dam water, may induce fish tolerance, a river reach or suppress normal activities such as, spawning.

The toxicity of most substances, and the vulnerability of organisms to these substances, are intensified as water temperature increases.

### **Measurement**

Water temperature is measured *in situ* using either a thermometer or a thermistor, and is expressed as the Celsius (EC). Ideally, water temperature should be recorded over a 24-hour period to establish diel variation, and in each season so that seasonal differences may be determined. Minimum-maximum thermometers enable the minimum and maximum values within a 24-hour period to be recorded. "Spot" or instantaneous measurements are of little use unless taken at exactly the same time of day at each site, or used to contribute to the calculation of the seasonal minimum and maximum temperatures.

### **Data Interpretation**

Changes in water temperatures that are unrelated to natural variation (e.g., diel and seasonal patterns) may have an effect at the organism, species and/or community level. Background temperature(s) needs to be established if deviation from "natural" temperature(s) for a particular water body at a particular time are to be assessed.

The effects of temperature changes on aquatic organisms depends on the extent, duration and timing of these changes. Relatively small temperature changes, if maintained for a period of time, may lead to alterations in community composition, as a result of the differential optimal temperatures of the respective organisms. Large, rapid shifts in temperature are lethal to aquatic organisms.

All water temperature measurements for the site in question should be within the Target Water Quality Range (TWQR).

## **Effects and Criteria**

### **Norms**

The norms for assessing the effect of water temperature on aquatic ecosystems are:

- ! acute and chronic physiological effects on aquatic organisms; and
- ! the effects of changes from *natural* site-specific temperature regimes which result in changes to ecosystem structure and function.

### **Effects**

The effects of temperature on aquatic organisms have been the subject of a number of literature reviews, predominantly conducted in the northern hemisphere. There is however, little information on the thermal tolerances of South African aquatic organisms, or their responses to temperature change.

Aquatic organisms have upper and lower thermal tolerance limits, optimal temperatures for growth, a preferred temperature range in thermal gradients, and temperature limitations for migration, spawning and egg incubation.



All organisms associated with freshwater, excluding birds and mammals, are poikilothermic. In other words, they are unable to control their body temperatures and are therefore highly dependent on ambient water temperature and very susceptible to changes in water temperature. Consequently, rapid changes in temperature may severely affect aquatic organisms and lead to mass mortality. Causes of thermal mortality in fish from acute exposure to elevated temperatures are basically the result of metabolic malfunctions (including fluid-electrolyte imbalance, alterations in gaseous exchange and osmoregulation, hypoxia of the central nervous system and inactivation of enzyme systems).

Less severe temperature changes in water bodies may have sub-lethal effects or lead to an alteration in the existing aquatic community. The qualitative and quantitative composition of the biota can change as a result of population shifts caused by the disappearance of stenothermal species (organisms adapted to a very narrow range of temperatures) from heated waters, and replacement by heat-tolerant species which increase in number and supplant the original species in the ecosystem.

Many organisms have life cycles in which temperature acts as a cue for the timing of migration, spawning or emergence. Artificial changes in temperature can interfere with temperature cues, thereby altering normal development.

**Criteria**

The water temperature TWQRs for aquatic ecosystems are:

Water Resource	Target Water Quality Range (TWQR)
All aquatic ecosystems	C Water temperature should not be allowed to vary from the background average daily water temperature considered to be normal for that specific site and time of day, by > 2 EC, <b>or</b> by > 10 %, <b>whichever estimate is the more conservative.</b>

**Note:**

C The TWQR for water temperature should be stated in terms of the case- and site-specific "natural" temperature regime. In all cases, local conditions should be determined (including diel and seasonal variability) before a water quality objective for an aquatic ecosystem is set. The 90th and 10th percentile values should be used to establish the "natural" temperature range.

Both spatial and temporal variability in temperature need to be taken into account.

Spatial variability includes:

- ! geographic differences;
- ! longitudinal differences (upper, middle and lower reaches of rivers and streams); and
- ! temperature differences with depth.

Temporal variability includes:

- ! diel differences;
- ! seasonal differences; and
- ! rapid rates of temperature change.

## **Modifications**

In certain areas, or at certain sites, it may be necessary to modify the water temperature criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to changes in water temperature;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow and water quality; and
- ! Where natural background water temperatures have a range of variation which is greater than that specified by the TWQR.

### *Conditions for Modification*

The following conditions should be satisfied before criteria for water temperature are altered:

- ! Adequate site-specific data, covering at least one annual cycle and several diel cycles, are available;
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in water temperature range.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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# Total Dissolved Salts/Solids

## Background Information

**Introduction** The total dissolved solids concentration, is a measure of the quantity of all compounds dissolved in water. The total dissolved salts concentration is a measure of the quantity of all dissolved compounds in water that carry an electrical charge. Since most dissolved substances in water carry an electrical charge, the TDSalts concentration is usually, used as an estimate of the concentration of total dissolved solids in the water.

The TDSalts concentration is directly proportional to the electrical conductivity (EC) of water. Because EC is much easier to measure than TDSalts, it is routinely used as an estimate of the TDSalts concentration. Therefore, it has become common practise to use the total dissolved salts concentration, as a measure for the total dissolved solids.

Electrical conductivity (EC) is a measure of the ability of water to conduct an electrical current. This ability is a result of the presence in water of ions such as carbonate, bicarbonate, chloride, sulphate, nitrate, sodium, potassium, calcium and magnesium, all of which carry an electrical charge. Many organic compounds dissolved in water do not dissociate into ions (ionise), and consequently they do not affect the EC.

**Occurrence** Natural waters contain varying quantities of TDS as a consequence of the dissolution of minerals in rocks, soils and decomposing plant material, the TDS concentrations of natural waters therefore being dependent at least in part on the characteristics of the geological formations which the water has been in contact with. The TDS concentration also depends on physical processes such as evaporation and rainfall.

The TDS concentrations are generally

- ! Low in rainwater, less than 1 mg/R;
- ! Low in water in contact with granite, siliceous sand and well-leached soils, less than 30 mg/R;
- ! Greater than 65 mg/R in water in contact with precambrian shield areas; and
- ! In the range of 200 - 1 100 mg/R in water in contact with palaeozoic and mesozoic sedimentary rock formations.
- ! High as a result of evapoconcentration, usually greater than 1 100 mg/mR.

Salts accumulate as water moves downstream because salts are continuously being added through natural and anthropogenic sources whilst very little is removed by precipitation or natural processes. Domestic and industrial effluent discharges and surface runoff from urban, industrial and cultivated areas are examples of the types of sources that may contribute to increased TDS concentrations. Evaporation also leads to an increase in the total salts.

**Interactions** The effects of the TDS are governed by the constituent inorganic salts. The proportional concentrations of the major ions affect the buffering capacity of the water and hence the metabolism of organisms. Secondary effects include those on water chemistry, which in turn affect the fate and impact on the aquatic environment of other chemical constituents or contaminants. Most commonly, the relative concentrations of the major ions tends to be:

- ! Cations:  $\text{Na}^+ > \text{Ca}^{2+}/\text{Mg}^{2+} > \text{K}^+$
- ! Anions:  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$

## Measurement

The TDS content of a water sample is measured gravimetrically. The water sample should be filtered through a 0.45 µm pore size filter, and the filtrate evaporated to dryness at 60 EC. The mass of the residue will approximate the TDS present in the filtrate. If the filtrate is evaporated at a high temperature (> 100 EC), some carbonate and all organic dissolved solids will be lost; at lower evaporation temperatures (65 - 85 EC), virtually no material is lost.

Electrical conductivity (EC) is a rapid and useful surrogate measure of the TDS content of those waters with a low organic content. Electrical Conductivity is determined by measuring the electrical conductance of water and is usually expressed in units of milli-Siemens per metre (mS/m). Owing to the dependence of EC measurements on temperature, EC measurements are reported at a standard reference temperature of 25 EC. Conversion factors for different temperatures are given in standard textbooks.

The TDS concentration of most natural waters can be estimated by multiplying EC by a constant. If EC is measured in units of mS/m and the TDS concentration is to be expressed in mg/l, this factor generally falls in the range 5.5 - 7.5. The following general relationship is commonly used as an approximation for TDS concentrations from EC for South African inland waters:

$$\text{TDS (mg/l)} = \text{EC (mS/m at 25 EC)} \times 6.5$$

The exact value of the conversion factor depends on the ratio of divalent to monovalent ions and the organic and inorganic content. Waters with a low or high pH typically require a conversion factor greater than 6.5. If very accurate estimates of the TDS concentration from EC measurements are required then the conversion factor should be experimentally determined for each specific site and for specific runoff event.

## Data Interpretation

Changes in the EC values provide useful and rapid estimates of changes in the TDS concentration, once the relationship between EC and TDS has been established for a particular water body. However, changes in EC values provide no information on the changes in the proportional concentrations of the major ions. Similarly, the relationship between TDS and EC will not reflect changes in the concentration of minor ions and nutrients such as phosphate and nitrate.

Changes in the long-term shifts in the TDS concentration are more important than single values. Therefore, mean or seasonal mean values for the concentrations in a data set should be compared with the Target Water Quality Range (TWQR).

## Effects and Criteria

### Norms

The norms for assessing the effects of the total dissolved solids on aquatic ecosystems are:

- ! chronic and acute physiological effects on aquatic biota; and
- ! changes in the "natural" site-specific TDS levels which cause changes in ecosystem structure and function.

## Effects

Plants and animals possess a wide range of physiological mechanisms and adaptations to maintain the necessary balance of water and dissolved ions in cells and tissues. This ability is extremely important in any consideration of the effects of changes in total dissolved solids on aquatic organisms. The individual ions making up the TDS also exert physiological effects on aquatic organisms.

Changes in the concentration of the total dissolved solids can affect aquatic organisms at three levels, namely:

- ! effects on, and adaptations of, individual species;
- ! effects on community structure; and
- ! effects on microbial and ecological processes such as rates of metabolism and nutrient cycling.

The rate of change of the TDS concentration, and the duration of change, appears to be more important than absolute changes in the TDS concentration, particularly in systems where the organisms may not be adapted to fluctuating levels of TDS. Seasonal timing of the change in TDS concentration may also have important synergistic effects with water temperature on the total community composition and functioning. Organisms adapted to low-salinity habitats are generally sensitive to changes in the TDS concentration.

## Criteria

The TWQR for TDS is stated in terms of case- and site-specific TDS concentrations. In all cases, local conditions should be determined (i.e. TDS concentrations, variability and seasonal changes) before water quality criteria are set.

Water Resource	Target Water Quality Range
All inland waters	<ul style="list-style-type: none"><li>Ⓒ TDS concentrations should not be changed by &gt; 15 % from the normal cycles of the water body under unimpacted conditions at any time of the year; <b>and</b></li><li>Ⓒ The amplitude and frequency of natural cycles in TDS concentrations should not be changed.</li></ul>

## Modifications

Modifications can be considered where case- and site-specific measurements indicate the TWQR to be too stringent or inappropriate. In particular, site-specific derivation of TDS criteria which are different from the TWQR should be considered in the cases of:

- ! naturally saline systems;
- ! rivers or streams which have been subjected to increased TDS concentrations over a long period of time, such that their original biota have either adapted to the new conditions or have been replaced by more salt-tolerant species; and
- ! where endemic or introduced organisms might be more sensitive to changes in TDS concentrations and may therefore have more stringent TDS requirements, e.g., in unimpacted cold-water habitats.

The following conditions should be satisfied before the TWQR for TDS concentrations is altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in TDS concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

## Sources of Information

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# Total Suspended Solids

## Background Information

**Introduction** The total suspended solids (TSS) concentration is a measure of the amount of material suspended in water. This definition includes a wide range of sizes of material, from colloids (0.1 Fm) through to large organic and inorganic particulates.

The concentration of suspended solids increases with the discharge of sediment washed into rivers due to rainfall and resuspension of deposited sediment. As flow decreases the suspended solids settle out, the rate of which is dependent on particle size and the hydrodynamics of the water body.

Water turbidity in the southern hemisphere is generally considered to be equivalent to some measure of the concentration of suspended solids. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through a water sample. The scattering of light is caused by suspended matter such as clay, silt and finely divided organic material, while the absorption of light is caused by inorganic matter, plankton and other microscopic organisms and soluble coloured organic compounds, such as fulvic, humic and tannic acids.

Correlation of turbidity with the concentration of suspended solids (mass/unit volume) is difficult because the size, shape and refractive index of particulates affects the light scattering properties of the suspension. The relationship between turbidity and suspended solids may however, be determined on a site-specific basis. A turbidimeter, calibrated with consideration of the site-specific characteristics, may then potentially be used to monitor suspended solids.

**Occurrence** Natural variations in rivers often result in changes in the TSS, the extent of which is governed by the hydrology and geomorphology of a particular region. In South Africa, all rivers, except some in the Natal foothills of the Drakensberg and in the south-western Cape, become highly turbid and laden with suspended solids during the rainy season. The major part of suspended material found in most natural waters is made up of soil particles derived from land surfaces. Erosion of land surfaces by wind and rain is a continuous and natural process. However, land use practices such as overgrazing, non-contour ploughing, removal of riparian vegetation and forestry operations accelerate erosion and result in increased loads of suspended solids in rivers.

Increases in total suspended solids may also result from anthropogenic sources, including:

- ! discharge of domestic sewage,
- ! discharge of industrial effluents (such as the pulp/papermill, china-clay, and brick and pottery industries),
- ! discharge from mining operations,
- ! fish-farm effluents (mostly organic suspended solids) and
- ! physical perturbations from road, bridge and dam construction.

**Interactions** An increase in the TSS may lead to a decrease in water temperature as more heat is reflected from the surface and less absorbed by the water. This may affect temperature-sensitive organisms.



Suspended inorganic material carries an electrical charge. The result is that a variety of dissolved substances, including nutrients, trace metal ions, and organic biocides, may become adsorbed onto the surfaces of these particles. Substances adsorbed onto particles are not available, and this may be advantageous in the case of toxic trace metal ions, but disadvantageous, in the case of nutrients.

If the suspended solids consist largely of organic solids, then the concentration of dissolved oxygen in the water body may decrease on oxidation of the solids by micro-organisms.

## Measurement

Turbidity may be measured in the field nephelometrically using a portable turbidimeter. Field measurements of turbidity are recommended because of rapid changes that may occur in stored water samples.

The nephelometric method is based on a comparison of the intensity of light scattered by the sample under defined conditions, with the intensity of light scattered by a standard reference suspension under the same conditions. The higher the intensity of scattered light, the higher the turbidity. A turbidimeter consists of a nephelometer with a light source and one or more photoelectric detectors. Turbidity values are expressed in Nephelometric Turbidity Units (NTUs).

The TSS concentration of a water sample can be measured gravimetrically and expressed as mg/l. A measured volume of water is filtered through a pre-weighed, pre-dried filter paper (0.45 µm pore size), which is dried at 60 °C for 48 hours and then re-weighed.

## Data Interpretation

All TSS measurements for the site in question should be within the Target Water Quality Range (TWQR). Changes in the TSS concentration that are unrelated to natural variation (e.g. diel and seasonal patterns) may have effects on organisms, species and communities. Background TSS levels need to be established if deviations from such "natural" levels for a particular water body at a particular time are assessed. Elevated levels of turbidity and TSS will have a greater effect in areas which have lower background TSS levels, for example, upper mountain catchment regions.

The significance to aquatic biota of changes in the TSS depends on the extent, duration, frequency and timing of these changes. If increases in TSS from anthropogenic sources result in the same amplitude as that of natural flooding, then these increases may well be tolerated by aquatic ecosystems. Continuous high-level inputs, may however have serious consequences.

## Effects and Criteria

### Norms

The norms for assessing the effects of the TSS concentration on aquatic ecosystems are:

- ! acute and chronic physiological effects on aquatic organisms;
- ! changes from "natural" site-specific TSS levels that cause changes to ecosystem structure and functioning.

### Effects

In turbid waters light penetration is reduced, leading to a decrease in photosynthesis. The resultant decrease in primary production reduces food availability for aquatic organisms higher up the food chain. Suspended solids may interfere with the feeding mechanisms of filter-feeding organisms such as certain macroinvertebrates, and the gill functioning, foraging efficiency (due to visual disturbances) and growth of fish.

Suspended solids that settle out may smother or abrade benthic plants and animals, and may result in changes to the nature of the substratum. This may then lead to changes in the structure of the biotic community by the decline of these organisms, through the replacement with organisms which burrow in soft sediments. Sensitive species may be permanently eliminated if the source of the suspended solids is not removed.

The recovery of a stream from sediment deposition is dependent on the elimination of the sediment source and the potential for the deposited material to be flushed out by stream flow.

**Criteria**

The TWQR for TSS in aquatic ecosystems are as follows:

<b>All Aquatic Ecosystems</b>	<b><i>Target Water Quality Range</i></b>
Background TSS concentrations are < 100 mg/R	C Any increase in TSS concentrations must be limited to < 10 % of the background TSS concentrations at a specific site and time.

**Modifications**

In certain areas, or at certain sites, it may be necessary to modify the TSS criteria. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where untested locally important species may be very sensitive to TSS;
- ! Where aquatic organisms in field situations may be stressed by diseases, parasites, predators, other contaminants, contaminated or insufficient food, and fluctuating or extreme conditions of flow and water quality; and
- ! Where natural background TSS concentrations are higher than the TWQR.

*Conditions for Modification*

The following conditions should be satisfied before criteria for turbidity or TSS are altered:

- ! Adequate site-specific analytical data, covering at least one annual cycle, are available;
- ! A site-specific study demonstrate that the particle size distribution of any additional TSS material will not significantly change the particle size distribution on the bed of the recipient system; and
- ! Site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in TSS concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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## Background Information

**Introduction** Zinc, a metallic element, is an essential micronutrient for all organisms as it forms the active site in various metalloenzymes. Zinc occurs in two oxidation states in aquatic ecosystems, namely as the metal, and as zinc(II).

In aquatic ecosystems the zinc(II) ion is toxic to fish and aquatic organisms at relatively low concentrations.

**Occurrence** Zinc occurs in rocks and ores and is readily refined into a pure stable metal. It can enter aquatic ecosystems through both natural processes such as weathering and erosion, and through industrial activity.

In aqueous solutions zinc is amphoteric, that is, it dissolves in acids to form the hydrated cations  $Zn^{2+}$  and in strong bases it forms zincate anions (probably of the form  $Zn(OH)_4^{2-}$ ). Organozinc complexes and compounds can also be formed. In most natural waters zinc exists mainly as the divalent cation, which is the potentially toxic form. The proportion of other forms such as inorganic compounds like  $ZnCO_3$ ; stable organic complexes like Zn-cysteinate; or colloids like  $Zn^{2+}$ -clay or  $Zn^{2+}$ -humic acid, depends on the chemistry of the water. The greatest dissolved zinc concentrations will occur in water with low pH, low alkalinity and high ionic strength. Chemical speciation of zinc is affected primarily by pH and alkalinity.

Soluble zinc salts (for example, zinc chloride and zinc sulphate) or insoluble precipitates of zinc salts (for example, zinc carbonate, zinc oxide and zinc sulphide) occur readily in industrial wastes. The carbonate, hydroxide and oxide forms of zinc are relatively resistant to corrosion and are used extensively in the following industries:

- ! metal galvanising;
- ! dye manufacture and processing;
- ! pigments (paints and cosmetics);
- ! pharmaceuticals; and
- ! fertilizer and insecticide.

**Interactions** A variety of interactions affect the toxicity of zinc in aquatic ecosystems. The toxicity of zinc is reduced in hard waters. In animals zinc is a metabolic antagonist of cadmium and its toxicity is reduced in the presence of zinc. Copper increases the zinc toxicity in soft, but not in hard water, and zinc toxicity increases at lower oxygen concentrations. Zinc is synergistically toxic with cyanide.

Although zinc toxicity can primarily be ascribed to the zinc(II) ion, toxicity has been associated with particular zinc salts, namely zinc chloride and zinc sulphate. In cases of toxicity associated with zinc nitrate, *Daphnia* was more resilient than fish or tadpoles.

Adsorption of zinc by hydrous metal oxides, clay minerals and organic materials is an important process in aquatic ecosystems since it affects the bio-availability and toxicity of zinc.

**Measurement** Zinc criteria for aquatic ecosystems are based on **dissolved zinc concentrations**. The reference methods for the determination of the total zinc concentration is by atomic absorption spectrophotometry (AAS) and inductively coupled plasma (ICP) emission spectrophotometry.

As with all trace metal determinations, care must be taken to prevent contamination of water samples. Polyethylene bottle which have been suitably pre-cleaned to remove metal contaminants are required.

**Data Interpretation** Ninety percent (90 %) of all dissolved zinc measurements for the site in question should be within the Target Water Quality Range (TWQR). All measurements should be below the Chronic Effect Value (CEV) to ensure protection of aquatic ecosystems. In the case of accidental spills, chronic and acute toxicity effects will occur if zinc measurements exceed the Acute Effect Value (AEV).

## Effects and Criteria

**Norms** The norms for assessing the effects of zinc on aquatic ecosystems are chronic and acute toxic effects of zinc on aquatic organisms.

**Effects** Zinc is a trace metal which is also an essential micronutrient in all organisms. The requirement for trace elements frequently varies substantially between species, but the optimal concentration range is generally narrow. Severe imbalances can cause death, whereas marginal imbalances contribute to reduced fitness.

The lethal effect of zinc on fish is thought to be from the formation of insoluble compounds in the mucus covering the gills. Sub-lethal concentrations at which toxic effects are evident depend on the concentration ratio of zinc to copper, since zinc interferes with copper absorption. Observed symptoms include depressed white blood cell-thrombocyte counts. Observed effects of prolonged exposure to sublethal concentrations of zinc in fish fry include oedema and liver necrosis.

Although invertebrate responses to zinc toxicity vary, molluscs are generally more resilient than are other organisms. Sub-lethal effects include reduced rates of shell growth, oxygen uptake and larval development. Algal photosynthesis can be inhibited by zinc.

**Criteria** The TWQR and criteria for dissolved zinc in aquatic ecosystems are:

<b>TWQR and Criteria</b>	<b>Zinc concentration (<math>\mu\text{g}/\text{R}</math>)</b>
<i>Target Water Quality Range (TWQR)</i>	<b># 2</b>
Chronic Effect Value (CEV)	3.6
Acute Effect Value (AEV)	36

**Note:**

C The data available **did not** satisfy the minimum chronic database requirement. A safety factor of 10 was used for the derivation of the CEV.

## Modifications

In certain areas, or at certain sites, it may be necessary to modify the zinc criteria provided in this guideline. Where any modification is anticipated, *the user of the guidelines must obtain expert advice*. All modifications must afford the same level of protection to aquatic ecosystems as stipulated by the criteria given in this guideline.

The following circumstances may require that case- and site-specific criteria be derived:

- ! Where the pH, alkalinity and ionic strength of local water may significantly alter zinc solubility;
- ! Where local water quality is characterised by ligands that variably affect zinc(II) ion availability; and
- ! Where a larger proportion of the dissolved zinc will be bound to suspended particles and thus not exert toxic effects on aquatic organisms.

### *Conditions for Modifications*

The following conditions should be satisfied before the criteria for zinc are altered:

- ! adequate site-specific analytical data, covering at least one annual cycle, are available;
- ! site-specific studies demonstrate that there are no adverse effects on the ecosystem for the proposed changes in zinc concentrations.

*All modifications that result in criteria that are higher than those specified here are subject to approval by the Department of Water Affairs and Forestry.*

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## **Chapter 7**

### **Appendices and Glossaries**



## APPENDIX 1

### LIST OF CONSTITUENTS ADDRESSED IN THE FIRST EDITION OF THE SOUTH AFRICAN WATER QUALITY GUIDELINES FOR AQUATIC ECOSYSTEMS

#### Toxic Constituents

##### *Inorganic*

Aluminium  
Ammonia  
Arsenic  
Cadmium  
Chlorine  
Chromium(III)  
Chromium(VI)  
Copper  
Cyanide  
Fluoride  
Iron  
Lead  
Manganese  
Mercury  
Selenium  
Zinc

##### *Organic*

Atrazine  
Endosulfan  
Phenol

#### System Variables

Dissolved Oxygen  
pH  
Temperature  
Total Suspended Solids/Salts (TSS)

#### Non-Toxic Inorganic Constituents

Total Dissolved Solids (TDS)

#### Nutrients

Inorganic Nitrogen (Nitrite + Nitrate + Ammonium)  
Inorganic Phosphorus (Ortho-Phosphate)

## APPENDIX 2

### DERIVATION OF CRITERIA FOR TOXIC CONSTITUENTS

*The methods described in this appendix were used in the derivation of the Acute Effect Values and the Chronic Effect Values given in these guidelines*

#### INTRODUCTION

#### DATA BASE REQUIREMENTS

##### **Final values used in the derivation of criteria**

##### **Procedures for calculating values used in the derivation of criteria**

*Final Acute Value*

*Final Chronic Value*

*Final Plant Value*

*Rounding off*

#### APPLICATION OF SAFETY FACTORS

#### EXAMPLE :

##### **Deriving criteria for cadmium**

**The information contained in appendix 2 has been extracted from:**

Roux, D.J., Jooste, S.H.J. and MacKay, H.M. (In press) Substance-specific water quality criteria for the protection of South African freshwater ecosystems: methods for derivation and initial results for some inorganic toxic substances. *South African Journal of Science*.

## Introduction

The derivation of a CEV and AEV for a particular toxic constituent entails a rigorous calculation procedure, based largely on the methodology developed by the United States Environmental Protection Agency. The procedure relies upon data generated from the results of toxicity tests on a representative range of aquatic organisms. Since the aim was to produce criteria specific to the South African situation, local source documents and research findings were used where possible. Locally derived data are, however, very limited and lacking for many indigenous species, especially fish. This study subsequently had to rely mainly on international toxicity data bases, of which the ASTER and AQUIRE data bases formed the main sources. ASTER and AQUIRE are being maintained by the United States EPA. These data bases contain data obtained from peer reviewed publications, with enough supporting information to indicate that acceptable test procedures were employed and that the results are reliable.

## Data Base Requirements

Quantity and quality of laboratory toxicity data play an important role in determining whether numerical criteria can be developed for a specific constituent. Confidence in a criterion usually increases with the amount of available data. The more comprehensive and representative the data that are gathered, the less the chance of deriving criteria that are severely overprotective or underprotective.

National criteria are derived only if adequate and appropriate data are available to provide reasonable confidence in such values. If data are not adequate, then tentative criteria are developed using the available information. Safety factors are applied at points in the calculation procedure to compensate for lacking data (discussed in more detail later). These tentative criteria can be reviewed as more data becomes available. No safety factor was applied if the data availability for a specific constituent complied with the following minimum data base requirement:

- < Results of acute toxicity tests on at least one species of freshwater animal in at least eight different families such that all of the following are included:
  - a representative of the cold-water fishes, e.g. from the family Salmonidae in the class Osteichthyes;
  - any family of freshwater fishes in the class Osteichthyes to represent the warm-water fishes (e.g. Cichlidae, Cyprinidae, Clariidae);
  - planktonic crustaceans (e.g. cladoceran, copepod etc.);
  - benthic crustaceans (e.g. ostracod, isopod, amphipod, crayfish);
  - insects (e.g. mayfly, dragonfly, damselfly, stonefly, caddisfly, mosquito, midge);
  - a family in a phylum other than Arthropoda or Chordata (e.g. Rotifera, Annelida, Mollusca),

*Only data on freshwater species were used. Data on cold and warm-water fish include species of which reproducing wild populations exist in southern African waters. If not indigenous to southern Africa, the species were selected on the basis of their local commercial or recreational importance. Species used under this specification include: Rainbow trout, Brown trout, Largemouth bass, Smallmouth bass and Common carp.*

- < Results of chronic toxicity tests or acute-chronic ratios (ACRs) of species of aquatic animals in at least three different families are used, provided that of the three species:
  - at least one is a fish, and
  - at least one is an invertebrate.

*Due to the general shortage of chronic toxicity data, ACRs for any freshwater fish in the class Osteichthyes were used. Although data on species specified under the acute test requirements were preferred, ACRs of other species were used for some metals.*

- < Results of at least one test with a freshwater alga or a vascular plant. If plants are among the aquatic biota that are most sensitive to the constituent, results of a test with a plant in another phylum (division) should also be available.

Two sets of criteria were calculated: I) when data on cold water fish species were excluded and ii) when data on cold water fish species were included in the data set. Values derived when excluding the data on cold water species were regarded as the criteria for national application. If, however, the inclusion of cold water species data resulted in a significant lowering of the calculated values, these lower values are given additionally as site-specific modifications for areas where endemic or exotic cold water-adapted species occur.

The following selection criteria were used in the collection and collation of data:

- < For each metal, all available data concerning toxicity to, and bio-accumulation by, aquatic animals and plants, were collected.
- < Questionable data were rejected. This included data from tests:
  - that did not contain a control treatment;
  - in which too many (usually >10 %) organisms in the control treatment died or showed signs of stress or disease;
  - in which distilled or deionized water was used as the diluent without addition of appropriate salts;
  - with organisms that were previously exposed to substantial concentrations of the test substance or other contaminants; and
  - where there was insufficient agreement of toxicity data within and between species.
- < Data on technical grade substances were used where appropriate, but data on formulated mixtures and emulsifiable concentrates of the material of concern were not used. All results are expressed in terms of the concentration of the metal of concern, and not of the test compound.

### **Final values used in the derivation of criteria**

Table 1 lists and defines the final values which are used in the derivation of criteria for toxic constituent.

**Table 1: Descriptions of the Final Values Used in the Derivation of Criteria for Toxic Constituents**

Value	Abbreviation	Description
Final Acute Value	FAV	Calculated from the EC <sub>50</sub> * values of acute toxicity tests on genera as per the prescribed data base requirements
Final Chronic Value	FCV	Calculated from either (i) results of chronic toxicity tests (LOEC or NOEC)***, or (ii) acute-chronic ratio (ACR)
Acute-Chronic Ratio	ACR	Ratio of geometric mean of acute values to geometric mean of chronic values
Final Plant Value	FPV	Lowest result of toxicity test on an important alga, or chronic toxicity test on an important vascular plant
Acute Effect Value	AEV	One-half of the FAV
Chronic Effect Value	CEV	Lowest value of the FCV and FPV

\* EC<sub>50</sub> is the toxicant concentration that corresponds to a cumulative probability of 50 % of an adverse effect at a specific time of observation. Where the desired effect is mortality, the term LC<sub>50</sub> (lethal concentration) is used  
 \*\* The LOEC (lowest observed effect concentration) is the lowest concentration used which led to an adverse response statistically different from the control. The NOEC (no observed effect concentration) is the highest concentration which led to no adverse effect statistically different from the control. Statistical significance was measured at the 95 % confidence level

**Procedures for calculating values used in the derivation of criteria**

*Final Acute Value*

For the purpose of deriving national criteria it is necessary to find a single figure to represent the plethora of acute toxicity data. A single acute toxicity value is usually presented as the n<sup>th</sup> percentile of acute effect concentrations (EC<sub>n</sub>). The test organisms include many different species in a number of different genera. The toxicity data for a species can be represented by the species mean acute value (SMAV). Where SMAVs for more than one species within a genus are available, the genus mean acute value (GMAV) is calculated.

The final acute value (FAV) is an estimate of the fifth percentile of a statistical population represented by the set of GMAV's for which acceptable acute tests have been conducted on the constituent. If, however, the SMAV of a commercially or recreationally important species is lower than the calculated FAV, then the smaller SMAV replaces the FAV in order to provide protection for that important species.

The procedure developed by the United States Environmental Protection Agency was followed in calculating the FAVs. This procedure involved five steps:

- Step 1: Suitable toxicity data were reduced to standard benchmark formats, such as  $LC_{50}$ s, to produce one value per test. For acute tests use was made of a **dose-response curve**, which plots the concentrations of the constituent against organisms' response. The concentration that corresponds to a cumulative probability of 50 % for death ( $LC_{50}$ ) of the test population was then calculated. The benchmark formats are reported in the AQUIRE data base.
- Step 2: The species mean acute values (SMAV) were calculated from individual toxicity test results. Results of individual tests have usually been found to conform to **skewed distributions**. However, there were often insufficient data to calculate a mean or modal value, and the geometric mean was used to approximate the distribution mean. This step produced one value to represent the tolerance of each selected species.
- Step 3: This step involved the calculation of a genus mean acute value (GMAV) from the relevant species mean acute values (SMAVs). Here, as in Step 2, the geometric mean was used to approximate the distribution mean. This produced one value to represent the tolerance of the genus. Where data for only one species per genus could be found, the SMAV became the GMAV.
- Step 4: Although the GMAVs often fitted a log normal distribution, or even a Weibul distribution, it was found that the calculation of the FAV was best served by assuming a **log triangular distribution**. The FAV was then calculated by:
- ! Assigning each GMAV the cumulative probability, **P**, calculated from  $P = R/(N+1)$  where **R** = rank and **N** = the number of GMAVs or SMAVs;
  - ! fitting a line to the  $\ln(\text{GMAV})$  versus **P** data set using the four points where **P** is closest to 0.05 and using the geometric mean functional relationship to estimate the slope (the factor of 0.05 was selected to give criteria that seemed neither too high nor too low in comparison to the sets of data from which they were calculated); and
  - ! calculating the FAV as the concentration corresponding to  $P = 0.05$  on this line.
- Step 5: The AEV was calculated as  $FAV/f$ , where *f* was the safety factor (Table 2). Where no safety factor was applicable, *f* had the value of 2.

Where there were enough data to demonstrate that acute toxicity to two or more species is similarly related to environmental characteristic(s) other than the toxic constituent (e.g. hardness, temperature or pH), then the SMAV (or GMAV) was calculated as follows:

- ! For each species the SMAV at a selected value, **Z**, of the water quality characteristic was calculated by:

$$SMAV = e^{-\frac{Z - X}{W}}$$

where **W** is the geometric mean of the acute toxicity values, **X** is the geometric mean of the water quality characteristic and **V** is the slope of the pooled normalized toxicity data of a species on the pooled normalized concentration of the water quality characteristic.

! The Final Acute Equation is written as:

$$R = e^{-A} \left[ \frac{1}{1 + \frac{A}{GMAV}} \right]$$

where A is the value of ln (GMAV) corresponding to P = 0.05

- ! In addition to the general criteria for acceptance of data, data were rejected when:
- the range of the pertinent environmental characteristic was not sufficiently wide to be useful,
  - acute values adjusted for the water quality characteristic for a species or genus differed by more than a factor 10,
  - correlation for at least one fish and one invertebrate was not available,
  - slopes from regression analysis of the pertinent environmental characteristic for different species were too dissimilar, or
  - too few data were available.

#### *Final Chronic Value*

The Final Chronic Value (FCV) was either calculated from available chronic toxicity data or was derived from the acute:chronic ratio (ACR). Where there are enough chronic exposure test data available, the species mean chronic value (SMCV), mean genus chronic value (MGCV) and FCV were calculated in a manner analogous to SMAV, GMAV and FAV.

In the case of having sufficient data, the following rules applied:

- ! Results of flow-through or renewal tests, i.e. where flowing water tanks were used or when water was replaced during the course of the experiment, were included.
- ! Survival, growth and reproduction of the control had to be acceptable for the species.
- ! If the total organic carbon (TOC) or suspended solids (SS) in the dilution water exceeded 5 mg/l, a relationship of either TOC or SS to chronic toxicity had to be known - whether there was an effect or not.
- ! Chronic values were based on end-points and exposures appropriate to the species. Full life-cycle tests were selected in preference to partial life-cycle tests.

The chronic value for a particular test was obtained from the geometric mean of the LOEC and the NOEC. In the case where there were insufficient chronic exposure data available to calculate a FCV, an ACR was calculated as follows:

- ! For each chronic value for which there is a corresponding acute value, i.e. the same species and the same constituent, the ACR was calculated as:

$$R = \frac{SMCV}{GMAV} \left[ \frac{1}{1 + \frac{A}{GMAV}} \right]$$

and the FCV was calculated as:

$$R = \frac{R}{R}$$

- ! For acute and chronic values to correspond, the same dilution water had to have been used.

- ! If there was no apparent correlation between the ACR and the SMAV, and the intra species ACR differed by less than a factor of 10, with no ACR less than 2, the final ACR was calculated as the geometric mean of the species ACR's.
- ! If the ACR appeared to be correlated to the SMAV, then the ACR was calculated for species whose SMAV's were close to the Final Acute Value.
- ! If a species ACR was less than 2 it was interpreted to mean that acclimation had probably taken place and, in order to ensure adequate protection in field situations, it was adjusted to 2.

If none of the above apply, toxicological mechanistic differences probably render the calculation of a meaningful Final Acute:Chronic Ratio invalid.

#### *Final Plant Value*

A final plant value (FPV) is the lowest result of a 96-hour test on an alga or a chronic toxicity test on a vascular plant.

In the case of metals, concentrations of strong complexing or chelating agents above about 0.7  $\mu\text{mol/l}$  were considered to invalidate the results.

#### *Rounding off*

For calculation purposes the data were used as reported and no rounding off was performed before the final result had been calculated. The criterion values were *rounded down* to the same number of significant figures as the lowest number of significant figures in the data set.

## **Application of Safety Factors**

Data generated with the prescribed list of test organisms do not exist for all toxic constituents or even for all trace metals. Safety factors - also termed application or extrapolation factors - are selected to compensate for the uncertainties associated with missing data. In the derivation of interim criteria for constituents for which data were inadequate, the final values, for example the FAV and FCV, were divided by the safety factor. The fewer data available, the higher the safety factor needs to be.

For the purpose of this study, safety factors were applied in the derivation of national criteria where the available data did not meet the specified data base requirements. Safety factors were mainly applied where the following issues arose:

- ! lack of data to evaluate interspecies variability;
- ! lack of data to evaluate intra species variability;
- ! lack of adequate chronic toxicity data.



**Table 2: The guidelines that were followed in applying safety factors for deriving AEVs, where safety factors are applied to the FAV**

Scenario	Acute Data Base Description	Safety Factor
1	Each of the six specified groups have at least one representative species, and the species mean can be calculated from at least two results for at least one species in at least three of the groups.	2
2	Each of the six specified groups have at least one representative species, but the intra species representation is less than in scenario 1.	3
3	Only four or five of the specified groups have at least one representative species, and the species mean can be calculated from at least two results for at least one species in at least three of those groups.	6
4	Only four or five of the specified groups have at least one representative species, and the intra species representation is less than in scenario 1.	15
5	The interspecies and/or intra species representation is less than in scenario 4. Even one acute result for one species can be used if the test procedures (including control and replicate tests) are adequate.	100

**Table 3: The guidelines that were followed in applying safety factors for deriving CEVs, where safety factors are applied to the FCV**

Scenario	Chronic Data Base Description	Safety Factor
1	ACR's or chronic exposure data are available for at least one species each from at least three different groups (including at least one fish)	1
2	ACR's or chronic data are available for at least one species each from at least three different groups not including a fish species.	10
3	ACR's or chronic data are available for species from one or two groups.	incl. fish - 10 excl. fish - 100
4	Only acute animal or plant data are available. (Factor applicable to the calculated FAV or FPV.)	1000

Although safety factors are sometimes used where a lack of data does not allow the evaluation of variability among different organism life stages, this application is not considered here. The majority of fish and invertebrate acute data that were used were for early life stages, and indications are that these life stages are generally the more sensitive ones. The degree to which a specific constituent is accumulated by aquatic organisms or persists in the aquatic environment is however, not reflected in the calculation or the application of safety factors for national criteria.

**EXAMPLE :**

**Deriving Criteria for Cadmium**

Table 4 contains the toxicological data used for calculating cadmium criteria, as summarised at the genus level. The data in Table 4 were compiled from species-level data obtained from the AQUIRE data base.

**Table 4: Genus-level chronic and acute toxicity data for cadmium as selected and summarised from AQUIRE**

Taxonomic grouping	GMAV ( $\mu\text{g}/\text{R}$ )	GMCV ( $\mu\text{g}/\text{R}$ )	ACR
<b>Cold water fish</b>			
<i>Oncorhynchus</i>	5.01	3.67	1.37
<i>Salmo</i>	7.37	3.59	2.05
<b>Other fish</b>			
<i>Carassius</i>	8 325		
<i>Cyprinus</i>	215.5		
<i>Gambusia</i>	7 685		
<i>Poecilia</i>	3 570		
<i>Pimephales</i>	30.5	15.2	2
<b>Planktonic crustaceans</b>			
<i>Daphnia</i>	9.9	0.135	65
<i>Moina</i>	40.8		251.9
<i>Simocephalus</i>	43.7		
<b>Benthic crustaceans</b>			
<i>Gammarus</i>	62.6		
<i>Hyaella</i>	204.9		
<b>Insects</b>			
<i>Chironomus</i>	1 200		
<i>Ephemerella</i>	2 130		
<i>Paraleptophlebia</i>	322.8		
Unidentified damselfly	8 100		
Unidentified caddisfly	3400		
<b>Rotifera, Annelida and Mollusca</b>			
<i>Aplexa</i>	104	4.841	21.48
<i>Branchiura</i>	3 018		
<i>Limnodrilus</i>	2 137		
<i>Physa</i>	157		
<i>Quistradrilus</i>	4 024		
<i>Tubifex</i>	4 024		
<i>Amnicola</i>	3 800		
<i>Nais</i>	1 700		
<b>Algae and Plants</b>			
<i>Anabaena flos aquae</i>	120		
<i>Ankistrodesmus</i>	2500		
<i>Chlorella</i>	153		
<i>Euglena</i>	5000		
<i>Lemna</i>	10		
<i>Microcystis</i>	70		
<i>Navicula</i>	310		
<i>Nitzschia</i>	480		
<i>Salvinia</i>	10		
<i>Scenedesmus</i>	168		
<i>Selenastrum</i>	113		

Using the data in Table 4, the following Final Acute Values (FAVs) were calculated:

FAV (excluding cold water fish) = 13.5 µg/R

FAV (including cold water fish) = 5.75 µg/R

The Final Chronic Value (FCV) was calculated from the GMCVs. This resulted in FCVs of 0.5 (excluding cold water fish) and 0.2 µg/R (including cold water fish).

Since this data set (Table 4) meet with the scenario 1 requirements (Tables 2 and 3), the safety factors for deriving an AEV and CEV are both equal to 1. Therefore the AEV and CEV for cadmium are respectively 6 (13.5/2) and 0.5 µg/R.

As the effect of water hardness and alkalinity on acute and chronic toxicity to aquatic organisms has been demonstrated, cadmium criteria were calculated in terms of water hardness, according to the following equations:

$$\text{AEV (excluding cold water fish)} = e^{(1.128[\ln(\text{hardness})]-3.284)}$$

$$\text{CEV (excluding cold water fish)} = e^{(0.7852[\ln(\text{hardness})]-4.226)}$$

$$\text{AEV (including cold water fish)} = e^{(1.128[\ln(\text{hardness})]-4.020)}$$

$$\text{CEV (including cold water fish)} = e^{(0.7852[\ln(\text{hardness})]-5.143)}$$

Subsequent recommended criteria for cadmium for waters of different hardness are presented in the section on cadmium.

## APPENDIX 3

### PROCEDURES FOR MODIFICATION OF CRITERIA

#### INTRODUCTION

#### CONDITIONS FOR MODIFICATION

#### **Derivation of Site-Specific Criteria**

#### **Procedures for Site-Specific Modifications of Criteria**

*Calculation of the Water Effect Ratio (WER)*

*Estimating the background concentration of a constituent*

## Introduction

Modification (i.e. the raising or lowering of values for the TWQR, CEV or AEV) of the criteria for a constituent may be considered when:

- ! Untested locally important species may show sensitivity to the water quality constituent of concern;
- ! Stress factors sensitize local aquatic organisms. Examples are disease, parasites, predators, other contaminants, insufficient food, extremes in flow, and changes in water quality and temperature;
- ! Natural background concentrations of the constituent of concern exceed the NER;
- ! Toxicity assays using ambient water as a diluent indicate that site-specific criteria, significantly different from the criteria given in the South Africa guidelines, may be appropriate for the water quality constituent of concern.

## Conditions for Modification

The following conditions should be met before the water quality criteria are modified:

- ! Adequate site-specific characteristic data covering at least one annual hydrological cycle (including inter-annual variation) must be available;
- ! Site-specific studies have demonstrated that the system is able to tolerate the modified criterion concentration; and
- ! It has been demonstrated that there is no increased risk to other local and downstream water users by the application of the modified criteria.
- ! Expert advice must be sought if modification of criteria is considered.

### Derivation of Site-Specific Criteria

Site-specific criteria should be derived only when sufficient data are available which address both the biotic effects and fate of the constituent. These data should be based on:

- ! Ambient toxicity tests or water effect ratio estimations;
- ! Physico-chemical data from the water column and benthos, including known biotic and abiotic transformations of the water quality constituent; and
- ! Site-specific hydrological information.

If ambient toxicity tests are used as the basis for the derivation of site-specific criteria, the general guidelines regarding the minimum data requirements (as described in **Appendix 2**) must apply.

If the water effect ratio (WER) is used for modification of the criteria, the modified criterion value is calculated from:

$$C_m = C_g \times WER \quad \text{Equation (1)}$$

### Procedures for Site-specific Modifications of Criteria

#### *Calculation of the Water Effect Ratio (WER)*

In the derivation of criteria for toxic constituents, data are used which are derived from toxicity assays performed under standard laboratory conditions on selected test cultures. Generally, the most important parameter that has an influence on the toxicity of a constituent to a specific species is the composition of the medium within which the test species is exposed to the constituent. Furthermore, toxicity is often highly species specific.

The water effect ratio (WER) is a means of correcting for unknown or unsuspected interactions between a toxic constituent and the receiving water into which it will be discharged, and its effect on locally important species.

Data for at least three locally important or significant species should be used. These species should include an alga, a fish and a crustacean. The general guidelines for the acceptability of data described in Appendix 2 are applicable. The WER is calculated from Equation (2):

$$WER = \frac{EC_r}{EC_t} \quad \text{Equation (2)}$$

where:  $EC_t$  = the geometric mean of the selected effect concentration (eg median lethal concentration,  $LC_{50}$ ) of the test species using ambient water as a diluent, and

$EC_r$  = the geometric mean of the selected effect concentration of the reference species under standard conditions.

The WER can be calculated from either acute or chronic data to be applied to the respective acute or chronic exposure criteria.

The value of the WER should be assumed to be equal to 1.0 if no significant difference of the test and reference data can be demonstrated at the 95 % confidence level.

*Estimating the background concentration of a constituent*

The background concentration of a water quality constituent is calculated from a data set covering at least one hydrological cycle for an unimpacted point at which:

- ! there are no identifiable point or diffuse sources upstream; and
- ! there are enough data available to be certain that there is no temporal trend at the 85 % confidence interval.

The background concentration is then taken to be the 90<sup>th</sup> percentile concentration of the water quality constituent in this data set.



**APPENDIX 4**

**TABLE OF TARGET GUIDELINE RANGES AND CRITERIA FOR TOXIC CONSTITUENTS**

<b>Constituent</b>	<b>Target Water Quality Range (TWQR - µg/l)</b>	<b>Chronic Effect Value (CEV - µg/l)</b>	<b>Acute Effect Value (AEV - µg/l)</b>
<b>Inorganic Constituents</b>			
Acid-soluble Aluminium	# 5	10	100
Un-ionised Ammonia	# 7	15	100
Total Arsenic	# 10	20	130
Total Cadmium	# 0.15	0.3	3
Total Residual Chlorine	# 0.2	0.35	5
Dissolved Chromium(III)	# 12	24	340
Dissolved Chromium (VI)	# 7	14	200
Dissolved Copper	# 0.3	0.53	1.6
Dissolved Fluoride	# 750	1 500	2 540
Dissolved Lead	# 0.2	0.5	4
Dissolved Manganese	# 180	370	1 300
Total Mercury	# 0.04	0.08	1.7
Total Selenium	# 2	5	30
Dissolved Zinc	# 2	3.6	36
<b>Organic Constituents</b>			
Atrazine	# 10	19	100
Free Cyanide	# 1	4	110
Endosulfan	# 0.01	0.02	0.2
Phenol	# 30	60	500

# Glossary of Terminology

<i>aerobic</i>	of organisms requiring oxygen for respiration <i>or</i> conditions where oxygen is available
<i>acclimation</i>	short-term adaptation of individual organisms to specific environmental conditions
<i>acute effect value</i>	the concentration at and above which statistically significant acute adverse effects are expected to occur
<i>adsorption/elution</i>	the attachment of molecules or ions to, and their removal from, a substrate by manipulation of electrical charge or pH
<i>agglomeration</i>	the coalescing of particles in water to form flocs; it can be promoted by gentle stirring or by adding chemicals.
<i>algogenic</i>	substances produced by algae.
<i>amphoteric</i>	is the capability of a substance to react as an acid or a base, hence of dissolving under basic or acidic conditions.
<i>anaerobic</i>	conditions where oxygen is lacking, or of organisms not requiring oxygen for respiration
<i>anionic</i>	characteristic behaviour or property of an ion that has a negative charge. Anions move to the anode in electrolysis
<i>anions</i>	negatively charged ions
<i>assimilative capacity</i>	is the capacity of a water body to accommodate, through processes such as dilution, dispersion and chemical and biological degradation, a quantity of substances without causing any known impairment of use
<i>benthic</i>	inhabiting the bottom of a waterbody
<i>biochemical oxygen demand (BOD)</i>	the amount of dissolved oxygen consumed by organisms in water rich in organic matter
<i>buffering capacity</i>	a measure of the relative sensitivity of a solution to pH changes on addition of acids or bases.
<i>carcinogenic</i>	capable of causing, promoting or giving rise to the development of cancer
<i>cationic</i>	the characteristic behaviour or property of an ion with a positive charge. Cations move to the cathode in electrolysis.
<i>chronic effect value</i>	the concentration limit which is safe for all or most populations even during continuous exposure

<i>chemical oxygen demand (COD)</i>	the amount of oxygen required to oxidise all the organic matter that is susceptible to oxidation by a strong chemical oxidant
<i>chlorophyll (a, b)</i>	the green pigment in plants and algae that during photosynthesis captures sunlight energy and converts into chemical energy in the form of carbohydrates. Chlorophyll <i>a</i> , <i>b</i> and <i>c</i> , are forms of chlorophyll, found in different proportions in different plants. Chlorophyll is used as a measure of the quantity of algae in water
<i>clarity</i>	refers to the depth to which light can penetrate in a water body and is measured by the depth to which a Secchi disk (a 20 cm diameter disk printed with black and white quadrants) is visible
<i>coagulation</i>	the agglutination of dispersed particles
<i>cyanosis</i>	the discolouration of the skin due to the presence of oxygen-deficient blood
<i>cytopathogenic or cytopathic</i>	refers to damage caused to cells
<i>diffuse pollutant source</i>	see <i>non-point pollutant source</i>
<i>dissolution</i>	the process of dissolving
<i>electron acceptor</i>	is an atom or part of a molecule that receives electrons from other substances in a chemical reaction binding the substances together with a covalent bond
<i>eutrophic</i>	a condition characterised by excess nutrients that stimulate excessive plant and algal growth
<i>fecundity</i>	the number of eggs produced by an individual or a species
<i>flocculation</i>	the coalescence of small dispersed particles in flocs through the processes of <i>coagulation</i> , aggregation or biochemical reaction of fine suspended particles or by addition of chemical reagents (flocculants)
<i>geosmin</i>	a tertiary alcohol and metabolite produced in trace concentrations by certain Cyanobacteria (blue-green algae), algae and bacteria. It is released into water and soil, where it imparts a typical earthy/muddy odour and taste. The odour and taste threshold for humans is extremely low (of the order of ng/R)
<i>haematology</i>	the study of blood
<i>haemoglobin</i>	the protein occurring in the red blood cells of vertebrates responsible for the transport of oxygen and carbon dioxide in the bloodstream
<i>haematocrit</i>	the ratio of red blood cells to plasma
<i>haemorrhagic inflammation</i>	inflammation due to the escape of blood from a ruptured blood vessel
<i>halophyte</i>	a salt-tolerant plant

<i>hard water</i>	water that contains high concentrations of calcium, magnesium, and to a lesser extent other alkaline earth metal ions. Under highly alkaline conditions, the calcium and magnesium of hard waters may precipitate out as scale or as some other insoluble salt of these two metal ions
<i>hardness</i>	defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per litre
<i>histopathology</i>	the study of the structure of abnormal tissue. Examination of tissues after death may serve to identify the cause of death and possibly the causative agent
<i>hygroscopic</i>	a substance that absorbs water
<i>hypoxia</i>	lack of sufficient oxygen
<i>igneous rock</i>	rock, formed from the cooling of magma that has not changed appreciably since its formation
<i>intensive systems</i>	farming systems where production is based on formulated artificial feeds
<i>ion exchange</i>	the interchange of ions of like charge, usually on a solid medium; used in water treatment, such as water softening
<i>lowest observed effect concentration</i>	the lowest concentration tested that leads to an adverse response statistically different of that of the control, where the statistical significance is measured at the 95 % confidence level
<i>macrophyte</i>	any macroscopic form of aquatic vegetation; encompasses certain species of algae, mosses and ferns as well as aquatic vascular plants
<i>mesotrophic</i>	refers to freshwater bodies that contain moderate quantities of plant nutrients and are moderately productive
<i>metamorphic rock</i>	rock that has been greatly altered from its previous condition through the combined action of heat and pressure
<i>microbes</i>	microscopic organisms such as bacteria or viruses
<i>mucilaginous</i>	the tacky or slimy property of extracellular substances secreted by certain groups of bacteria, such as the slime-producing bacteria
<i>mutagenic</i>	the capability of inducing mutations, eg. chemicals, radiation
<i>necrosis</i>	the death of cells or tissues
<i>no observed effect concentration</i>	the highest concentration that gives no adverse effects statistically different to that of the controls, where the statistical significance is measured at the 95 % confidence level
<i>non-point pollutant sources</i>	diffuse discharges of pollutants from surface run off, infiltration or atmospheric sources

<i>osmoregulation</i>	the regulation of the osmotic pressure of body fluids by controlling the amount of water and/or salts in the body
<i>osmosis</i>	the diffusion of a solvent, usually water, through a semi-permeable membrane, into a more concentrated solution
<i>pelagic</i>	refers to animals able to swim in the water column
<i>permeability</i>	the condition of allowing the passing of fluid molecules through a particular medium such as soil, etc.
<i>photosynthesis</i>	the trapping of solar energy and its conversion to chemical energy by plants and algae, which use the energy in manufacturing food molecules from carbon dioxide and water
<i>physico-chemical</i>	refers to a physical characteristic of water which derives from a single or combination of chemical constituent(s) of water (e.g. conductivity, redox potential)
<i>point pollutant sources</i>	are discharges of pollutants from known discrete sources, e.g. an effluent discharge from an industry. The volume and quality of the discharge can normally be measured
<i>polyvalent metallic ions</i>	ions of metals having more than one oxidation state, e.g. Cr(III) and Cr(VI)
<i>poikilothermic</i>	animals whose temperatures vary with that of the surrounding medium
<i>raw water</i>	source water in its untreated state
<i>redox potential</i>	an expression of the oxidising or reducing power of a solution relative to a reference potential. This potential is dependent on the nature of the substances dissolved in the water, as well as on the proportion of their oxidised and reduced components
<i>reducing conditions</i>	conditions prevailing within an aquatic environment in which the redox potential is such that substances become reduced
<i>salinity</i>	a measure of the salt content of soil or water
<i>scaling</i>	the formation of a dense coating of predominantly inorganic material formed from the precipitation of water soluble constituents. The most common substances forming scale are carbonates and sulphates of calcium and magnesium hydroxide
<i>site-specific</i>	refers to conditions that are unique or specific to a certain site or locality
<i>sub-lethal</i>	the concentration or dose of a toxic substance below the threshold
<i>supersaturation</i>	refers to a solution containing more solute than equilibrium conditions will allow
<i>surficial deposits</i>	unconsolidated alluvial, residual or glacial deposits overlying bedrock or occurring on or near the surface of the earth

<i>teratogenic</i>	of agent or factor causing deformed embryos or offspring
<i>titratable bases</i>	bases that are capable of being analysed quantitatively through the addition of known amounts of a standardised acid solution until a given reaction is produced (colour change, precipitation)
<i>toxic substance</i>	natural or synthetic chemical substance that may cause adverse effects on living organisms, even when present at low concentrations
<i>valency</i>	the number of electrons required to be gained or lost by an atom to reach a state where the outermost electron shell is full
<i>vascular plants</i>	plants with woody conducting vessels (i.e. most terrestrial plants)
<i>zeolites</i>	minerals, consisting mainly of hydrous silicates of calcium, sodium and aluminium, which are able to act as cation exchangers and are utilised in the treatment of water to fulfil this function

## Glossary of abbreviations / acronyms

<b>AEV</b>	acute effect value
<b>ANZECC</b>	Australian and New Zealand Environmental and Conservation Council
<b>AOC</b>	assimilable organic carbon
<b>ACR</b>	acute:chronic ratio
<b>AWWA</b>	American Water Works Association
<b>BOD</b>	biological oxygen demand
<b>CCREM</b>	Canadian Council of Resources and Environmental Ministers
<b>CEV</b>	chronic effect value
<b>COD</b>	chemical oxygen demand
<b>CSIR</b>	Council for Scientific and Industrial Research
<b>DOC</b>	dissolved organic carbon
<b>DWAF</b>	Department of Water Affairs and Forestry
<b>EC</b>	electrical conductivity
<b>EC<sub>50</sub></b>	the toxicant concentration that corresponds to a cumulative probability of 50% of an adverse effect at a specific time of observation
<b>FAV</b>	final acute value
<b>FCV</b>	final chronic value
<b>FPV</b>	final plant value
<b>GMAV</b>	genus mean acute value
<b>HOCl</b>	hypochlorous acid
<b>HPLC</b>	high performance liquid chromatography
<b>IAWPRC</b>	International Association for Water Pollution Research and Control
<b>IC</b>	inorganic carbon
<b>IR</b>	infiltration rate

<b>LC<sub>50</sub></b>	the concentration that corresponds to a cumulative probability of 50 % for death of the test population
<b>LOEC</b>	lowest observed effect concentration
<b>NAS/NAE</b>	National Academy of Sciences/National Academy of Engineering (USA)
<b>NDOC</b>	non-dissolved organic carbon
<b>NOAEL</b>	no observed adverse effect level. Refers to that test concentration of a toxicant in a toxicological experiment at which no adverse effect on the test organism is observed or measured
<b>NOEC</b>	no observed effect concentration
<b>NTU</b>	nephelometric turbidity units
<b>RO</b>	reverse osmosis
<b>SMAV</b>	species mean acute value
<b>TDS</b>	total dissolved solids
<b>TOC</b>	total organic carbon
<b>TSS</b>	total suspended solids
<b>TWQR</b>	Target Water Quality Range
<b>US EPA</b>	United States Environmental Protection Agency



## Glossary of units of measure

<b>µg/R</b>	micrograms per litre
<b>µS/cm</b>	micro-Siemens per centimetre
<b>mg/R</b>	milligrams per litre
<b>mM/R</b>	millimoles per litre
<b>ng/R</b>	nanograms per litre
<b>nm</b>	nanometre
<b>NTU</b>	nephelometric turbidity units
<b>EC</b>	degrees centigrade