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GOVERNMENT NOTICES • GOEWERMENTSKENNISGEWINGS

DEPARTMENT OF ENVIRONMENTAL AFFAIRS

NO. 404 **15 MARCH 2019**

NATIONAL ENVIRONMENTAL MANAGEMENT: INTEGRATED COASTAL MANAGEMENT ACT, 2008 (ACT NO. 24 OF 2008)

SOUTH AFRICAN WATER QUALITY GUIDELINES FOR COASTAL MARINE WATERS - NATURAL ENVIRONMENT AND MARICULTURE USE

I, Nomvula Paula Mokonyane, Minister of Environmental Affairs, hereby publish the Draft South African Water Quality Guidelines for Coastal Marine Waters - Natural Environment and Mariculture Use in terms of sections 69 and 83(1)*(f)*(v) of the National Environmental Management: Integrated Coastal Management Act, 2008 (Act No. 24 of 2008) for public comment.

Any person who wishes to submit representations or comments in connection with the South African Water Quality Guidelines for Coastal Marine Waters - Natural Environment and Mariculture Use is invited to do so within 30 calendar days from the date of the publication of this notice. Comments received after this time may not be considered. The Draft South African Water Quality Guidelines for Coastal Marine Waters - Natural Environment and Mariculture Use is a 160 page document and is available on the Department's website at https://www.environment.gov.za/legislation/gazetted_notices.

All representations and comments must be submitted in writing to the Deputy Director-General of the national Department of Environmental Affairs, Branch: Oceans and Coasts:

By hand: The Deputy Director-General
Attention: Ms N. Baijnath-Pillay
National Department of Environmental Affairs
Branch: Oceans & Coasts
2 East Pier Building, East Pier Road
Victoria & Alfred Waterfront, Cape Town

By post to: The Deputy Director-General
Attention: Ms. N. Baijnath-Pillay
National Department of Environmental Affairs
Branch: Oceans & Coasts
P.O. Box / Private Bag x4390
Cape Town, 8002

By email: Nbpillay@environment.gov.za

NOMVULA PAULA MOKONYANE
MINISTER OF ENVIRONMENTAL AFFAIRS

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South African Water Quality Guidelines for Coastal Marine Waters – Volume 1: Natural Environment and Mariculture Use

environmental affairs

Department:
Environmental Affairs
REPUBLIC OF SOUTH AFRICA

South African Water Quality Guidelines for Coastal Marine Waters – Volume 1: Natural Environment and Mariculture Use

DEPARTMENT OF ENVIRONMENTAL AFFAIRS

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EXECUTIVE SUMMARY

Contemporary coastal water quality management strategies employed around the world, including in South Africa, focus on maintaining or achieving receiving water quality such that the water body remains or becomes fit for all designated uses. Designated uses of the marine environment includes aquaculture, recreational use, industrial use, as well as the protection of biodiversity and ecosystem functioning. This goal oriented management approach arose from the recognition that enforcing end of the pipe effluent limits in the absence of an established context, i.e. not recognising the assimilative capacity and requirements of receiving environments, would reach a point where water bodies would only be marginally fit for their designated uses.

Water quality guidelines, criteria or standards (hereinafter collectively referred to as GCSs[1]) are an important tool for managing water quality and typically comprise of a suite of numerical concentration limits or narrative statements for particular properties (physico-chemical) or constituent (nutrient or toxic substance) of or in water. These guidelines are derived with the objective of maintaining water bodies in a state that is fit for designated water uses. The Department of Water and Sanitation (DWS) developed a set of four Water Quality Guidelines in 1992, which was thereafter updated in 1995, and were aimed at managing coastal and marine water quality for designated uses. These guidelines consists of:

- Volume 1: Natural Environment
- Volume 2: Recreational Use (updated and re-launched by the DEA in 2012)
- Volume 3: Industrial Use
- Volume 4: Mariculture

The responsibility of managing coastal waters was transferred to the Department of Environmental Affairs, Branch Oceans and Coasts (DEA: O&C) in terms of the National Environmental Management: Integrated Coastal Management Act (NEM: ICMA), which was promulgated in February 2009. The DEA: O&C commissioned a project in 2016/17 to gather evidence in support of updating these guidelines to ensure that they remain relevant in the context of an updated information base and updated water use requirements.

Approaches followed for the development of water quality GCSs from 14 countries, their states/provinces, politico-economic unions (e.g. European Union), and/or ecoregions (e.g. Benguela Current Large Marine Ecosystem Programme, Western Indian Ocean Region) (hereinafter referred to as '*other jurisdictions*') have been reviewed as part of the project. This process assisted in the identification of structural and technical shortcomings of the 1995 Guidelines and provided a starting point for their revision.

The international review demonstrated that South Africa's guidelines for physico-chemical properties are very outdated with regards to (1) the level of protection awarded to the designated uses (i.e. lack of a definition for the term '*ambient conditions*'); and (2) the practicality for implementation. It was therefore recommended that the Final Guidelines are aligned with current international practices by adopting the site-specific, so-called r*eference system water quality data approach*. First and foremost this means that the term '*ambient condition*' should be defined as the natural range of conditions at a particular site (seasonal and/or event driven). To ensure appropriate protection of all designated uses, the Final Guidelines should move away from guidelines, which specify fixed ranges and proportions (fixed number or percentage) of ambient conditions. Instead, it was recommended that the approach of the ANZECC 2000 Guidelines be implemented, which requires that guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should be determined as the range defined by the 20th and 80th %iles of the seasonal distribution (also consider event-driven changes) for the reference system.

The international review indicated that, unlike the 1995 Guidelines Water Quality Guidelines, GCSs for various designated uses are generally not presented in separate documents. This seems to be in the interest of avoiding unnecessary repetition that may occur with separate GCSs documents. Following this trend, a single Final Guideline South African Water Quality Guideline for Coastal Marine Waters has therefore been produced (hereinafter referred to as '*the Final Guidelines*'), which contains background information profiles on a range of properties and common contaminants found in seawater as well as recommended guideline values for all designated beneficial uses.

The international review also revealed that water quality GCSs for industrial use are generally no longer

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[1] Water quality guidelines and criteria themselves are not legally binding and represent recommended but non-mandatory controls. Note, however, that guidelines and criteria become legally binding when a legal document (i.e. act, regulation or permit) explicitly requires compliance with the guideline document/values. In contrast, water quality standards are legally binding and must be met by all users of the water resource, including organs of state.

adopted owing to the enormous variation in water quality requirements within and between industries and also in recognition of the fact that requirements for industrial use of water are generally coincident with those for the natural environment and/or mariculture. The same approach has thus been recommended for South Africa, and guidelines for industrial use have been omitted from the Final Guidelines.

The 1995 Guidelines contain narrative statements and guideline values along with relevant background information for 29 properties (temperature, salinity, dissolved oxygen etc.) and constituents (nutrients, toxic substances, pathogens). Background information and guidelines for these properties/constituent have all been updated in the Final Guidelines and additional narrative statements and guideline values have been developed for a further 28 constituents using information from the scientific literature and also from profiles and guideline documents that have been adopted in other jurisdictions. The Final Guidelines thus contain narrative statements and guideline values for 57 properties and constituents.

Properties and constituents have been separated into the following categories:

(1) Objectionable matter,

(2) Physico-chemical properties,

(3) Nutrients,

(4) Toxic substances,

(5) Human pathogens, and

(6) Organoleptic substances (i.e. smell, taste, and appearance which reduce palatability of mariculture organisms).

This corresponds with the approach adopted for the 1995 Guidelines, and is in line with international practice. A complete summary table of all recommended narrative statements and guideline values is included in Table 1. Note that many of the narrative statements and guideline values are applicable to both Natural Environment and Mariculture (which makes sense given that these organisms are no less sensitive to conditions in the environment than other biota) while others (e.g. microbiological indicators such as *E. coli* and faecal coliforms and organoleptic substances) are applicable to Mariculture only owing to the fact that these organisms need to be suitable (safe and palatable) for human consumption as well.

The Final Guidelines are intended to provide reasonable confidence that, if they are indeed achieved, there will be no significant impact on South Africa's designated uses of coastal marine waters with regards to those properties and constituents that have been included in the guidelines. Compliance with the water quality guidelines for the protection of marine aquatic ecosystems should be achieved in all coastal waters, except within approved sacrificial (mixing) zones. Effluent (and its associated contaminants) discharged into the marine environment from land-based sources typically undergoes initial dilution and dispersion at the outfall point (or pipe end) and naturally, water quality guidelines are likely to be exceeded in this area.

GLOSSARY OF TERMS

Acute toxicity	The adverse effects of a substance that result either from a single expo- sure or from multiple exposures in a short period of time (usually less than 24 hours). To be described as acute toxicity, the adverse effects should occur within 14 days of the administration of the substance.
Adsorption	The adhesion in an extremely thin layer of molecules (as of gases, solutes, or liquids) to the surfaces of solid bodies or liquids with which they are in contact.
Bioaccumulation	The process where the chemical concentration in an aquatic organism achieves a level that exceeds that in the water as a result of chemical uptake through all routes of chemical exposure (e.g. dietary absorption, transport across the respiratory surface, dermal absorption).
Bioconcentration	The intake and retention of a substance in an organism entirely by respiration from water in aquatic ecosystems or from air in terrestrial organisms.
Bioconcentration factor	The concentration of test substance in/on the fish or specified tissues thereof divided by the concentration of the chemical in the surrounding medium at steady state. The higher the factor the more a substance bioconcentrates in an organism.
Biomagnification	Synonym: bioamplification or biological magnification. The increasing concentration of a substance, such as a toxic chemical, in the tissues of organisms at successively higher levels in a food chain.
Biotic ligand model (BLM)	The BLM allows users to develop protective chronic and acute values based on site-specific water quality variables including temperature, dis- solved organic carbon (DOC), salinity, and pH, which influence the bio- availability and toxicity of copper in estuarine/marine environments.
CAS RN	A unique numerical identifier assigned by Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature (currently including those described from at least 1957 through the present), including organic and inorganic compounds, minerals, isotopes, alloys and nonstructurable materials (UVCBs, of unknown, variable composition, or biological origin).
Chlorine produced oxidants (CPO)	Reactive oxygen species that are formed during the chlorination of seawater. These include hypobromous acid, hypobromite ion and bromamines.
Chronic toxicity	The development of adverse effects as the result of long term exposure to a toxicant or other stressor. It can manifest as direct lethality but more commonly refers to sublethal endpoints such as decreased growth, reduced reproduction, or behavioural changes such as impacted swimming performance.
Coliforms	Gram-negative, non-spore-forming, oxidase-negative, rod-shaped facultative anaerobic bacteria that ferment lactose (with β-galactosidase) to acid and gas within 24– 48h at 36±2°C. Not specific indicators of faecal pollution.
Combined chlorine	Synonym: Combined available chlorine (CAC). Chloramines, which are formed in chlorinated freshwater containing ammonia.

Complexation	The combination of individual atom groups, ions or molecules to create one large ion or molecule. One atom or ion is the focal point of the complex.
Congener (chemistry)	One of many variants or configurations of a common chemical structure.
Conservative-type distribution	Trace metals that interact only weakly with particles, have oceanic residence times greater than 10,000 years (much greater than the mixing time of the oceans), and have concentrations that maintain a relatively constant ratio to salinity. Trace metals with this distribution exhibit an al- most uniform distribution in the oceans with only a slight depletion at the surface.
Dissolved metal	Metal compounds, which pass through a 45 μm filter.
Eh	Measure of oxidation/reduction potential.
Enterococci and faecal streptococci	Enterococci and faecal streptococci both refer to vaguely defined groups of Gram-positive spherical bacteria, some of which are members of the natural flora of various environments. Because of the limited specificity of tests commonly used for these groups, they can, for all practical purposes be considered to be the same.
Erosion	The action of surface processes (such as water flow or wind) that remove soil, rock, or dissolved material from one location on the Earth's crust, then transport it away to another location.
Escherichia coli	Member of the group of faecal coliform bacteria. Highly specific to the faeces of warm-blooded animals and cannot multiply in any natural water environment.
Euphotic zone	In a water body, the layer closer to the surface that receives enough light for photosynthesis to occur.
Free residual chlorine (FRC)	Synonym: Free available chlorine (FAC). Hypochlorous acid and hypochlorite ion, which are formed in chlorinated freshwater.
Jurisdiction	Countries, their states/provinces, politico-economic unions (e.g. European Union), ecoregions (e.g. Benguela Current Large Marine Ecosystem Programme, Western Indian Ocean Region)
Ligand	An ion or molecule that binds to a central metal atom to form a complex (alternatively known as a coordination entity). Ligands are atoms or molecules with electron pairs available; they may be neutral or negatively charged.
Lowest observed effect level (LOEL)	The lowest concentration or amount of a substance found by experiment or observation that causes an adverse alteration of morphology, function, capacity, growth, development, or lifespan of a target organism distinguished from normal organisms of the same species.
Microbial indicator organisms	Micro-organisms that may not pose a major human health risk, but that are indicative of the presence of human pathogens.
Mixing zone	An administrative construct which defines a limited area or volume of the receiving water where the initial dilution of a discharge is allowed to occur, until the water quality standards are met. In practice, it may occur within the near-field or far-field of a hydrodynamic mixing process and therefore depends on source, ambient, and regulatory constraints.

Nitrification	The biological (nitrifying bacteria) oxidation of ammonium to nitrate with nitrite as an intermediate in the reaction sequence.
Nutrient-type distribution	Trace metals with nutrient-type distributions are dominated by the internal cycle of assimilation by plankton in surface waters. Consequently, their concentrations are lowest in surface waters where they are assimilated by phytoplankton and/or adsorbed by biogenic particles, and increase in the subsurface waters as sinking particles undergo decomposition or dissolution, followed by oxidation and remineralization in deeper waters. Oceanic residence times of nutrient-type, recycled elements are inter- mediate (a few thousand to one hundred thousand years).
Octanol-water partitioning coefficient (Kow)	The ratio of a chemical's concentration in the octanol phase to its con- centration in the aqueous phase of a two-phase octanol/water system. Kow = Concentration in octanol phase / Concentration in aqueous phase.
Organoleptic effects	Synonym for tainting substances
Orthophosphate	Synonyms: phosphate, filterable reactive phosphate, reactive phosphorus, soluble reactive phosphate. The phosphate form which is most readily utilised by biota and provides a good estimation of the amount of phosphorus available for algae and plant growth.
Oxidation	The loss of electrons or an increase in oxidation state by a molecule, atom, or ion.
Oxidation state	Synonym: oxidation number. This is an indicator of the degree of oxidation (loss of electrons) of an atom in a chemical compound.
Percentile	A measure used in statistics indicating the value below which a given percentage of observations fall. E.g. Measuring water temperature in a lagoon: Water temperature is measured 100 times from January to December in a given year. 80 percent of the 100 measurements fall be- low 25°C, which means that 25°C represents the 80th percentile value. Similarly, 20 percent of the 100 measurements fall below 16°C, which means that 16°C represents the 20th percentile value.
Persistent organic pollutants (POP)	Organic compounds (of either natural of anthropogenic origin) that are toxic and also persist in the environment by resisting photolytic, chemical and biological degradation.
Phytoplankton	Mostly microscopic, single-celled photosynthetic organisms that live suspended in water. Like land plants, they take up carbon dioxide, make carbohydrates using light energy, and release oxygen.
Point of Departure	The lower confidence bound on the lowest experimental dose that showed an effect. The critical study used for all quantitative risk assessments has a Point of Departure. However, at present, the POD acronym is primarily used in deriving the AWQC for a type of cancer that does not show a linear response to dose.
Precipitate (chemistry)	The solid that is formed during chemical precipitation.
Precipitation (chemistry)	The chemical reaction that causes a solid to form from solution.

Primary nursery areas (PNA)	Tidal salt waters which provide essential habitat for the early development of commercially important fish and shellfish and are so designated by the Marine Fisheries Commission.
Reactive oxygen species	Chemically reactive chemical species containing oxygen. They are known to harm living organisms by damaging DNA, through oxidations of polyunsaturated fatty acids in lipids (lipid peroxidation), oxidations of amino acids in proteins and oxidative deactivation of specific enzymes by oxidation of co-factors.
Reduction	The gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.
Reference Dose	An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to humans (including sensitive subgroups) that is likely to be without an appreciable risk of adverse effects over a lifetime.
Risk Specific Dose	The concentration in water that has a specific associated risk, such as a one-in-a-million extra risk for an adverse effect. This dose-response parameter is used for chemicals that have no safe dose and where the risk increases linearly as the dose increases from no exposure to doses where the tumours have been experimentally observed in one or more toxicological studies.
Safety factor	A factor that is applied to the lowest credible toxicity datum to account for uncertainty when deriving a water quality GCS from a small dataset.
Scavenged-type distribution	Trace metals that have strong interactions with particles and short oceanic residence times (ca. 100 to 1,000 yrs). These residence times that are less than the ventilation or mixing time of the oceans. Their concentrations tend to be maximal near major sources such as rivers, atmospheric dust, bottom sediments, and hydrothermal vents. Concentrations decrease with distance from the sources.
Speciation (chemistry)	The chemical form or compound in which an element occurs in both non-living and living systems. It may also refer to the quantitative distribution of an element.
Stormwater	Rain that washes off driveways, parking lots, roads, yards, rooftops, and other hard surfaces and s carried away through a system of pipes that is separate from the sewerage system. Stormwater is not treated and is often highly polluted.
Thermotolerant coliforms	Coliforms that produce acid and gas from lactose at 44.5 ±0.2°C within 24 ±2h, also known as faecal coliforms due to their role as faecal indicators. Escherichia coli (E. coli): Thermophilic coliforms that produce in- dole from tryptophan, but also defined now as coliforms able to produce β-glucuronidase (although taxonomically up to 10% of environmental E. coli may not). Most appropriate group of coliforms to indicate faecal pollution from warm-blooded animals.
Total Ammonia Nitrogen	The sum of ammonia (NH3) and ammonium (NH4+).
Total recoverable metal	Synonym: Total metal. Dissolved and particulate metal.

Total residual chlorine (TRC)	Synonyms: Total available chlorine (TAC), combined reactive chlorine (CRA), reactive chlorine (RA). Reactive oxygen species formed through chlorination of freshwater. The term refers to the sum of free residual chlorine (FRC) (hypochlorous acid and hypochlorite ion) and combined chlorine (chloramines) in fresh water.
Total residual oxidants (TRO)	The reactive oxygen species that are formed when chlorine is added to water.
Total Suspended Solids (TSS)	Is the dry-weight of particles trapped by a filter. It is a water quality parameter.
Turbidity	The cloudiness or haziness of a fluid caused by large numbers of individual organic and/or inorganic particles that are generally invisible to the naked eye, similar to smoke in air. The measurement of turbidity is a key test of water quality.
Upwelling	A process that is induced by offshore winds transporting coastal surface water offshore, which is replaced by rising deep, cold and nutrient-rich water.
Water hardness	The amount of dissolved calcium and magnesium in the water. Hard water is high in dissolved minerals, both calcium and magnesium.
Weathering process	The breaking down of rocks, soil, and minerals as well as wood and artificial materials through contact with the Earth's atmosphere, waters, and biological organisms.

LIST OF ABBREVIATIONS

ACR	Acute-chronic ratio
ANCECC	Australian and New Zealand Environment and Conservation Council
ANZECC	Australian and New Zealand Environment Conservation Council
BAFs	Bioaccumulation Factors
BCLME	Benguela Current Large Marine Ecosystem
BFA	Bioconcentration Factor Approach
BLM	Biotic Ligand Model
BOD	Biological Oxygen Demand
CAS RN	Chemical Abstracts Service Registry Number
CCME	Canadian Council of Ministers of the Environment
CPO	Chlorine produced oxidants
CRC	Combined reactive chlorine
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodephenlydichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DEA	Department of Environmental Affairs
DEA:O&C	Department of Environmental Affairs Branch: Oceans & Coasts
DNA	Deoxyribonucleic acid
DO	Dissolved oxygen

DOC	Dissolved organic carbon
DOP	Dissolved organic phosphorus
DSP	Diarrhetic shellfish poisoning
DWA	Department of Water Affairs
DWS	Department of Water and Sanitation
EC	Effect concentration
EU	European Union
FAC	Free available chlorine
FRC	Free residual chlorine
GCSs	Guidelines, criteria and standards
GDA	General Discharge Authorisation
ICMA	National Environmental Management: Integrated Coastal Management Act (Act 24 of 2008)
K_{ow}	Octanol-water partitioning coefficient
LC	Lethal concentration
LOEC	Lowest observed effect concentration
MATC	Maximum acceptable toxicant concentration
MF	Membrane Filter
MPA	Marine Protected Area
MPN	Most probable number
NOEC	No observed effect concentration
NSP	Neurotoxic shellfish poisoning
NTU	Nephelometric Turbidity Unit
PAH	Polyaromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PNA	Primary nursery areas
POD	Point of Departure
POPs	Persistent organic pollutants
PSP	Paralytic shellfish poisoning
PSU	Practical salinity unit
RC	Reactive chlorine
RfD	Reference Dose
RSC	Relative Source Contribution
RSD	Risk Specific Dose
RWQF	Receiving water quality framework
SSD	Species sensitivity distribution
TAC	Total available chlorine

TAN	Total Ammonia Nitrogen
TBT	Tributyltin
TRC	Total residual chlorine
TRO	Total residual oxidants
TSS	Total Suspended Solids
U.S.	United States
UFs	Uncertainty Factors
US-EPA	United States Environmental Protection Agency
WIOR	Western Indian Ocean Region

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1. INTRODUCTION AND BACKGROUND

Contemporary coastal water quality management strategies employed around the world, including in South Africa, focus on maintaining or achieving receiving water quality such that the water body remains or becomes fit for all designated uses. Designated uses of the marine environment includes aquaculture, recreational use, industrial use, as well as the protection of biodiversity and ecosystem functioning. This goal oriented management approach arose from the recognition that enforcing end of the pipe effluent limits in the absence of an established context, i.e. not recognising the assimilative capacity and requirements of receiving environments, would reach a point where water bodies would only be marginally fit for their designated uses.

Water quality guidelines, criteria or standards (hereinafter collectively referred to as GCSs[2]) are an important tool for managing water quality and typically comprise of a suite of numerical concentration limits or narrative statements for particular properties (physico-chemical) or constituent (nutrient or toxic substance) of or in water. These guidelines are derived with the objective of maintaining water bodies in a state that is fit for designated water uses. The Department of Water and Sanitation (DWS) developed a set of four Water Quality Guidelines in 1992, which were updated in 1995, and were aimed at managing coastal and marine water quality for designated uses. These guidelines consists of:

- Volume 1: Natural Environment
- Volume 2: Recreational Use (updated and re-launched by the DEA in 2012)
- Volume 3: Industrial Use
- Volume 4: Mariculture

Responsibility of managing coastal waters was transferred to the Department of Environmental Affairs, Branch Oceans and Coasts (DEA: O&C) in terms of the National Environmental Management: Integrated Coastal Management Act (NEM: ICMA), which was promulgated in February 2009.

2. INTERNATIONAL REVIEW AND BEST PRACTICE GUIDELINES

The DEA: O&C commissioned a project in 2016/17 to gather evidence in support of updating these guidelines to ensure that they remain relevant in the context of an updated information base and updated water use requirements. Approaches followed for the development of water quality GCSs from 14 countries, their states/provinces, politico-economic unions (e.g. European Union), and/or ecoregions (e.g. Benguela Current Large Marine Ecosystem Programme, Western Indian Ocean Region) (hereinafter referred to as '*other jurisdictions*') have been reviewed as part of the project. This process assisted in the identification of structural and technical shortcomings of the 1995 Guidelines and provided a starting point for their revision.

The international review showed that owing to the high level of natural variability of physico-chemical properties in coastal marine and estuarine waters, both temporally and geographically, it is generally accepted that guideline values should be as site-specific as possible to each ecosystem[4,24–27, 17, 12 5, 6,28]. The 1995 Guidelines partially adopted this approach by specifying that temperature of the receiving water should not exceed ±1°C of ambient conditions, suspended solids should not vary by more than 10% from ambient, and turbidity/visibility should not be decreased by more than 10% from ambient. Specifications for salinity and pH are, however, not in line with current international practice inasmuch as these are expressed as fixed ranges (33-36 ppt for salinity and 7.3-8.2 for pH). Australia and New Zealand are exceptional in this respect, in that ranges for certain properties of sea water are ecoregion-specific and correspond with ecosystem requirements. Note that these physico-chemical property ranges have been developed from extensive *in situ* measurements and yet, the ANZECC 2000 Guidelines emphasise the importance of developing site-specific guidelines wherever possible.

Although the term *ambient condition* is not explicitly defined in the 1995 Guidelines, it has been common practice to apply an average value from *in situ* measurements of varying quality and quantity. Experience has shown that it is extremely difficult to implement guidelines that are expressed as a fixed range or as a proportion (fixed number or percentage) of *average* ambient conditions. This is owing to physical and chemical properties of inshore waters, especially in semi-enclosed bays and estuaries, which are inherently highly variable in both space and time. It follows that the environment is seldom at average levels and that a range above or below average ambient condition is likely to be meaningless.

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[2] Water quality guidelines and criteria themselves are not legally binding and represent recommended but non-mandatory controls. Note, however, that guidelines and criteria become legally binding when a legal document (i.e. act, regulation or permit) explicitly requires compliance with the guideline document/values. In contrast, water quality standards are legally binding and must be met by all users of the water resource, including organs of state.

Internationally, the term *ambient* most commonly refers to the natural range of conditions at a particular site (seasonal and/or event driven). If this definition was adopted by the Final Guidelines, but in combination with the original physico-chemical property guidelines of 1995, organisms would likely be exposed to conditions that lie outside of their natural tolerance ranges (assuming that the natural tolerance ranges of the organism in question corresponds with the limits of natural variability in the environment).

The international review demonstrated that South Africa's guidelines for physico-chemical properties are very outdated with regards to (1) the level of protection awarded to the designated uses (i.e. lack of a definition for the term '*ambient conditions*'); and (2) the practicality for implementation. It was therefore recommended that the Final Guidelines are aligned with current international practices by adopting the site-specific, so-called *reference system water quality data approach*. First and foremost this means that the term '*ambient condition'* should be defined as the natural range of conditions at a particular site (seasonal and/or event driven). To ensure appropriate protection of all designated uses, the Final Guidelines should move away from guidelines, which specify fixed ranges and proportions (fixed number or percentage) of ambient conditions. Instead, it was recommended that the approach of the ANZECC 2000 Guidelines be implemented, which requires that guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should be determined as the range defined by the 20th and 80th %iles of the seasonal distribution (also consider event-driven changes) for the reference system.

The 1995 Guidelines for nutrients require that '*waters should not contain concentrations of dissolved nutrients that are capable of causing excessive or nuisance growth of algae or other aquatic plants or reducing dissolved oxygen concentrations below the target range indicated for dissolved oxygen*'. This narrative guidelline is in line with international water quality GCSs but should be revised to include chlorophyll *a* and turbidity in addition to dissolved oxygen levels. It has been shown internationally that when deriving site-specific water quality guidelines, the *predictive modelling approach* can help to establish indirect relationships between stressors and biological responses and should be applied whenever possible to derive site-specific guideline values. Where the *predictive modelling approach* is difficult to implement (this approach is computationally demanding), the above-mentioned *reference system data approach* should be applied to derive site-spe- cific nutrient guideline values. Where insufficient or no reference data exists, single guideline values could be derived from available data based on professional judgement, as an interim measure.

With regards to toxic substances the USA, Australia and Europe have invested substantial resources towards improving water quality management by revising existing GCSs and deriving new GCSs for known and emerging toxic substances. Many substances have long been known for their toxicity and have been identified as 'priority pollutants' (refer to Callahan *et al*. 1979, Water-Related Environmental Fate of 129 Priority Pollutants). Deriving GCSs for toxic substances requires three steps, each of which is research intensive and expensive to execute. First, a toxic substance needs to be characterised by describing its chemical composition and water-related environmental fate. Secondly, toxicity testing on a range of organisms needs to be conducted. Toxicity tests experimentally measure the response of living organisms to toxic substances. These responses may be lethal effects, e.g. death of the organism over 96 hours, or sub-lethal effects such as inhibition of growth, reproduction or enzyme activity[30]. Finally, the water quality guideline can be derived from all availa- ble toxicity testing data. The more data is available the more statistically sophisticated are the methods used to derive water quality GCSs for toxic substances. Since 1995, the quality of GCSs for toxic substances have improved dramatically through the use of statistically sophisticated methods. The 1995 Guidelines should be updated to ensure that the guideline limits reflect the latest research conducted internationally.

The international review indicated that, unlike the 1995 Guidelines Water Quality Guidelines, GCSs for various designated uses are generally not presented in separate documents, as is the case of the 4 separate guidelines produced by the Department of Water and Sanitation. This seems to be in the interest of avoiding unnecessary repetition that may occur with separate GCSs documents. Following this trend, a single Final Guidelines South African Water Quality Guideline for Coastal Marine Waters has therefore been produced (hereinafter referred to as '*the Final Guidelines*'), which contains background information profiles on a range of properties and common contaminants found in seawater as well as recommended guideline values for all designated beneficial uses.

The international review also revealed that water quality GCSs for industrial use are generally no longer adopted owing to the enormous variation in water quality requirements within and between industries and also in recognition of the fact that requirements for industrial use of water are generally coincident with those for the natural environment and/or mariculture. The same approach has thus been recommended for South Africa, and guidelines for industrial use have been omitted from the Final Guidelines.

The 1995 Guidelines contain narrative statements and guideline values along with relevant background information for 29 properties (temperature, salinity, dissolved oxygen etc.) and constituents (nutrients, toxic substances, pathogens). Background information and guidelines for these properties/constituent have all been updated in the Final Guidelines and additional narrative statements and guideline values have been developed for a further 28 constituents using information from the scientific literature and also from profiles and guideline documents that have been adopted in other jurisdictions. The Final Guidelines thus contain narrative statements and guideline values for 57 properties and constituents.

Properties and constituents have been separated into the following categories:

(1) Objectionable matter,

(2) Physico-chemical properties,

(3) Nutrients,

(4) Toxic substances,

(5) Human pathogens, and

(6) Organoleptic substances (i.e. smell, taste, and appearance which reduce palatability of mariculture organisms).

This corresponds with the approach adopted for the 1995 Guidelines, and is in line with international practice. A complete summary table of all recommended narrative statements and guideline values is included in Table 1. Note that many of the narrative statements and guideline values are applicable to both Natural Environment and Mariculture (which makes sense given that these organisms are no less sensitive to conditions in the environment than other biota) while others (e.g. microbiological indicators such as *E. coli* and faecal coliforms and organoleptic substances) are applicable to Mariculture only owing to the fact that these organisms need to be suitable (safe and palatable) for human consumption as well.

The Final Guidelines are intended to provide reasonable confidence that, if they are indeed achieved, there will be no significant impact on South Africa's designated uses of coastal marine waters with regards to those properties and constituents that have been included in the guidelines. Compliance with the water quality guidelines for the protection of marine aquatic ecosystems should be achieved in all coastal waters, except within approved sacrificial (mixing) zones. Effluent (and its associated contaminants) discharged into the marine environment from land-based sources typically undergoes initial dilution and dispersion at the outfall point (or pipe end) and naturally, water quality guidelines are likely to be exceeded in this area. This initial dilution and dispersion zone is termed the 'mixing zone', and the size of this zone is allowed to vary depending on the assimilative capacity and sensitivity of the receiving environment (mixing zone sizes for the South African coastal marine environment were recommended in the *Assessment Framework for the Management of Effluent from Land-Based Sources Discharged to the Marine Environment* (AEC 2015)[19]).

This initial dilution and dispersion zone is termed the 'mixing zone', and the size of this zone is allowed to vary in size depending on the assimilative capacity and sensitive of the receiving environment. As such, guidelines values and narrative statements are applicable for all marine habitats (including estuaries) in spite of the fact that some marine habitats (e.g. sheltered bays and estuaries) are generally considered more sensitive than the rest of the marine environment. It is assumed that such enhanced sensitivity will be addressed by varying the size of the mixing zone around licenced outfalls (reduced mixing zone size applicable for sensitive habitats). The only exception here is in instances where the level of toxicity for a particular substance is dependent on salinity, in which case different guidelines values are specified for different salinity levels.

The following recommendations were made:

(1) These guidelines be reviewed regularly (e.g. every five years), as the data on the relative toxicity of contaminants included in the Final Guidelines are constantly being updated.

(2) Microplastics are an important case in point here. Their impact on marine organisms is currently being researched in South Africa and elsewhere and it is strongly recommended that once enough data is available, a guideline value for the protection of marine organisms be included in the guidelines.

(3) Data are currently available on 168 other less common contaminants which could potentially also be included in this, or future revisions of the South African Water Quality Guidelines.

(4) A list of these 161 toxic substances, ranked according to the number of international water quality GCSs developed, has been included in this report. Those toxic substances for which water quality GCSs have been developed in several jurisdictions should be prioritised.

Table 1: Recommended water quality guidelines for the Natural Environmental and Mariculture in South Africa. Note that guideline values for the protection of mariculture organism health are identical to the recommended guidelines for the natural environment except where organoleptic effects indicate the need for more conservative guideline val- ues for mariculture organisms. Where relevant, a distinction is made between "acute" and "chronic" guideline values. Generally though, only chronic exposure values are presented for precautionary reasons.

Category	Subcategory	Name	CAS RN	Guideline value/narrative		Reference guideline*	Profile section
				Natural Environment	Mariculture		
Objectionable matter	N/A	Objection-able matter	N/A	Coastal and marine waters should not contain - • floating particulate matter, debris, oil, grease, wax, scum, foam or any similar floating materials and residues from land-based sources in concentrations that may cause nuisance; • materials from non-natural land-based sources which will settle to form putrescence; • submerged objects and other subsurface hazards which arise from non-natural origins and which would be a danger, cause nuisance or interfere with any esignated/recognized use		South Africa 1995[3]	§4.1
Physico-chemical properties	N/A	Temperature	N/A	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should be determined as the range defined by the 20th and 80th %iles of the seasonal and/ or event-driven distributions for the reference system. Test data: Median concentration		ANZECC 2000[4] BCLME 2006[5] WIOR 2009[6]	§4.2.1
Physico-chemical properties	N/A	Salinity	N/A	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should be determined as the range defined by the 20th and 80th %iles of seasonal and/ or event-driven distributions, depending upon whether low salinity or high salinity effects are being considered. Test data: Median concentration		ANZECC 2000[4] BCLME 2006[5] WIOR 2009[6]	§4.2.2

Category	Subcategory	Name	CAS RN	Guideline value/narrative		Reference guideline*	Profile section
				Natural Environment	Mariculture		
Physico-chemical properties	N/A	pH	N/A	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should be determined as the range defined by the 20th and 80th %iles of the of seasonal and/or event-driven distributions for the reference system. pH changes of more than 0.5 pH units from the seasonal maximum or minimum defined by the reference systems should be fully investigated. Test data: Median concentration for the period		ANZECC 2000[4] BCLME 2006[5] WIOR 2009[6]	§4.2.3
Physico-chemical properties	N/A	Suspended solids	N/A	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should not exceed the 80th %ile of the seasonal and/ or event-driven distributions. Additionally, the natural euphotic depth (Z_{eu}) should not be permitted to change by more than 10%. Test data: Median concentration for period.		ANZECC 2000[4] BCLME 2006[5] WIOR 2009[6]	§4.2.4
Physico-chemical properties	N/A	Turbidity	N/A	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should not exceed the 80th %ile of seasonal and/or event-driven distributions. Additionally, the natural euphotic depth (Z_{eu}) should not be permitted to change by more than 10%. Test data: Median concentration for period.		ANZECC 2000[4] BCLME 2006[5] WIOR 2009[6]	§4.2.5

Category	Subcategory	Name	CAS RN	Guideline value/narrative		Reference guideline*	Profile section
				Natural Environment	Mariculture		
Physico-chemical properties	N/A	Dissolved oxygen	N/A	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should not be allowed to drop below the 20%ile of the seasonal and/or event-driven distributions. Where possible, guideline values should be obtained during low flow and high temperature periods when DO concentrations are likely to be at their lowest. Test data: Median DO concentration for the period, calculated using the lowest diurnal DO concentrations.		ANZECC 2000[4] BCLME 2006[5] WIOR 2009[6]	§4.2.6
Nutrients	N/A	Ammonium and ammonia	14798-03-9 7664-41-7	*As a nutrient:* Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range. This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the *reference system data approach*: where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution. Where insufficient or no reference data exists, single guideline values could be derived from available data based on professional judgement, as an interim measure.		ANZECC 2000[4] BCLME 2006[5] WIOR 2009[6]	§4.3.1
	N/A	Nitrite	14797-65-0				
	N/A	Nitrate	14797-55-8				
	N/A	Phosphorus	7723-14-0				
	N/A	Silicon (as reactive silicate)	7440-21-3				
Toxic substances	Metals	Arsenic	7440-38-2	8 µg/L as total recoverable arsenic (Chronic)		EPA California 2013[7]	§4.4.1
		Cadmium	7440-43-9	0.12 µg/L as total recoverable cadmium (Chronic)		CCME 2014[8]	§4.4.2
		Chromium	7440-47-3	2 µg/L as total recoverable hexavalent chromium (Cr^{6+}) (Chronic)		EPA California 2013[7]	§4.4.3

Category	Subcategory	Name	CAS RN	Guideline value/narrative		Reference guideline*	Profile section
				Natural Environment	Mariculture		
		Copper	7440-50-8	3 µg/L as total recoverable copper (Chronic)		EPA California 2013[7]	§4.4.4
		Lead	7439-92-1	2 µg/L as total recoverable lead (Chronic)		EPA California 2013[7]	§4.4.5
		Mercury	7439-97-6	0.016 µg/L as total recoverable mercury (Chronic)		CCME 2003[9]	§4.4.6
		Nickel	7440-02-0	5 µg/L as total recoverable nickel (Chronic)		EPA California 2013[7]	§4.4.7
		Silver	7440-22-4	0.7 µg/L as total recoverable silver (Chronic)		EPA California 2013[7]	§4.4.8
		Zinc	7440-66-6	20 µg/L as total recoverable zinc (Chronic)		EPA California 2013[7]	§4.4.9
Toxic substances	Inorganic constituents	Ammonia	7782-50-5	600 µg/L as total ammonia nitrogen (Chronic)		EPA California 2013[7]	§4.3.1
		Chlorine	7782-50-5	2 µg/L Chlorine-produced oxidants (CPO) (Chronic)		EPA California 2013[7]	§4.5.2
		Fluoride	16984-48-8	Seawater: 1500 µg/L (Acute)		Canada, BC 1990[10]	§4.5.3
				Estuaries: 1160 µg/L (Acute)		Fleiss 2011[11]	
		Cyanide (as free cyanide)	57-12-5	1 µg/L measured in free cyanide (Chronic)		EPA California 2013[7]	§4.5.4
		Sulphide (as hydrogen sulphide)	S^{2-}: 18496-25-8 H_2S: 7783-06-4	2 µg/L measured as hydrogen sulphide (Chronic)		EPA North Carolina 2016[12]	§4.5.5
		Nitrate	14797-55-8	Nitrate (NO_3) = 200 000 (Chronic) Nitrate as nitrogen (NO_3– N) = 45 000 (Chronic)		CCME 2012[13]	§4.3.2
		Nitrite	14797-65-0	*Toxicity:* Insufficient data. Note that in the absence of eutrophication, surface waters are well oxygenated and consequently most reactive nitrogen exists in the form of nitrate, a considerably less toxic compound to marine animals. Preventing eutrophication will therefore also protect marine animals from nitrite toxicity[14].		N/A	§4.3.3

Category	Subcategory	Name	CAS RN	Guideline value/narrative		Reference guideline*	Profile section
				Natural Environment	Mariculture		
Toxic substances	Organic constituents; Organic pesticides; Organochlorine compounds	Aldrin	309-00-2	0.003 µg/L (Chronic)		EPA North Carolina 2016[12]	§4.6.1
		Dieldrin	60-57-1	0.003 µg/L (Chronic)		EPA North Carolina 2016[1]	§4.6.1
		Total DDT (DDT, DDE & DDD)	50-29-3 72-55-9 72-54-8	0.025 µg/l (Chronic)		European Union 2013[15]	§4.6.2
		Endosulfan	115-29-7	0.0005 µg/L endosulfan (Chronic)		European Union 2013[15]	§4.6.3
Toxic substances	Organic constituents; Polyaromatic hydrocarbons (PAHs)	Acenaphtene	83-32-9	20 (Chronic)		EPA North Carolina 2016[12]	§4.6.4
		Anthracene	120-12-7	0.1 (Chronic)		European Union 2013[15]	§4.6.4
		Benzo(a) pyrene	50-32-8	0.00017 (Chronic)		European Union 2013[15]	§4.6.4
		Benzo(b) fluor-anthene	205-99-2	Benzo(a)pyrene serves as a marker for these PAHs.		European Union 2013[15]	§4.6.4
		Benzo(g,h,i)-perylene	191-24-2				
		Benzo(k) fluor-anthene	207-08-9				
		Indeno1,2,3-(cd)Pyrene	193-39-5				
		Fluoranthene	206-44-0	0.0063 (Chronic)		European Union 2013[15]	§4.6.4
		Naphthalene	91-20-3	2 (Chronic)		European Union 2013[15]	§4.6.4

Category	Subcategory	Name	CAS RN	Guideline value/narrative		Reference guideline*	Profile section
				Natural Environment	Mariculture		
Toxic substances	Chlorinated phenols	2-Chlorophenol	95-57-8	-	0.1 (Organoleptic effects)	EPA 1986[16]	§4.6.5
		3-Chlorophenol	108-43-0	-	0.1[A] (Organoleptic effects)	EPA South Carolina 2014[17]	§4.6.5
		4-Chlorophenol	106-48-9	-	0.1 (Organoleptic effects)	EPA South Carolina 2014[17]	§4.6.5
		2,3-Dichlorophenol	576-24-9	-	0.04 (Organoleptic effects)	EPA South Carolina 2014[17]	§4.6.5
		2,4-Dichlorophenol	120-83-2	0.42 (Chronic)		United Kingdom 2014[18]	§4.6.5
		2,5-Dichlorophenol	583-78-8	-	0.5 (Organoleptic effects)	EPA South Carolina 2014[17]	§4.6.5
		2,6-Dichlorophenol	87-65-0	-	0.2 (Organoleptic effects)	EPA South Carolina 2014[17]	§4.6.5
		3,4-Dichlorophenol	95-77-2	-	0.3 (Organoleptic effects)	EPA South Carolina 2014[17]	§4.6.5
		2,3,5-Trichlorophenol	933-78-8	-	1 (Organoleptic effects)	ANZECC 2000[4]	§4.6.5
		2,4,5-Trichlorophenol	95-95-4	-	1 (Organoleptic effects)	EPA South Carolina 2014[17]	§4.6.5
		2,4,6-Trichlorophenol	88-06-2	6.5 (Chronic)	1 (Organoleptic effects)	EPA Florida 2015[19] EPA South Carolina 2014[17]	§4.6.5
		2,3,4,6-Tetrachlorophenol	58-90-2	-	0.1 (Organoleptic effects)	ANZECC 2000[4]	§4.6.5
		Pentachlorophenol	87-86-5	0.4 (Chronic)		European Union 2013[15]	§4.6.5
Toxic substances	Polychlorinated biphenyls	Polychlorinated biphenyls	1336-36-3 (Category, unique CAS numbers assigned to 209 PCB congeners)	0.000045 (Chronic)	0.000045 (Chronic)	EPA Florida 2015[19]	§4.6.6
Toxic substances	Organotin compounds	Tributyltin	36643-28-4	0.0002 µg/L (Chronic) measured in tributyltin cation 0.0002 µg/L (Chronic) measured in tributyltin cation		European Union 2013[15]	§4.6.7

Category	Subcategory	Name	CAS RN	Guideline value/narrative		Reference guideline*	Profile section
				Natural Environment	Mariculture		
Human pathogens	Microbiological indicators	Faecal Indicators – Faecal coliform	N/A	-	Most Probable Number (MPN) or Membrane Filter (MF) counts (reported as colony-forming units (CFU) shall not exceed a median value of 14 MPN/MF with not more than 10% of the samples exceeding 43 for MPN or 31 for MF, nor exceed 800 MPN/MF on any one day.	EPA Florida 2015[19]	§4.7.1

1) South Africa 1995[3]: South African Water Quality Guidelines for Coastal and Marine Waters. Volume 1: Natural Environment

2) ANZECC 2000[4]: Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council (ANZECC).

3) BCLME 2006[5]: The Development of a Common set of Water and Sediment Quality Guidelines for the Coastal Zone of the Benguela Current Large Marine Ecosystem.

4) WIOR 2009[6]: Guidelines for the Establishment of Environmental Quality Objectives and Targets in the Coastal Zone the Western Indian Ocean (WIO) Region.

5) EPA California 2013[7]: Water Quality Standards Regulations: California. United States Environmental Protection Agency

6) CCME 2014[8]: Canadian water quality guidelines for the protection of aquatic life: Cadmium. Canadian Council of Ministers of the Environment (CCME).

7) CCME 2003[9]: Canadian water quality guidelines for the protection of aquatic life: Inorganic mercury and methylmercury. Canadian Council of Ministers of the Environment (CCME).

8) Canada, British Columbia 1990[10]: Ambient Water Quality Criteria for Fluoride: Overview report. Government of British Columbia.

9) Fleiss 2011[11]: Review of Fluoride Toxicity to Aquatic Organisms and its Toxicity Contribution in Volvo Wastewater.

10) EPA North Carolina 2016[12]: Water Quality Standards Regulations: North Carolina. United States Environmental Protection Agency.

11) European Union 2013[15]: Directive 2013/39/EU of the European parliament and of the council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.

12) CCME 2012[13]: Canadian water quality guidelines for the protection of aquatic life: Nitrate. Canadian Council of Ministers of the Environment (CCME).

13) EPA South Carolina 2014[17]: Water Quality Standards Regulations: South Carolina. United States Environmental Protection Agency.

14) EPA 1986[16]: Quality Criteria for Water. United States Environmental Protection Agency.

15) EPA Florida[19]: Water Quality Standards Regulations: Florida. United States Environmental Protection Agency.

3. APPROACHES AND METHODOLOGIES FOR DEVELOPMENT OF WATER QUALITY GUIDELINES, CRITERIA AND STANDARDS

3.1 Summary of water quality guidelines, criteria / standards adopted in other jurisdictions

Approaches followed for the development of water quality GCSs from 14 countries, their states/provinces, politico-economic unions (e.g. European Union), and/or ecoregions (e.g. Benguela Current Large Marine Ecosystem Programme, Western Indian Ocean Region) (hereinafter referred to as '*other jurisdictions*') were reviewed as part of a project commissioned by the DEA in 2016/2017. This process assisted in the identification of structural and technical shortcomings of the 1995 Guidelines and provided a starting point for their revision.

GCSs from all of these jurisdictions are applicable to the protection of the natural marine environment. GCSs applicable to the mariculture sector have been adopted in eight of these jurisdictions but GCSs have not been adopted for industrial use of coastal marine waters (excluding mariculture) in any of these jurisdictions except for the State of Florida. A list of those GCSs, their geographic applicability, and short-hand used here inafter are listed in Tables 2a and 2b.

Objectionable matter, physico-chemical properties and constituent categories (i.e. nutrients, toxic substances, human pathogens, biotoxins and organoleptic substances) are not equally applicable to all beneficial uses (Table 2). For example, it is generally understood that the health of mariculture organisms will be protected if requirements as set out in guidelines protecting coastal marine aquatic environments are met. This is especially true when indigenous organisms are farmed in suitable conditions[4,22].

Additionally though, mariculture organisms also need to be suitable (safe and palatable) for human consumption, which necessitates the addition of guidelines for microbiological indicators (i.e. *E. coli* and faecal coliform) and organoleptic substances for mariculture guidelines. While guidelines for nutrients are fundamentally important in maintaining a healthy natural environment, nutrients are not important for industrial use. Finally, water used for recreational purposes must protect human health and should be aesthetically pleas- ing. Physico-chemical properties (i.e. tolerable temperature and pH), toxic substances, human pathogens and organoleptic effects are therefore relevant.

The sections below summarise the findings for the natural environment, mariculture and industrial use. Note that different methodologies are used to derive guidelines for objectionable matter, physico-chemical properties and constituents (i.e. nutrients, toxic substances, human pathogens, biotoxins and organoleptic substances).

Table 2a: Summary of water quality guidelines, criteria or standards adopted in other jurisdictions that were reviewed

Jurisdiction	Guideline/Criteria/ Standard (GCS) name	Types of guidelines (i.e. end user categories)	Implementing Agency	Year	Short hand used in this Guideline
Canada	Canadian Environmental Quality Guidelines	• Natural Environment	Canadian Council of Ministers of the Environment	Various	CCME + [Year]
Canada, British Columbia	Ambient Water Quality Criteria for Fluoride	• Natural Environment	Government of British Columbia: Environmental Protection Division	1990	Canada, BC 1990
Australia and New Zealand	Australian and New Zealand Guidelines for Fresh and Marine Water Quality	• Natural Environment • Mariculture (protection of organisms and organoleptic effects)	Australian and New Zealand Environment and Conservation Council (ANZECC)	2000	ANZECC 2000
United States of America (USA)*	National Recommended Water Quality Criteria	• Natural Environment • Mariculture (protection of organism and human health, and organoleptic effects)	United States Environmental Protection Agency (EPA)	Natural Environment: Continuously updated Organoleptic effects: 1986 Human health: Continuously updated	EPA + [Year]
USA California State*	Water Quality Control Plan: Ocean Waters of California	• Natural Environment • Mariculture (protection of human health and organoleptic effects)	California Environmental Protection Agency	2012	EPA California 2012
USA Oregon*	Water Quality Standards: Beneficial Uses, Policies, and Criteria for Oregon	• Natural Environment	Department of Environmental Quality	2013	EPA Oregon 2013
USA Florida*	Surface Water Quality Standards: Chapter 62-302	• Natural Environment • Mariculture (protection of organism and human health) • Industrial Use	Florida Department of Environmental Protection	2015	EPA Florida 2015
USA North Carolina*	North Carolina 15A NCAC 02B Surface Water Quality Standards	• Natural Environment • Mariculture (protection of organism and human health)	North Carolina Department of Environmental Quality	Continuously updated	EPA North Carolina 2016

Jurisdiction	Guideline/Criteria/ Standard (GCS) name	Types of guidelines (i.e. end user categories)	Implementing Agency	Year	Short hand used in this Guideline
USA South Carolina*	R.61-68, Water Classifications & Standards	• Natural Environment • Mariculture (protection of human health and organoleptic effects)	South Carolina Department of Health and Environmental Control	2014	EPA South Carolina 2014
European Union	Directive 2013/39/ EU	• Natural Environment	European Environment Agency	2013	EU 2013
United Kingdom	Water Framework Directive implementation in England and Wales: new and updated standards to protect the water environment	• Natural Environment	Department for Environment Food & Rural Affairs Welsh Government	2014	UK 2014
Benguela Current Large Marine Ecosystem (BCLME) (Angola, Namibia and South Africa)	Development of a Common Set of Water and Sediment Quality guidelines for the Coastal Zone of the BCLME	• Natural Environment • Mariculture (protection of organism and organoleptic effects)	Respective agencies in the various countries	2006	BCLME 2006
Western Indian Ocean (WIO) Region (Kenya, Tanzania, Mozambique, South Africa, Madagascar, Seychelles, Comoros and Mauritius)	Guidelines for the Establishment of Environmental Quality Objectives and Targets in the Coastal Zone of the Western Indian Ocean (WIO) Region	• Natural Environment • Mariculture (protection of organism and organoleptic effects)	Respective agencies in the various countries	2009	WIOR 2009
Estuarine environments (Europe)	Fleiss 2011 – Predicted No Effect Concentration (PNEC) for estuarine environments[10]	• Natural Environment	N/A	2011	Fleiss 2011

*EPA Water Quality Standards (legally binding) are approved by the federal government on a State by State basis

Table 2b: Applicability of various guideline categories to the protection of the natural environment, mariculture, industrial use and recreation.

Guideline categories	Natural Environment	Mariculture			Industrial use	Recreation (DEA 2012)1
		Protection of mariculture organism health	Protection of human health	Palatability (organoleptic effects)		
Objectionable matter	Yes	Yes	-	Yes	Yes	Yes
Physico-chemical properties	Yes	Yes	-	-	Yes	Yes
Nutrients	Yes	Yes	Yes (toxic algal blooms)	-	-	-
Toxic substances	Yes	Yes	Yes	-	Yes	Yes
Human pathogens	-	-	Yes	-	Yes	Yes
Organoleptic effects	-	-	-	Yes	Yes	Yes

3.2 Water quality constituents and properties

Three types of stressors on the natural environment and its organisms have been identified, depending on whether they have direct or indirect effects on the ecosystem[3]. Stressors include physico-chemical properties of seawater (i.e. temperature, dissolved oxygen, salinity etc.) as well as constituents (organic and inorganic, including nutrients and toxic substances).

Properties and constituents can either be directly toxic to biota, or can be non-toxic but are associated with changes to the ecosystem (e.g. biodiversity, species composition, Figure 1). Non-toxic direct-effect stressors include for example:

- Excess nutrients cause prolific algal growth and cyanobacterial blooms (refer to Section 4.3 for more detail);
- Suspended particulate matter can reduce light penetration into a waterbody and result in reduced primary production, possible deleterious effects on phytoplankton, macrophytes and seagrasses, or smother benthic organisms and their habitats (refer to Sections 4.2.4 and 4.2.5 for details); and
- Organic matter decay processes can significantly reduce the dissolved oxygen concentration and cause death of aquatic organisms, particularly fish (refer to Section 4.2.6).

Despite the toxicity and potential to impact ecosystems, some of the constituents covered in these Guidelines are essential at low concentrations for the effective functioning of the biota. These include nutrients such as nitrogen and phosphorous, as well as certain heavy metals such as copper and zinc[3].

Indirect stressors can influence the toxicity of other stressors while not directly affecting biota. Dissolved oxygen, for example, can influence redox conditions as well as the uptake or release of nutrients by sediments. Equally, pH, dissolved organic carbon (DOC) and suspended particulate matter, can have a major effect on the bioavailability of metals[3].

Approaches and methodologies followed for the development of water quality GCSs from 14 jurisdictions were reviewed. A list of these guidelines, their geographic applicability, and short-hand used hereinafter are listed in (Tables 2a and 2b).

‘Different approaches and methodologies for deriving water quality GCSs are applied for the sub-categories listed below:

- Objectionable matter;
- Physico-chemical properties (temperature, salinity, pH, suspended solids, turbidity, dissolved oxygen);
- Nutrients (ammonium, ammonia, nitrite, nitrate, phosphorus, silicon); and
- Toxic substances (metals, inorganic and organic constituents).

The following sections elaborate on the approaches and methodologies used to derive water quality GCSs for the protection of the natural environment in the coastal and marine waters in other jurisdictions.

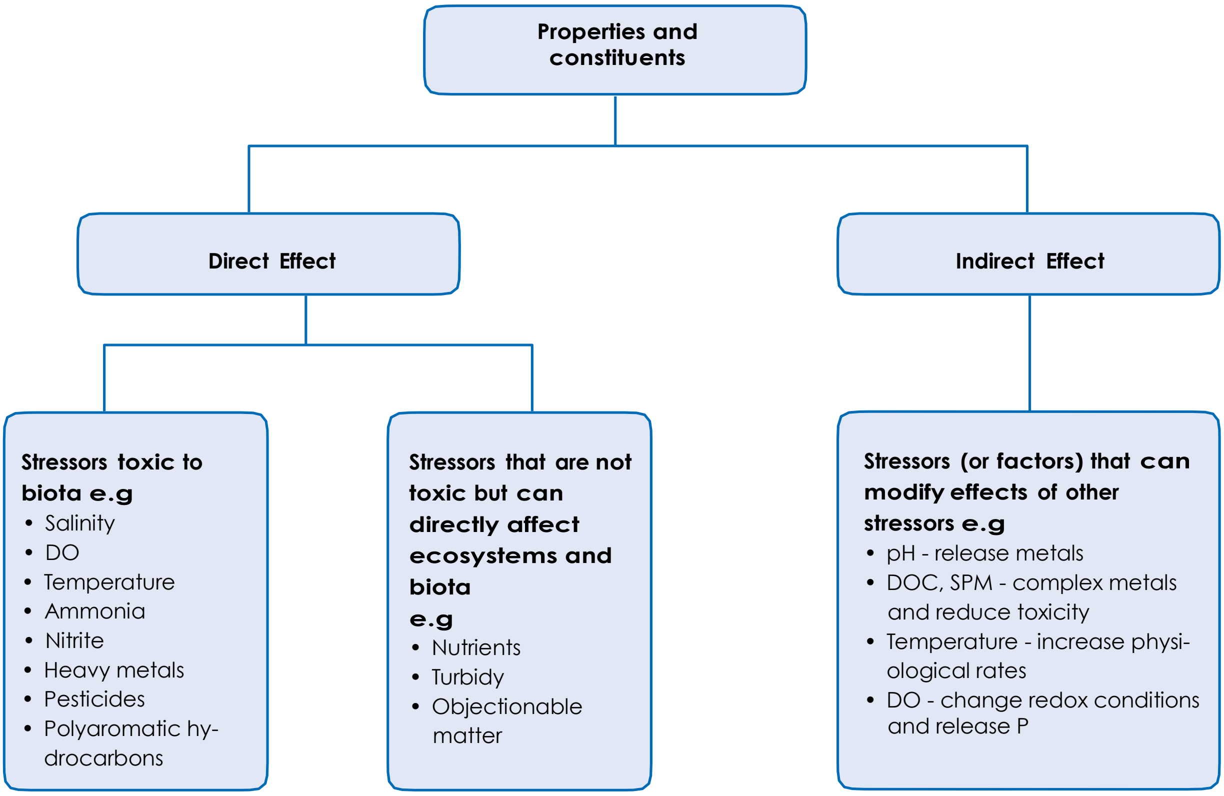


Figure 1: Types of physical and chemical stressors on the natural environment (Figure adapted from the Australian and New Zealand Guidelines for Fresh and Marine Water Quality[3]).

3.2.1 Objectionable matter

Objectionable matter refers to debris, plastic litter, oil, grease, wax, scum, foam, and submerged (just below water surface) objects in the water column. Marine animals can be affected through entanglement in and ingestion of plastic litter. Ingestion of plastic can cause digestive issues (including starvation) and/or death. It has been shown that marine organisms absorb polychlorinated biphenyls from the plastic, which contributes to the bioconcentration and bioaccumulation of this contaminant in the food chain[23]. Water quality guidelines related to objectionable matter are usually narrative and typically require that objectionable matter should not represent a nuisance in the marine environment. Objectionable matter includes:

- Objectionable floating matter or oily films;
- Non-natural matter that will settle to form objectionable deposits on the seabed;
- Submerged objects and other subsurface hazards that arise from non-natural origins and which would be a danger to recreational users; and
- Objectionable smells or odours.

3.2.2 Physico-chemical properties and nutrients

Physico-chemical properties of seawater typically include temperature, salinity, pH, suspended solids, turbidity, and dissolved oxygen. The main nutrients required for primary production in nearshore marine environ ments include nitrogen (ammonia, ammonium, nitrate and nitrite), phosphorus (phosphate), silicate and iron. Marine ecosystems are generally nitrogen (i.e. ammonium, ammonia, nitrite, and nitrate) limited, although phosphorus and reactive silicate are also important nutrients (refer to Section 4.3 for details on nutrient cycling in the ocean). Owing to the high level of natural variability of physico-chemical properties and nutrients in coastal marine and estuarine waters both temporally and geographically, it is generally accepted that guideline values should be as site-specific as possible to each ecosystem[3,24–27, 16, 11 4, 5,28]. The ANZECC 2000 Guidelines recommend four different approaches in deriving site-specific water quality guidelines for physico-chemical properties and nutrients[3]:

1. *Biological and ecological effects data approach*. This approach determines an acceptable change in biological and ecological condition from the reference condition as a result of changes in water quality. Data can either be obtained using local biota and local waters, or from applicable scientific literature;
2. *Reference system water quality data approach*. Water quality data can be obtained from the same undisturbed ecosystem or from a local but different system, or from regional reference ecosystems. Reference system water quality data should be collected to detect natural variability (seasonal or event-driven). It is recommended that monthly data is collected for two years to produce a representative distribution of the data. An appropriate percentile of the reference data distribution (data may be normally distributed or not) should be used to derive the water quality guidelines range. Depending on the management objective, a more or less conservative percentile value can be determined to improve (preferred approach) or maintain water quality. When following a precautionary approach, it is generally accepted that water quality at the edge of a mixing zone should be higher than the 20th percentile value and lower than the 80th percentile value of the reference system. It is advisable to compare the median of replicate samples from a monitoring site with the site-specific guideline values (the sampling period at a monitoring site, i.e. monthly, seasonally and/or event driven, should be determined on a case by case basis). This approach is graphically illustrated by way of an example in Figure 2.
3. *Predictive modelling approach*. This approach is particularly useful for properties and constituents, whose disturbance occurs through transformations in the environment (e.g. nutrients, biodegradable organic matter etc.). Predictive modelling can help to establish indirect relationships between stressors and biological responses; and
4. *Professional judgement* may be used in cases where it is not possible to obtain appropriate data for a reference ecosystem. Such judgement should be supported by appropriate scientific information.

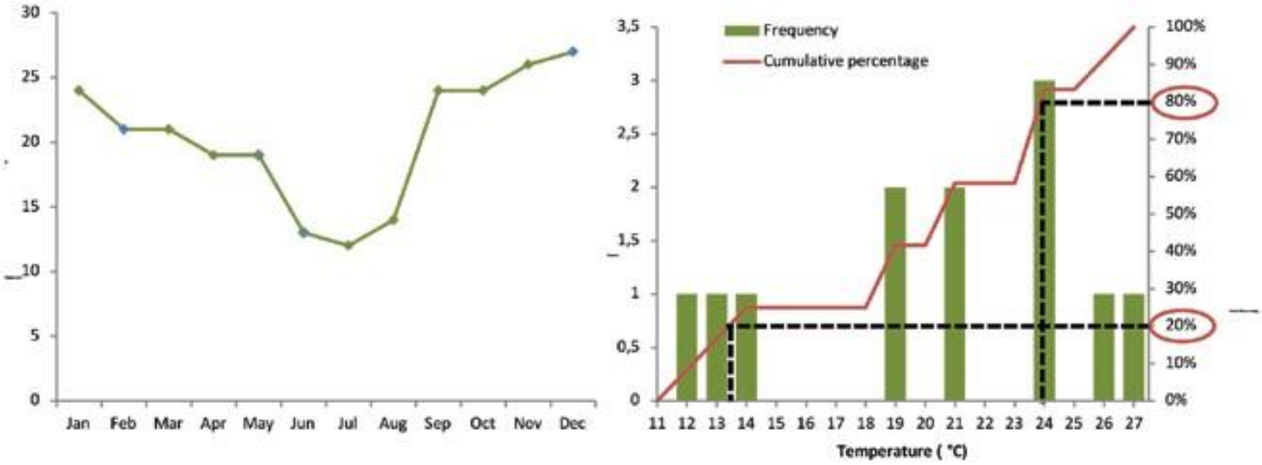


Figure 2: Illustration of the reference system water quality data approach. When following a precautionary approach, it is generally ac- cepted that water quality at the edge of a mixing zone should be higher than the 20th percentile value and lower than the 80th percentile value of the reference system. The percentile is a measure used in statistics indicating the value below which a given percentage of observations fall. For example: Water temperature is measured every month in a lagoon (figure on left). 80 percent of the 12 meas- urements fall below 24°C, which means that 24°C represents the 80th percentile value (figure on right). Similarly, 20 percent of the 12 measurements fall below 13.3°C, which means that 13.3°C represents the 20th percentile value (figure on right). The median of replicate samples from a monitoring site should then be compared with these site-specific guideline values (i.e. between 13.3 and 24 °C).

Most guidelines or standards from countries other than Australia and New Zealand do not explicitly state the approach taken to derive site-specific water quality guidelines for physico-chemical properties or nutrients (exceptions are the BCLME 2006[4] and WIOR 2009[5] Guidelines which follow the ANZECC 2000 Guidelines). The *reference system water quality data* approach, however, seems to be most commonly implemented for physico-chemical properties, and is used in combination with the *predictive modelling approach* to derive nutrient water quality criteria (e.g. US-EPA[29], CCME[28], ANZECC 2000[3]). For example the US-EPA recommends the following process for coastal and estuarine criteria development (please refer to the detailed technical guideline document 'Nutrient Criteria Technical Guidance Manual for Estuarine and Coastal Marine Waters' compiled by the US-EPA for more details[29]):

(1) Investigation of historical information to reveal the nutrient quality in the past and to deduce the ambient, natural nutrient levels prior to anthropogenic disturbance;

(2) Determination of present-day or historical reference conditions for the waterbody segment based on the least affected sites remaining, such as areas of minimally developed shoreline, of least intrusive use, fed by those tributaries of least developed watersheds;

(3) Use of loading and hydrologic models to best understand the density and flow gradients, including tides, affecting the nutrient concentrations;

(4) The best interpretation of this information by specialists responsible for developing the criteria to project future consequences of nutrient enrichment scenarios; and

(5) Consideration of the consequences of any proposed criteria on the coastal marine waters that ultimately receive these nutrients to ensure that the developed criteria provide for the attainment and maintenance of these coastal uses.

The Canadian Council of Ministers of the Environment have adopted the approach taken by the US-EPA, which is summarised in the Canadian guidance framework for the Management of nutrients in nearshore marine systems[28].

3.2.3 Toxic substances

Protection of aquatic ecosystems from toxic substances, which act according to their bioavailable concentration in solution, is best achieved by adopting water quality GCSs based on aquatic toxicological studies. Aquatic toxicological studies are most effective if they are adapted to local conditions, i.e. take into account the sensitivity of local marine species. Toxicity tests experimentally measure the response of living organisms to toxic substances. These responses may be lethal effects, e.g. death of the organism over 96 hours, or sub-lethal effects such as inhibition of growth, reproduction or enzyme activity[30]. Toxicity is a generic meas- ure of the particular biological response (also referred to as end-point) and can be assessed at any level of biological organisation. Toxicological testing can be conducted using a range of endpoints and test species spanning different trophic levels[30]. Adverse effects on an organism can either be acute (exposure over a short period of time relative to the lifespan of the test organism) or chronic (exposure over multiple genera- tions or a significant portion of the organisms' lifespan).

Acute toxicity data is ideally derived by assessing mortality as the end-point, measuring the lethal concentration that kills 50% of test organisms in a given time (lethal concentration or LC_{50}), usually after 96 hours for fish and 48 hours for some invertebrates[30,31,32]. EC_{50}, the *effect concentration*, is generally used when it is difficult to accurately determine mortality. EC_{50} can consist of a surrogate end-point such as immobility or other specific behavior.

Chronic toxicity data includes a wide variety of biological end-points, including biological functioning (mortality, reproduction, immobilisation, and growth), behaviour (mobility, motility, burial rate, ventilation rates, swimming rate, phototactic responses and feeding rate) and biochemical responses (inhibition of bioluminescence, induction, enzyme activity, DNA changes, lesions, immune responses). Biological endpoints of survival, growth and reproduction have direct relevance for ecosystems and should be prioritised when deriving water quality GCSs[30]. *No observed effect concentration* (NOEC) and *lowest observed effect concentration* (LOEC) end-points with concurrent gathering of EC_{50} data is currently recommended for chronic toxicity testing[30]. NOEC is the highest concentration that does not cause a significant effect, while LOEC is the lowest test concentration that does cause an effect.

The dataset for acute tests is very much more extensive than that for chronic tests, although the latter is preferable for protecting ecosystems. Chronic values can be generated by extrapolating from acute data, using (1) chemical-specific acute-chronic ratios (ACR), (2) extrapolation by regression analysis[33,34]or (3) by applying default assessment factors (a default factor of 10 is common used unless a larger factor is warranted)[30].

Toxicity tests include single species tests or multispecies and community bioassays. Single species tests are used almost exclusively in deriving water quality GCSs as they are relatively simple, easy to standardise, and are reproducible and rapid. Their ability to predict responses in natural waters is limited, however. Extrapolation from laboratory tests to even the same or similar species in the field, and to whole ecosystem effects, introduces large uncertainties in the estimation of risk. Multispecies bioassays are thus used to study community responses to chemicals under laboratory conditions. The most complex approach is the addition of organisms or manipulations of natural populations in *in situ* bioassays. Results obtained using the latter approach are environmentally realistic but are inherently highly variable, with interpretation and application being significantly more challenging than using laboratory experiments.

3.2.3.1 Extrapolation of toxicity test results in deriving water quality GCSs

Derivation of all water quality GCSs for toxic substances requires some form of extrapolation from available data to estimate a threshold that takes into account uncertainties such as inter- and intra-species variation and laboratory to field extrapolation. Extrapolations inherently involve a number of uncertainties and value judgements. Two main approaches can be adopted, namely the deterministic and probabilistic methods[35].

Historically, in the absence of extensive toxicity data, the deterministic approach was often employed in establishing water quality GCS values for toxic substances by applying a '*safety factor*' (synonyms include assessment factors and application factors) to the lowest credible toxicity datum. A carefully chosen safety factor, which can range between 1 and 10 000, can account for uncertainty when deriving a water quality GCS[35]. Quantity and quality of the toxicity data have to be considered when determining the level of uncertainty. Where uncertainty is high, a larger safety factor is recommended (e.g. European Union minimum data requirements as detailed in Table 3).

More recently, knowledge of aquatic toxicology and the environmental impact of toxic substances has advanced to a point where it is possible to derive water quality GCSs using statistical extrapolation. Statistical extrapolation for deriving water quality GCSs is internationally implemented by means of species sensitivity distributions (SSD)[31,35,32]. Ideally the dataset for an SSD should be statistically and ecologically representative of the community of interest. An SSD is constructed by log-transforming data and fitting it to a distribution function from which a percentile (normally the 5th percentile) is used as the basis for a water quality GCS. Several distribution functions have been proposed. The US EPA (1985)[32] assumes a log-triangular function, Kooijman (1987)[36] and Van Straalen and Denneman (1989)[37], a log-logistic function, and Wagner and Løkke (1991)[38], a log-normal function. Aldenberg and Slob (1993)[39] and Aldenberg and Jaworska (2000)[40] further refined the methodology for estimating the uncertainty of the 5th percentile by introducing confidence levels. The SSD approach is illustrated in Figure 3.

Species sensitivity distribution models explicitly account for differences in sensitivity between species, although a further safety factor can be applied to the 5th percentile from model extrapolation to account for 'residual' uncertainties that are not accounted for in SSD models[35]. Larger safety factors are, however, applied to the extrapolation when using a deterministic approach. A thorough discussion of the use of the SSD approaches in ecotoxicology and a description of the most appropriate regression models can be found in Posthuma *et al.* (2002)[41] and Zajdlik (2005)[42], respectively.

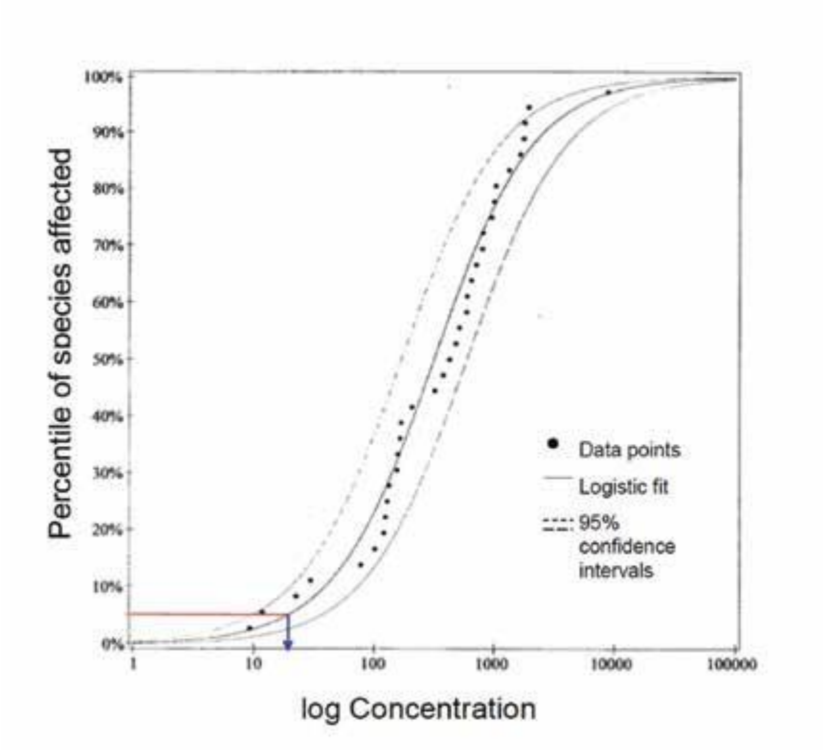


Figure 3: Schematic of a relationship between concentration of a substance and the percent of species affected, illustrating the approach for deriving a specific guideline level, in this case being the intercept of the 5th percentile and the fitted curve. Also shown are the upper and lower 95% confidence limits (Source: Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life, Canadian Council of Ministers of the Environment 2007).

3.2.3.2 Summary of international approaches

The methodologies and approaches employed by developed countries reviewed as part of this study (i.e. Canada, Australia and New Zealand, United States and European Union) had the following commonalities:

- Guiding principles;
- Protocol for collecting data;
- Minimum requirements for toxicological data. For some substances the minimum requirements can, however, not be met and the policymaker may decide that a standard is too uncertain to be used in a statutory context;
- Protocols on how to account for indirect stressors (or factors), which can influence the bioavailability of a toxic substance;
- Approaches and procedures for calculating chronic and acute water quality GCSs (i.e. deterministic approach versus statistical extrapolation, note though that the ANZECC 2000 Guidelines only specify chronic guideline values); and
- Data confidence category (only applied in Canada, New Zealand and Australia). For example, in the case of insufficient data for the statistical extrapolation approach, the deterministic approach can be adopted instead and the water quality guideline value is categorised as less reliable[30, 31, 32,35].

All documents consulted provide detailed guidance for implementing stringent data evaluation processes when deriving water quality GCSs. The most important components, including data confidence categories, minimum toxicological data requirements, and safety factors, the approach adopted (i.e. deterministic versus statistical extrapolation), as well as the assessment period, have been summarised in Table 3 for Canada, Australia and New Zealand, the United States and the European Union. These documents are too comprehensive for a more detailed discussion on further differences and the reader is referred to the relevant literature listed in Table 3 for this. Deriving water quality GCSs using the approaches and methodologies outlined above is very expensive, as it is time and data intensive (note that the ANZECC Guidelines have been in revision since 2009) and has, as a result, not been adopted in any of the developing countries investigated as part of this project[4,5]. Developing countries have mostly focused their efforts on reviewing guidelines from developed countries and have typically customised these as necessary to suit their own requirements (e.g. Benguela Current Large Marine Ecosystem (BCLME) guidelines applicable in Namibia, Angola and South Africa), and corresponding guidelines for countries in the Western Indian Ocean Region (South Africa, Mozambique, Tanzania, Kenya, Somalia, Mauritius, Seychelles, Madagascar).

Table 3: Summary of the approach and minimum toxicological data requirements for the derivation of water quality GCSs for toxic substances applicable to the protection of marine ecosystems (Table adapted from the BCLME Guidelines[4]).

Jurisdiction	Confidence category	Approach	Minimum toxicological data requirements	Assessment period
Canada	Type A	Statistical extrapolation, i.e. species sensitivity distribution (SSD) assuming a log-logistic function	Minimum data requirements for derivation of a long-term exposure guideline for marine environments: • At least three (A&B1)/two (B2) studies on three (A&B1)/two (B2) or more marine fish species, at least one of which is a temperate species. • At least two studies on two or more marine species from different classes, at least one of which is a temperate species (A&B1). • At least two studies on two or more marine species (B2). • At least one study on a temperate marine vascular plant or marine algal species (A&B1). • If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and three (A)/two (B1&B2) studies on non-target marine plant or algal species are required. • A: The acceptable endpoints representing the no-effects threshold and EC10/IC10 for a species are plotted. The other, less preferred, endpoints may be added sequentially to the data set to fulfil the minimum data requirement condition and improve the result of the modelling for the guideline derivation if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: Most appropriate ECx/ICx representing a no-effects threshold > EC10/IC10 > EC11-25/IC11-25 > Maximum acceptable toxicant concentration (MATC) > NOEC > LOEC > EC26-49/IC26-49 > nonlethal EC50/IC50. • B1&B2: The most preferred acceptable endpoint representing a low-effects threshold for a species is used as the critical study; the next less preferred endpoint will be used sequentially only if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: Most appropriate ECx/ICx representing a low-effects threshold > EC15-25/IC15-25 > LOEC > MATC EC26- 49/IC26-49 > nonlethal EC50/IC50 > LC50. • A: Primary and secondary no-effects and low-effects level data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropri- ate goodness-of-fit test.	None specified.

Jurisdiction	Confidence category	Approach	Minimum toxicological data requirements	Assessment period
	Type B1	Deterministic approach: i.e. extrapolation from the lowest available and acceptable toxicity endpoint by using an assessment/ application/ safety factor	• B1: The minimum data requirement must be met with primary data. The value used to set the guideline must be primary. Only low-effect data can be used to fulfil the minimum data requirement. • Secondary data are acceptable. The value used to set the guideline may be secondary. Only low-effect data can be used to fulfil the minimum data requirement. Minimum data requirements for derivation of a short-term exposure guideline for marine environments: • At least three (A&B1)/two (B2) studies on three (A&B1)/two (B2) or more marine fish species, at least one of which is a temperate species. • At least two studies on two or more marine species from different classes, at least one of which is a temperate species (A&B1). • At least two studies on two or more marine species (B2). • At least one study on a temperate marine vascular plant or marine algal species (A&B1). • Toxicity data for marine plants are highly desirable, but not necessary (B2). • If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on non-target marine plant or algal species are required (A,B1&B2). • Acceptable LC50 or equivalent (e.g., EC50 for immobility in small invertebrates) (A,B1&B2). • A: Primary and secondary LC50 (or equivalents) data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test. • B1: The minimum data requirement must be met with primary LC50 (or equivalents) data. The value used to set the guideline must be primary. • B2: The minimum data requirement must be met with primary LC50 (or equivalents) data. Secondary data are acceptable. The value used to set the guideline may be secondary.	
	Type B2			

Jurisdiction	Confidence category	Approach	Minimum toxicological data requirements	Assessment period
Australia and New Zealand	High	Field or mesocosm NOEC Data: Deterministic approach, i.e. extrapolation from the lowest available and acceptable toxicity endpoint by using an assessment/ application/ safety factor.	No-Observable-Effect Concentration (NOEC) data of suitable quality from chronic or sub-chronic tests for 5 or more species belonging to at least four different taxonomic groups. Alternatively, NOEC data from at least 3 well-conducted field or mesocosm (model ecosystem) studies that: • Include fish and shellfish or data related to these; • Include components that represent basic properties of ecosystems (e.g. nutrient cycling, trophic structures); • Are of sufficient duration to account for life-history of organisms and fate of the toxic substance; • Have rigorous experimental design with adequate controls and exposure/effect data (i.e. at least 3 treatments plus control); and • Have sufficient replication to give adequate statistical power. Assessment factor (synonyms: application factor, safety factor) of 10 was applied to the lowest field NOEC to account in the mesocosm types and the fact that more sensitive species may not have lived in the test system.	None specified. Note that all guideline values protect the natural environment from chronic toxicity only.
		Chronic NOEC data: Species sensitivity distribution (SSD) assuming a log-logistic function.	• Chronic NOEC data for at least 5 different species from at least 4 different taxonomic groups • When there were multiple data points for any one species, then the following rules also applied (as per Aldenberg & Slob 1993): o If several toxicity values were derived for different effects or end-points, the lowest NOEC was taken to represent the sensitivity of that species; and o If several toxicity values were derived for the same effect, the geometric mean of the values was taken to represent the sensitivity of that species.	
	Medium	Acute LC50 or EC50 data was converted to extrapolated chronic data by means of the acute-to-chronic ratio (ACR). Species sensitivity distribution (SSD) assuming a log-logistic function was used to derive chronic guideline values	• LC50 or EC50 of suitable quality for at least 5 different species from at least four different taxonomic groups.	

Jurisdiction	Confidence category	Approach	Minimum toxicological data requirements	Assessment period
	Low	Deterministic approach, i.e. extrapolation from the lowest available and acceptable toxicity endpoint by using an assessment/ application/ safety factor.	Note that low reliability trigger values are calculated from insufficient datasets and are not included in the guideline table. Values should be used with caution. • At least 3 chronic NOEC values → AF = 20 • At least 3 acute LC_{50} or EC_{50} values → AF = 100 • If the minimum requirements stated above could not be met, lowest acute LC50 or EC50 → AF = 1000 • Organic or non-metallic inorganic toxic substances: Use freshwater quality guideline, where available.	
United States of America	Not specified	Statistical extrapolation, i.e. species sensitivity distribution (SSD) assuming a log-triangular function.	1. Results of acceptable (rules are explicitly stated in source document) tests with at least one species of saltwater animal in at least eight different families such that all of the following are included: a. two families in the phylum Chordata; b. a family in a phylum other than Arthropoda or Chordata; c. either the Mysidae or Penaeidae family; d. three other families not in the phylum Chordata (may include Mysidae or Penaeidae, whichever was not used above); and e. any other family. 2. Acute-chronic ratios (methodology explained further in source document) with species of aquatic animals in at least three different families provided that of the three species: a. At least one is a fish; b. At least one is an invertebrate; and c. At least one is an acutely sensitive saltwater species (the other two may be freshwater species). • Results of at least one acceptable test with a saltwater alga or vascular plant (see Section VIII). If plants are among the aquatic organisms most sensitive to the material, results of a test with a plant in another phylum (division) should also be available; and • At least one acceptable bio-concentration factor determined with an appropriate saltwater species, if a maximum permissible tissue concentration is available.	One-hour and four-day period averages for criteria maximum concentration (CMC). Criteria continuous concentration (CCC) cannot be exceeded more than once every three years.

Jurisdiction	Confidence category	Approach	Minimum toxicological data requirements	Assessment period
European Union (including the United Kingdom)	None specified	Deterministic: extrapolation from the lowest available and acceptable toxicity endpoint by using an assessment/application/safety factor.	Long-term standard derivation: • Assessment factors (AF) (synonym: safety factors) to be applied to aquatic toxicity data: o Lowest short-term $L(E)C_{50}$ from freshwater or saltwater representatives of three taxonomic groups (algae, crustaceans and fish i.e. base set) of three trophic levels → AF = 10 000 o Lowest short-term $L(E)C_{50}$ from freshwater or saltwater representatives of three taxonomic groups (algae, crustaceans and fish) of three trophic levels, plus two additional marine taxonomic groups (e.g. echinoderms, molluscs) → AF = 1000 o One long-term result (e.g. EC_{10} or NOEC) (from freshwater or saltwater crustacean reproduction or fish growth studies) → AF = 1000 o Two long-term results (e.g. EC_{10} or NOEC) from freshwater or saltwater species representing two trophic levels (algae and/or crustaceans and/or fish) → AF = 500 o Lowest long-term results (e.g. EC_{10} or NOEC) from three freshwater or saltwater species (normally algae and/or crustaceans and/or fish) representing three trophic levels→ AF = 100 o Two long-term results (e.g. EC_{10} or NOEC) from freshwater or saltwater species representing two trophic levels (algae and/or crustaceans and/or fish) plus one long-term result from an additional marine taxonomic group (e.g. echinoderms, molluscs) → AF = 50 o Lowest long-term results (e.g. EC_{10} or NOEC) from three freshwater or saltwater species (normally algae and/or crustaceans and/or fish) representing three trophic levels + two long-term results from additional marine taxonomic groups (e.g. echinoderms, molluscs) → AF = 10 Short-term standard derivation: • Quality assessed acute $L(E)C_{50}$ data for fish, crustaceans and algae (base set). No guideline value can be derived if the set is not complete. • Assessment factors (AF) (synonym: safety factors) to be applied to aquatic toxicity data: o At least one short-term $L(E)C_{50}$ from each of three trophic levels of the base set (fish, crustaceans and algae) → AF = 1000	Long-term standard is expressed as an annual average concentration based on chronic toxicity data. Short-term standard is expressed as a maximum acceptable concentration based on acute toxicity data.

Jurisdiction	Confidence category	Approach	Minimum toxicological data requirements	Assessment period
			o At least one short-term L(E)C$_{50}$ from each of three trophic levels of the base set (fish, crustaceans and algae). Acute toxicity data for different species do not have a higher standard deviation than a factor of 3 in both directions) OR known mode of toxic action and representative species for most sensitive taxonomic group included in data set. → AF = 100 o At least one short-term L(E)C$_{50}$ from each of three trophic levels of the base set (fish, crustaceans and algae) + one short-term L(E)C$_{50}$ from an additional specific saltwater taxonomic group. → AF = 500 o At least one short-term L(E)C$_{50}$ from each of three trophic levels of the base set (fish, crustaceans and algae) + one short-term L(E)C50 from an additional specific saltwater taxonomic group. Acute toxicity data for different species do not have a higher standard deviation than a factor of 3 in both directions) OR known mode of toxic action and representative species for most sensitive taxonomic group included in data set. → AF = 50 o At least one short-term L(E)C$_{50}$ from each of three trophic levels of the base set (fish, crustaceans and algae) + two or more short-term L(E)C50s from additional specific saltwater taxonomic groups→ AF = 100 o At least one short-term L(E)C$_{50}$ from each of three trophic levels of the base set (fish, crustaceans and algae) + two or more short-term L(E)C$_{50s}$ from additional specific saltwater taxonomic groups. Acute toxicity data for different species do not have a higher standard deviation than a factor of 3 in both directions) OR known mode of toxic action and representative species for most sensitive taxonomic group included in data set. → AF = 10	

Jurisdiction	Confidence category	Approach	Minimum toxicological data requirements	Assessment period
		Statistical extrapolation, i.e. species sensitivity distribution (SSD) assuming a log-normal function.	Long-term and short-term standard derivation: • Quality-assessed chronic NOEC or EC$_{10}$ data (long-term); • Quality assessed acute L(E)C$_{50}$ data (one value per species); • The output from an SSD-based quality standard is considered reliable if the database contains preferably more than 15, but at least 10 NOECs/EC$_{10s}$, from different species covering at least 8 taxonomic groups; • The following taxa need to be represented (applicable to fresh and seawater): o Fish (species frequently tested include salmonids, minnows, bluegill sunfish, channel catfish, etc.); o A second family in the phylum Chordata (e.g. fish, amphibian, etc.); o A crustacean (e.g. cladoceran, copepod, ostracod, isopod, amphipod, crayfish etc.); o An insect (e.g. mayfly, dragonfly, damselfly, stonefly, caddisfly, mosquito, midge, etc.) (Only applicable to freshwater, replace by more typical marine taxa, including molluscs, echinoderms, annelids, marine crustaceans or coelenterata); o A family in a phylum other than Arthropoda or Chordata (e.g. Rotifera, Annelida, Mollusca, etc.); o A family in any order of insect or any phylum not already represented; and o Algae; • Long-term standard: A default assessment factor of 5 is applied to the model outcome. The AF value can be reduced if an evaluation of the uncertainties around the derivation of the 5th percentile shows low uncertainty. • Short-term standard: A default assessment factor of 10 is applied to the model outcome. The AF value can be reduced if an evaluation of the uncertainties around the derivation of the 5th percentile shows low uncertainty. An additional AF of 5 is applied when freshwater and saltwater data is combined.	

Canadian Council of Ministers of the Environment (CCME). 2000. Volume 2: Aquatic Ecosystems - Rationale and Background Information. In *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* Australian and New Zealand Environment and Conservation Council; Agriculture and Resource Management Council of Australia and New Zealand;

Canadian Council of Ministers of the Environment (CCME). 2007. A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life 2007. In *Canadian Water Quality Guidelines for the Protection of Aquatic Life* Canadian Council of Ministers of the Environment: Winnipeg;

European Communities. 2011. Technical Guidance for Deriving Environmental Quality Standards. In *Common Implementation Strategy for the Water Framework Directive* Technical Report - 2011 - 055. Guidance Document No. 27. European Commission;

United States Environmental Protection Agency (USEPA). 1985. *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection Of Aquatic Organisms and Their Uses*. PB85-227049 United States Environmental Protection Agency.

4. GUIDELINES FOR THE NATURAL ENVIRONMENT AND MARICULTURE

Narrative statements, guideline values and background information profiles (i.e. description, sources, fate in the environment, occurrence in South African coastal marine waters etc.) for 57 properties are provided.

Properties and constituents are separated into the following categories: (1) Objectionable matter, (2) Physico-chemical properties, (3) Nutrients, (4) Toxic substances, (5) Human pathogens, and (6) Organoleptic substances (i.e. smell, taste, and appearance which reduce palatability of mariculture organisms). This corresponds with the approach adopted for the 1995 Guidelines, and is in line with international practice.

Note that many of the narrative statements and guideline values are applicable to both the Natural Environment and Mariculture (which makes sense given that these organisms are no less sensitive to conditions in the environment than other biota). Other guideline categories (e.g. microbiological indicators such as *E. coli* and faecal coliforms and organoleptic substances) are applicable to the mariculture sector only owing to the fact that these organisms need to be suitable (safe and palatable) for human consumption as well.

4.1 Objectionable matter

Description	Objectionable matter refers to debris, plastic litter, oil, grease, wax, scum, foam, submerged (just below water surface) objects or any other visible substances that float in the water column.
Recommended guideline*	**Mariculture and Natural Environment** Coastal and marine waters should not contain - • floating particulate matter, debris, oil, grease, wax, scum, foam or any similar floating materials and residues from land-based sources in concentrations that may cause nuisance; • materials from non-natural land-based sources which will settle to form putrescence; • submerged objects and other subsurface hazards which arise from non-natural origins and which would be a danger, cause nuisance or interfere with any designated/recognized use
Sources	Naturally occurring floating matter is usually limited to macrophytes and algae. Anthropogenic source of objectionable floating matter include: • raw sewage (municipal waste); • stormwater run-off (litter, debris, oil and grease); • accidental oil spills (oil and grease); • paper and pulp waste water (foaming); and • illegal dumping of ship refuse.
Environmental fate and behaviour	Objectionable floating matter may end up on beaches or in sheltered areas or is ingested by marine organisms.
Interdependence with other constituents/ properties	Not relevant to floating matter.
Mode of action/toxicity	Objectionable floating matter may smother or physically injure marine life, e.g. benthic communities, sea birds and seals. Marine animals can be affected through entanglement in and ingestion of plastic litter. Ingestion of plastic can cause digestive issues (including starvation) and/or death. It has been shown that marine organisms absorb polychlorinated biphenyls from the plastic, which contributes to the bioconcentration and bioaccumulation of this contaminant in the food chain[23]. Although it has not been quantified, the presence of oil may result in a reduction in light penetration which could harm primary production. The presence of crude oil has been shown to inhibit growth in algae substantially[60].
Natural occurrence in South African waters	Naturally occurring floating matter is usually limited to macrophytes and algae.

Guideline levels adopted by other countries/ states/ ecoregions	EPA Florida 2015[18]	No undissolved oil, or visible oil defined as iridescence, shall be present so as to cause taste or odour, or otherwise interfere with the beneficial use of waters.[A]
	EPA South Carolina 2014[16]	All surface waters of the State shall at all places and at all times be free from domestic, industrial, agricultural, or other man-introduced non-thermal components of discharges which, alone or in combination with other substances, or in combination with other components of discharges (whether thermal or non-thermal) float as debris, scum, oil or other matter in degree as to create a nuisance.[A]
	BCLME 2006[4]	1500 µg/L[B]
	WIOR 2009[5]	1500 µg/L[B]

**The existing South African Water Quality Guideline remains unchanged.

A Protection of mariculture organism health

B Human consumption, organoleptic effects

4.2 Physico-chemical properties

4.2.1 Temperature

Constituent	Temperature (°C)
Category	Physico-chemical property
Description	Temperature is a basic property of water. Temperature, or changes in temperature, is important in the regulation or triggering of many physiological processes in marine organisms.
Recommended guidelines for temperature (°C)	**Mariculture and Natural Environment**
	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should be determined as the range defined by the 20th and 80th %iles of the seasonal and/or event-driven distributions for the reference system. Test data: Median concentration for the period.
Notes on guidelines	Owing to the high level of natural variability in sea surface temperature in coastal marine waters both temporally and geographically, it is not possible to provide fixed guideline values for this parameter. The most recent annual average sea surface temperature ranges for the coastal regions in South Africa are shown below[61]. Note that these temperature ranges were calculated from interpolated *in situ* data and have limited local applicability. **West Coast (Cool Temperate):** 12-16°C, depending on upwelling conditions **South Coast (Warm Temperate):** 16-18.5°C **East Coast (Subtropical):** 17.5-25°C

Natural occurrence in South African waters	The temperature regime for South African marine waters differs from one coastal region to another: **West Coast (Cool Temperate):** The natural temperature regime along the South African West Coast is largely influenced by wind-induced upwelling (south-easterly and southerly winds) which varies seasonally. Seasonality is strongest in the south where south-easterly winds are rare in winter but common in summer. Seasonality diminishes to the north-west where winds blow from the south throughout the year, although velocities are lower in winter[62]. Sea surface temperatures of the upwelled coastal waters range from 9-16°C and depend upon the 'strength' of the upwelling process[61,62]. These temperatures can increase to above 16°C in summer through solar warming after upwelling[2]. Surface temperatures of the west coast are usually between 11 and 18°C during summer and 11-14° C during winter[61]. Temperatures of oceanic water in the area are about 20°C[62]. **South Coast (Warm Temperate)**: Surface temperatures of the south coast are usually between 18 and 23°C during summer and 13.5-17° C during winter (temperature ranges were calculated from interpolated *in situ* data)[61]. During summer, thermoclines are formed by the sun heating the surface water, while during winter months the water column is generally well mixed. Upwelling may also influence the temperature regime in the coastal zone, albeit not on the same scale as along the west coast[63]. **East Coast (Subtropical):** The waters of the east coast are of tropical origin. Surface temperatures over most of the east coast are between 19 and 27°C during summer and 16-22.5° C during winter[61]. Offshore surface waters (upper 50 m) are also warmer in summer than in winter with summer maxima greater than 26°C[64]. Short-term fluctuations in surface waters may be as high as 8-9°C, often exceeding seasonal variations. There is evidence of localised upwelling on the inner shore along various areas of the coastline[64]. **Estuaries:** Water temperature in estuaries is typically more variable than in the adjacent marine environment due to their shallow depth, low water volume and freshwater input from land drainage. Water temperatures fluctuate widely in response to changes in air temperature, insolation, tidal state and river flow. Temperatures vary from as low as 8°C to as high as 35°C or more[65].
Interdependence with other constituents/ properties	Not relevant to temperature. Generally, temperature is not interdependent on any other water quality property or constituent.
Pollution Sources	Anthropogenic sources which may influence water temperature in the marine environment are usually related to the discharge of cooling water from power stations and certain industries.
Mode of action/ toxicity	Typical water quality problems which may be associated with temperature include: • eutrophication; • general growth deficiencies; • lowered reproduction; • changes in feeding habits; • changes in respiration patterns[2].
Measurement in seawater	For marine waters, temperature is usually measured *in situ*, using a Conductivity-Temperature-Depth (CTD) meter. An ordinary thermometer or UTR (Underwater Temperature Recorder) can also be used. On a large scale, satellite-derived SST (Sea Surface Temperature) is used for measurement. Units: °C.

Guideline levels adopted in other jurisdictions		**Natural Environment**	**Mariculture**
	CCME 1999[27]	Human activities should not cause changes in ambient temperature of marine and estuarine water to exceed ±1°C at any time, location, or depth. The natural temperature cycle characteristic of the site should not be altered in amplitude of frequency by human activities. The maximum rate of any human-induced temperature change should not exceed 0.5°C per hour.	No guideline
	ANZECC 2000[3]	The desired range for the median concentration is defined by the 20th and 80th percentiles of the ecosystem's reference distribution.	<2.0°C change over one hour
	EPA South Carolina 2014[16]	Ambient temperature shall not exceed 2.2°C above natural conditions during fall, winter or spring, and 0.8°C in summer.	Same as natural environment
	EPA North Carolina 2016[11]"	Temperature shall not be increased above the natural water temperature by more than 0.8°C during the months of June, July, and August not more than 2.2°C dur- ing other months, and in no cases to exceed 32°C due to the discharge of heated liquids.	
	EPA Florida 2015[18]	Focus is on restricting effluent temperature at the end of pipe rather than specifying what the receiving environment should be.	Not listed
	BCLME 2006[4] WIOR 2009[5]	Where an appropriate reference system(s) is available, and there are sufficient data for the reference system, the guideline value should be determined as the range defined by the 20th and 80th %iles of the seasonal distribution for the reference system. Test data: Median concentration for the period.	Same as natural environment

4.2.2 Salinity

Constituent	Salinity
Category	Physico-chemical property
Description	Salinity refers to the dissolved salt content in seawater. Typically, the major constituents in 1 kg of average seawater with a salinity of 35 x 10^{-3} (~35 PSU) in decreasing proportions are [66]: Cl^- (19.35 g) → Na^+ (10.78 g) → SO^{2-} (2.71 g) → Mg^{2+} (1.28 g) → Ca^{2+} (0.41 g) → K^+ (0.40 g) → HCO^{-4} (0.11 g) → Br^- (0.07 g) → $B(OH)_3{}^-$ (0.02 g) → $CO_3{}^-$ (0.01 g) → Sr^{2+} (0.01 g) → $B(OH)_4{}^-$ (0.001 g)
Recommended guidelines for salinity (ppt)	**Mariculture and Natural Environment**
	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should be determined as the range defined by the 20th and 80th %iles of seasonal and/or event-driven distributions, depending upon whether low salinity or high salinity effects are being considered. Test data: Median concentration for the period.
Guideline notes	Owing to the high level of natural variability in salinity in coastal marine waters both temporally and geographically, it is not possible to provide fixed guideline values for this parameter.
Natural occurrence in South African waters	The salinity regime for South African marine waters differs from one coastal region to another: **West coast:** Salinities fall in the narrow range of 34.7 to 35.4 PSU with lower salinities being associat- ed with cold upwelling water[62] (warm surface waters are more saline due to evaporation). Land run-off is low along the west coast and intermittent and thus dilution of these salinities only occurs locally at the Orange, Olifants and Berg River mouths and smaller estuaries further south. Due to evaporative losses, salinities as high as 37.0 PSU have been recorded in Langebaan lagoon[67]. **South coast:** Salinities measured in coastal water of the south coast have revealed slight seasonal variations with highest salinities in summer (35.4 PSU) and lowest values in winter (35.0 PSU)[68]. **East coast:** Subtropical surface waters are usually characterised by relatively high salinities (>35.0 PSU) caused by greater evaporation rates. However, input of fresh water from large rivers to the north (Zambezi and Limpopo) as well as input from east coast rivers result in slightly reduced summer salinities. There is generally a slight positive salinity gradient from the shoreline to the core of the Agulhas Current[64]. **Estuaries:** Salinity in estuaries is typically much more variable than in the adjacent marine environment due to their location at the terminal end of river systems and the combined influences of the sea and freshwater derived from land drainage. This is especially true of temporally open closed estuaries which are periodically cut off from the influences of the sea due to the formation of a sand bar at the mouth where salinities frequently drop to 0 PSU for extended periods and may rise as high as 300 PSU or more due to water loss by evaporation[65].
Interdependence with other constituents/ properties	Generally, salinity is not interdependent on other water quality properties or constituents.
Pollution Sources	Anthropogenic influences on salinity in the marine environment can originate from wastewater discharges which, depending on the volume discharged, may result in a short-term decrease in salin- ity in the immediate vicinity of the discharge. More serious impacts can be caused by hypersaline discharges from reverse osmosis plants. Reverse osmosis involves forcing saline water through a semi-permeable membrane under high pressure, leaving the dissolved salts and other solutes behind on the surface of the membrane. Negatively buoyant brine effluent is discharged by these plants and has the potential to decimate benthic ecosystems in the absence of adequate dilution or dispersion[69]water softening, quality of sewage effluents.
Environmental fate and behaviour	Not relevant to salinity.
Mode of action/toxicity	Typical water quality problems which may be associated with salinity include: • general growth deficiencies; • lowered reproduction; • changes in water pumping rates; • changes in moulting patterns; • mortalities.

Measurement in seawater

According to *The International System of Units (SI) in Oceanography* salinity's unit is dimensinless, and is defined in terms of the condyuctivity ration K_{15}. The conductivity ratio is calculated by dividing the conductivity of the seawater sample (at 15°C and 1 atm pressure) by the conductivity of standard KCl solution (32.4356 g/kg)[70]. In marine waters, salinity is usually measured *in situ*, using a Conductivity -Depth-Salinity (CTDS) meter.

Where the ionic strength ('salt content') of seawater has been measured as Electrical Conductivity (EC in mS/m) conversion factors can be used to calculate PSU using the following equation: Salinity (PSU) = (EC (mS/m) x factor)/1000

Conversion factors from EC to PSU in the range 32-36, at different temperatures are[71]:

Electrical Conductivity (mSm-1)	**Temperature (°C)**			
	25	**20**	**15**	**10**
5437.4	6.62			
5302.5	6.6			
5167.1	6.58			
531.4	6.56			
4895.1	6.54			
4910.5		7.33		
4788.2		7.31		
4665.6		7.29		
4542.6		7.26		
4419.2		7.24		
4399.6			8.18	
4289.6			8.16	
4179.4			8.13	
468.8			8.11	
3957.9			8.08	
3906.1				9.22
3808				9.19
3709.6				9.16
3611				9.14
3512.2				9.11

Where the salt content has been measured as mg/L total dissolved solids (TDS), it can be converted to salinity by dividing the TDS value by 1000.

Guideline levels adopted in other jurisdic-tions		Natural Environment	Mariculture
	CCME 1999[27]	Human activities should not cause the salinity (expressed as, parts per thousand) of marine and estuarine waters to fluctuate by more than 10% of the natural level expected at that time and depth.	No guideline
	ANZECC 2000[3]	The desired range for the median concentration is defined by the 20th and 80th percentiles of the ecosystem's reference distribution.	Marine: 33-37 Brackish: 3-35
	EPA North Carolina 2016[11]	Changes in salinity due to hydrological modifications shall not result in removal of the functions of a Primary Nursery Areas (PNA)[A]	Not listed
	BCLME 2006[4] WIOR 2009[5]	Where an appropriate reference system(s) is available, and there are sufficient data for the reference system, the guideline value should be determined as the range defined by the 20th and 80th %iles of the seasonal distribution for the reference system. Test data: Median concentration for the period.	Same as natural environment guideline

[A] Primary Nursery Areas (PNAs) are tidal salt waters which provide essential habitat for the early development of commercially important fish and shellfish and are so designated by the Marine Fisheries Commission.

4.2.3 pH

Constituent	pH
Category	Physico-chemical property
Description	pH is a measure of the concentration of hydrogen ions in solution, according to the expression: pH = $-\log_{10}$ [H^+], where H^+ is the hydrogen ion concentration. Water with a pH less than seven is acidic, while alkaline water has a pH of greater than 7.
Recommended guidelines for pH	**Mariculture and Natural Environment**
	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should be determined as the range defined by the 20th and 80th %iles of the of seasonal and/or event-driven distributions for the reference system. pH changes of more than 0.5 pH units from the seasonal maximum or minimum defined by the reference systems should be fully investigated. Test data: Median concentration for the period
Guideline notes	Owing to the high level of natural variability in pH in coastal marine waters both temporally and geographically, it is not possible to provide fixed guideline values for this parameter.
Natural occurrence in South African waters	The pH of seawater usually ranges between 7.9 and 8.2[72]. Seawater in equilibrium with atmospheric CO_2 is slightly alkaline, with a pH of about 8.1-8.3. The pH may rise slightly through the rapid abstraction of CO_2 from surface waters during photosynthesis[73]. Decomposition of organic matter under anaerobic (anoxic) conditions involves the reduction of CO itself, and leads to the formation of hydrocarbons, such as methane. Under these conditions, the pH may rise to a value as high as 12.0[73]. pH levels in estuaries is typically more variable than in the sea due to reduced concentrations of buffering ions (salt). pH levels in the upper reaches of estuaries in the fynbos region (west and south coasts) are often acidic (pH <7) due to the presence of humic acid in water flowing off areas with fynbos vegetation, and may be alkaline (pH >7) due to geological influences in other areas.
Interdependence with other constituents/properties	The pH of seawater can be influenced by certain gases which are soluble in seawater, such as carbon dioxide, ammonia (unionised) and hydrogen sulphide. For example, carbon dioxide can be abstracted from seawater during phytoplankton blooms thereby causing an increase in pH. In seawater CO^2 [gas] + $H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$ In seawater remote from contaminated or anoxic regions, the pH is mainly controlled by the CO_2/HCO_3^- / CO^{2-} system. Other weak electrolytes slightly augment this effect (e.g. borate, phosphate, silicate and arsenate) [71]
Pollution Sources	Anthropogenic sources which may influence the pH of water are usually related to highly acidic or alkaline industrial waste waters.
Environmental fate and behaviour	Aqueous solutions containing salts of weak acids or bases, such as seawater, show a resistance to pH change (known as buffering), on the addition of acids and bases[71].
Mode of action/ toxicity	Typical water quality problems which may be associated with pH include: • general growth deficiencies; • changes in respiration patterns; • changes in water pumping rates; • shell deformation; • mortalities.
Measurement in seawater	pH is measured using a pH meter. The pH of seawater cannot be measured against the low ionic strength National Bureau of Standards (USA) buffers. Seawater has a high ionic strength resulting in significant errors in measurements. Artificial seawater buffers should be used[49].

Guideline levels adopted in other jurisdictions		**Natural Environment**	**Mariculture**
	CCME 1999[27]	The pH of marine and estuarine waters should fall within the range of 7.0-8.7 units unless it can be demonstrated that such a pH is a result of natural processes. Within this range, pH should not vary by more than 0.2 pH units from the natural pH expected at that time. Where pH is naturally outside this range, human activities should not cause pH to change by more than 0.2 pH units from the natural pH expected at that time, and any change should tend towards the recommended range.	No guideline
	ANZECC 2000[3]	Ambient pH ranges are specified for different ecoregions (differentiated between inshore and offshore, where the former is in some instances classified as an estuary).[A]	6.0-9.0[A]
	EPA 1986[15]	6.5-8.5 For open ocean wa- ters where the depth is substantially greater than the euphotic zone, the pH should not be changed more than 0.2 units from the naturally occurring variation or any case outside the range of 6.5 to 8.5. For shallow, highly productive coastal and estuarine areas where naturally occurring pH variations approach the lethal limits of some species, changes in pH should be avoided but in any case should not exceed the limits established for fresh water, i.e., 6.5-9.0.	No guideline
	EPA California 2013[6]	The pH shall not be changed at any time more than 0.2 units from that which occurs naturally.	Not listed

	EPA Florida 2015[18]	In coastal water, the pH shall not vary more than one unit above or below natural background. In open waters, the pH should change no more than two-tenths of a unit above or below natural background. The pH should range from 6.5-8.5.	Same as natural environment guideline
	EPA South Carolina 2014[16]	pH shall not vary more than one-half of a pH unit above or below that of effluent-free waters in the same geological area having a similar total salinity, alkalinity and temperature, but not lower than 6.5 or above 8.5. South Carolina has also developed some site-specific criteria.	Same as natural environment guideline
	EPA North Carolina 2016[11]	6.8-8.5	Not listed
	BCLME 2006[4] WIOR 2009[5]	Where an appropriate reference system(s) is available, and there are sufficient data for the reference system, the guideline value should be determined as the range defined by the 20th and 80th %iles of the seasonal distribution for the reference system. Test data: Median concentration for the period.[A]	Same as natural environment guideline

A Protection of mariculture organism health

4.2.4 Total suspended solids

Constituent	Total suspended solids (TSS)
Category	Physico-chemical property
Description	Suspended matter consists of silt, clay, fine particles of organic and inorganic matter, soluble organic compounds, plankton, and other microscopic organisms. The presence of suspended solids is usually attributed to a reduction in the clarity of water, i.e. light penetration or visibility. For the purpose of deriving water quality guidelines, the non-filterable residues, containing both biotic and abiotic components, will be referred to as total suspended sediments.
Recommended guidelines for total suspended solids (mg/L)	**Mariculture and Natural Environment** Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should not exceed the 80th %ile of the seasonal and/or event-driven distributions. Additionally, the natural euphotic depth (Z_{eu}) should not be permitted to change by more than 10%. Test data: Median concentration for period.
Guideline notes	Owing to the high natural variability in total suspended solids (TSS) levels in coastal marine waters both temporally and geographically, it is not possible to provide fixed guideline values for this parameter.
Sources	Sediments enter fresh surface waters predominantly through natural erosion of geological formations. The rate of erosion depends on climate, geology, exposure, slope, soil type, and vegetation cover. Deposited sediment may remain stored in river channels and banks until mobilised by water with critical velocities, transporting sediment into coastal environments[74]. Apart from freshwater inputs, a large proportion of suspended solids in estuarine and coastal waters originates from resuspension of fine, unconsolidated sediments and detritus by means of wave action and currents[75]. Natural levels of suspended solids fluctuate widely with large daily and seasonal variations[74]. Anthropogenic activities such as agriculture, deforestation, surface hardening (i.e. urbanisation), dredging, gravel pit operations, mining, and municipal/industrial wastewater discharge into rivers can dramatically increase sediment input into the coastal environment.
Environmental fate and behaviour	Suspended solids usually remain in suspension in the water column since their density is similar to that of sea-water and turbulence in the water column. Under calmer conditions, solids may settle out from the water column and be deposited onto the substratum.
Interdependence with other constituents/ properties	The type and concentration of suspended matter controls the turbidity and transparency of seawater. The relationships between turbidity and suspended sediments is site-specific, as turbidity is affected by factors such as the concentration, size, shape, and refractive index of suspended sediments and the water colour [76,74,77,78]. The composition (grain size, organic vs. inorganic) and concentration of suspended solids is an important factor in determining the fate of some constituents in seawater.
Mode of action/ toxicity	When the TSS concentration is elevated above background levels, it may have an impact on the ecosystem as a whole and/or on individual species. For example, the energy available to seaweed may be reduced due to light attenuation due to elevated TSS levels. Conversely, reduced nutrient availability in the water column may occur through adsorption and subsequent sedimentation of settleable solids. At high concentrations, TSS may cause abrasion or clogging of sensitive organs such as gills, which in turn, results in stress and increased disease susceptibility.
Natural occurrence in South African waters	The overall trend in TSS along the coast of South Africa could not be established from the literature. Although turbidity data is available, relationships between turbidity and suspended sediments cannot be assumed, as turbidity is affected by factors such as the concentration, size, shape, and refractive index of suspended sediments and the water colour[76,74,77,78].
Measurement in Seawater	Suspended matter is measured in the laboratory by both filterable and non-filterable residues of a water sample. Undissolved particles make up the non-filterable residues, these varying in size from approximately 10 nm to 0.1 mm in diameter, although it is usually accepted that the suspended solids are the fraction that will not pass through a 0.45 µm pore diameter glass fibre filter[24].

Guideline levels adopted in other jurisdictions		**Natural Environment**	**Mariculture**
	CCME 2002[24]	**Clear flow**: Maximum increase of 25 mg/L from background levels for any short-term exposure (e.g., 24-h period). **Maximum average** increase of 5 mg/L from background levels for longer term exposures (e.g., inputs lasting between 24 h and 30 d). **High flow**: Maximum increase of 25 mg/L from back- ground levels at any time when background levels are between 25 and 250 mg/L. Should not increase more than 10% above back- ground levels when background is ≥ 250 mg/L.	No guideline
	ANZECC 2000[3]	Not listed	Marine waters: <10 mg/L Brackish waters: <75 mg/L
	EPA 1986[15]	Settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonally established norm for aquatic life.	No guideline
	EPA North Carolina 2016[11]	Not listed	Settleable solids: None attributable to sewage, industrial wastes or other wastes;
	BCLME 2006[4] WIOR 2009[5]	Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline values should be determined as the 80th %ile of the reference system(s) distribution. Additionally, the natural euphotic depth (Z_{eu}) should not be permitted to change by more than 10%. Test data: Median concentration for period.	Same as natural environment guidelines

4.2.5 Turbidity (including colour and euphotic zone)

Constituent	Turbidity
Category	Physico-chemical property
Description	Turbidity is a measure of the lack of clarity or transparency of water caused by biotic and abiotic suspended or dissolved substances (colloidal particles with size between 0.001 and 0.1 µm). The higher the concentration of these substances in water, the more turbid the water becomes. The colour of turbid water changes according to the types of dissolved substances. Turbidity is an expression of the optical properties of substances that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample[24].
Recommended guidelines for turbidity (NTU)	**Mariculture and Natural Environment**
	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should not exceed the 80th %ile of seasonal and/or event-driven distributions. Additionally, the natural euphotic depth (Z_{eu}) should not be permitted to change by more than 10%. Test data: Median concentration for period.
Guideline notes	Owing to the high natural variability in turbidity in coastal marine waters both temporally and geographically, it is not possible to provide fixed guideline values for this parameter.
Sources	Natural turbidity in water is caused by colloidal suspension (particle size between 0.001 µm and 0.1 µm) of, for example, clays and silt, usually introduced through river run-off. Turbidity may also be introduced to the water column through resuspension of natural debris during turbulent conditions, usually caused by strong wind and wave action. Natural colour in water may result from the presence of natural metallic ions and humic substances, usually introduced through river run-off.

Environmental fate and behaviour	Owing to the high salt content of seawater, natural colloidal suspension (causing turbidity) and humic substances (natural colour) usually coagulate with specific ions and precipitate out.		
Interdependence with other constituents/ properties	Turbidity and transparency of seawater is controlled by the type and concentration of suspended solids. The relationships between turbidity and suspended solids are site-specific, as turbidity is affected by factors such as the concentration, size, shape, and refractive index of suspended sediments and the wate colour[76,74,77, 78]. Turbidity can serve as an indicator for TSS at sites where this relationship has been established[24]. Salinity stratification plays an important role in the suppression of turbulence in estuarine surface waters by trapping suspended solids near the so called turbidity maximum. A turbidity maximum describes a layer of very high turbidity which is trapped underneath a less dense, freshwater body[79]		
Mode of action/ toxicity	Unnaturally high turbidity levels reduce light penetration into the water column, which can supress photosynthetic productivity and consequently impact on higher trophic levels. Substances impacting on water colour may change the quantity and quality of transmitted light, which can induce a shift in species composition of phytoplankton, benthic microalgae and aquatic macrophytes. Marine organisms which rely on visual cues for feeding or reproduction may also be impacted by altered turbidity levels.		
Natural occurrence in South African waters	Turbidity in estuarine systems has been shown to be positively correlated to the amount of seasonal rainfall in the biogeographic regions of South Africa[80,81,82]. For example, lower rainfall and runoff in cool and warm-temperate estuaries results in lower turbidity, while high rainfall and runoff results in high turbidity, particularly in subtropical estuaries[83].		
Measurement in Seawater	Turbidity can be measured using a turbidity meter (Nephelometer) *Units:* NTU (Nephelometric turbidity units)[84] 'True colour', i.e. the colour in water caused by substances in solution, can be measured through visual comparison methods using the platinum cobalt method or a Lovibond comparator[84]. *Units:* Pt-Co mg/L (defined as the colour being produced by 1 mg Pt -l1 in the form of the chloroplatinate ion or Hazen unit. (1 Hazen unit = 1 Pt-Co mg/L). The clarity of water (combined effect of colour, turbidity and suspended solids) can be measured by using a Secchi disc (a disc about 8 inches in diameter, divided into quadrants painted alternately black and white like the target of a level-rod). The Secchi depth is reached when the reflectance equals the intensity of light backscattered from the water. *Units:* metres below water surface[84].		
Guideline levels adopted in other jurisdictions		**Natural Environment**	**Mariculture**
	CCME 2002[24]	**Clear flow:** Maximum increase of 8 NTU from background levels for a short-term exposure (e.g. 24-h period). Maximum average increase of 2 NTU from background levels for a longer term exposure (e.g. 30-d period). **High flow or turbid waters:** Maximum increase of 8 NTU from background levels at any one time when back- ground levels are between 8 and 80 NTU. Should not increase more than 10% of background levels when background is > 80 NTU.	No guideline
	ANZECC 2000[3]	An ambient turbidity range is specified for each ecoregion (differentiated between inshore and offshore, where the former is in some instances classified as estuary).[A]	*Colour:* 30-40 Pt-Co units[A]

	EPA 1986[15]	Settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonally established norm for aquatic life.	No guideline
	EPA California 2013[6]		Not listed
	EPA Florida 2015[18]	29 NTU above background concentration. All surface waters of the State shall at all places and at all times be free from domestic, industrial, agricultural, or other man-introduced non-thermal components of discharges which, alone or in combination with other substances or in combination with other components of discharges (whether thermal or non-thermal) produce colour, odour, taste, turbidity, or other conditions in degree as to create a nuisance.	*Turbidity:* 29 NTU above background concentration.[A] Euphotic zone: The annual average value shall not be reduced by more than 10% as compared to the natural background value. Annual average values shall be based on a minimum of three samples, with each sample collected at least three months apart[A].
	EPA South Carolina 2014[16]	Not to exceed 25 NTU provided existing uses are maintained. Free from: Sewage, industrial, or other waste which produce taste or odour or change the existing colour or physical, chemical, or biological conditions in the receiving waters or aquifers to such a degree as to create a nuisance, or interfere with classified water uses (except classified uses within mixing zones as described in this regulation) or existing water uses.[B]	Same as natural environment guideline
	EPA North Carolina 2016[11]	The turbidity in the receiving water shall not exceed 25 NTU; if turbidity exceeds this level due to natural background conditions, the existing turbidity level shall not be increased.	Not listed
	BCLME 2006[4] WIOR 2009[5]	Where an appropriate reference system(s) is available and there are suf- ficient data for the reference system, the guideline values should be deter- mined as the 80th %ile of the reference system(s) distribution. Additionally, the natural euphotic depth (Z_{eu}) should not be permitted to change by more than 10%. Test data: Median concentration for period.	Same as natural environment guideline

A Protection of mariculture organism health

B Protection of human health, consumption of organisms only

4.2.6 Dissolved oxygen

Constituent	Dissolved Oxygen
Chemical grouping	Physico-chemical property
Description	This property refers to the amount of dissolved oxygen present in the water. Dissolved oxygen is an essential requirement for most heterotrophic marine life.
Recommended guidelines for dissolved oxygen (mg/L)	**Mariculture and Natural Environment**
	Guideline values must be derived from a reference system (data set) that is appropriate to the discharge locality and should not be allowed to drop below the 20%ile of the seasonal and/or event-driven distributions. Where possible, guideline values should be obtained during low flow and high temperature periods when DO concentrations are likely to be at their lowest. Test data: Median DO concentration for the period, calculated using the lowest diurnal DO concentrations.
Guideline notes	Owing to the high level of natural variability in levels of dissolved oxygen in coastal marine waters both temporally and geographically, it is not possible to provide fixed guideline values for this parameter.
Pollution Sources	Anthropogenic sources which may influence the dissolved oxygen in marine waters are those with high oxygen demand (reflected in high organic content, high biochemical oxygen demand or chemical oxygen demand) including: • stormwater run-off; • sewage discharges; • certain industrial wastes.

Interdependence with other constituents/ properties

The dissolved oxygen of water is a non-conservative property. The solubility of oxygen in water is largely dependent on the salinity and temperature of the water. The solubility of oxygen (mg/L) in seawater for a range of salinities and temperatures are (1 atm pressure)[85]"type" : "article-journal", "volume" : "29" }, "uris" : ["http://www.mendeley.com/documents/?uuid=81857181-61c5-453f-b912-e76b97b35ea7"] }], "mendeley" : { "formattedCitation" : "⁸⁵", "plainTextFormattedCitation" : "85", "previouslyFormattedCitation" : "⁸⁶" }, "properties" : { "noteIndex" : 0 }, "schema" : "https://github.com/citation-style-language/schema/raw/master/csl-citation.json" }:

Temperature (°C)	Salinity (ppt)			
	25x10^{-3}	30x10^{-3}	35x10^{-3}	40x10^{-3}
10	9.621	9.318	9.024	8.739
11	9.412	9.117	8.832	8.556
12	9.210	8.925	8.648	8.379
13	9.017	8.739	8.470	8.210
14	8.830	8.561	8.300	8.046
15	8.651	8.389	8.135	7.888
16	8.478	8.233	7.976	7.737
17	8.311	8.064	7.823	7.590
18	8.151	7.910	7.676	7.449
19	7.995	7.761	7.533	7.312
20	7.846	7.617	7.395	7.180
21	7.701	7.479	7.262	7.052
22	7.561	7.344	7.134	6.929
23	7.426	7.214	7.009	6.809
24	7.295	7.089	6.888	6.693
25	7.168	6.967	6.771	6.581
26	7.045	6.849	6.658	6.472
27	6.926	6.734	6.548	6.366
28	6.810	6.623	6.441	6.263
29	6.698	6.515	6.337	6.164
30	6.589	6.410	6.236	6.066

Mode of action/toxicity

Typical problems which may be associated with dissolved oxygen include:

- general growth deficiencies;
- lowered reproduction;
- changes in feeding habits;
- changes in respiration patterns;
- changes in moulting patterns;
- formation of air blisters;
- mortalities;
- abnormalities in movement.

Natural occurrence in South African waters	Dissolved oxygen is a non-conservative property of seawater and its natural levels in surface waters are largely governed by local temperature/salinity regimes, as well as organic content. Dissolved oxygen levels in seawater below the thermocline are usually lower, owing to biological demand and limited replenishment from the air. The surface waters along high energy coastlines, such as those found along most parts of the South African coast, are usually saturated with oxygen. Low oxygen waters are also a feature of the Benguela system (west coast). Chapman and Shannon[86] identified two local zones for formation of oxygen-deficient water along the west coast: one in the vicinity of the Orange River mouth and the other in St Helena Bay[87]. Water from both these zones can advect southwards as compensation flow for the surface north-westerly drift[88]. This low-oxygen water rarely penetrates south of the Cape Peninsula, but oxygen-depleted water that occasionally develops on the Agulhas Bank, can impact this area[86].
Measurement in sea-water	In a receiving water body, it is important to measure the actual amount of oxygen in solution in the water, expressed as dissolved oxygen (DO). Dissolved oxygen in natural waters is usually measured titrametrically according to the Winkler method [89] or using an oxygen sensor – either an electrode (electro- chemical sensor) or an optode (optical sensor). *Units:* mg/L O_2 Where O_2 concentrations are given as ml/L, it can be converted to mg/L: O_2 in mg/L = O_2 in ml/L x (1.4290 / density of seawater at specific °C) **Note:** Often the chemical characteristics of *effluents* are given in terms that are not necessarily identical to those properties or constituents used to describe the receiving water quality. It is often more informative to measure the amount of oxygen which might be consumed by the effluent when it is discharged into a receiving water body, rather than available oxygen itself (i.e. dissolved oxygen). The oxygen demand of an effluent is normally expressed as: • five-day biochemical oxygen demand (BOD)[90] • chemical oxygen demand (COD); or • Oxygen absorbed (OA).

Guideline levels adopted in other jurisdictions		**Natural Environment**	**Mariculture**
	CCME 1992[91]	The recommended minimum concentration of DO in marine and estuarine waters is 8.0 mg/L. Depression of DO below the recommended value should only occur as a result of natural processes. When the natural DO level is less than the recommended interim guideline, the natural concentration should become the interim guideline at that site. When ambient DO concentrations are >8.0 mg/L, human activities should not cause DO levels to decrease by more than 10% of the natural concentration expected in the receiving environment at that time.	No guideline
	ANZECC 2000[3]	Ambient dissolved oxygen ranges are specified for individual ecoregions (differentiated between inshore and offshore, where the former is in some instances classified as estuary).[A]	>5 mg/L[A]
	EPA 1986[15]		No guideline
	EPA California 2013[6]		Not listed
	EPA Florida 2015[18]	9.1	The daily average percent DO saturation shall not be below 42 percent saturation in more than 10 percent of the values; The seven-day average DO percent saturation shall not be below 51 percent more than once in any twelve week period; and The 30-day average DO percent saturation shall not be below 56 percent more than once per year. If it is determined that the natural background DO saturation in the waterbody (including values that are naturally low due to vertical stratification) is less than the applicable criteria stated above, the applicable criteria shall be 0.1 mg/l below the DO concentration associated with the natural background DO saturation level. For predominately marine waters, a decrease in magnitude of up to 10 percent from the natural background condition is allowed if it is demonstrated that sensitive resident aquatic species will not be adversely affected.[A]

	EPA South Carolina 2014[16]	Daily average not less than 5.0 mg/l with a low of 4 mg/l.	Same as natural environment guidelines[A]
	EPA North Carolina 2016[11]	Dissolved oxygen: not less than 5.0 mg/l, except that swamp waters, poorly flushed tidally influenced streams or embayments, or estuarine bottom waters may have lower values if caused by natural conditions;	
	BCLME 2006[4] WIOR 2009[5]	Where an appropriate reference system(s) is available, and there are sufficient data for the reference system, the guideline value should be determined as the 20%ile of the reference system(s) distribution. Where possible, the guideline value should be obtained during low flow and high temperature periods when DO concentrations are likely to be at their lowest. Test data: Median DO concentration for the period, calculated using the lowest diurnal DO concentrations.	Same as natural environment guideline

A Protection of mariculture organism health
B Protection of human health, organism consumption only

4.3 Nutrients

The main nutrients required for primary production in nearshore marine environments include nitrogen (ammonia, ammonium, nitrate and nitrite), phosphorus (phosphate), silicate and iron.

In contrast to freshwater systems, where phosphorus is usually the limiting nutrient, temperate marine systems (including estuaries) are thought to be nitrogen limited[28, 92,93]. It is thought that differences in nitrogen fixation and denitrification rates as well as nutrient loading ratios may be responsible for this phenomenon. However, phosphorus can be temporarily limiting to phytoplankton in coastal marine systems during periods of high freshwater inflow, such as those that occur during the rainy season[28]. Phosphorus may also be limiting in anthropogenically impacted systems that have exceptionally high nitrogen inputs combined with stringent phosphorus input controls[94]. Thus, both phosphorus and nitrogen must be considered in plans designed to manage nutrient over-enrichment in nearshore marine systems[95]. Although less intensively studied than phytoplankton, marine macroalgae growth in temperate systems appears to be limited primarily by nitrogen[96,28]. The fate of nitrogen in form of ammonium, ammonia, nitrite and nitrate in the marine environment is controlled by the nitrogen cycle, which is explained and shown in Box 1.

Excess inputs of phosphorus and nitrogen in nearshore marine ecosystems can cause changes in both structure (biological communities) and function (ecological processes)[29]. Over-enrichment of biologically available phosphorus and nitrogen initially stimulates diatom growth. Diatoms also require silicate as an essential nutrient and consequently, excessive diatom growth can deplete silicate in the water column[97,28]. In coastal systems with high nutrient inputs, this decline in silicate is often responsible for a shift from a diatom based phytoplankton community to one in which flagellates dominate[28,98]. Concurrently, harmful algal blooms may occur more frequently. Such red and brown tides can be toxic to shellfish, fish, marine mammals, resulting in changes in biodiversity, and in some cases, become a direct threat to humans[99,29]. In shallow marine environments and intertidal zones where sufficient light reaches the bottom, fast growing macroalgae (e.g. *Enteromorpha*, *Ulva*, *Cladophora spp.*) may proliferate, eliminating slower growing macroalgae and sea grasses (e.g. *Zostera capensis*). High phytoplankton concentrations may also reduce light penetration to the point where sea grasses and other benthic plants are completely eliminated[29,28].

One of the most serious consequences of nutrient over-enrichment to marine ecosystems is the decreased level of dissolved oxygen (DO) within the water column[100]. Bacterial decomposition of excess biological material depletes DO, causing hypoxic or anoxic conditions in sediments and the water column. In shallow systems, excessive macroal- gal growth can result in anoxic conditions within the water column, especially during periods of warm water temper- atures and during the night when photosynthesis cannot occur. This is when dissolved oxygen reaches a minimum and may result in the death of aerobic benthic organisms and, in severe cases, fish kills[101,28,100].

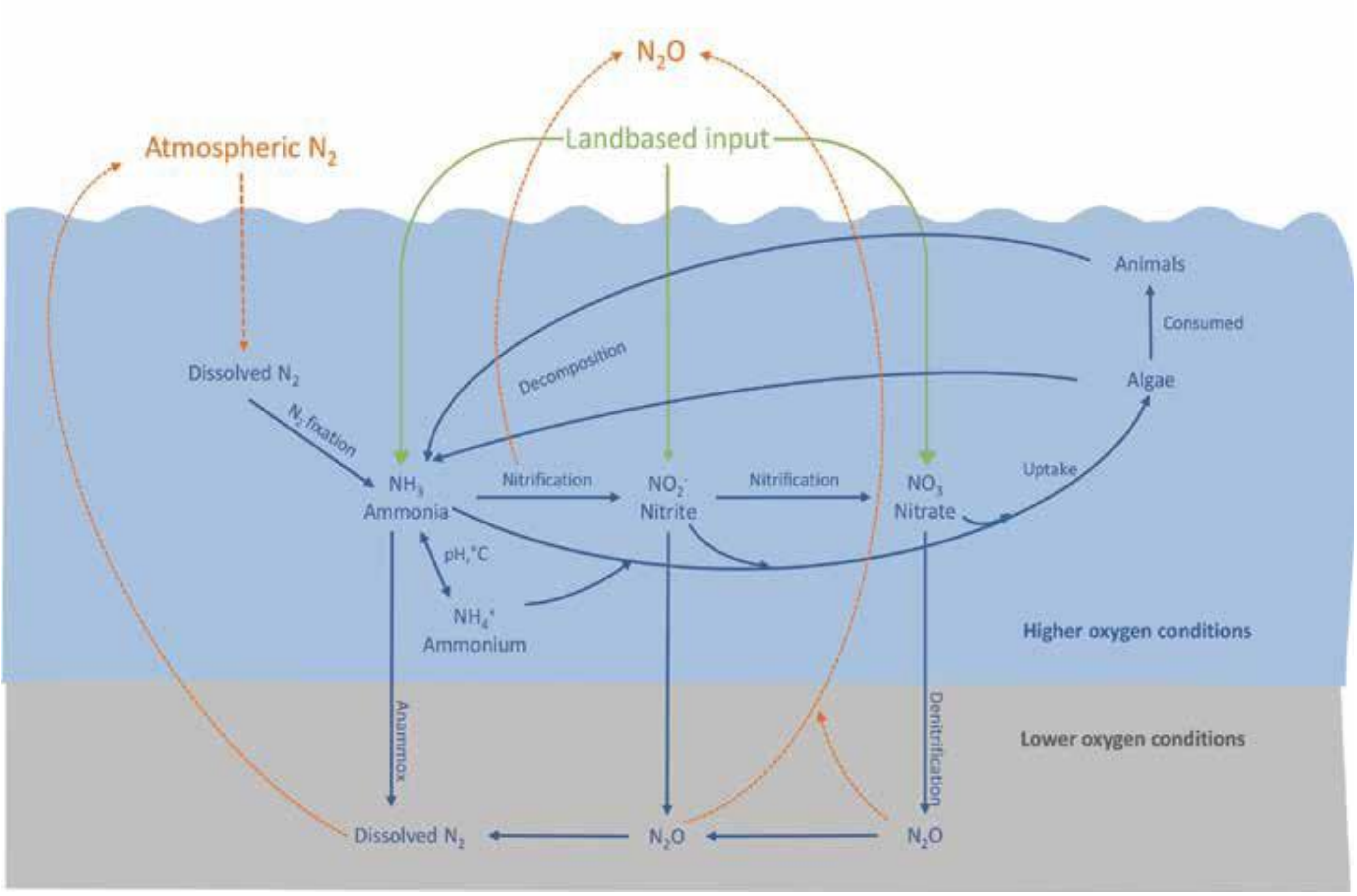
Iron is also an important trace element for primary producers and nitrogen fixing organisms and has been shown to be a limiting nutrient in some offshore oceanic marine systems[102]. It is considered unlikely that iron limits primary production in estuaries and coastal seas, although it may partially limit nitrogen-fixing cyanobacteria in estuaries[103].

Since pre-industrial times, the amount of biologically available nitrogen entering the marine environment has in- creased dramatically each year and there is a strong relationship between nitrogen inputs to a coastal system and the human population density within its catchment[28]. The most important sources of anthropogenic nutrient inputs to coastal systems are wastewater discharges, fertilizers and atmospheric deposition[104]. Nitrogen, unlike phosphorus, is not retained in soils after the application of fertilisers and is easily leached from soils into waterways and into the ocean. Nitrogen input via groundwater may also be important in areas where aquifers are hydraulically connected to the sea through permeable soils[104,28].

Furthermore, aquaculture operations can be important sources of nutrient inputs to coastal areas[105,28]. About 40% of the nitrogen contained in fish foods is incorporated into fish biomass, the rest is released to the environment as metabolic wastes, faeces and uneaten food fragments[106]. Fish and seafood processing plants are also considered as important potential sources of nutrients in coastal waters[28]. For effluent management purposes, it has been recommended to consider seasonal loading rates in relation to the time at which the system is most susceptible to eutrophication, for example, in the summer when freshwater inputs and flushing rates are lowest[28].

In some coastal areas, the transport of nitrogen into coastal areas from offshore waters can be greater than land- based input[94]. This is true for many coastal areas, such as areas along the west coast of South Africa, where nutrient-rich, deep-oceanic water upwells along the coast.

Not all coastal waters are equally susceptible to nutrient over-enrichment. The most susceptible systems are those with limited tidal exchange and mixing, long retention time, vertically stratified water masses, and relatively low background concentrations of suspended sediments[107,94]. This means that controlling nutrient inputs is of relatively little importance for achieving a healthy coastal environment in some areas, while it is of critical importance in others and highlights the need for site specific understanding and data.



Box 1: The fate of ammonium, ammonia, nitrite and nitrate in the marine environment is determined by the nitrogen cycle as depicted in the figure on the right. The marine nitrogen cycle is one of the most complicated biochemical cycles in the oceans. Nitrogen is a biologically limiting nutrient, which changes in its form, or concentration, and can cause changes in the cycling of carbon or phosphorus.

Nitrogen gas (N$_2$) makes up 78% of Earth's atmosphere and dissolves into the ocean's surface waters. Nitrogen gas is biologically accessible to *Trichodesmium spp.* bacteria, which convert nitrogen gas into ammonia$_3$(NH) (nitrogen fixation). Some of the ammonia is converted to ammonium (NH$_4^+$) through protonation and the relative concentration of these two compounds depends largely on the pH and temperature of the water body.

Under higher oxygen conditions, the microbial oxidation of ammonia to nitrate (NO$_3$) with nitrite (NO$_2$) as an intermediate in the reaction sequence is termed nitrification. During this process, nitrous oxide gas (N^{2}O) is also produced and is released into the atmosphere. Ammonia, ammonium, nitrite and nitrate can all be taken up by marine algae for the synthesis of proteins and DNA, although nitrate is most commonly available and ammonium is most readily assimilated by plants. Marine animals in turn feed on algae and specialised microbes decompose biological material back into ammonia.

Under lower oxygen conditions, anammox microbacteria use ammonia and nitrite to make nitrogen gas, which also rises to the sea surface and escapes into the atmosphere. Denitrifying microorganisms also convert nitrate to nitrite, which is partially converted into nitrous oxide and then to nitrogen gas. Both gases are released back into the atmosphere. In upwelling systems, nitrate can be transported from deeper waters to the euphotic zone, where it becomes available to for the uptake by marine algae.

Nitrogen is also introduced into the marine environment from land-based sources. During the past two centuries, humans have substantially altered the global nitrogen cycle, increasing both the availability and mobility of nitrogen. This is phenomenon is causing significant effects on many aquatic organisms and are contributing to the degradation of freshwater, estuarine, and coastal marine ecosystems[13].

4.3.1 Ammonium and ammonia

Constituent	Ammonium (NH_4^+) and ammonia (NH_3) Measured as total ammonia nitrogen (TAN)	
	Ammonium (NH_4^+)	Ammonia (NH_3)
IUPAC Names	Ammonium	Azane
CAS RN	14798-03-9	7664-41-7
Category	Dissolved inorganic nutrient and toxic substance (in the form of ammonia)	
Description	The ammonium cation is a positively charged polyatomic ion with the chemical formula NH_4^+. Ammonium (NH_3) is formed by the protonation of ammonia. In the marine environment, the relative concentration of these two compounds depends largely on the pH and temperature (see below for more detail) of the water body. Ammonia is uncharged and lipid soluble and therefore acutely toxic to marine organisms at low concentrations. In contrast, the hydrated ammonium ion is non-toxic and a nutrient to primary producers. The permeability of plasma membranes to charged particles, such as ammonium ions, is relatively low[108].	
Recommended guidelines for ammonium and ammonia (Total ammonia nitrogen measured in µg/L)	**Natural Environment and Mariculture** *As a nutrient:* Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range. This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, total ammonia nitrogen (TAN) (i.e. NH_3 and NH_4^+) concentrations can be derived using the *reference system data approach*: where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution. Where insufficient or no reference data exists, single guideline values could be derived from available data based on professional judgement, as an interim measure. *Toxicity:* 600 µg/L (Chronic)	
Notes on guidelines	Due to the acute toxicity of ammonia (NH_3), the most conservative receiving water quality guideline value (ambient versus toxicity) is applicable following the derivation of seasonal site-specific guideline ranges for TAN.	

<table>
<tr>
<td>Sources</td>
<td>
<p>Nitrogen is the most abundant chemical element of the Earth's atmosphere (almost 80%) and ranks fourth behind carbon, oxygen and hydrogen as the commonest chemical element in living tissues[109]. Ammonium and ammonia occur abundantly in the atmosphere, soil, surface water and biological organisms and cycles through these media as part of the nitrogen cycle (Box 1). They are important nutrients for living organisms and are used for the synthesis of proteins and DNA.</p>
<p>Ammonium and ammonia can be present naturally from atmospheric deposition, surface and groundwater runoff, weathering of nitrogen-rich geological deposits, N_2 fixation by certain prokaryotes, and biological degradation of organic matter[13].</p>
<p>Anthropogenic sources of ammonium and ammonia include[13]:</p>

Wastewaters from livestock farming
Effluent releases from aquaculture operations
Municipal sewage effluents (including sewage treatment plants that are not performing tertiary treatments)
Industrial wastewater effluents (e.g. textile manufacturers, pharmaceutical industry and cleaning products industry)
Runoff and infiltration from waste disposal sites
Runoff from operational mines, oil fields, and unsewered industrial sites
Overflows of combined storm and sanitary sewers
Cultivation of N_2-fixing crop species
Agriculture utilising animal manure and inorganic nitrogen fertilisers
Runoff from burned forests and grasslands
Urban runoff
Septic tank leachate and runoff from failed septic systems
Runoff from construction sites and abandoned mines
Emissions to the atmosphere of reduced (from volatilisation of manure and fertilisers) and oxidised (from combustion of fossil fuels) nitrogen compounds, and subsequent deposition over surface waters
Other activities that can mobilise nitrogen from long-term storage pools such as biomass burning, land clearing and conversion, and wetland drainage.

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<tr>
<td>Environmental fate and behaviour</td>
<td>
<p>Ammonium and ammonia are important components of the nitrogen cycle. Ammonia undergoes nitrification and constitutes a large source of available nitrogen in the marine environment. Refer to Box 1 for more details on the nitrogen cycle.</p>
<p>Ammonia is highly soluble in water and its speciation is affected by a wide variety of environmental parameters, including pH, temperature, and ionic strength[110]. In aqueous solution, protonation of ammonia leads to the formation of ammonium (NH^{+}). These two compounds exist in equilibrium depending on the environmental conditions.</p>
<p>Ionised ammonium salts can form when ammonia dissolves in dilute acids[111].</p>
</td>
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<tr>
<td>Interdependence with other constituents/ properties</td>
<td>
<p>The relative proportions of NH_3 and NH_4^{+} in solutions depend primarily on temperature and pH and, to a lesser extent, on salinity. Concentrations of NH_3 increase with elevated temperatures and pH values, and decrease with higher salinities[108].</p>
<p>Percent unionised ammonia (NH_3) in seawater (S = 32-40 PSU) at different temperatures and pH levels at 1 ATM pressure[2]:</p>
<table>
<tr><th></th><th colspan="4">pH</th></tr>
<tr><th>Temp °C</th><th>7.5</th><th>8.0</th><th>8.5</th><th>9.0</th></tr>
<tr><td>10</td><td>0.46</td><td>1.44</td><td>4.41</td><td>12.60</td></tr>
<tr><td>15</td><td>0.67</td><td>2.07</td><td>6.28</td><td>17.60</td></tr>
<tr><td>20</td><td>0.96</td><td>2.98</td><td>8.87</td><td>23.60</td></tr>
<tr><td>25</td><td>1.39</td><td>4.28</td><td>12.40</td><td>30.90</td></tr>
</table>
<p>At salinities common in seawater (32-40 PSU) there is up to one fifth less unionised ammonia (NH_3) than in fresh water at the same temperature and pH[2].</p>
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</table>

Mode of action/ toxicity	Ammonia is uncharged and lipid soluble and therefore acutely toxic to marine organisms at low concentrations. In vertebrates ammonia can cause convulsions, coma and death. This has been attributed to elevated NH_4^+ displacing K^+ and depolarizes neurons, causing activation of NMDA type glutamate receptor, which leads to an influx of excessive Ca^{2+} and subsequent cell death in the central nervous system[112] coma and death, probably because elevated NH 4 + displaces K + and depolarizes neurons, causing activation of NMDA type glutamate receptor, which leads to an influx of excessive Ca 2+ and subsequent cell death in the central nerv- ous system. Present ammonia criteria for aquatic systems are based on toxicity tests carried out on, starved, resting, non-stressed fish. This is doubly inappropriate. During exhaustive exercise and stress, fish increase am- monia production and are more sensitive to external ammonia. Present criteria do not protect swimming fish. Fish have strategies to protect them from the ammonia pulse following feeding, and this also protects them from increases in external ammonia, as a result starved fish are more sensitive to external ammonia than fed fish. There are a number of fish species that can tolerate high environmental ammonia. Glutamine formation is an important ammonia detoxification strategy in the brain of fish, especially after feeding. Detoxification of ammonia to urea has also been observed in elasmobranches and some teleosts. Reduction in the rate of proteolysis and the rate of amino acid catabolism, which results in a decrease in ammonia production, may be another strategy to reduce ammonia toxicity. The weather loach volatilizes NH_3, and the mudskipper, P. schlosseri, utilizes yet another unique strategy, it actively pumps NH_4 + out of the body. In contrast, the hydrated ammonium ion is non-toxic and a nutrient to primary producers. The permeability of plasma membranes to charged particles, such as ammonium ions, is relatively low[108].
Natural occur- rence in South African waters	In oxygenated unpolluted seawater samples, total ammonia nitrogen (TAN) rarely exceeds 70 µg/L. In deep anoxic stagnant water, such as in the Black Sea, ammonium concentrations can be as high as 2 100 µg/L[89]. Levels of ammonia in estuaries can also reach very high levels due to natural and anthropogenically-linked contributions from the catchment (>1 mg/L) especially in systems that receive large volumes of organically rich effluent (e.g. from WWTWs). In the absence of anthropogenic inputs, ammonia levels in estuaries are generally less than 50 µg/L[65,113,114]. The concentration of ammonium/ammonia in seawater exhibits considerable spatial and temporal variations, which can be attributed to the complex processes that determine its fate in the marine environment.
Measurement in seawater	Total ammonia nitrogen ($NH_4^+ + NH_3$) can be determined photometrically in seawater[108]. *Units:* µg/L (NH $^+$ + NH) –N or µmol/L (NH $^+$ + NH)–N (the latter can be converted to µg/L [$NH_4^+ + NH_3$]-N by multiplying with the atomic mass of N, i.e. 14).

A Values for alternative levels of protection (% species). Alternative levels include 80% = 1300 µ/l, 90% = 1200 µ/l, 95% = 910 µ/l and 99% = 500 µ/l.

B Measured in µg/L for slightly disturbed ecosystems. Overall, the limits for estuaries, inshore and offshore habitats are as follows: Estuaries: 40-50; Inshore 1-15; Offshore 1-15. Please refer to the ANZECC Guidelines 2000 for more detail[3].

Table 4: Water quality guidelines/criteria/standards for ammonium and ammonia as a nutrient and toxic substance adopted in other jurisdictions.

Jurisdiction	Natural Environment		Mariculture	
	As a nutrient	As a toxin (µg/L)	As a nutrient	As a toxin (µg/L)
CCME 2002[24]	Site-specific guideline values must be derived using the reference condition approach using empirical data.			
ANZECC 2000[3]	Ambient ammonium ranges are specified for different ecoregions (differentiated between inshore and offshore, where the former is in some instances classified as estuary).[A]	TAN: 500 – 1700[B]		Ammonia: <100
EPA California 2013[6]	Nutrient materials shall not cause objectionable aquatic growths or degrade indigenous biota.	TAN: 600		
EPA Florida 2015[18]	Narrative nutrient criteria: The discharge of nutrients shall continue to be limited as needed to prevent violations of other standards contained in this chapter. In no case shall nutrient concentrations of a body of water be altered so as to cause an imbalance in natural populations of aquatic flora or fauna. Phosphorus limits are specified per estuary.		Same as guidelines for the natural environment	
UK 2014[17]		Ammonia: 21		
BCLME 2006[4] WIOR 2009[5]	Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range (see above). This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the Reference system data approach: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution.	TAN: 910	Same as the natural environment.	TAN: 910

A Measured in µg/L for slightly disturbed ecosystems. Overall, the limits for estuaries, inshore and offshore habitats are as follows: Estuaries: 40-50; Inshore 1-15; Offshore 1-15. Please refer to the ANZECC Guidelines 2000 for more detail[3].

B Values for alternative levels of protection (% species). Alternative levels include 80% = 1300 µ/l, 90% = 1200 µ/l, 95% = 910 µ/l and 99% = 500 µ/l.

4.3.2 Nitrate

Constituent	Nitrate (NO_3^-)
IUPAC Name CAS RN	Nitrate 14797-55-8
Category	Dissolved inorganic nutrient and toxic substance
Description	Nitrate is the final oxidation product of nitrogen compounds in seawater and is considered to be the only thermodynamically stable oxidation level of nitrogen in the presence of oxygen in seawater[89]: $N_2 \leftrightarrow N2\ O \leftrightarrow NO \leftrightarrow NO_2^- \leftrightarrow NO_3^-$
Recommended guide-lines for nitrate (µg/L)	**Mariculture and Natural Environment**
	As a nutrient: Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range. This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the *reference system data approach*: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution. Where insufficient or no reference data exists, single guideline values could be derived from available data based on professional judgement, as an interim measure. *Toxicity:* Nitrate (NO_3) = 200 000 (Chronic) Nitrate as nitrogen (NO_3 – N) = 45 000 (Chronic)
Notes on guidelines	Nitrate has the chemical formula NO_3 . The symbol NO_3 –N stands for "nitrate as nitrogen", which means that this is a test for nitrate but the concentration units are being reported as nitrogen only. Concentration is units of mass per volume (e.g. µg/L. Changing the way nitrate is reported, therefore changes the value of the concentration. Taking into account the molecular weight of nitrate and nitrogen, the conversion factor is calculated and applied in the following way: 62 (weight of NO_3)/14 (weight of N) = 4.428 45 000 µg/L of nitrate as nitrogen x 4.428 = 199 260 µg/L of nitrate Measurements of nitrate as nitrogen (NO_3 -N) in µmol/L can be converted to µg/L by multiplying with the atomic mass of N, i.e. 14. Due to the risk of eutrophication and/or potential toxicity, the more conservative receiving water quality guideline value (ambient versus toxicity) is applicable following the derivation of seasonal site-specific guideline ranges for nitrate.

Sources	Nitrogen is the most abundant chemical element of the Earth's atmosphere (almost 80%) and ranks fourth behind carbon, oxygen and hydrogen as the commonest chemical element in living tissues[109]. Nitrate occurs abundantly in the atmosphere, soil, surface water and biological organisms and cycles through these media as part of the nitrogen cycle (Box 1). Nitrate is an important nutrient for living organisms and is used for the synthesis of proteins and DNA. Nitrate can be present naturally from atmospheric deposition, surface and groundwater runoff, weathering of nitrogen-rich geological deposits, N_2fixation by certain prokaryotes, and biological degradation of organic matter[13]. Anthropogenic sources of nitrate include[13]: • Wastewaters from livestock farming • Effluent releases from aquaculture operations • Municipal sewage effluents (including sewage treatment plants that are not performing tertiary treatments) • Industrial wastewater effluents • Runoff and infiltration from waste disposal sites • Runoff from operational mines, oil fields, and unsewered industrial sites • Overflows of combined storm and sanitary sewers • Cultivation of N_2-fxing crop species • Agriculture utilising animal manure and inorganic nitrogen fertilisers • Runoff from burned forests and grasslands • Urban runoff • Septic tank leachate and runoff from failed septic systems • Runoff from construction sites and abandoned mines • Emissions to the atmosphere of reduced (from volatilisation of manure and fertilisers) and oxidised (from combustion of fossil fuels) nitrogen compounds, and subsequent deposition over surface waters • Other activities that can mobilise nitrogen from long-term storage pools such as biomass burning, land clearing and conversion, and wetland drainage.
Environmental fate and behaviour	Nitrate is an important component of the nitrogen cycle. Nitrate is the final oxidation product of nitrogen compounds in seawater and is considered to be the only thermodynamically stable oxidation level of nitrogen in the presence of oxygen in seawater[89]. In general, nitrate constitutes two-thirds to four-fifths of the total available nitrogen in surface waters[115] and constitutes a largest direct source of bioavailable nitrogen in the marine environment. Refer to Box 1 for more details on the nitrogen cycle. The concentration of nitrate in these layers is governed by the advective transport of nitrate into surface layers, the microbial oxidation of ammonia and the uptake by the primary producers. If the light penetration into the water is sufficient, the uptake rate is usually much faster than the processes transporting the nitrate into the surface layers. Therefore, the nitrate concentration in most ocean surface waters is close to zero[89]. In temperate climatic zones, where winter cooling of the surface waters produces deep-reaching vertical mixing, the nitrate content of seawater follows a fairly regular cycle with high values in autumn, winter and early spring and low values in spring and summer. In upwelling areas, the supply rate of nitrate is very often considerably higher than the uptake rate. For this reason, the concentration of nitrate can be usefully applied as an indicator for upwelling and, together with temperature measurements, as a means to separate the apparent decrease of micronutrients downstream of an upwelling area by a physical mixing process and biological uptake[89]. Nitrate and phosphate are used to form the soft tissue of organisms and the molar ratio of nitrate to phosphate in ocean water is close to the ratio of 15:1 for organic tissues; thus, when all the dissolved phosphate in surface waters has been used up, so has all of the dissolved nitrate. Why nitrate and phosphate should occur in seawater in the same ratio required by those organisms remains one of the intriguing mysteries of seawater chemistry[116].

Interdependence with other constituents/ properties	If the oxygen content of seawater becomes depleted as a result of microbial remineralisation, nitrate may be used as an alternative electron acceptor instead of oxygen. This process, called denitrification, leads to the reduction of a portion of nitrate to molecular nitrogen (N_2). The reduction of sulphate commences only after the available nitrate has been quantitatively used up. It is, therefore, very unlikely that nitrate may co-exist for any length of time in the presence of hydrogen sulphide. Usually the nitrate reduction zone is separated from waters containing sulphide by a layer in which the nitrate concentration has been reduced to less than 1.4 µg/LNO_3^- - N and where oxygen values are below 0.02 ml/L. The presence of nitrate in sulphide containing water indicates turbulent mixing processes between anoxic water and the water from the transition layer, or it may be the result of analytical errors[89].
Mode of action/toxicity	At high concentrations, nitrate can be toxic to a wide variety of aquatic animals[117]. Its toxicity, how- ever, is considerably lower than that of ammonia or nitrite with acute median lethal concentrations of NO_3^- -N being up to two orders of magnitude higher than for NH_3 -N and NO_2^- - N [118]. The ameliorating effect of water salinity on the toxicity of inorganic nitrogenous compounds to seawater animals has been established[13]. Nitrate toxicity is thought to cause growth deficiencies and mortality through (a) methaemoglobin for- mation, resulting in a reduction in the oxygen carrying capacity of blood and (b) through the inability of the organisms to maintain osmoregulation under high salt contents associated with elevated nitrate levels[118].
Natural occurrence in South African waters	Nitrate in oxygenated seawater with a salinity of 35 PSU ranges from less than 1.4 to 630 µg/L NO_3^--N, with an average concentration of 420 µg/L NO_3^--N. Nitrate concentrations usually increase with depth, i.e. surface depletion and enrichment at depth. This distribution is referre$_3$ to as a nutrient type distribution[119]. **West coast:** Nutrient supply to the surface water occurs via the upwelling process[86]. The supply of nutrients to the euphotic zone by the upwelling process triggers the high biological productivity of the Benguela ecosystem and is the major feature driving the important commercial fish populations that occur in the area. The average nitrate concentration (as NO_3^--N) reported for the west coast is 16.4 µg/L[120], while upwelled areas can be as high as 280 ± 56 µg/L[121]. **South coast:** Along the south coast, coastal upwelling brings water rich in nutrients to the surface. The average nitrate concentration (as NO_3^--N) reported for the south coast is 81 µg/L[120] **East coast:** Waters of tropical origin are usually poor in nutrients resulting in generally low primary productivity. Average nitrate (as NO_3^- -N) concentrations such as those reported for the east coast are[122]: Port Edward 35 µg/L Durban 47 µg/L Richards Bay 38 µg/L. **Estuaries.** Levels of nitrate in estuaries are often higher than coastal waters due to natural and anthropogenically linked contributions from the catchment and can reach very high levels (>1 mg/L) in estuaries that receive significant volumes of organically rich effluent (e.g. from WWTWs). In the absence of anthropogenic inputs, nitrate levels in estuaries are generally less than 100 µg/L[65,113,114]. It is important to note that the nitrate concentration in seawater exhibits considerable spatial and temporal variations, which can be attributed to the complex processes that determine its fate in the marine environment. Establishing site-specific water quality guidelines using adequate *in-situ* data is therefore of paramount importance.

Table 5: Water quality guidelines/criteria/standards for nitrate as a nutrient and toxic substance adopted in other jurisdictions.

Jurisdiction	Natural Environment		Mariculture	
	As a nutrient	As a toxin (µg/L)	As a nutrient	As a toxin (µg/L)
CCME 2012[12]	Site-specific guideline values must be derived using the reference condition approach using empirical data.	Nitrate = 1 500 000 (Acute); 200 000 (Chronic) Nitrate as nitrogen = 339 000 (Acute); 45 000 (Chronic)	No mariculture guidelines	
ANZECC 2000[3]	Insufficient data	Insufficient data	Insufficient data	<100 000[A]
EPA California 2013[6]	Nutrient materials shall not cause objectionable aquatic growths or degrade indigenous biota.	Insufficient data	Not listed	Not listed
EPA Florida 2015[18]	Narrative nutrient criteria: The discharge of nutrients shall continue to be limited as needed to prevent violations of other standards contained in this chapter. In no case shall nutrient concentrations of a body of water be altered so as to cause an imbalance in natural populations of aquatic flora or fauna. Phosphorus limits are specified per estuary.	Insufficient data	Same as guidelines for the natural environment.	Not listed

BCLME 2006[4]	Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range (see above). This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the Reference system data approach: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s)	Insufficient data	Same as guidelines for the natural environment.	Not listed
WIOR 2009[5]				

A Protection of mariculture organism health.

4.3.3 Nitrite

Constituent		Nitrite (NO_2^-)
IUPAC Name CAS RN		Nitrite 14797-65-0
Category		Dissolved inorganic nutrient and toxic substance
Description		Nitrite occurs in seawater as an intermediate compound in the microbial reduction of nitrate or in the oxidation of ammonia[89] : $NO_3^- \leftrightarrow NO_2^- \leftrightarrow NO_2 \leftrightarrow N\,O_2 \leftrightarrow N_3$ *or* $NO_2^- \leftrightarrow NO_4^- \leftrightarrow NH^+$
Recommended guidelines for nitrite (µg/L)		**Mariculture and Natural Environment**
		As a nutrient: Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range. This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the *reference system data approach*: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution. Where insufficient or no reference data exists, single guideline values could be derived from available data based on professional judgement, as an interim measure. *Toxicity:* Insufficient information
Notes on guidelines		In the absence of eutrophication, surface waters are well oxygenated and consequently most reactive nitrogen exists in the form of nitrate, a considerably less toxic compound to marine animals. Preventing eutrophication will therefore also protect marine animals from nitrite toxicity[13]. Due to the risk of eutrophication and/or potential toxicity, the more conservative receiving water quality guideline value (ambient versus toxicity) is applicable following the derivation of seasonal site-specific guideline ranges for nitrite.

Sources		Nitrogen is the most abundant chemical element of the Earth's atmosphere (almost 80%) and ranks fourth behind carbon, oxygen and hydrogen as the commonest chemical element in living tissues[109]. Nitrite occurs abundantly in the atmosphere, soil, surface water and biological organisms and cycles through these media as part of the nitrogen cycle (Box 1). Nitrite is an important nutrient for living organisms and is used for the synthesis of proteins and DNA. Nitrite can be present naturally from atmospheric deposition, surface and ground water runoff, weathering of nitrogen-rich geological deposits, N_2 fixation by certain prokaryotes, and biological degradation of organic matter[13]. Anthropogenic sources of nitrite include[13]: • Wastewaters from livestock farming • Effluent releases from aquaculture operations • Municipal sewage effluents (including sewage treatment plants that are not performing tertiary treatments) • Industrial wastewater effluents • Runoff and infiltration from waste disposal sites • Runoff from operational mines, oil fields, and unsewered industrial sites • Overflows of combined storm and sanitary sewers • Cultivation of N_2- fxing crop species • Agriculture utilising animal manure and inorganic nitrogen fertilisers • Runoff from burned forests and grasslands • Urban runoff • Septic tank leachate and runoff from failed septic systems • Runoff from construction sites and abandoned mines • Emissions to the atmosphere of reduced (from volatilisation of manure and fertilisers) and oxidised (from combustion of fossil fuels) nitrogen compounds, and subsequent deposition over surface waters • Other activities that can mobilise nitrogen from long-term storage pools such as biomass burning, land clearing and conversion, and wetland drainage.
Environmental fate and behaviour		Nitrite is an important component of the nitrogen cycle. Nitrite undergoes nitrification to NO_3^- under higher oxygen conditions and constitutes a large source of available nitrogen in the marine environment. Refer to Box 1 for more details on the nitrogen cycle. Nitrite may be excreted by phytoplankton, especially during periods of luxury feeding, i.e. when a surplus of nitrate and phosphate stimulates a heavy bloom of plankton[89]. The natural level of nitrite in seawater is usually very low, but in transition zones, where higher oxygen conditions change to lower oxygen conditions, thin layers of high nitrite concentrations may occur together with low levels of dissolved oxygen[89]. In upwelling areas, elevated nitrite values indicate high activity of the primary producers[89].
Interdependence with other constituents/ properties		Low dissolved oxygen concentrations favour the formation of nitrite. Nitrite photolysis gives rise to a 10^4- fold supersaturation of nitrogen oxide in water with respect to its concentration in the air[71]. The toxicity of nitrite, while still formidable, is significantly reduced in seawater due to the high concentration of chloride and calcium[123].
Mode of action/ toxicity		Nitrite is known to be very toxic to a wide variety of aquatic animals[117]. The ameliorating effect of salinity on the toxicity of inorganic nitrogenous compounds to seawater animals is well established though[13]. Furthermore, in the absence of eu- trophication, surface waters are well oxygenated and consequently most reactive nitrogen exists in the form of nitrate, a considerably less toxic compound to marine animals[13].

Natural occurrence in South African waters		The natural level of nitrite in seawater is less than 1.4 µg/L NO_2^--N. In anoxic zones with low levels of oxygen (less than 0.15 ml/L), nitrite concentrations in excess of 28 µg/L NO_4^--N have been measured. Under upwelling conditions, levels can be between 14 and 28 µg/L NO_2^--N[89]. Limited information is available on the natural occurrence of nitrite along the South African coast. Higher nitrite levels can be expected in coastal regions that experience upwelling. On the west coast of South Africa for example, an average of 4.2 µg/L has been reported[120]. Coastal areas on the south coast of South Africa, on the other hand, have on average lower nitrite levels (2.8 µg/L). Subtropical waters along the east coast of South Africa are expected to have low nitrite concentration. Levels of nitrite in estuaries are often higher than coastal waters due to natural and anthropogenically-linked contributions from the catchment and can reach very high levels (>1 mg/L) in estuaries that receive large volumes of organically rich efflu- ent (e.g. from WWTWs).[65,113,114] In the absence of anthropogenic inputs, nitrite levels in estuaries are generally less than 10 µg/L. It is important to note that the nitrite concentration in seawater exhibits considerable spatial and temporal variations, which can be attributed to the complex processes that determine its fate in the marine environment. Establishing site-specific water quality guidelines using sufficient *in-situ* data is therefore of paramount importance.
Measurement in seawater		Dissolved nitrite can be determined photometrically in seawater[89] . Units: µg/L NO_2^--N or µmol l^{-1} NO_2^-- N (the latter can be converted to µg/L NO_2^--N by multiplying with the atomic mass of N, i.e. 14).

Table 6: Water quality guidelines/criteria/standards for nitrite as a nutrient and toxic substance adopted in other jurisdictions.

Jurisdiction	**Natural Environment**		**Mariculture**	
	As a nutrient	**As a toxin (µg/L)**	**As a nutrient**	**As a toxin (µg/L)**
CCME 2012[12]	Site-specific guideline values must be derived using the reference condition approach using empirical data.	Insufficient data	No mariculture guidelines	
ANZECC 2000[3]	Insufficient data	Insufficient data	Insufficient data	<100[A]
EPA California 2013[6]	Nutrient materials shall not cause objectionable aquatic growths or degrade indigenous biota.	Insufficient data	Not listed	Not listed
EPA Florida 2015[18]	Narrative nutrient criteria: The discharge of nutrients shall continue to be limited as needed to prevent violations of other standards contained in this chapter. In no case shall nutrient concentrations of a body of water be altered so as to cause an imbalance in natural populations of aquatic flora or fauna. Phosphorus limits are specified per estuary.	Insufficient data	Same as guidelines for the natural environment.	Not listed
BCLME 2006[4]	Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range (see above). This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the Reference system data approach: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution.	Insufficient data	Same as guidelines for the natural environment.	Not listed
WIOR 2009[5]				

4.3.4 Phosphorus

Constituent	Phosphorus (P)
IUPAC Name CAS RN	Phosphorus 7723-14-0
Category	Nutrient (inorganic and organic)
Description	Phosphorus occurs naturally and abundantly in rocks and other mineral deposits. Phosphorus is gradually released from weathering rocks and mineral deposits as phosphate ions, which are soluble in water. Phosphates are classified as reactive phosphates (synonym orthophosphates), condensed phosphates (pyro, meta, and polyphosphates) and organic phosphates. Reactive phosphate is the form which is most readily utilised by biota and therefore provides a good estimation of the amount of phosphorus available for algae and plant growth. The most probable species in oxygenated seawater are HPO_4^{2}, $NaHPO_4^{-}$ and $MgHPO_4$ [119]. Phosphorus is non-toxic to aquatic organisms at levels and forms present in the environment. Excessive biologically available phosphorus will however lead to eutrophication in marine ecosystems, which are not nitrogen limited and can result in secondary toxicity (lack of oxygen, hydrogen sulphide etc.)[124,125].
Recommended guidelines for phosphorus	**Mariculture and Natural Environment** *As a nutrient:* Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range. This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the *reference system data approach*: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution. Where insufficient or no reference data exists, single guideline values could be derived from available data based on professional judgement, as an interim measure.

Notes on guidelines	Elemental phosphorus never occurs by itself in water, but always as some type of compound. The main types of phosphorus in water include orthophosphate (synonyms: phosphate, filterable reactive phosphate, reactive phosphorus, soluble reactive phosphate), (2) condensed phosphates (pyro, meta, and polyphosphates) and (3) organically bound phosphates (inside or bonded to organic compounds). These types of phosphorus can either occur as dissolved or particulate forms. It is therefore critical to clarify whether the sample was filtered first (i.e. dissolved) or not (dissolved and particulate) and what type of filter was used (most commonly a 0.45 µm filter is used)[126]. Three types of tests are available to measure these three types of phosphorus in water, namely the orthophosphate test, the acid hydrolysable phosphate test and the total phosphorus test (synonym: total phosphate). Results from the *orthophosphate test* can be reported in two different ways: • PO_4 spoken as “orthophosphate” • PO_4^{3-} - P spoken as “orthophosphate as phosphorus” The $PO_4{}^{3-}$ results combine both the phosphorus and the oxygen in the compound, whereas PO_4 – P only considers the phosphorus in the compound. Results are reported in concentration (i.e. units of mass per volume e.g. µg/L) and therefore, changing the way orthophosphate is reported changes the value of the concentration. Taking into account the molecular weight of orthophosphate and phosphorus, the conversion factor is calculated and applied in the following way: 95 (weight of PO_4^{3-}) / 31 (weight of P) = 3.06 62 µg/L as PO -P 62 µg/L of PO_4 - P x 3.06 = 190 µg/L of $PO_4{}^{3-}$ Orthophosphate provides a good estimation of the amount of phosphorus available for algae and plant growth, as this is the form which is most readily utilised by biota. Orthophosphate is therefore commonly analysed for monitoring phosphorus in natural waters. Orthophosphate is commonly reported as dissolved orthophosphate and is generally measured in PO_4 -P. The acid hydrolysable phosphate test measures condensed phosphates (pyro, meta, and polyphosphates), which are multiple orthophosphate molecules “condensed” together. The total phosphorus test can detect the amount of all phosphorous in a given sample. Using further intermediate steps, this test also allows the isolation of organically bound phosphate. Organic phosphates are contained inside, or are bonded to organic compounds. Test results for measuring condensed phosphates and organically bound phosphates are reported as orthophosphate and therefore either $PO_4{}^{3-}$ or PO_4 -P can be used to describe the results. The results for total phosphorus are usually reported as P. It is very important that the same methodology is used for collecting, analysing and reporting on *in situ* baseline and routine monitoring (receiving environment and effluent) data. A report should always answer the following questions: a) What type of phosphorus was measured? b) Was the sample filtered? If so what pore size did the filter have? c) What test(s) was (were) used? (Refer to Dabkowski and White 2003[126] for more information) In what form is the result displayed? Orthophosphate ($PO_4{}^{3-}$) or orthophosphate as phosphorus (PO_4 –P)?
Sources	Phosphorus enters the aquatic environment as phosphate ions, through weathering and erosion of phosphate rock and soils containing the mineral apatite (an impure tri-calcium phosphate)[127]. Anthropogenic activities can elevate phosphate levels in surface waters. Sources of anthropogenic phosphate include[49]: • waste products from manufacturing phosphoric acid for fertilizer production; • phosphatisation of metals in plating and metal processing industries; • sewage discharges (including household detergents); • agricultural run-off (over fertilization with super-phosphates is a common problem and enormous amounts are brought to the sea by rivers in some areas[89]; • run-off from dairy farms and piggeries.

Environmental fate and behaviour	The most probable species in oxygenated seawater are HPO_4^{2-}, $NaHPO_4^{-}$ and $MgHPO_4$[119]. Other sources state that 1% of the orthophosphate is present as $H_2PO_4^{-}$, 87% as HPO_4^{2-} and 12% as PO_4^{3-}, also that 96% of the PO_4^{3-} and 44% of the HPO_4^{2-} are apparently present in seawater as ion pairs, probably with calcium and magnesium. As a result, calcium phosphate is more soluble in seawater than in distilled water (ion pair and complex formation)[71]. The phosphate concentration at the surface is low because of the steady uptake by phytoplankton in the photic zone. Phytoplankton is consumed by zooplankton and other animals that package most of their waste products into faecal pellets. A variety of dissolved organic phosphorus (DOP) compounds are present in the upper layers of the sea. Although inorganic phosphorus is usually the preferred substrate for phytoplankton, some photosynthetic organisms can access dissolved organic nutrients[128]"ISBN" : "01659936", "ISSN" : "01659936", "abstract" : "Over much of the world's surface oceans, nitrate and phosphate concentrations are below the limit of detection (LOD). Organic debris slowly drifts down and as the pressure increases with depth, most of this debris is crushed and its phosphate is released before it reaches the bottom. Only about 1% of this organic matter actually reaches the sediments129. Consequently, in contrast to inorganic phosphate, organic phosphorus occurs at high concentrations near the surface and is depleted in the deep ocean. Upwelling conditions can introduce phosphates to surface waters, while anoxic conditions will facilitate the return of phosphate from the sediment back into solution. Phosphate which is held in sediment as insoluble $FePO_4$ will be reduced to soluble Fe_3 (P_4O_2), and insoluble CaH PO_4 will be acidified to soluble Ca_2 (H_4PO_2)[129]. Phosphate and nitrate are used to form the soft tissue of organisms. The molar ratio of nitrate to phosphate in ocean water is close to the ratio of 16:1 for organic tissues; thus, when all the dissolved phosphate in surface waters has been used up, so has all the dissolved nitrate. It remains unknown whether organisms evolved to use the 16:1 molar ratio of N:P because it was there, or whether marine organisms themselves established the ratio through time[130].
Interdependence with other constituents/ properties	Precipitated inorganic phosphorus in sediment can re-solubilise in anoxic conditions, i.e. under low pH and low dissolved oxygen levels[129].
Mode of action/ toxicity	Phosphorus is non-toxic to aquatic organisms at levels and forms present in the environment. Excessive biologically available phosphorus will lead to eutrophication in marine ecosystems, which are not nitrogen limited[124,125].
Natural occurrence in South African waters	The mean concentration of reactive phosphate in seawater has been estimated to be about 62 µg/L as PO_4 -P[89]. Reactive phosphate in seawater with salinity 35 ppt has been shown to range between 109 µg/L in deeper waters, and less than 31 µg/L PO_4 -P in surface waters[119]. Surface depletion and bottom enrichment is characteristic for nutrients in seawater (nutrient type distribution). **West Coast.** Nutrient supply to the surface water occurs via the upwelling process[131]. Average total phosphorus concentrations (as P) reported for the west coast[120], as well as those specifically reported for upwelled waters (as PO_4 -P) are[121] 53 and 47 ± 1.6 µg/L, respectively. **South Coast.** Along the south coast, coastal upwelling brings water rich in nutrients to the surface. The following average concentration for total Phosphorus (as P) has been reported as 37 µg/L[120]. **East Coast.** Waters of tropical origin are generally poor in nutrients resulting in generally low primary productivity. Higher nutrient concentrations are usually associated with upwelling. Average phosphate (PO_4 -P) concentrations reported for the east coast range from 19 µg/L (Port Edward and Durban) to 24 µg/L (Richards Bay)[132]. **Estuaries.** Levels of phosphate (PO_4 -P) in estuaries are generally higher than coastal waters due to natural and anthropogenically linked contributions from the catchment and can reach very high levels (>1 mg/L) in estuaries that receive significant volumes of organically rich effluent (e.g. from WWTWs). In the absence of anthropogenic inputs, phosphate levels in estuaries are generally less than 50 µg/L[65,113,114]. It is important to note that the reactive phosphate concentration in seawater exhibits considerable spatial and temporal variations. Establishing site-specific water quality guidelines using adequate *in-situ* data is therefore of paramount importance.

Guideline levels adopted in other jurisdictions		**Natural Environment**	**Mariculture**
	CCME 2002[24]	Site-specific guideline values.	No guideline
	ANZECC 2000[3]	Ambient phosphate (reactive filterable) and phosphorus ranges are specified for each ecoregion (differentiated between inshore and offshore, where the former is in some instances classified as estuary).	Not listed
	EPA California 2013[6]	Nutrient materials shall not cause objectionable aquatic growths or degrade indigenous biota.	Not listed
	EPA Florida 2015[18]	Narrative nutrient criteria: The discharge of nutrients shall continue to be limited as needed to prevent violations of other standards contained in this chapter. n no case shall nutrient concentra- tions of a body of water be altered so as to cause an imbalance in natural populations of aquatic flora or fauna. Phosphorus limits have been specified per estuary.	Same as natural environment
	BCLME 2006[4] WIOR 2009[5]	Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range. This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the Reference system data approach: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution.	Same as natural environment

4.3.5 Silicon (as reactive silicate)

Constituent	Silicon (Si) as reactive silicate
IUPAC Name CAS RN	Silicon 7440-21-3 Reactive silicate: various, depending on the compound
Category	Dissolved inorganic nutrient
Description	Silicon is a non-toxic, essential, and, in some cases, a growth-limiting micronutrient for marine organisms. Dissolved silicon exists in seawater almost entirely as undissociated orthosilicic acid ($Si(OH)_4$)[133]. Reactive silicate is probably the only silicon species in seawater that can be used by siliceous organisms[131].
Recommended guidelines (natural environment and mariculture)	**Mariculture and Natural Environment** *As a nutrient:* Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range. This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the *reference system data approach*: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution. Where insufficient or no reference data exists, single guideline values could be derived from available data based on professional judgement, as an interim measure.
Sources	During weathering of silicate material, silicon is brought into ionic solution, probably in the form of alkali salts of the orthosilicic acid, $Si(OH)_4$. High concentrations of silicon are found dissolved in rivers emanating from volcanic sources. It has been estimated that the total annual river output to oceans is about 200 million tons of dissolved silicon with over double this amount added by glacial weathering of rocks in Antarctica89.
Environmental fate and behaviour	About half of the suspended matter in seawater is of inorganic origin and this part contains a large proportion of silicon identified in clays and other minerals. In surface waters, the concentration of suspended silicon generally exceeds that in solution, but at depths greater than about 100 m, it represents only a few percent of the total[89]. Silicon probably existing as hydrated silica, is a major constituent of diatoms, which form a large proportion of marine phytoplankton. Some fungi and siliceous sponges also have structural parts containing silica. Diatoms and radiolarian can also excrete silica in the form of opal, amorphous hydrated silica ($SiO_2\ nH_2O$). When siliceous organisms die, silica is liberated into the seawater. Silica is a biolimiting nutrient, but is used only to make the hard parts of some planktonic organisms (diatoms, radiolarians). The skeletal remains dissolve slowly as they sink into deep water after death, and accumulate in sediments on the sea floor. Because it is a biolimiting nutrient whose availability in surface waters limits biological production, its characteristic vertical profiles show almost total depletion in surface waters because they are controlled principally by biological processes[130].
Interdependence with other constituents/ properties	The solubility of silica decreases as the temperature decreases. The solubility of amorphous opaline silica decreases by about 30% for a drop in temperature from 25 to 5°C. In deep oceans, because of high pressure, the solubility increases slightly[130,134].
Mode of action/toxicity	Excessive biologically available silicate will lead to eutrophication in marine environments that are not nitrogen limited.

Natural occurrence in South African waters	Solubility of silicate is approximately 50 mg/L (as Si)[89]. The silicon in solution in seawater is probably in the form of orthosilicic acid, $H_4 SiO_4$ [119]. The concentrations in surface waters to deep waters range from less than 28 to 5 040 (as Si), with an average concentration of 2 800 µg/L. This distribution is called a nutrient type distribution[119]. **West coast.** Nutrient supply to the surface water occurs via the upwelling process[86]. Average reactive silicate concentrations (as Si) reported for the west coast[120], as well as those specifically reported for upwelled waters are 391 and 420±140 µg/L, respectively[121]. **South coast.** Along the south coast, coastal upwelling brings water rich in nutrients to the surface. The average reactive silicate concentrations (as Si) have been reported as 146 µg/L[120]. **East coast.** Waters of tropical origin are generally poor in nutrients resulting in generally low prima- ry productivity. Higher nutrient concentrations are usually associated with upwelling. Average silicate (as Si) concentrations reported for Port Edward, Durban and Richards Bay are 83, 104 and 97 µg/L respectively[132]. **Estuaries.** River water generally contains a greater concentration of silicon than seawater; levels of silicon in estuaries are consequently normally higher than in the adjacent marine environment. There is limited data available on levels of silicon in estuaries in South Africa but data that is available indicates that levels are generally in the order of mg/L rather than µg/L as is the case for seawater [65,113,114]. It is important to note that the reactive silicate concentration in seawater exhibits considerable spatial and temporal variations. Establishing site-specific water quality guidelines using adequate *in-situ* data is therefore of paramount importance.		
Guideline levels adopted in other jurisdictions		**Natural Environment**	**Mariculture**
	EPA California 2013[6]	Nutrient materials shall not cause objectionable aquatic growths or de- grade indigenous biota.	Not listed
	EPA Florida 2015[18]	Narrative nutrient criteria: The discharge of nutrients shall continue to be limited as needed to prevent violations of other standards contained in this chapter. In no case shall nutrient concentrations of a body of water be altered so as to cause an imbalance in natural populations of aquatic flora or fauna. Phosphorus limits have been specified per	Same as natural environment

	BCLME 2006[4] WIOR 2009[5]	Nutrient concentrations in the water column should not result in chlorophyll a, turbidity and/or dissolved oxygen levels that are outside the recommended water quality guideline range. This range should be established by using either suitable statistical or mathematical modelling techniques. Alternatively, where a modelling approach may be difficult to implement, nutrient concentrations can be derived using the Reference system data approach: Where an appropriate reference system(s) is available and there are sufficient data for the reference system, the guideline value should be determined as the 80th %ile of the reference system(s) distribution.	Same as natural environment

4.4 Toxic substances – Metals

Unlike most organic substances, metals are neither created nor destroyed by biological or chemical processes. Rather, they are transformed from one chemical form to another. Trace metals are normally found in low to very low concentrations in the environment and include elements such as mercury, cadmium, arsenic, lead, chromium, zinc and copper. These metals occur naturally in the earth's crust and are released through chemical weathering processes at very slow rates. Mining and the use of these metals as catalysts in industrial processes, however, result in discharges of trace metals at levels that are far greater than those associated with "normal" chemical weathering processes.

While some trace metals are known to be important micronutrients for living organisms (e.g. iron, zinc, manganese, zinc, copper, cobalt, molybdenum and nickel), others, including lead, silver and mercury are biological inhibitors without known metabolic function[135,136]. However, at elevated levels, all trace metals become toxic and otherwise important micronutrients can become toxic[135]. Trace metals exist in a variety of chemical species in seawater, which strongly influences if, how, and at what quantities they are taken up by marine organisms[135]. Furthermore, the effect of trace metals at the biomolecular level (requirements for nutrient metals versus toxicity) varies at the species level. For example, trace metals variably influence growth and productivity of phytoplankton and as a result, bioavailable trace metal composition and concentration can determine community composition[135].

Overall, elevated trace metal concentrations in the marine environment as a result of anthropogenic activity have been shown to decrease aquatic diversity[137]. Trace metals accumulate in the tissue of marine organisms[138,139] and become increasingly concentrated higher up the food chain[137]. Consumption of biota containing high levels of trace metals by humans poses a serious health risk and has resulted in the implementation of measures to reduce trace metal input into the environment[140].

The fact that metals naturally occur as inorganic forms in environmental compartments (e.g. sediments) and are cycled through the biotic components of an ecosystem, complicate the evaluation of toxicity data for inorganic metal substances and have a major influence on the way we derive water quality GCSs for metals. When evaluating toxicity data to derive water quality GCSs for metals, total metal concentrations are not usually directly related to ecotoxicological effects because many abiotic and biotic processes can modify the availability of metals, even rendering them unavailable for uptake. This means that the fraction available for uptake and toxicity may be a very small part of the total metal present. Bioavailability may be affected by several physicochemical parameters such as the pH, hardness of water and the dissolved organic carbon (DOC). Organic carbon (OC) and sulphides levels are key influencing factors for the sediment compartment[35].

Ideally, the derivation of water quality GCSs for metals requires an explicit consideration of bioavailability using speciation models or, failing that, to utilise dissolved concentrations instead of total concentrations. Background concentrations may also need to be taken into account[35].

4.4.1 Arsenic

Constituent	Arsenic
IUPAC Name	Arsenic (As)
CAS RN	7440-38-2
Category	Toxic substances: metals
Description	Arsenic (elemental) is a naturally occurring, silver-grey crystalline metallic material. Elemental arsenic is insoluble in water. Arsenic occurs in four oxidation states in the natural environment. The [-3] state is present in gaseous arsine (AsH_3) and the metallic [0] state occurs in certain types of mineral deposits. Arsenic in the As^{3+} and As^{5+} states is common in a variety of complex minerals and in dissolved salts in natural waters [141]. Arsenic occurs as inorganic salts and organic compounds, which vary in their physical and chemical[141]. Major forms of arsenic in seawater include[129]: • arsenite (As^{3+}) (regarded as the most toxic and the predominant form under anaerobic conditions) • arsenate (As^{5+}) (the stable form in aerobic conditions) • methylarsonic acid (CH_3 As O $(OH)_2$) • dimethylarsinic acid ($(CH_3)_2$ As O (OH)) At the normal pH value for surface seawater (8.2), arsenite exists mainly as an uncharged species, e.g. $As(OH)_3$ and arsenate as the ion $HAsO_4^{2-}$. The latter is the predominant form at equilibrium[89,119]. Arsenic is harmful to aquaculture organism and human health. Arsenic does not cause tainting.
Recommended Guidelines for total recoverable arsenic (µg/L)	**Natural Environment and Mariculture** 8 (Chronic)
Notes on guidelines	Most detection methods measure *total recoverable* or *dissolved arsenic* in a sample, where "dissolved" is defined operationally as arsenic which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable* arsenic are compared to the guidelines. The differential determination of arsenic (i.e. arsenite As^{3+} and arsenate As^{5+} is possible by hydride generation-atomic absorption spectrophotometry (HGA-AS)[142]. South Africa's laboratories, however, have currently no conventional method available for the differential measurement of arsenite and arsenate.
Sources	Arsenic is a naturally occurring element and the average abundance in the earth's crust is approximately 5 ppm[143]. Arsenic enters the environment through weathering and erosion of rock and soils, and volcanic eruptions[144]. Anthropogenic activities release arsenic into the air, water (freshwater and sea water) and soil[140]. Arsenic is mined or is extracted as a by-product in the smelting of other metals including lead, copper, and gold140. Arsenic trioxide (As_2O_3) is used in wood preservatives, agriculture (herbicide, fungicide), livestock (sheep dips, feed additives), medicine (human and veterinarian), electronics, industry, and metallurgy[145]. Arsenic can also be mobilised during cement manufacturing or combustion of fossil fuels. Arsenic in the air will eventually return to the land or ocean as dust or in precipitation[146]. Dissolved and particulate arsenic enters the ocean via rivers (enriched through overland flow or waste discharges) or directly from land-based discharges into coastal waters. The distinction is important, as adsorption is most effective in aerobic, acidic, freshwaters and remobilisation does not readily occur. Consequently, arsenic entering the ocean via rivers is likely to be adsorbed with much reduced bioavailability. However, under favourable conditions (see section on environmental fate and behaviour below), direct discharges from land-based facilities into the ocean could lead to high levels of dissolved, bioavailable arsenic.

Environmental fate and behaviour	Arsenic is extremely mobile in the aquatic environment and cycles through the water column, sediments and biota. The ocean acts a primary sink for arsenic. Arsenic has an unusually complex chemistry with oxidation-reduction, ligand exchange, precipitation, and adsorption reactions all taking place[141]. The fate of arsenic in the aquatic environment depends on prevailing pH and oxidation potential. Chemical speciation is important in determining arsenic distribution and mobility. Interconversions of As^{3+} and As^{5+} arsenic states and organic complexation are most important. Biological activity or highly reducing conditions can produce gaseous arsine (e.g. di- and tr-imethylarsine) and volatilisation to the atmosphere can occur[141]. Gaseous arsines are extremely toxic to aquatic organisms. Dissolved arsenic compounds can be removed from the water column through adsorption to clays, iron oxides, and organic material, which leads to the enrichment of sediments[147,148]. Arsenic adsorbed to particulates does not disassociate and accumulates in sediment, where remobilisation has only a small effect on the dissolved arsenic concentration (<7%)[149]. Furthermore, adsorption is most effective in aerobic, acidic, freshwaters and more arsenic can be found in solution as conditions become more reducing, alkaline, and/or saline[150]. Furthermore, arsenic can form complexes with a number of organic compounds, most of which increase solubility. Arsenate may isomorphously substitute phosphate[151]. Arsenic bioaccumulates in living organisms, with greatest levels observed in lower trophic levels. However, high toxicity or arsenic lowers overall accumulation by aquatic organisms. There is no evidence of biomagnification[152]. Inorganic arsenic is metabolised by a number of aquatic (including marine) organisms to organic arsenicals, increasing the mobility in the environment[141,153].
Mode of action/toxicity	Arsenic is not known to be an essential trace element for living organisms[154], although some micro-organisms are known to use arsenic for energy generation[155]. Inorganic arsenic is most toxic to living organisms and includes trivalent inorganic arsenic (arsenite As^{3+}) and pentavalent inorganic arsenic (arsenate As^{5+})[156]. The former is predominant under anoxic conditions and readily binds to sulfhydryl groups of enzymes leading to enzyme inhibition. Arsenate is more prevalent in aerobic conditions and is structurally similar to phosphate and may disrupt metabolic reactions that require phosphorylation[156]. Arsenic can lead to general growth deficiencies, lowered reproduction, changes in respiration patterns and mortalities. High toxicity of arsenic lowers overall bioaccumulation by aquatic organisms.
Natural occurrence in South African waters	The concentration of arsenic in seawater at a salinity of 35 ppt has been given as 2.3 µg/L[157]. Dissolved arsenic in seawater was also found to range between 1-3 µg/L. A range between 1.12 and 1.87 µg/L with an average of 1,72 µg/L has been reported for the most probable species ($HASO_4^{2-}$) in ocean water with a salinity of 42- 35[119]. The occurrence of methylarsenic compounds is usually associated with phytoplankton activity[149]. Ranges of <1 to 4 ng/l for CH As O (OH) (methylarsonic acid) and 0.2 to 1 ng/l for $(CH_3)_2$ As O (OH)(dimethylarsinic acid) have been reported for seawater[131].

Guideline levels adopted in other jurisdictions (Total µg/L unless otherwise stated)		**Natural Environment**	**Mariculture**
	CCME 2001[158]	12.5 (Chronic)[A]	
	ANZECC 2000[3]		<30[B,D]
	EPA 1992[45]		0.14[B,F]
	EPA 1995[159]	69 (Acute); 36 (Chronic)[B]	
	EPA California 2013[6]	8-80[A,C]	
	EPA Florida 2015[18]	50 (Acute)[A] As^{3+}: 36 (Acute)	50 (Acute)[A,D] As^{3+}: 36 (Acute) [A,D]
	EPA South Carolina 2014[16]	69 (Acute); 36 (Chronic)[A]	10[A,E]
	EPA North Carolina 2016[11]	69 (Acute); 36 (Chronic)[B]	
	UK 2014[17]	25 (Long-term)	
	BCLME 2006[4]	As^{3+}: 2.3 (Chronic) [A,C] As^{5+}: 4.5 (Chronic) [A,C]	
	WIOR 2009[5]	As^{3+}: 2.3 (Chronic) [A,C] As^{5+}: 4.5 (Chronic) [A,C]	

A Expressed as total recoverable metal.
B Expressed as dissolved metal.
C Values for alternative measurements. Alternative measurements include 6-month average = 8 µg/L, Daily maximum = 32 µg/L, Instantaneous maximum = 80 µg/L.
D Protection of mariculture organism health
E Protection of human health, for consumption of organisms only
F Protection of human health, for consumption of organisms and water.

4.4.2 Cadmium

Constituent	Cadmium
IUPAC Name CAS RN	Cadmium 7440-43-9
Category	Toxic substances: metals
Description	Cadmium exists in two oxidation states, namely metallic (Cd^0) and divalent (Cd^{2+}). Most natural cadmium deposits can be found in its divalent oxidative state[160]. While metallic cadmium is insoluble in water, several of its divalent salts are freely soluble[161]. Cadmium is harmful to aquaculture organism and human health. Cadmium does not cause tainting.
Recommended Guidelines for total recoverable cadmium (µg/L)	**Natural Environment and Mariculture** 0.12 (Chronic)
Notes on guidelines	Cadmium toxicity increases with decreasing salinity (see section on environmental fate and behaviour for more detail). Therefore estuarine organisms will be at greater risk and a more conservative guideline value should be applied in future. Most detection methods measure total or dissolved cadmium in a sample, where "dissolved" is defined operationally as cadmium which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable* cadmium are compared to the guidelines. Although speciation of cadmium in seawater is often related to the observed toxicity, speciation of cadmium can only be predicted using geochemical models, for example the Windermere Humic Aqueous Model (WHAM)[162,163]. South Africa's laboratories, however, do not have accredited tests available to separately analyse cadmium speciation.
Sources	The average concentration of cadmium in the continental crust ranges from 0.15-0.2 mg/kg cadmium[164]. While igneous and metamorphic rocks have relatively low average cadmium concentrations (0.082 and 0.06 ppm respectively), sedimentary rock contains substantially higher amounts with an average of 3.42 ppm (range 0.05-500 ppm)[164]. Cadmium is commonly associated with zinc, lead, and copper ores[164,165]. Cadmium enters the environment through weathering and erosion of rock and soils, natural combustion from volcanoes and forest fires. Anthropogenic activities accelerate cadmium mobilisation through the release of wastewater streams from mining operations, agriculture, urban areas, and various industries into surface waters (fresh and salt water)[166,167,168,169]. Nickel-Cadmium (NiCd) batteries account for the majority (over 80%) of global cadmium consumption, followed by its use in pigments, coatings and plating, stabilizers for plastics, nonferrous alloys and other emerging specialized uses (e.g., use of cadmium selenide or cadmium sulphide in the manufacture of nanoparticles used as a semiconductor in photovoltaic devices[170]. Cadmium is also present as an impurity in zinc, lead and copper ore mine wastes, fossil fuels, iron and steel, cement, and fertilizers[171]. Although cadmium is not mined in South Africa, cadmium containing products are manufactured locally and are often dumped together with household waste by consumers[172].
Environmental fate and behaviour	Compared to other heavy metals, cadmium is relatively mobile in the aquatic environment and may be transported in solution as either hydrated cations or as organic or inorganic complexes[141]. Cadmium mobility in aquatic environments is enhanced by low pH, low hardness, low suspended matter levels, high redox potential and low salinity. The most probable main species of cadmium in oxygenated seawater is $CdCl_2$[119]. Various sorption processes reduce the mobility of cadmium and result in the enrichment of suspended and bed sediments relative to the water column[141]. In unpolluted water, sorption onto clay minerals, hydrous iron and manganese oxides are controlling factors, while sorption onto organic materials plays a greater role in polluted waters[141]. Dissolved cadmium is also assimilated by marine diatom *Thalassiosira weissflogii* when zinc concentrations are insufficient for phytoplankton growth[173,174]. The assimilation and subsequent cycling of dissolved cadmium in the euphotic zone until it is transported to deeper waters means that this trace metal can be Characterised as having a nutrient-like depth profile (i.e. surface depletion and deep water enrichment)[173,174]. Once cadmium is removed from the water column, it may not be bioavailable except to benthic feeders and bottom dwellers[141]. Cadmium can be re-suspended in particulate form and/or can undergo hydrolysis to become bioavailable in its dissolved form. Coastal upwelling systems can transport cadmium back to surface waters[175].

Mode of action/toxicity	For most organisms cadmium is a non-essential metal without biological function[176,177,178]. The marine diatom *Thalassiosira weissflogii* is, however, known to assimilate cadmium when zinc concentrations are insufficient for phytoplankton growth[173,174]. The main toxic form of cadmium is the free Cd^{2+} ion; however other forms of cadmium, for example those bound to various ligands, may also cause adverse effects. Cadmium, exerts its toxic effects in aquatic organisms by blocking the uptake of calcium of manganese from water[179]. Calcium (Ca^{2+}) is an essential element which is taken up by organisms from water via specialized calcium channels. However, when cadmium (Cd^{2+}) is present in water, this metal competes with calcium for binding sites, inhibiting calcium uptake and resulting in hypocalcaemia[180]. Cadmium is a known teratogen and carcinogen, is a probable mutagen and is known to induce a variety of other short- and long-term adverse physiological effects in fish and wildlife at both the cellular and whole-animal level[176,181,182]. Chronic exposure leads to adverse effects on growth, reproduction, immune and endo- crine systems, development, and behaviour in aquatic organisms[177]. Increasing water hardness reduces toxicity to organisms[183]. The organic content of seawater generally decreases the uptake and toxic effect by binding cadmium and reducing its availability to organisms. Although a general trend of decreasing toxicity with increasing salinity was observed for close to ten genera, this relationship could not be statistically verified[169]. Increased ambient tempera- ture has been shown to elevate toxicity of cadmium in wild oysters (*Crassostrea virginica*)[184]. This has the important implication that regulatory standards for water pollution derived in one area may not offer adequate protection in other (warmer) climates[185]. Furthermore, the enhanced bioavailability of cadmium at higher temperature and lower salinity implies that cadmium could be more toxic for estuarine species than marine species[186]. pH and alkalinity have been shown to have little or no effect on cadmium toxicity[187,188]. Cadmium bioaccumulates in all levels of the food chain[169,185].
Natural occurrence in South African waters	The average cadmium content of sea water has been reported to approximately 0.1 µg/L or less[165,189]. The most probable species found in oxygenated seawater with a salinity of 35 ppt is cadmium chloride ($CdCl_2$) and has an average concentration of 0.079 µg/L (0.00011-0.12 µg/L)[119]. Although elevated cadmium concentrations can often be traced back to anthropogenic activities, spatial and temporal variability in natural background concentrations of cadmium in the marine environment could also occur due to site-specific geochemical processes, as well as abiotic processes such as weathering, climate, soil type, pH, redox potential and dilution (i.e. seasonal precipitation patterns). The average cadmium concentration in South African surface offshore marine waters was reported as 0,108 µg/L in 1984[190]. Coastal cadmium concentrations were generally higher, ranging from "none detectable "to 3.5 µg/L (average of 0.4 µg/L) [191]. Most values were low and compared favourably with the cadmium concentration reported elsewhere in coastal waters[192,193]. High concentrations off Umbogintwini and Fynnlands could be explained by nearby pipeline outfalls carrying industrial effluent, high concentrations near the Knysna estuary were accredited to favourable biochemical and abiotic processes[191].

Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	CCME 2014[7]	0.12 (Chronic)[A]	
	ANZECC 2000[3]	0.7-36[B,C]	0.5-5[B,F,D]
	EPA 2016[169]	33 (Acute); 7.9 (Chronic)[B]	
	EPA Oregon 2013[194]	40 (Acute); 8.8 (Chronic)[B]	
	EPA California 2013[6]	1-10[A,D]	
	EPA Florida 2015[18]	8.8 (Acute)[A]	8.8 (Acute)[A,G]
	EPA South Carolina 2014[16]	43 (Acute); 9.9 (Chronic)[A]	
	EPA North Carolina 2016[11]	40 (Acute); 8.8 (Chronic)[B]	
	European Union 2013[14]	0.2 (Chronic); 0.45-1.5 (Acute)[B,E]	
	BCLME 2006[4]	5.5[A]	5.5[A,G]
	WIOR 2009[5]	5.5[A]	5.5[A,G]

A Expressed as total recoverable metal.
B Expressed as dissolved metal.
C Values for alternative levels of protection (% species). Alternative levels include 80% = 36 µg/L, 90% = 14 µg/L, 95% = 5.5 µg/L and 99% = 0.7 µg/L.
D Values for alternative measurements. Alternative measurements include 6-month average = 1 µg/L, Daily maximum = 4 µg/L, Instantaneous maximum = 10 µg/L.
E Class 1 = 0.45 µg/L (< 40 mg Ca CO_3 /l); Class 2 = 0,45 µg/L (40 to < 50 mg $CaCO_3$/l); Class 3 = 0.6 µg/L (50 to < 100 mg $CaCO_3$ /l); Class 4 = 0.9 µg/L (100 to < 200 mg $CaCO_3$ /l); Class 5 = 1.5 µg/L (≥ 200 mg $CaCO_3$ /l).
F Varies with hardness.
G Protection of mariculture organism health.

4.4.3 Chromium

Constituent	Chromium (Cr)
IUPAC Name CAS RN	Chromium 7440-47-3
Category	Toxic substances: metals
Description	Chromium is a hard but brittle shiny, grey metal. Chromium can exist in nine different oxidation states from -2 to +6[195]. In aqueous systems, however, chromium exists in oxidation states Cr^{3+} (stable) and Cr^{6+} (strongly oxidising)[141,195]. Cr^{6+} is the principal oxidation state found in surface waters and aerobic soils[195] and is almost exclusively sourced from human activities[141]. The most probable species in oxygenated seawater with pH>6.5 is the chromate ion, CrO_4^{-2}. Chromium is harmful to aquaculture organism and human health. Chromium does not cause tainting.
Recommended Guidelines for total recoverable hexavalent chromium (Cr^{6+}) (µg/L)	**Natural Environment and Mariculture** 2 (Chronic)
Notes on guidelines	Hexavalent chromium (Cr^{6+}) is the principal oxidation state found in surface waters and aerobic soils[195] and is considered much more toxic than trivalent chromium (Cr^{3+}). Recently reviewed guidelines therefore no longer specify a limit for Cr^{3+}. Most detection methods measure total or dissolved chromium in a sample, where "dissolved" is defined operationally as cadmium which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable* chromium are compared to the guidelines.
Sources	Chromium is a naturally occurring element and is found in the earth's crust in concentrations of approximately 10-100 ppb[141]. Naturally, chromium enters the aquatic environment through weathering and erosion of rock and soils, forest fires and vegetative debris and volcanic eruptions[195]. Chromium is mined, smelted and refined for use in various industries. Chromium oxide, chromium chloride and chromium sulphate are the most commonly used compounds for metal plating and finishing, pigments and paints, leather tanning, wood preservation, corrosion inhibition and as catalysts. Smaller quantities are also used in cosmetics, toners for copying machines, magnetic tapes, fertilisers, rubber products, plastics, soaps and cleaning products[195]. South Africa is the world's largest single producer of ferrochrome and supplies much of the world's stainless steel producers[196]. Ferrochrome is mined in Limpopo, Mpumalanga and North West Provinces of South Africa[196]. Cr^{6+}enrichment can therefore be expected in coastal environments that are fed by rivers originating in or passing through these provinces. Furthermore, effluents originating from industries that produce chromium containing products and municipal sewage can contain high concentrations of Cr^{6+}. Chromium also enters the aquatic environment in via waste sites and atmospheric deposition[195].

<table>
<tr><td>Environmental fate and behaviour</td><td colspan="3">Chromium is usually found in the trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) oxidation state in aquatic systems[141]. Chromium compounds with other valences (-2,-1,0,+1,+2,+4,+5) are extremely rare[195] and are not important when discussing the fate of chromium in the aquatic environment.

Cr^{3+} is the most stable form in natural waters and sediments. It quickly hydrolyses and precipitates as insoluble hydroxide or oxide in water with pH>5[197]. It also has a strong tendency to form hexacoordinate octahedral complexes with a great variety of ligands, including water, ammonia, urea, halides, sulphates, ethylendiamine, and organic acids[141]. Cr^{3+} is only weakly adsorbed into inorganic solids[141].

Cr^{6+} is released into the aquatic environment mainly from anthropogenic sources and is highly toxic[141]. The most probable form in natural waters (pH>6.5) is the chromate ion, CrO_4^{-2}, which is stable and soluble, and therefore mobile in the aquatic environment[198]. Cr^{6+} is not easily adsorbed by clays, ferric hydroxide, or ferric and manganese oxides[199]. However, Cr^{6+} is efficiently removed by activated carbon, which may indicate that it is adsorbed by organic materials[200].

Cr^{3+} and Cr^{6+} are readily interconvertible under natural conditions[201]. Cr^{6+} can be reduced by Fe^{2+}, dissolved sulphides, and certain organic compounds with sulfhydryl groups. Various microorganisms have been shown to catalyse Cr^{6+} reduction under varying conditions[202]North-West Province (South Africa. Cr^{3+} can be oxidised by a large excess of MnO_2 and at a slower rate by O_2 under natural water conditions. Conditions favourable to the formation of Cr^{6+} keeps chromium dissolved in the water column, while conditions favourable to Cr^{3+} lead to precipitation and adsorption of chromium in sediments[201].

Chromium is weakly bioaccumulates in aquatic organisms[141]. Although chromium has been shown to transfer through the food chain, the concentration decreases with increasing trophic levels[203].</td></tr>
<tr><td>Mode of action/ toxicity</td><td colspan="3">The high oxidizing potential, high solubility, and ease of permeation of biological membranes make Cr^{6+} generally more toxic than Cr^{3+}[195].

Chronic Cr^{3+} toxicity reduced filtration rate of molluscs (*Mytilus edulis* and *Mya arenaria*) and hatching success of *Artemia salina*. Acute toxicity lead to reduced filtration rate of *Perna perna* and mortality of various organisms[195].

Chronic impacts of Cr^{6+} on marine organisms include organ damage (*Pleuronectes platessa*), reduced respiration (*Callinectes simulis*) and mortality (various species). Acute toxicity reduces filtering rate (*Villorita cyprinoides*), reduced growth and impaired photosynthesis (marine algae), and mortality[195]. Cr^{6+} also causes cancer in humans [202] (North-West Province in South Africa).</td></tr>
<tr><td>Natural occurrence in South African waters</td><td colspan="3">Dissolved chromium concentrations in marine water have been found to range from 0.2 to 2 µg/L[131]. A range between 0.1 and 0.26 µg/L, with an average of 0.21 µg/L, has been reported for the most probable species (CrO_4^{2-} and $NaCrO_4^{-}$) in oxygenated seawater[119].

The average chromium concentration in South African offshore surface waters was reported as 0.071 µg/L in 1984[190].</td></tr>
<tr><td rowspan="10">Guideline levels adopted in other jurisdictions (µg/L)</td><td></td><td>**Natural Environment**</td><td>**Mariculture**</td></tr>
<tr><td>CCME 1999[195]</td><td>Cr^{3+}: 56 (Chronic)[A]
Cr^{6+}: 1.5 (Chronic)[A]</td><td></td></tr>
<tr><td>ANZECC 2000[3]</td><td>Cr^{3+}: 7.7-90.6[B,C]
Cr^{6+}: 0.14-85[B,D]</td><td>Total Cr: <20</td></tr>
<tr><td>EPA California 2013[6]</td><td>Cr^{6+}: 2-20[A,E]</td><td></td></tr>
<tr><td>EPA Florida 2015[18]</td><td>Cr^{6+}: 50 (Acute)[A]</td><td>Cr^{6+}: 50 (Acute)[A,F]</td></tr>
<tr><td>EPA South Carolina 2014[16]</td><td>Cr^{6+}: 1100 (Acute);
50 (Chronic)[A]</td><td></td></tr>
<tr><td>EPA North Carolina 2016[11]</td><td>Cr^{6+}: 1100 (Acute);
50 (Chronic)[B]</td><td></td></tr>
<tr><td>European Union 2013[14]</td><td>Cr^{6+}: 32 (Acute);
0.6 (Chronic)[B]</td><td></td></tr>
<tr><td>BCLME 2006[4]</td><td>Cr^{3+}: 10 (Chronic)[A]
Cr^{6+}: 4.4 (Chronic)[A]</td><td>Cr^{3+}: 10 (Chronic)[A,F]
Cr^{6+}: 4.4 (Chronic)[A,F]</td></tr>
<tr><td>WIOR 2009[5]</td><td>Cr^{3+}: 10 (Chronic)[A]
Cr^{6+}: 4.4 (Chronic)[A]</td><td>Cr^{3+}: 10 (Chronic)[A,F]
Cr^{6+}: 4.4 (Chronic)[A,F]</td></tr>
</table>

A Expressed as total recoverable metal.

B Expressed as dissolved metal.

C Values for alternative levels of protection (% species) for Cr^{3+}. Alternative levels include 80% = 90.6 µg/L, 90% = 48.6 µg/L, 95% = 27.4 µg/L and 99% = 7.7 µg/L.

D Values for alternative levels of protection (% species) for Cr^{6+}. Alternative levels include 80% = 85 µg/L, 90% = 20 µg/L, 95% = 4.4 µg/L and 99% = 0.14 µg/L.

E Values for alternative measurements for Cr^{6+}. Alternative measurements include 6-month median = 2 µg/L, Daily maximum = 8 µg/L, Instantaneous maximum = 20 µg/L.

F Protection of mariculture organism health.

4.4.4 Copper

Constituent	Copper (Cu)
IUPAC Name CAS RN	Copper 7440-50-8
Category	Toxic substances: metals
Description	Copper is an abundant inorganic trace element (Cu) that occurs naturally in earth's crust. Copper has a high thermal and electrical conductivity. Copper can be harmful to aquaculture organism and human health. Copper causes tainting.
Recommended Guidelines for total recoverable copper (µg/L)	**Natural Environment and Mariculture** 3 (Chronic)
Notes on Guidelines	Most detection methods measure *total recoverable* or *dissolved copper* in a sample, where "dissolved" is defined operationally as copper which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable* copper are compared to the guidelines.
Sources	Copper enters the marine environment through geological processes such as weathering, erosion, deposition and volcanic eruptions. Copper mining and the use of this metal in the agricultural sector (pesticides), and for metal and electrical manufacturing can accelerate the naturally low rates of copper supply to the marine environment. Furthermore, copper containing antifouling paints used for ship hulls, buoys and underwater surfaces, as well as chromated copper arsenate (CCA) treated timber structures have contributed considerably to anthropogenically elevated copper levels in the marine environment.
Environmental fate and behaviour	Copper in oxygenated seawater exists most commonly as copper carbonate ($CuCO_3$) copper hydroxide ($CuOH^+$) and as Cu^{2+}. Observations suggest that seawater can retain a maximum of 50 µg/L of copper. At high concentrations, the copper is present in a colloidal form[204]. A significant fraction of Cu^{2+} may exist as complexes with dissolved organic compounds. Upon degradation, it results in an increase in the amount of free copper[204]. Anoxic near-shore sediments represent a significant sink for copper when compared with the accumulation rates for pelagic sediments[131]. The surface distributions of copper have been shown to be influenced by continental sources from river and/or shelf sediments. As a result, copper has been shown to have much higher concentrations in shelf water than in oceanic surface waters[157]. Cu^{2+} can also be adsorbed onto dead or living bacteria[66]. In addition to adsorption processes, active uptake of copper by phytoplankton in the photic zone can also be important, playing an important role in metal-requiring and metal-activated enzyme systems[119]. Copper is incorporated in haemocyanin, the blood pigment of molluscs and crustaceans[134].
Mode of action/ toxicity	At low concentrations copper is an essential nutrient to marine organisms. At higher concentrations however, copper becomes toxic. Chronic exposure can adversely affect survival, growth, reproduction, brain function, enzyme activity, blood chemistry, and metabolism of organisms. At very high concentrations copper in seawater can cause mortality of marine organisms.
Natural occurrence in South African waters	The average copper concentration in South African surface marine waters has been reported as 0,899 µg/l[190]. A review of the metal concentrations in South African coastal water, sediments and marine organisms was undertaken by Hennig in 1985[191].

Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	ANZECC 2000[3]	0.3-8[B,C]	<5[B,F]; 1000[B,G]
	EPA Draft 2016[205]	To be calculated using a biotic ligand model.[E] Using reference conditions with temperature = 22°C; pH=8; Dissolved Organic Carbon = 1.0 mg/L and Salinity = 32 ppt 2.0 (Acute); 1.3 (Chronic)[B]	
	EPA Oregon 2013[194]	4.8 (Acute); 3.1 (Chronic)[B]	
	EPA California 2013[6]	3-30[A,D]	
	EPA Florida 2015[18]	3.7 (Acute)[A]	3.7 (Acute)[A,F]
	EPA South Carolina 2014[16]	5.8 (Acute); 3.7 (Chronic)[A]	1000[A,G]
	EPA North Carolina 2016[11]	4.8 (Acute) 3.1 (Chronic)[B]	
	UK 2014[17]	3.76 µg/l, where DOC ≤1mg/l. Where DOC >1mg/l, 3.76 + (2.677 x ((DOC/2) – 0.5)) µg/l (Chronic)[B]	
	BCLME 2006[4]	1.3[A]	1.3[A,F]; 1000[A,G]
	WIOR 2009[5]	1.3[A]	1.3[A,F]; 1000[A,G]

A Expressed as total recoverable metal.

B Expressed as dissolved metal.

C Values for alternative levels of protection (% species). Alternative levels include 80% = 8 µ/l, 90% = 3 µ/l, 95% = 1.3 µ/l and 99% = 0.3 µ/l.

D Values for alternative measurements. Alternative measurements include 6-month average = 3 µ/l, Daily maximum = 12 µ/l, Instantaneous maximum = 30 µ/l.

E The BLM allows users to develop protective chronic and acute values based on site-specific water quality variables including temperature, dissolved organic carbon (DOC), salinity, and pH, which influence the bioavailability and toxicity of copper in estuarine/marine environments.

F Protection of mariculture organism health.

G Organoleptic effects (not toxic to humans).

4.4.5 Lead

Constituent	Lead (Pb)
IUPAC Name CAS RN	Lead 7440-43-9
Category	Toxic substances: metals
Description	Lead is a naturally occurring, soft, bluish-grey heavy metal. The most probable species in marine waters are $PbCO_3^{0}$, $(PbCO_3)_2^{2-}$, $Pb Cl^{+}$[119]. Lead is harmful to aquaculture organism and human health. Lead does not cause tainting.
Recommended Guidelines for total recoverable lead (µg/L)	**Natural Environment and Mariculture** 2 (Chronic)
Notes for guidelines	Most detection methods measure *total recoverable* or *dissolved lead* in a sample, where "dissolved" is defined operationally as lead which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable* lead are compared to the guidelines.
Sources	Lead is a naturally occurring element and the average abundance in the earth's crust is approximately 15 ppm[206]. Lead enters the environment through weathering and erosion of rock and soils, natural combustion from volcanoes and forest fires[119]. Lead is a major constituent of three minerals, which are found in sufficient abundance to form mineable deposits. These include galena (PbS), angelesite ($PbSO_4$), and cerrusite ($PbCO_3$). By far the most abundant is galena, which is the primary constituent of the sulphide ore deposits from which most lead is mined[141]. Lead is used for a wide range of products, including the manufacturing of car batteries, metal plating, bullets, explosives, matches, ballast keel of sailboats, scuba diving weight belts, and sound proofing (sheet-lead)[49,207]. Lead has many uses in the construction industry and lead-based semiconductors are finding applications in photovoltaic (solar energy) cells and infrared detectors[208]1800. Infrared detectors are in general used to detect, image, and measure patterns of the thermal heat radiation which all objects emit. At the beginning, their development was connected with thermal detectors, such as thermocouples and bolometers, which are still used today and which are generally sensitive to all infrared wavelengths and operate at room temperature. The second kind of detectors, called the photon detectors, was mainly developed during the 20th Century to improve sensitivity and response time. These detectors have been extensively developed since the 1940's. Lead sulphide (PbS) is also used for electrodes and in solder for electronics (in some countries) and for radiation shielding purposes. In most countries, lead as an additive to fuel and paint has been phased out due to associated health risks. In the past, release of lead to the atmosphere largely originated from leaded petrol[129]. By the mid-1980s, a significant shift in lead end-use patterns had taken place. Much of this shift was a result of the environmental regulations originating in the U.S. and EU that significantly reduced or eliminated the use of lead in non-battery products, including gasoline, paints, solders, and water systems.

Environmental fate and behaviour	Neither metallic lead nor the common lead minerals are soluble in water. Naturally occurring metallic lead or lead minerals are not usually mobile in ground or surface water, as they are adsorbed by ferric hydroxide or tend to combine with carbonate or sulphate ions to form insoluble compounds[209]. Lead can, however, be dissolved in some acids and as a result, compounds produced industrially are considerably water soluble[141]. The dominant mechanism controlling the fate of lead appears to be sorption. Sorption processes are effective in reducing the concentration of soluble lead in natural waters and result in enrichment of bed sediments near the source[141]. Lead has a tendency to form complexes with naturally occurring organic materials (e.g. humic and fulvic acids). This increases its adsorptive affinity for clays and other mineral surfaces. Precipitation of $PbSO_4$, $PbCO_3$, and PbS may also be important. At low pH values, sorption and precipitation are not nearly as effective in removing lead from solution, so that lead is much more mobile in acidic waters[141]. Benthic microbes can methylate lead to form tetramethyl lead which is volatile and more toxic than inorganic lead. Biomethylation may, in this manner, also provide a mechanism for remobilisation of lead from the bed sediments[141]. Lead is bioaccumulated by aquatic organisms but not in the food chain (i.e. no biomagnification). For example, fish accumulate very little lead in edible tissue while high levels can be found in oysters and mussels. Bioconcentration factors tend to decrease as trophic level increases[141].
Mode of action/toxicity	Both dissolved and particulate metal species may be toxic[210] and are not known to be an essential trace element for aquatic organisms[129]. A decrease in pH increases availability of divalent lead, the principal form accumulated by aquatic animals[141]. Marine organisms exposed to lead may experience general growth deficiencies, lowered reproduction and mortality. Juvenile fish are more sensitive to lead than adults or eggs. Typical symptoms of lead toxicity include spinal deformity[211] and blackening of the caudal region. Organic compounds of lead are more toxic to fish than inorganic lead salts[212]. Invertebrate community structure may be adversely affected by lead contamination. For example, adaptation to hypoxic conditions can be hindered by high lead concentrations[212].
Natural occurrence in South African waters	Lead concentrations in marine waters typically range from 0.004-0.09 µg/L in the open ocean (average of 0.03 µg/L) and between 0.007 and 0.2 µg/L in coastal waters (average of 0.08 µg/L)[213] together with analysis of recent IAEA data, suggests that marine pollutants can be divided into three broad categories: 1. those that are more concentrated in the open ocean environment than in coastal waters, including PCBs and (arguably. The most probable species in oxygenated sea water (35 ppt) are $PbCO_3{}^0$, $(Pb_3\ CO_2)^{2-}$, and $Pb\ Cl^+$ which have been reported to range between 0.0004 and 0.037 µg/L (average of 0.002 µg/L)[119]. In deep ocean waters, the lead concentrations have been measured at a level of 0.01 to 0.05, µg/L. Other measurements suggest that deep ocean lead levels may be as low as 0.002 µg/L[129]. In South African surface offshore marine waters, lead was reported as 0.521 µg/L in 1984[190]. Coastal lead concentrations were generally higher with a median of 2.6 µg/L (ranging from "none detectable "to 287 µg/L) [191]. Anomalies were observed at St Lucia, Durban Bay and Bashee River and Swartkops River[191]. Note that all values listed above reflect concentrations in a marine environment impacted by anthropogenic activities and should not serve as a baseline.

Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	ANZECC 2000[3]	2.2-12[B,C]	1-7[B,E,F]
	EPA 1980[214]	210 (Acute);8.1 (Chronic)[B]	
	EPA Oregon 2013[194]	210 (Acute); 8.1 (Chronic)[B]	
	EPA California 2013[6]	2-20[A,D]	
	EPA Florida 2015[18]	8.5 (Acute)[A]	8.5 (Acute)[A,F]
	EPA South Carolina 2014[16]	220 (Acute); 8.5 (Chronic)[A]	
	EPA North Carolina 2016[11]	210 (Acute); 8.1 (Chronic)[B]	
	European Union 2013[14]	14 (Acute); 1.3 (Chronic)[B]	
	BCLME 2006[4]	4.4[A]	4.4[A,F]
	WIOR 2009[5]	4.4[A]	4.4[A,F]

A Expressed as total recoverable metal.
B Expressed as dissolved metal.
C Values for alternative levels of protection (% species). Alternative levels include 80% = 12 µg/L, 90% = 6.6 µg/L, 95% = 4.4 µg/L and 99% = 2.2 µg/L.
D Values for alternative measurements. Alternative measurements include 6-month average = 2 µg/L, Daily maximum = 8 µg/L, Instantaneous maximum = 20 µg/L.
E Varies with hardness.
F Protection of mariculture organism health.

4.4.6 Mercury

Constituent	Mercury (Hg)
IUPAC Name CAS RN	Mercury 7439-97-6
Category	Toxic substances: metals
Description	Mercury is a metal which is liquid at normal temperatures and pressures. Mercury exists in one of three oxidation states, namely elementary mercury (Hg), mercurous ion (Hg^{1+}) and mercuric ion (Hg^{2+})[141]. Elementary mercury is volatile and not readily soluble in water[215]. Inorganic mercury in seawater occurs primarily as Hg^{2+}[216]. The most probable Hg^{2+} form in seawater is $Hg Cl_3^-$ and $Hg Cl_4^{2-}$[215]. Complexes with bromide ions are also significant in seawater[216]. Mercury is harmful to aquaculture organism and human health. Mercury does not cause tainting.
Recommended guidelines for total recoverable mercury (µg/L)	**Natural Environment and Mariculture** 0.016 (Chronic)
Notes for guidelines	Guideline values vary considerably. The most recent acute value was derived by EPA Florida in 2015 (0.025 µg/L), which is equal to or lower than all other recently derived chronic values (0.025-1.1). Conceptually, a chronic value must be lower than the acute value and therefore, the 0.016 µg/L chronic CCME 2001 Guideline[158] was adopted for mercury. Most detection methods measure *total recoverable* or *dissolved mercury* in a sample, where "dissolved" is defined operationally as mercury which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable* mercury are compared to the guidelines.
Sources	Mercury is a naturally occurring element and the average abundance in the earth's crust is approximately 80 ppb (ranging from 5 ppb to 1000 ppb in common natural materials)[217]. Mercury enters the aquatic environment through weathering and erosion of rock and soils, forest fires, volcanic eruptions, hot springs and a portion of the volatilisation from the oceans[8]. When compared to natural sources, anthropogenic activities release significant amounts of mercury into the air, water (freshwater and sea water) and soil[8]. Such activities include gold mining, metal smelting, coal-burning power plants, production of chlorine and sodium hydroxide, wood pulping, agriculture (application of mercury containing fungicide), preparation of exterior paint, municipal and hospital waste incineration, coal and fossil fuel combustion, cement manufacturing, and mercury waste in landfills or storage[8,218].
Environmental fate and behaviour	Inorganic mercury in seawater occurs primarily as Hg^{2+}. Hg^{2+} can undergo reduction to elemental mercury. Elemental mercury occurs primarily in the surface of the ocean[219] and can be lost to the atmosphere by volatisation[216]. Apart from the dime Hg^{2+}, which occurs at extremely low concentrations in sea water, complexes of mercury in the intermediate oxidation state Hg^{1+} are not stable[215]. Although dissolved stable mercury (i.e. Hg^{2+}) is readily adsorbed onto organic and inorganic particles, high levels of chloride in seawater under oxygenated conditions favours the formation of mercuric chloride complexes ($Hg Cl_3^-$ and $Hg Cl_4^{2-}$)[220]. This increases the solubility of mercury[141]. Organic and inorganic particles associated with inorganic mercury compounds settle near the source and sediments are therefore considered the primary sink in the mercury cycle[141]. Mercury in sediments can precipitate as mercury sulphide[141]. Abiotic and biotic (microbial) processes can transform inorganic mercury in the water column or in sediments to organic alkylmercury compounds such as methylmercury[216], dimethylmercury, as well as aryl compounds (e.g. phenyl mercury)[221]. Methylation rates tend to be highest in surface sediments with freshly deposited organic matter and in warm shallow sediments where abundant bacterial activity takes place[222,223]. Inorganic and organic forms of mercury may release ionic or metallic mercury into the water column (as a result of turbulence or activities of benthic organisms) as part of the mercury cycling process[141]. Only a small proportion of dissolved inorganic mercury is ingested by the aquatic biota or transported by current movement[141]. However, methylmercury uptake by living organisms is most important when considering the toxicity of mercury. Mercury readily bioaccumulates[224] and biomagnifies in upper trophic levels of aquatic food webs[225,226,227].

<table>
<tr><td>Mode of action/toxicity</td><td colspan="3">Bioavailability and toxicity of mercury in the ocean depends on its speciation in water216. The most toxic mercury species commonly found in seawaters is methylmercury (CH_3Hg), which is produced by the methylation of the reactive, ionic form, primarily Hg^{2+}[215,228]. Methylmercury is a potent neurotoxin and is present in most marine organisms[229].
Toxicity of mercury is negatively correlated with salinity, selenium concentration, and oxygen content, and positively correlated with temperature. Water hardness has a negligible effect on mercury toxicity[8].
Organisms at lower trophic levels usually contain the lowest proportion of total mercury as methylmercury and uptake is primarily a passive process occurring by adsorption to or absorption within the cell[224]. In organisms at higher trophic levels, methylmercury compounds bind strongly with sulphydryl groups in proteins and pass easily through the digestive wall. Methylmercury bioconcentrates in tissues, while inorganic mercury is more likely to be excreted. This increases the proportion of methylmercury in tissues[230].
Chronic mercury poisoning can reduce growth and survival and can cause general growth deficiencies/deformities, changes in respiratory patterns, burrowing abnormalities (benthic invertebrates) and mortalities[8].</td></tr>
<tr><td>Natural occurrence in South African waters</td><td colspan="3">Dissolved mercury concentrations reported for ocean waters range between 0.0005 and 0.003 µg/L, while those for coastal waters range between 0.002 and 0.015 µg/L[218]. Local variations from these values are considerable, especially in coastal seawater where mercury associated with suspended material may also contribute to the total load.
In South African surface offshore marine waters, mercury was reported as 0.055 µg/L in 1984[190]. Coastal mercury concentrations were generally higher with a median of 0.13 µg/L (ranging from 0.006 to 3.9 µg/L) [191]. Anomalies were observed at St Lucia, Durban Bay and Umgababa[191].</td></tr>
<tr><td rowspan="11">Guideline levels adopted in other jurisdictions (µg/L)</td><td></td><td>Natural Environment</td><td>Mariculture</td></tr>
<tr><td>CCME 2003[8]</td><td>0.016 (Chronic)[A]</td><td></td></tr>
<tr><td>ANZECC 2000[3]</td><td>0.1-1.4[B,C]</td><td><1[B,C]</td></tr>
<tr><td>EPA 1995[159]</td><td>1.8 (Acute); 0.94 (Chronic)[B]</td><td></td></tr>
<tr><td>EPA California 2013[6]</td><td>0.04-0.4[A,D]</td><td></td></tr>
<tr><td>EPA Florida 2015[18]</td><td>0.025 (Acute)[A]</td><td>0.025 (Acute)[A,E]</td></tr>
<tr><td>EPA South Carolina 2014[16]</td><td>2.1 (Acute); 1.1 (Chronic)[A]</td><td>0.051[A,F]</td></tr>
<tr><td>EPA North Carolina 2016[11]</td><td>0.025 (Chronic)[A]</td><td></td></tr>
<tr><td>European Union 2013[14]</td><td>0.07 (Acute)[B]</td><td></td></tr>
<tr><td>BCLME 2006[4]</td><td>0.4 (Chronic)[A]</td><td>0.4 (Chronic)[A,E]</td></tr>
<tr><td>WIOR 2009[5]</td><td>0.4 (Chronic)[A]</td><td>0.4 (Chronic)[A,E]</td></tr>
</table>

A Expressed as total recoverable metal.
B Expressed as dissolved metal.
C Values for alternative levels of protection (% species). Alternative levels include 80% = 1.4 µg/L, 90% = 0.7 µg/L, 95% = 0.4 µg/L and 99% = 0.1 µg/L.
D Values for alternative measurements. Alternative measurements include 6-month average = 0.04 µg/L, Daily maximum = 0.16 µg/L, Instantaneous maximum = 0.4 µg/L. E Protection of mariculture organism health.
F Protection of human health, for consumption of organisms only.

4.4.7 Nickel

Constituent	Nickel (Ni)
IUPAC Name CAS RN	Nickel 7440-02-0
Category	Toxic substances: metals
Description	Nickel is a hard but brittle, silvery-white metal at normal temperatures and pressures. Nickel is usually found in the divalent oxidation state in aquatic systems[197]. Elemental nickel is insoluble in water[197]. The most probable species in oxygenated seawater is $NiCO_3$, Ni^{2+}, and $NiCl^{+}$[19]. Nickel is harmful to aquaculture organism and human health. Nickel does not cause tainting.
Recommended Guidelines for total recoverable nickel (µg/L)	**Natural Environment and Mariculture**
	5 (Chronic)
Notes for guidelines	Most detection methods measure *total recoverable* or *dissolved nickel* in a sample, where "dissolved" is defined operationally as nickel which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable nickel* are compared to the guidelines.
Sources	Nickel is a naturally occurring element and the average abundance in the earth's crust is approximately 80 ppb[143], ranking 24th in crustal abundance of all elements[231]. Nickel possesses high thermal and electrical conductivities[232]. Nickel enters the aquatic environment through weathering and erosion of rock and soils, forest fires, and volcanic eruptions (nickel sulphide)[233]. Nickel is mined, smelted and refined for use in various industries. Metallic nickel is used in various alloys that have wide range of applications[234]. Nickel alloys are used in stainless steel production, in the electric industry and in shipbuilding[232]. Nickel compounds are also useful in various industries, including nickel plating, electronics, production of jewellery and nickel-containing batteries[235]. Nickel salts are of commercial importance and include nickel chloride, sulphate, nitrate, carbonate, hydroxide, acetate and oxide[236]. Globally, the largest anthropogenic releases into atmospheric, terrestrial and aquatic systems are from fossil fuel combustion, nickel mining and smelting[237]. Nickel enters the aquatic environment in effluents, via leaching (e.g. landfills) and through atmospheric deposition[238, 232].
Environmental fate and behaviour	Nickel is usually found in the divalent oxidation state in aquatic systems[197]. Nickel compounds with other valences (0, +1, +3, and +4) are extremely rare and are not important when discussing the fate of nickel in the aquatic environment. Nickel is the most mobile metal in the aquatic environment of all metals, as only a small proportion of the dissolved nickel is precipitated or adsorbed[141]. In unpolluted waters, sorption processes are moderately effective in limiting the mobility of nickel in the aquatic environment. In polluted, organically enriched waters, little or no sorption takes place and nickel remains in solution[141]. Nickel has an affinity for organic materials, hydrous iron and manganese oxides, which scavenge nickel from solution[141]. The most common aqueous ligands that are formed under aerobic conditions with a pH less than 9 include hydroxide, carbonate, sulphate, and halide compounds[197], which are sufficiently soluble to allow toxic levels of nickel to persist in solution. Insoluble nickel sulphide can form in reducing environments through precipitation[141]. The presence of humic acid, however, prevents precipitation of nickel[239]. Nickel may be deposited in sediment by precipitation, complexation, adsorption, and via uptake by biota. Nickel can subsequently be released from the sediment due to a change in pH, ionic strength, and particle concentration, which can reverse adsorption[240]. Nickel is bioaccumulated by some marine organisms at insignificant levels but biomagnification does not occur[141].

Mode of action/ toxicity	Although nickel essentiality in terrestrial to terrestrial vertebrates has been established, limited information exists for the role of nickel in sustaining aquatic life[238]. Nickel is an essential nutrient for algae and cyanobacteria[238]. It is currently unclear whether nickel is essential to aquatic invertebrates and vertebrates, as nickel-containing metallo-enzyme has yet to be recovered from animal tissue[241]. Nickel can replace essential metals in metallo-enzymes, thereby causing disruptions in metabolic pathways[237]. Nickel adversely affected growth and morphology of the marine bacterium *Arthrobacter marinus*[242]. It also inhibited growth of the diatom *Phaeodactylum tricornutum*[243], of the alga *Thalassiosira aestevalis*, and of a natural marine phytoplanktonic community[244]. Chronic exposure to nickel resulted in reduced hatching success and survival of the topsmelt (*Atherinops affinis*)[245]. Acute nickel poisoning leads to mortality of marine organisms[245]. Toxicity of nickel increased with increasing hydrostatic pressure[246]. Toxicity to marine bacterium *Acinetobacter sp.* also increased with increasing pH (from 5.5 to 8.5)[247]. Seawater decreases the toxicity of nickel to microbes due to the competitive interaction between magnesium and nickel for common binding sites on cell surfaces[247].
Natural occurrence in South African waters	Nickel concentrations in marine water have been found to range from 0.2 to 3 µg/L[119,131]. A range between 0.12 and 0.70 µg/L, with an average of 0.23 µg/L, has been reported for the most probable species ($NiCO_3$, Ni^{2+}, NiCl) in oxygenated seawater[119]. The average nickel concentration in South African offshore surface waters was reported as 0.563 µg/L in 1984[190]. Coastal nickel concentrations were generally higher with a median of 1.1 µg/L (ranging from 0.16 to 26 µg/L) [191]. Higher nickel concentrations in South Africa occurred around Richards Bay and Durban, Knysna, Green Point and the Olifants River[191]. It has been established that input from mixed industrial urban sources may elevate nickel concentrations to 10–50 µg/L[248].

Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	ANZECC 2000[3]	7-560[B,C]	<100[B,E]
	EPA 1995[159]	74 (Acute); 8.2 (Chronic)[B]	
	EPA 1998[45]		4600[B,F]
	EPA Oregon 2013[194]	74 (Acute); 8.2 (Chronic)[B]	
	EPA California 2013[6]	5-50[A,D]	
	EPA Florida 2015[18]	8.8 (Acute)[A]	8.3 (Acute)[A,E]
	EPA South Carolina 2014[16]	75 (Acute); 8.3 (Chronic)[A]	4600[A,G]
	EPA North Carolina 2016[11]	74 (Acute); 8.2 (Chronic)[B]	
	European Union 2013[14]	34 (Acute); 8.3 (Chronic)[B,E]	
	BCLME 2006[4]	70 (Chronic)[A]	70 (Chronic)[A,E]
	WIOR 2009[5]	70 (Chronic)[A]	70 (Chronic)[A,E]

A Expressed as total recoverable metal.
B Expressed as dissolved metal.
C Values for alternative levels of protection (% species). Alternative levels include 80% = 560 µg/L, 90% = 200 µg/L, 95% = 70 µg/L and 99% = 7 µg/L.
D Values for alternative measurements. Alternative measurements include 6-month median = 5 µg/L, Daily maximum = 20 µg/L, Instantaneous maximum = 50 µg/L.
E Protection of mariculture organism health.
F Protection of human health, for consumption of organisms and water.
G Protection of human health, for consumption of organisms only.

4.4.8 Silver

Constituent	Silver (Ag)
IUPAC Names	Silver
CAS RN	7440-22-4
Category	Toxic substances: metals
Description	Silver is a naturally occurring soft element[105]. Nano-sized silver particles (nanosilver) in the aquatic environment are a relatively recent concern and not enough data is available to date to derive a guideline for nanosilver[105]. Silver occurs at extremely low concentrations in the aquatic environment, primarily in the +I oxidation state as the $AgCl_2^-$ complexes in seawater[119]. Silver is harmful to aquaculture organism and human health. Silver does not cause tainting.
Recommended Guidelines for total recoverable silver (µg/L)	**Natural Environment and Mariculture**
	0.7 (Chronic)
Notes for guidelines	Most detection methods measure *total recoverable* or *dissolved silver* in a sample, where "dissolved" is defined operationally as silver which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable silver* are compared to the guidelines.
Source	Silver is a naturally occurring rare element and is found in the earth's crust in concentrations of approximately 0.1 ppm[143]. Naturally, silver enters the aquatic environment through weathering and erosion of rock and soils[195]. Roughly 60% of silver in water originates from natural sources. The remaining 40% are introduced into the aquatic environment from anthropogenic inputs[105]. Silver is mined, smelted and refined for use in various industries. The metallic form of silver is used to make jewellery, silverware, electronic equipment and dental fillings. Silver also occurs in powdery white (silver nitrate and silver chloride) or dark-grey to black compounds (silver sulphide and silver oxide). Silver compounds are used in the photographic industry[249]. Effluent originating from mines, manufacturing facilities and municipal waste water treatment plants release silver into the aquatic environment. The mining and photographic industries have been identified as the major contributors to anthropogenically introduced silver in the marine environment[249]. Naturally, silver in the aquatic environment is higher near mineral deposits and are very low elsewhere in the environment[250]. South Africa is not a producer of silver and anthropogenic sources of silver in the aquatic environment in South Africa are likely to originate mostly from industries that use silver in the production of above mentioned products.
Environmental fate and behaviour	Silver is usually found in the oxidation states 0 and +1, with +2 and +3 rarely occurring in the natural environments[105]. Chloride, bromide and iodide ions control the levels of hydrated silver cations in the aquatic environment[141]. Dissolved silver concentrations are typically very low due to stable complexes formed with dissolved organic carbon (DOC) or inorganic or organic suphides[105]. Chlorides play a key role in silver speciation in estuarine and marine environments[105]. As salinity increases, colloid-bound silver dissociates and silver complexation with chloride predominates. Crystalline, metallic silver and silver sulphides may precipitate under reducing conditions. Sorption is the major controlling mechanism in determining the fate of silver in the aquatic environment. Silver is strongly adsorbed onto hydrous manganese and iron oxides, clay minerals and organics[141]. Silver accumulates in sediments relatively close to the source. Numerous plants and primary consumer organisms accumulate silver and bioavailability is dependent on the presence of free Ag^+ ions, which readily dissociate from salts such as $AgNO_3$ [141,105]. There is no evidence for silver biomagnification[251,252].

<table>
<tr><td>Mode of action/toxicity</td><td colspan="3">There is no evidence that silver has any essential biological function in aquatic life[105]. Silver is toxic to aquatic bacteria, invertebrate and fish. Its toxicity ranks second only to mercury among the heavy metals[253]. Marine fish actively transport ions to combat water loss, which facilitates excretion of excess ions at the gills, reducing accumulation within the organism. In contrast, silver enters freshwater fish via the apical surface of gills, which leads to ionoregulatory imbalance and ultimately death[105, 254].
Bioavailability is dependent on speciation reactions that enhance silver solubility[255]. Toxicity is decreased in natural waters containing abundant negatively-charged organic matter and sulphides for silver complexation[105]. In seawater, silver predominantly forms chloride complexes, which has been shown to reduce toxicity[255]. Neither hardness nor alkalinity has an effect on accumulation and toxicity of silver[256].
In comparison to $AgNO_3$, inorganic silver complexes such as silver thiosuphate, silver chloride and silver sulphide were found to exert very low toxicity[257].</td></tr>
<tr><td>Natural occurrence in South African waters</td><td colspan="3">Silver is generally found in extremely low concentrations in the aquatic environment when compared to other metals[105]. This is chiefly due to its low crustal abundance and effective controls on its mobility in water[141]. Silver probably has a nutrient-type chemistry which is substantially depleted in the surface waters relative to deep water[119].
Concentration of silver in seawater has been given as 0.1 µg/L[119]. A range between 0.00000539 and 0.00378 µg/L, with an average concentration of 0.003 µg/L has been reported for the most probable species ($AgCl_2^-$) in seawater[119].
A range between 0.01 and 0.08 µg/L has been reported for dissolved silver in ocean water. Considerably higher concentrations (up to at least 0.5 µg/L) may occur in coastal waters[131].
Data on silver concentrations in South African coastal waters could not be obtained.</td></tr>
<tr><td rowspan="11">Guideline levels adopted in other jurisdictions (µg/L)</td><td></td><td>Natural Environment</td><td>Mariculture</td></tr>
<tr><td>CCME 2015[105]</td><td>7.5 (Acute)[A]</td><td></td></tr>
<tr><td>ANZECC 2000[3]</td><td>0.8-2.6[B,C]</td><td><3[B,E]</td></tr>
<tr><td>EPA 1995[159]</td><td>1.9 (Acute)[B]</td><td></td></tr>
<tr><td>EPA Oregon 2013[194]</td><td>1.9 (Acute)[B]</td><td></td></tr>
<tr><td>EPA California 2013[6]</td><td>0.7-7[A,D]</td><td></td></tr>
<tr><td>EPA Florida 2015[18]</td><td>2.3 (Acute)[A]</td><td></td></tr>
<tr><td>EPA South Carolina 2014[16]</td><td>2.3 (Acute)[A]</td><td></td></tr>
<tr><td>EPA North Carolina 2016[11]</td><td>1.9 (Acute); 0.1 (Chronic)[B]</td><td></td></tr>
<tr><td>BCLME 2006[4]</td><td>1.4 (Chronic)[A]</td><td>1.4 (Chronic)[A,E]</td></tr>
<tr><td>WIOR 2009[5]</td><td>1.4 (Chronic)[A]</td><td>1.4 (Chronic)[A,E]</td></tr>
</table>

A Expressed as total recoverable metal.
B Expressed as dissolved metal.
C Values for alternative levels of protection (% species). Alternative levels include 80% = 2.6 µg/L, 90% = 1.8 µg/L, 95% = 1.4 µg/L and 99% = 0.8 µg/L.
D Values for alternative measurements. Alternative measurements include 6-month median = 0,7 µg/L, Daily maximum = 2,8 µg/L, Instantaneous maximum = 7 µg/L.
E Protection of mariculture organism health.

4.4.9 Zinc

Constituent	Zinc (Zn)
IUPAC Names CAS RN Chemical grouping	Zinc 7440-66-6 Inorganic constituents
Category	Toxic substances: metals
Description	Zinc is a bluish-white, shiny and brittle metal, which occurs abundantly in nature and is comparatively non-toxic. In aqueous solution, zinc always has a valence of +II[258]. In the marine environment the equilibrium species of zinc are Zn^{2+}, $ZnOH^{+}$, $ZnCO_3$, $ZnCl^{+}$ [119]. Zinc can be harmful to aquaculture organism and human health. Zinc causes tainting.
Recommended Guidelines for total recoverable zinc (µg/L)	**Natural Environment and Mariculture** 20 (Chronic)
Notes for guidelines	Most detection methods measure *total recoverable* or *dissolved zinc* in a sample, where "dissolved" is defined operationally as zinc which passes through a 0.45 µm filter. In South Africa, however, water quality testing laboratories most commonly offer total recoverable metal. Care must be taken that analytical results of *total recoverable zinc* are compared to the guidelines.
Source	Zinc is a naturally occurring element and is found in the earth's crust in concentrations of approximately 123 ppm[143]. In nature, zinc occurs mainly as a sulphide mineral usually associated with lead, iron, and copper suphides[259]. Naturally, zinc enters the aquatic environment through weathering and erosion of rock and soils[260]. Zinc is mined, smelted and refined for use in various industries. Zinc is primarily used in the production of brass, noncorrosive alloys, and white pigments; in galvanisation of iron and steel products; in agriculture as a fungicide and as a protective agent against soil zinc deficiency; and therapeutically in human medicine[260]. Major sources of anthropogenic zinc in the environment include smelting and ore processors, mine drainage, domestic and industrial sewage, combustion of solid wastes and fossil fuels, road surface runoff, corrosion of zinc alloys and galvanised surfaces, and erosion of agricultural soils[260]. Nano zinc oxide (nZnO) particles (with diameter smaller than 100 nm) are used more and more frequently in the manufacture of sunscreens[261]. nZnO is also used in ceramics and rubber processing, wastewater treatment, and as a fungicide[262]. At least 25% of the amount of sunscreen applied onto the skin is washed off during bathing and swimming[263], implying that around 250 tonnes of these nanomaterials can be potentially discharged into the marine environment. South Africa is self-sufficient in zinc[259] and anthropogenic sources of zinc in the aquatic environment in South Africa are likely to originate to a large extent from smelting and ore processing and mine drainage.
Environmental fate and behaviour	In aqueous solution, zinc always has a valence of +II[258]. Compounds of zinc with the common ligands of surface waters are soluble in neutral and acidic solutions, which makes zinc one of the most mobile of the heavy metals[141]. In most unpolluted and/or freshwaters, the majority of zinc will exist as the hydrated divalent cation. In polluted and or sea waters, complexation is expected to predominate[141]. The dominant fate of zinc in aerobic waters is sorption by hydrous iron and manganese oxides, clay minerals, and organic material[239, 264] and results in enrichment of suspended and bed sediments relative to the water column[265,266]. The efficiency of these materials in removing zinc from solution depends on various factors. In waters where solids are primarily dissolved, most of the zinc is transported in solution in form of hydrated cations or complex species[267,268]. In contrast, most of the zinc will be adsorbed to suspended and colloidal organic and inorganic particles if suspended solids are predominant[239,266,269]. Adsorption increases with pH and concentration of ligands[270], as well as hydrous oxides of iron and manganese[264]. Zinc is desorbed from sediments as salinity increases[271]. In reducing environments, sulphide exerts an important control on the mobility of zinc through precipitation. In aerobic conditions, precipitation of the hydroxide, carbonate, or basic sulphate can occur when zinc is present in high concentrations[141]. As an essential nutrient, zinc is strongly bioaccumulated in all organisms with bioconcentration factors ranging from 100-100 000[141]. However, compared to the amount of zinc found in sediments, bioaccumulated zinc represents only a small proportion of the total reservoir[141].

Mode of action/ toxicity	Zinc is one of the most important metals in biological systems[258] and over 25 zinc-containing enzymes have been identified. However, at higher concentrations, zinc is toxic to marine algae (inhibition of cellular manganese uptake), invertebrate and fish[179,272,273]. Overall, invertebrate species are more sensitive to acute zinc toxicity than fish species (EPA Zinc). Zinc can inhibit algae growth, lead to abnormal shell development and reduced development in oyster larvae[274] and reduce liver functioning in fish[275]. Nano zinc oxide (nZnO), which is an active ingredient in sunscreen, has been shown to be less toxic to marine organisms than to freshwater organisms due to reduced solubility of nZnO in seawater[276]. Zinc toxicity is reduced with increasing salinity and water hardness[277,278].

Natural occurrence in South African waters	Zinc occurs abundantly in nature. The average concentration of zinc for unpolluted seawater has been given as 5 µg/L[157]. The concentration of dissolved zinc in the ocean ranges between 0.5 and 4 µg/L[131]. A range between 0.003 and 0.59 µg/L, with an average concentration of 0.39 µg/L has been reported for the most probable species (Zn^{2+}, $ZnOH^+$, $ZnCO_3$, $ZnCl^+$) in oxygenated seawater with a salinity of 35 ppt[119]. The average zinc concentration in South African offshore surface waters was reported as 6.59 µg/L in 1984[190]. Coastal zinc concentrations were generally similar with a median of 5.7 µg/L (ranging from 0.094 to 287 µg/L) [191]. Industrialised areas in South Africa showed very high zinc concentrations, including St Lucia, Richards Bay, Durban, Port Elizabeth (Swartkops River) and Saldanha Bay[191].		
Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	ANZECC 2000[3]	7-43[B,C]	<5[B,E] ; 5000[B,F]
	EPA 1986[15]		
	EPA 1995[159]		
	EPA 2002[159]		26000[A,G]
	EPA Oregon 2013[194]	90 (Acute); 81 (Chronic)[B]	
	EPA California 2013[6]	90 (Acute); 81 (Chronic)[B]	
	EPA Florida 2015[18]	20-200[A,D]	86 (Acute)[A,E]
	EPA South Carolina 2014[16]	86 (Acute)[A]	26000[A,I] ; 5000[A,H]
	EPA North Carolina 2016[11]	95 (Acute); 86 (Chronic)[A]	
	UK 2014[17]	90 (Acute); 81 (Chronic)[B]	
	BCLME 2006[4]	6.8 + ambient (Long-term)[B]	15 (Chronic)[A,E]; 5[A,H]
	WIOR 2009[5]	15 (Chronic)[A]	15 (Chronic)[A,E]; 5[A,H]

A Expressed as total recoverable metal.

B Expressed as dissolved metal.

C Values for alternative levels of protection (% species). Alternative levels include 80% = 43 µg/L, 90% = 23 µg/L, 95% = 15 µg/L and 99% = 7 µg/L.

D Values for alternative measurements. Alternative measurements include 6-month median = 20 µg/L, Daily maximum = 80 µg/L, Instantaneous maximum = 200 µg/L.

E Protection of mariculture organism health.

F Human consumption (not specified whether Protection of human health or organoleptic effect).

G Protection of human health, for consumption of organisms and water.

H Organoleptic effects (not toxic to humans).

I Protection of human health, for consumption of organisms only.

4.5 Toxic substances - Inorganic constituents

4.5.1 Ammonia

Refer to Section 4.3 for information for guideline values for ammonia toxicity to marine organisms.

4.5.2 Chlorine (as chlorine produced oxidants)

Constituent	Chlorine (Cl)
IUPAC Names	Chlorine
CAS RN	7782-50-5
	Chlorine produced oxidants: various, depending on the compound
Category	Toxic substances: inorganic constituents
Description	Chlorine is widely used as a disinfectant and therefore chlorinated discharges may affect non-target organsms[279]containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1. Chlorine is harmful to aquaculture organism and human health. Chlorine does not cause tainting.
Recommended Guidelines for chlorine-produced oxidants (CPO) (µg/L)	**Natural Environment and Mariculture**
	2 (Chronic)

Note on guideline

Note on terminology and analysis of chlorine in seawater:

The table below and accompanying text aims to clarify the complicated terminology used to describe chlorine chemistry and analysis in aqueous environments. When chlorine is added to water, the resulting reactive oxygen species that can harm aquatic organisms are termed *total residual oxidants* (TRO). In the literature, TRO is also referred to as *total residual chlorine (TRC)* (synonyms: total available chlorine, combined reactive chlorine, and reactive chlorine) in the context of freshwater chlorine analysis, and as *chlorine-produced oxidants (CPO)* in the context of seawater chlorine analysis. TRC and CPO consist of the following reactive species:

Freshwater	**Total residual chlorine (TRC)**[A]	
	Free residual chlorine (FRC)[B]:	Combined chlorine[C]:
	• Hypochlorous acid • Hypochlorite ion	• Choramines
Seawater Addition of bromide ions	**Chlorine produced oxidants (CPOs)**[D]	
	• Hypobromous acid • Hypobromite ion	• Bromamines

A Synonyms: Total available chlorine (TAC), combined reactive chlorine (CRA), reactive chlorine (RA)

B Synonyms: Free available chlorine (FAC)

C Synonyms: Combined available chlorine (CAC)

D CPOs do not contain chlorine. Terminology describing the two types of components of CPOs is not available (i.e. equivalent of FRC and combined chlorine).

The term "*total residual chlorine*" (TRC) is used to refer to the sum of free residual chlorine (FRC) (hypochlorous acid and hypochlorite ion) and combined chlorine (chloramines) in fresh water. Sea water and estuary water, however, contain natural levels of bromide ions (the average bromide ion concentration in seawater is 67 mg/ L[279]containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1). The addition of chlorine (or chlorinated wastewaters) to waters containing bromide results in the production of so called "*chlorine-produced oxidants*" (CPO), which include hypobromous acid, hypobromite ions, as well as bromamines in the presence of ammonia (refer to section on Environmental fate and behaviour for more detail on this issue). This means that a variety of oxidants (i.e. biocidal products) not containing chlorine are likely to be present in a sea- or estuarine water body into which chlorinated wastewater is discharged[280].

The Total Residual Chlorine Test (synonyms: Total Available Chlorine, Combined Reactive Chlorine, and Reactive Chlorine Test) is widely used to quantify chlorine-containing reactive oxygen species that could harm freshwater organisms (i.e. TRC). It is important to note that the analytical results of the Total Residual Chlorine Test indicate the total oxidising capacity of the sample (i.e. not only chlorine-containing reactive oxygen species)[280]. This means that the Total Residual Chlorine Test can be used to measure CPO (i.e. oxidants that can harm marine organisms as a result of seawater chlorination).

Although the term CPO is used in the context of seawater chlorine analysis only, the analytical results refer to the sum of all oxidative products (e.g. estuaries with low salinities may have both chlorine-and bromide-containing oxidants), as the Total Residual Chlorine Test used for measuring CPO is incapable of differentiating these oxidants[281].

The detection of the total oxidising capacity of chlorinated seawater should be determined through the Total Residual Chlorine Test. Results obtained from this test however, should be reported as µg/L of CPO.

Interference: CPO can be underestimated in water containing peroxide or with a high organic content. Organic particles remove the reagent iodide by reduction or sorption prior to determination of CPO[282]

Sources	Sources of chlorine in the marine environment include[279]containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1[,283]: • disinfection of municipal waste waters. Here, a complex water is chlorinated and then released into marine waters; • chlorination of seawater for cooling systems to protect installation against fouling organisms. Continuous chlorination at about 1 mg/L is a very cheap, convenient and efficient way to protect the installation against biofouling from bacteria and mussels (at nuclear power stations and paper mills). Seawater is pumped through the installation, chlorinated and released back into the sea • waste from manufacturing chlorinated lime, bleaching of fabrics, defining and dezincing iron, synthetic rubber and plastics, chlorinating hydrocarbons.
Environmental fate and behaviour	When inorganic chloramine-treated water is discharged to the estuarine or marine environment, a number of possible oxidants may be formed[284]. Collectively, these oxidants are called chlorine-produced oxidants (CPO)[281]. Seawater chlorination differs greatly from that of fresh water primarily due to the high bromide concentration of seawater (average bromide concentration in seawater is 67 mg/L). The chemistry associated with seawater chlorination is complex. Thus, for the purpose of these water quality guidelines, only a few of the reactions have been highlighted below. In the presence of bromide, free residual chlorine cannot exist in seawater as it instantaneously oxidises bromide into bromine. When chlorine additions remain below bromide concentrations (i.e. 67 mg/L), the oxidation of bromide is quantitative in less than ten seconds at a pH of 8 (the pH of seawater)[279]containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1. Due to the rapid hydrolysis of bromine, hypobromous acid (HOBr) and its ionic counterpart OBr^- are the active species. Under normal seawater conditions (pH between 7.8 and 8.2) the undissociated form (HOBr) predominates, with consequent higher reactivity and biocidal activity. In chlorinat- ed seawater, bromine and any other oxidants disappear very rapidly. Naturally occurring organic substances contribute to a large proportion of oxidant consumption[279]containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1. In coastal seawater, ammonia concentrations are usually lower (typically less than 28 µg/L) and therefore bromine remains as hypobromous acid. When ammonia increases, bromamines may be formed. At pH 8.1, ammonia and bromine react with chlorine at comparable rates. Monochloramine, the more persistent species among the various oxidised chlorine-pro- duced oxidants, may be found when ammonia concentrations increase, or in lower pH conditions[279]containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1. In most cases, bromamines are the only combined forms and tri-and dibromamines are the main species. These bromamines are high oxidising species and thus behave similarly to free bromine. Bromamines disappear rapidly; organic bromamines are rapidly formed. Hypobromous acid can also disproportionate into bromide and bromate. Bromate is formed during seawater chlorination and this reaction is accelerated by sunlight-containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1)[279]. Paradoxically, chlorine chemistry establishes that no chlorine is found in chlorinated water; neither in seawater where bromide oxidation is instantaneous, nor in waste water where monochloramine is the main reactive species[279]containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1). The largest part of the added chlorine is consumed by organic compounds through oxidation reactions. Therefore, the identification of organic chloro-derivatives is of great environmental significance because of the formation of many persistent and hazardous substances. Organic chloro-derivatives are addressed separately in these guidelines (Section 4.6)

Mode of action/ toxicity	Chemical oxygen species (i.e. CPO) are known to harm living organisms by damaging DNA, through oxidations of polyunsaturated fatty acids in lipids (lipid peroxidation), oxidations of amino acids in proteins and oxidative deactivation of specific enzymes by oxidation of co-factors. Dilution of effluent at the point of discharge as well as the consumption of CPO by the oxygen demand of the receiving waters, are factors that reduce biological effects. Acute toxicity of CPO reduced egg fertility success of sand dollar (*Dendraster excentricus*) and green sea urchin (*Strongylocentrotus droebachiensis*) during a five minute exposure at 2 and 5 µg/L respectively[285]. Mortality of various invertebrate and fish species have been reported to occur between 5 and 190 µg/L ranging in exposure time from 8 min to 96 h[286]. Chronic exposure to CPO has been shown to inhibit shell growth of littleneck clams (*Protothaca staminea*) during a period of 239 days at 25 µg/L[287]. Inhibition of photosynthesis and growth of algae has also been reported at concentrations from 10-30 µg/L[286]. Chronic exposure has also been shown to lead to a phytoplankton community shift after 30 days of exposure at 50 µg/L[288]. Fish, invertebrates and algae have been reported to experience at least 50% mortality when exposed to CPO concentrations of 30-140 µg/L for a period between 8 and 25 days[286]. Apart from CPO, chlorinated by-products also represent a hazard to marine life due to their toxic nature, and their higher persistence and bioaccumulation potential. Chlorinated by-products have also been shown to be carcinogenic[289].
Natural occurrence in South African waters	Chlorine does not occur naturally in seawater. However, compounds such as chloroform and bromoform, as well as other halogenated compounds are produced naturally in the marine environment, mainly by algae-containing high concentrations of organic carbon and ammonia, requires higher chlorine dosage (5-20 mg\u00b71-1) [279].

Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	CCME 1999[286]	0.5 (Acute)[A]	
	ANZECC 2000[3]		<3[C,E]
	EPA 1986[15]	13 (Acute); 7.5 (Chronic)[C]	
	EPA Oregon 2013[194]	13 (Acute); 7.5 (Chronic)[C]	
	EPA California 2013[6]	2-60[C,D]	
	EPA Florida 2015[18]	100 (Acute)[C]	100 (Acute)[C,E]
	EPA South Carolina 2014[16]	13 (Acute); 7.5 (Chronic)[C]	
	EPA North Carolina 2016[11]	7.5 (Chronic)[C]	
	UK 2014[17]	10 (Acute)[B]	
	BCLME 2006[4]	3 (Chronic)[C]	3 (Chronic)[C,E]
	WIOR 2009[5]	3 (Chronic)[C]	3 (Chronic)[C,E]

A Recorded as chlorine-produced oxidant (CPO) which are the reactive chlorine species formed under marine conditions.
B Recorded as total residual oxidant (TRO), free and combined bromine and chlorine.
C Recorded as total residual chlorine (TRC).
D Values for alternative measurements. Alternative measurements include 6-month average = 2 µg/L, Daily maximum = 8 µg/L, Instantaneous maximum = 60 µg/L.
E Protection of mariculture organism health.

4.5.3 Fluoride

Constituent	Fluoride (F^-)
IUPAC Name CAS RN	Fluoride 16984-48-8
Category	Toxic substances: inorganic
Description	Fluoride is an inorganic, monatomic anion of fluorine. Fluoride is the simplest anion of fluorine and its salts and minerals are important chemical reagents and industrial chemicals. Fluoride is harmful to aquaculture organism health. Fluoride is not considered toxic to human health and does not cause tainting.
Recommended Guidelines for Fluoride (µg/L)	**Natural Environment and Mariculture** Marine: 1500 (Acute) Estuarine: 1160 (Acute)
Notes on guidelines	No chronic values have been derived for fluoride, except as listed in BCLME 2006[4] and WIOR 2009[5]. These limits are likely to have been adopted from the 1995 South African Water Quality Guideline limit of 5000 µg/L, which were based on only one study[290]. Since then, acute limits lower than this have been published using more recent literature.
Source	Fluoride is present in the environment as the stable form of the very reactive element fluorine. Fluorine is very abundant in the earth's crust and is detectable in almost all minerals. Fluoride naturally enters the aquatic environment through weathering of alkali and silicic igneous and sedimentary rocks. Fluoride is also emitted into the atmosphere during volcanic eruptions. Atmospheric fluoride (particulate and soluble gaseous) enters the aquatic environment via precipitation[291]. Fluorite contains approximately 49% fluoride by mass[292]. Fluoride is mined, smelted and refined for use in various industries. Fluoride is primarily used in the manufacturing of aluminium and steel, production of phosphate fertiliser, metal producing and processing industries, steel and electrometallurgical fluxing, as well as ceramics and glass manufacture. Combustion of fluoride-containing coal releases fluoride into the atmosphere. Major sources of anthropogenic fluoride in the environment include smelting and ore processors, mine drainage, domestic and industrial sewage, and erosion of agricultural soils. Fluoride is released into the environment as hydrogen fluoride, silicon tetrafluoride or fluoride particulates[291]. Hydrogen fluoride is the most important manufactured fluoride as it is the intermediary from which all other fluorides are prepared[291].
Environmental fate and behaviour	Fluoride is present in the environment as the stable form of the very reactive element fluorine. In water, dissolved fluoride is present as the ion F^-, especially in dilute solutions and at neutral pH[293]. As pH increases undissociated hydrogen fluoride (HF) and bifluoride (HF_2^-) become predominant in solution. Dissolved fluorides readily precipitate as sediments in waters high in calcium. In marine waters, about 4 x 10^{11} g of fluoride per year are removed by incorporation into calcium carbonates. The residence time of fluoride in the ocean has been estimated to 2-3 million years[294]. Fluoride bioaccumulates in marine and intertidal organisms[295].
Mode of action/ toxicity	It is currently unknown whether fluoride is an essential nutrient for any biological systems[9]. Prolonged exposure to excess fluoride can lead to fluorosis (retention of excess fluoride), which can lead to deleterious integration into biochemical pathways, often as a substitute for calcium[296]. A number of cellular processes can be disrupted, including enzyme activity, inhibition of protein secretion and synthesis, generation of reactive oxygen species (ROS), and alteration of gene expression[296]. Fluoride has also been associated with oxidative stress. Oxidative stress can lead to the degradation of cellular membranes and reduce mitochondrial fitness[296]. An increase in background concentration from 0.9 mg/L to 1.9 mg/L near an effluent outfall resulted in encrusting marine rocky shore communities modification[297]. Overall, juvenile life stages are generally most susceptible to elevated fluoride concentrations[10]. An increase in temperature stimulates the fluoride uptake rate of organisms, increasing toxicity[9,298]. There is no relationship between fluoride toxicity and calculated dissolved calcium concentration[299]. It has been shown that toxicity of fluoride to the algae *Chlorella vilgaris* was higher at lower pH[300]. Toxicity of fluoride is lower in seawater. This phenomenon has been attributed to chloride ions, which may facilitate fluoride excretion from the organism. Local populations of marine species may have adapted to fluoride exposure. This highlights the importance of knowing local background concentrations of fluoride.

Natural occurrence in South African waters	The average concentration of the probable main species (F^- and MgF^+) in oxygenated seawater at a salinity of 35 ppt was given as 1.292 mg /L[119]. Fluorides in the South African east coast waters showed fluoride concentrations ranging from 1.2 – 1.7 mg/L in unpolluted seawater[301].		
Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	Canada, BC 1990[9]	1500 (Acute)	
	EPA Florida 2015[18]	5000 (Acute)	1500 (Acute)[A]
	BCLME 2006[4]	5000 (Chronic)	5000 (Chronic) [A]
	WIOR 2009[5]	5000 (Chronic)	5000 (Chronic) [A]
	Fleiss 2011 – Predicted No Effect Concentration PNEC for estuarine environments[10]	1160 (Acute)	

[A] Protection of mariculture organism health

4.5.4 Cyanide (as free cyanide)

Constituent	Cyanide (CN^-) as free cyanide (CN^- + HCN)
IUPAC Names CAS RN	Cyanide 57-12-5
Category	Toxic substances: inorganic
Description	Cyanide occurs in water as simple cyanides e.g. hydrogen cyanide (HCN), the cyanide ion (CN), Sodium cyanide (NaCN), Potassium cyanide (KCN)), metallocyanide complexes, cyanates and nitriles[141,302]. Free cyanide is the primary toxic agent in the aquatic environment. Free cyanide is defined as the sum of the cyanide present as hydrogen cyanide (HCN) and as the cyanide ion (CN-) (regard- less of origin)[303]. The relative concentration of these two cyanide forms depends primarily on pH and temperature[141]. In aqueous solution with pH <9.2 and temperature <20°C, the majority (>90%) of the free cyanide is in the form of molecular HCN[4]. HCN is considered the most toxic form[141]. Cyanide is harmful to aquaculture organism and human health. Cyanide does not cause tainting.
Recommended Guidelines for Cyanide as free cyanide (CN^- + HCN) (µg/L)	**Natural Environment and Mariculture** 1 (Chronic)
Notes on guidelines	Free cyanide refers to the sum of the cyanide ion (CN^-) and hydrogen cyanide (HCN) in a sample. At a pH of 7 or less free cyanide consists entirely of HCN[304]. For analytical purposes free cyanide is defined as the amount of HCN liberated from a solution at pH 6.0. Free cyanide is the primary toxic agent in the aquatic environment and is therefore considered to be the most appropriate measure of cyanide. Other cyanide types and associated tests are also available. Weak Acid Dissociable (WAD) Cyanide describes metal cyanide complexes that dissociate under weak acid conditions of pH 4.5-6. Cyanide Amenable to Chlorination (CATC) refers to cyanide complexes that dissociate and oxidise when exposed to chlorine under alkaline conditions and consist of free cyanide and weak acid dissociable cyanide complexes. Testing for CATC is intended to measure the effectiveness of cyanide destruction by chlorination.
Sources	Cyanide is ubiquitous in the environment, originating from both manmade and natural sources[303]. Cyanide is formed, excreted, and degraded naturally by animals, plants, insects, fungi, and bacteria[305] and can be found in many foods and plants. However, levels tend to be elevated in the vicinity of industries that produce and make use of large quantities of Cyanide[305]. Cyanide is widely used in electroplating, metallurgy, gold-mining facilities, oil refineries, power plants, solid waste combustion, production of organic chemicals, and plastics, photographic developing, fumigation, and mining[305,306,307]. These activities lead to the release of large quantities of cyanide into surface waters (freshwater and seawater). Although an illegal practice today, NaCN has also been used for the collection of tropical marine fish for the aquarium trade and the restaurant industry since 1962[308]. This fishing practice has had devastating impacts on coral reef ecosystems and fish populations[309].
Environmental fate and behaviour	HCN and CN^- readily dissociate and hydrolyse from inorganic cyanides such as NaCN and KCN. HCN and CN^- can also dissociate easily from some metallocyanide complex anions, including zinc and cadmium cyanide. In contrast, other metallocyanide complex anions are stable unless subjected to a change in pH or exposed to natural light (photodecomposition)[141,303]. The form of cyanide is dependent on pH, but is also influenced by temperature, dissolved oxygen, salinity, sunlight and complexing agents. Therefore a multitude of complex metallocyanides can exist in an aquatic environment, each with its own physical and chemical properties. Loss of free cyanide from the water column is primarily through sedimentation, microbial degradation, volatilization[303] and uptake by living organisms. There are no reports of cyanide biomagnification or cycling in living organisms, probably owing to its rapid detoxification of sublethal doses by most species, and death at higher doses[305]. Biodegradation of cyanide via microbial organisms has facilitated the development of biotechnologies for the treatment of wastewaters containing cyanide prior to discharge into surface waters[305].

Mode of action/toxicity	The toxicity of cyanide to aquatic organisms is predominantly due to the presence of HCN derived from dissociation, photodecomposition and hydrolysis[310,311]. The toxicity of cyanide increases if the pH levels decreases, forming extremely toxic HCN[141]. Cyanide is a potent toxic agent that is readily absorbed from all routes, including skin, mucous membranes, and inhalation[303]. Cyanide interferes with oxygen metabolism by locking ferric metal centres and thus stopping the electron flow in the respiratory chain in mitochondria, which can lead to the death of the affected organism[312]. At sublethal levels, cyanide can cause developmental abnormalities, lower reproductive potential and negatively affect endocrine function. Conversely, low levels of cyanide can also stimulate fish growth (hormesis)[305]. Adverse effects of cyanide on aquatic plants are unlikely at concentrations that cause acute effects to most marine fishes and invertebrates[305]. Numerous biological and abiotic factors are known to modify the biocidal properties of free cyanide, including water pH, temperature, and oxygen content; life stage, condition, and species assayed; previous exposure to cyanide compounds; presence of other chemicals; and initial dose tested[305].
Natural occurrence in South African waters	Information on natural concentrations of cyanide in marine water could not be obtained.

Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	ANZECC 2000[3]	2-14[A]	<5[C]
	EPA 1984[313]	1 (Acute); 1 (Chronic)	
	EPA 2015[45]		400[D]
	EPA California 2013[6]	1-10[B]	
	EPA Florida 2015[18]	1(Acute)	1 (Acute)[C]
	EPA South Carolina 2014[16]	1 (Acute); 1 (Chronic)	140[E]
	EPA North Carolina 2016[11]	1 (Chronic)	
	UK 2014[17]	5 (Acute); 1 (Chronic)	
	BCLME 2006[4]	4 (Chronic)	4 (Chronic)[C]
	WIOR 2009[5]	4 (Chronic)	4 (Chronic)[C]

A Values for alternative levels of protection (% species). Alternative levels include 80% = 14 µg/L, 90% = 7 µg/L, 95% = 4 µg/L and 99% = 2 µg/L.

B Values for alternative measurements. Alternative measurements include 6-month average = 1 µg/L, Daily maximum = 4 µg/L, Instantaneous maximum = 10 µg/L.

C Protection of mariculture organism health

D Protection of human health, consumption of water and organism

E Protection of human health, consumption of organisms only

4.5.5 Sulphide (as hydrogen sulphide)

Constituent	Sulphide (S^{2-})
IUPAC Names CAS RN	Sulphide(S^2) as Hydrogen sulphide (H_2 S) S^{2-}: 18496-25-8 H_2S: 7783-06-4
Category	Toxic substances: inorganic
Description	Hydrogen sulphide is a poisonous gas which readily dissolves in water. No heterotrophic life can exist in water containing hydrogen sulphide, and such affected areas are therefore transformed into oceanic 'deserts'[89]. The speciation of H_2S in seawater at 25°C, pH of 8.1 and salinity of 35 ppt is HS^- (96.93%), H_2 S (3.07%), and S^{2-} (0.00019%)[314]. Sulphide is harmful to aquaculture organism health. Sulphide is not considered toxic to human health and does not cause tainting.
Recommended Guidelines for Sulphide as hydrogen sulphide (µg/L)	**Natural Environment and Mariculture** 2 (Chronic)
Notes on guidelines	When soluble sulphides are added to water they react with hydrogen ions to form sulphanide HS^- or hydrogen sulphide H_2S, the proportion of each depending on the pH[15]. The speciation of H_2S in seawater at 25°C, pH of 8.1 and salinity of 35 ppt is sulphanide HS^- (96.93%), hydrogen sulphide H_2S (3.07%), and sulphide ion S^{2-} (0.00019%)[314]. The toxicity of sulphides derives primarily from hydrogen sulphide rather than from the sulphanide or sulphide ions[15]. Sulphide toxicity is therefore generally determined by testing for hydrogen sulphide only.
Source	Although hydrogen sulphide is usually not directly introduced to the marine environment through anthropogenic sources, those with high oxygen demand (reflected in high organic content, high biochemical oxygen demand or chemical oxygen demand) can favour conditions for the formation of hydrogen sulphide[15]. On the west coast of South Africa, strong upwelling conditions during the summer months bring nutrient rich waters to the surface, which stimulates phytoplankton growth. High biomass blooms consisting of mostly dinoflagellate decompose, leading to low oxygen conditions and the formation of hydrogen sulphide. Faunal mass mortalities, during which large numbers of west coast rock lobster *Jasus lalandii* 'walk out' of the sea in search of oxygen, occur sporadically but are not uncommon[315].
Environmental fate and behaviour	Dissolved oxygen in seawater is utilised by bacteria for oxidising organic matter to carbon dioxide, water and inorganic ions. In deep water of stagnant basins and in sea areas with a very slow water exchange or a high load of organic matter, all the dissolved oxygen may be utilised, leading to anoxic conditions[131]. Hydrogen sulphide behaves as a weak acid, and is present in natural waters as both the undissociated compound and the HS^- ion (below pH 12 the concentration of S^{2-} ion is negligible). Hydrogen sulphide is very volatile and reacts rapidly with oxygen[131]. Hydrogen sulphide is produced in anaerobic environments by the activities of sulphate-reducing bacteria (desulfovibria) which derive energy from a process of anaerobic respiration. $2CH_2\ O + SO_4{}^{2-} \rightarrow 2\ HCO_3{}^- + H_4S$ Probably only a small fraction of H_2 S is released into the atmosphere. In many environments, it reacts instead with iron to form insoluble iron sulphide, an abundant constituent of anaerobic organic rich sediments. Much of the sulphide that is not immobilised in this fashion is oxidised by bacteria that derives energy from the following reaction as soon as it reaches the aerobic level of the water profile[129]: $H_2\ S + 2\ O_2 \rightarrow SO_4{}^{2-} + 2H^+$ Therefore H_2S is slowly oxidised to sulphate in seawater. Evidence of this is that molecular sulphur does not accumulate in sediments in natural stagnant sea basins e.g. the Black Sea[129]. The solubility of hydrogen sulphide decreases with increasing temperature and salinity[316].
Mode of action/toxicity	Typical water quality problems that may be associated with acute exposure to hydrogen sulphide include failure of fish eggs to hatch and mortalities. Chronic exposure has been shown to lead to general growth deficiencies, growth reductions, reduced egg fish deposition[15].

Natural occurrence in South African waters	Hydrogen sulphide is a frequent component of anoxic waters, attaining concentrations as high as 70 mg/L under extreme conditions[129].		
Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	ANZECC 2000[3]		H_2S: <2[A]
	EPA 1986[15]	H_2 S: 2 (Chronic)	
	EPA California 2013[6]	The dissolved sulphide concentration of waters in and near sediments shall not be significantly increased above that present under natural conditions.	
	EPA South Carolina 2014[16]	H_2 S: 2 (Chronic)	
	EPA North Carolina 2016[11]	H_2 S: 2 (Chronic)	
	BCLME 2006[4]		S: 1 (Chronic)[A]
	WIOR 2009[5]		S: 1 (Chronic)[A]

A Protection of mariculture organism health

4.5.6 Nitrite and nitrate

Refer to Sections 4.3.2 and 4.3.3 for information and guideline values for nitrate and nitrite toxicity to marine organisms.

4.6 Toxic substances - Organic constituents

Persistent organic pollutants (POPs) (Section 4.6) are organic compounds (of either natural of anthropogenic origin) that are toxic and also persist in the environment by resisting photolytic, chemical and biological degradation. Many of these compounds are more soluble in lipids than in water and readily become stored in animals fat stores and bioaccumulate up the food chain. These chemicals are also easily transported around the globe in the atmosphere when volatised from soil or water surfaces. As such, these chemicals have a much broader impact than the area in which they are applied.

Concern over their accumulation and broad reaching effects on the environment has led to many of these compounds being restricted or banned under worldwide conventions. The Stockholm Convention on Persistent Organic Pollutants came into force in 2004. A number of pesticides were originally listed under this convention including: aldrin, dieldrin, DDT, endrin, heptachlor, chlordane, hexachlorobenzene, mirez and toxaphene. Since 2004, the list has been expanded to include further pesticides like endosulfan.

The Stockholm Convention, of which South Africa is a signatory prohibits or restricts the use of many of these POP pesticides. There are some, however, like DDT which can be used by government agencies to control human disease vectors such as malarial mosquitos. Despite not being actively used, many of these obsolete pesticides may still be stored, often inappropriately, and can still act as a source of pollution to the environment.

4.6.1 Aldrin and Dieldrin

Constituents	Aldrin (C_{12} H_6 Cl_6) and Dieldrin ($C1_2$ H8 Cl_6 O)	
	Aldrin	Dieldrin
IUPAC Names	1,2,3,4,10,20–Hexachloro-1,4,4a,5,8,8a–Hexahydro–1,4:5,8-dimethanonaphthalene	(1aR,2R,2aS,3S,6R,6aR,7S,7aS)-3,4,5,6,9,9-hexa-chloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-di-methanonaphtho[2,3-b]oxirene
CAS RN	309-00-2	60-57-1
Category	Toxic substances; Organic constituents; Organic pesticides; Organochlorine compounds	
Description	Aldrin and dieldrin are two structurally similar organochlorine pesticides. Here these two compounds are grouped together because aldrin quickly breaks down to dieldrin in the environment and within organisms. Aldrin is a white odourless solid when pure, whereas dieldrin is a white to light tan crystalline flakes. Historically, Aldrin was widely used to treat soils in order to kill soil pests like termites, cotton rootworm and grasshoppers. Dieldrin was mainly used as an insecticide on seeds, fruit as well as soils and occasionally for the control of malarial mosquitos. Both were originally created as alternatives to DDT. Organochlorine pesticide use peaked world-wide in the 1970s before the threats to Protection of human health and the environment were well understood. Aldrin and dieldrin were some of the original organic pollutants to be banned under the Stockholm Convention of Persistent Organic Pollutants. Their production is currently banned worldwide and use is restricted and is being phased out. Aldrin and Dieldrin are harmful to aquaculture organism and human health. Aldrin and Dieldrin do not cause tainting.	
Recommended Guidelines for Aldrin and Dieldrin (µg/L)	**Natural Environment**	**Mariculture**
	Aldrin: 0.003 (Chronic)	Aldrin: 0.00005[A]
	Dieldrin: 0.002 (Chronic)	Dieldrin: 0.000054
Notes for guidelines	A Protection of human health, for consumption of organisms only Detection limits are approximately 0.001 µg/L for aldrin and 0.002 µg/L for dieldrin [317]	
Sources	Aldrin and dieldrin are manmade compounds, which do not occur in the natural environment. These chemicals have historically been directly applied to soils as well as crops. In South Africa, Aldrin was withdrawn from use in 1992 and dieldrin were banned in 1983[318]. In 2004, aldrin and dieldrin were banned globally under the Stockholm Convention of Persistent Organic Pollutants. As such there should be no recent, local sources of aldrin or dieldrin in South Africa. Despite bans on these chemicals, volatilisation of these compounds from soils means that they can be transported far from usage sites. The long lasting nature and ability to bioaccumulation has seen residues of these compounds found in many ocean animals, especially those at higher trophic levels[319].	

Environmental fate and behaviour	Within the environment, aldrin readily oxidises to form dieldrin. Aldrin and Dieldrin both have relatively low solubility of 0.03 mg/L and 0.14 mg/L respectively[319]. They both also have relatively high adsorption coefficients, meaning that they are not easily leached from soils[319]. Both Aldrin and dieldrin can be volatized from the soil and water surfaces[141]. In aquatic systems, the volatilization half-life of aldrin is in the order of a few hours to few days[141]. The volatilisation of aldrin is higher than that of dieldrin. This volatilization can lead to these compounds being spread far from their site of use. Aldrin typically has an aerobic half-life 28 days whereas dieldrin is much more persistent with an aerobic half-life of approximately 1400 days[319]. Sorption in aquatic systems and bioaccumulation are also probably important processes in the environmental fate of aldrin, although, mostly dieldrin is bioaccumulated rather than aldrin itself[141]. Biotransformation and biodegradation for both pesticides is considered very slow[141].
Mode of action/toxicity	Similar to other polychlorinated ring insecticides like endosulfan and endrin, aldrin and dieldrin primarily affect the nervous system through impairing the function of GABA (gamma amino butyric acid) which is an inhibitory neurotransmitter in the central nervous system[320,321]"title" : "Canadian Water Quality Guidelines for the Protection of Aquatic Life: Endosulfan", "type" : "chapter" }, "uris" : ["http://www.mendeley.com/documents/?uuid=3aa-faa21-470a-4ed4-bad8-51cc8df19301"] }, { "id" : "ITEM-2", "itemData" : { "DOI" : "10.1289/ehp.9087255", "ISBN" : "0091-6765 (Print. This neurotoxicity can lead to convulsions, respiratory failure and death in some animals[322]. Aldrin and dieldrin are listed as category B2 carcinogens by the U.S. EPA meaning they have sufficient evidence of carcinogenicity from animal studies, but inadequate data from human studies[319]. Both compounds are listed a known endocrine disruptors to humans as well[319]. Estuarine and marine invertebrates exposed to aldrin have a variable response with reduced abundances recorded for polychaete worms at 1 µg/L, mortality of hermit crabs at between 33-300 µg/L , mortality of copepods at over 1 mg/L and enzyme disruption of shrimp at 6.3 µg/L[5,319]. American oysters' growth and shell deposition have been shown to be affected at aldrin concentrations between 15-25 µg/L for 96 hrs. Developmental changes have been recorded in echinoderms at 7000 µg/L for 2 hrs. Accumulation has also been recorded in algae at doses over 50 µg/L for 24 hrs as well as changes in physiology when exposed for longer periods of time[319] Similarly to aldrin, varying responses to dieldrin have been recorded in different taxa, however, effects are seen at lower values. Dieldrin accumulation is recorded in diatoms at 1.7 µg/L and mortality of amphipods at 60 µg/L. Respiratory effect as well as mortality are only recorded in alga at concen- trations over 1 mg/L. The average acute toxicity for different taxa range for aldrin as rated by the Pesticide Action Network ranged from slightly toxic to very highly toxic and for dieldrin from moderately toxic to very highly toxic[319].
Natural occurrence in South African waters	Aldrin and dieldrin are not naturally occurring chemicals and therefore have no natural levels of occurrence within South African waters. Considering aldrin readily converts to dieldrin in the environment, dieldrin is more commonly found in sampled areas.

Guideline levels adopted in other jurisdictions (µg/L)		**Natural Environment**	**Mariculture**
	EPA 1980[323]	Aldrin: 1.3 (Acute)	
	EPA 1995[159]	Dieldrin: 0.71 (Acute); 0.0019 (Chronic)	
	EPA 2015[45]		Aldrin: 0.00000077[B] Dieldrin: 0.0000012[B]
	EPA Florida 2015[18]	Aldrin: 1.3 (Acute); 0.00014 (Chronic) Dieldrin: 0.0019 (Acute); 0.00014 (Chronic)	Aldrin: 1.3 (Acute); 0.00014 (Chronic)[C] Dieldrin: 0.0019 (Acute); 0.00014 (Chronic)[C]
	EPA South Carolina 2014[16]	Aldrin: 1.3 (Acute) Dieldrin: 0.71 (Acute); 0.0019 (Chronic)	Aldrin: 0.00005[D] Dieldrin: 0.000054[D]
	EPA North Carolina 2016[11]	Aldrin: 0.003 (Chronic) Dieldrin: 0.002 (Chronic)	
	European Union 2013[14]	Total: 0.005(Chronic)[A]	
	BCLME 2006[4]	Dieldrin: 0.002 (Acute)	Dieldrin: 0.002 (Acute)[B]
	WIOR 2009[5]	Aldrin: 3.15 (Acute) Dieldrin: 0.002 (Acute)	Aldrin: 3.15 (Acute)[B] Dieldrin: 0.002 (Acute)[B]

A Sum of cyclodiene pesticides Aldrin, Dieldrin, Endrin and Isodrin.
B Protection of human health, for consumption of organisms and water
C Protection of mariculture organism health
D Protection of human health, for consumption of organisms only

4.6.2 Dichlorodiphenyltrichloroethane (DDT), Dichlorodephenlydichloroethylene (DDE) & Dichlorodiphenyldichloroethane (DDD)

Constituents	DDT ($C_{14}H_9Cl_5$), DDE ($C_{14}H_8Cl_4$) & DDD ($C_{14}H_{10}Cl_4$)		
	DDT	DDE	DDD
IUPAC Names	1,1'-(1,1,1-Trichloroethane-1,1-diyl) bis(4-chlorobensene)	1,1-bis-(4-chlorophenyl)-2,2,-di-chloroethene	1-chloto-4-[2,2,-dochloro-1-(4-chlorophenyl)ethyl]benzene
CAS RN	50-29-3	72-55-9	72-54-8
Category	Toxic substances; Organic constituents; Organic pesticides; Organochlorine compounds		
Description	Dichlorodiphenyltrichloroethane (DDT) is a broad spectrum organochlorine pesticide. DDT is a colourless, tasteless and almost odourless crystalline compound known primarily for its insecticidal properties. DDT was used widely before it was banned in many countries due to ecological considerations. Commercially available DDT is often a mixture of compounds that are very closely related. The p,p' isomer is the major component often making up two thirds of the mixture, with the o,p' isomer is the next most prevalent. The remainder of the mixture is made up of DDE and DDD which are the major metabolites that DDT breaks down into in the environment. DDE and DDD are rarely found as pure compounds but rather with DDT isomers. All these compounds are often collectively referred to as total DDT. DDT is considered a persistent organic pesticide which is not readily broken down and is known to bioaccumulate in the environment leading to health problems in top predators[324]. DDT has been cited as a threat to top marine predator populations[325,326]. DDT, DDE and DDD are harmful to aquaculture organism and human health. DDT, DDE and DDD do not cause tainting.		
Recommended Guidelines for DDT (µg/L)	**Natural Environment**	**Mariculture**	
	Total DDT (DDT, DDE & DDD): 0.025 (Chronic)	DDT: 0.00022[A] DDE 0.00022[A] DDD: 0.00031[A]	
Notes for guidelines	A Protection of human health, consumption of organisms only		
Sources	DDT was first synthesised in 1974. Technical grade DDT is a mixture of DDT isomers and also contains small amounts of DDE and DDD. DDE is not synthesised singularly for use, whereas DDD was also used as a pesticide for a limited time. Most DDE and DDD in the environmental are a result of the breakdown of DDT. During the second world war, DDT was used extensively to help control malaria and typhus. Often DDT was sprayed over large areas of land, but also applied directly to buildings, soil and people. Afterward WWII, DDT was used as an agricultural insecticide often sprayed on crops aerially. When DDT is sprayed, and residue that does not adhere to surfaces drift away and is often vaporised. This can lead to long distance movement of the chemical which can then be deposited in areas far from initial release[324,327]. Production and use of DDT peaked in late 1960s and early 1970s. In 1972, DDT was banned for agricultural use within the United States after its potential detrimental environmental effects became apparent. Many countries subsequently started to ban and phase out the use of DDT. Effective as of 2004, DDT was also banned as one of the original organic pollutants to be listed under the Stockholm Convention of Persistent Organic Pollutants. Their production is currently banned worldwide and use is restricted to disease vector control. Within South Africa, DDT was banned in 1983 except for the control of Malaria by the Government[318]. During current use, DDT is often applied directly to houses rather than sprayed aerially reducing the potential for environmental impact. The risk of contamination and waste accumulation is, however, still present. The main modes of contamination include drift/volatilization, leaching and run off[318].		

Environmental fate and behaviour	DDT has very low solubility at 0.006 mg/L in addition to a very high adsorption coefficients (151 000) which means that DDT is not easily leached from soils nor does it remain dissolved for long[319]. These properties are similar for both DDE and DDD [324]. Most DDT found in aquatic environments is either within organisms or attached to sediment particles[141]. DDT metabolises within organisms to DDE and DDD through either dehydrochlorination or dehalogenation respectively[318]. These metabolites eventually further break down into DDA (2,2-bis(4-chlorophenyl)acetic acid) through a series of reductive chlorinations and oxidative steps[318]. These breakdown processes are slow with DDE taking the longest to breakdown. Often the DDE or DDD metabolites are excreted before fully broken down or are stored with the bodies' fat reserves, sometimes for many years[324]. Because of their storage within an organisms lipid stores, DDT, DDE and DDD often accumulate in higher order predators. Within the environment, both photolysis and hydrolysis of DDT are considered slow process and have halflives of over 150 years and 80 years at pH 9[141]. The global concentrations of DDT in the atmosphere indicates, however, that volatilization of DDT is an important process. DDT may be volatized from water in less than a week, however, atmospheric transformations seem to be slow[141]. Overall in an aerobic conditions, DDT has a half-life of approximate 6200 days (~17 years)[319,324]. This half-life can be considerably shorter in tropical environments (e.g. less than a year) but can also extend to more than 30 years under certain circumstances[324,327]. These long half-lives can lead to DDT, DDD and DDE persisting in the environment for potentially hundreds of years after application[324]. In aquatic systems sorption and bioaccumulation are also probably important processes in the environmental fate of DDT, DDD and DDE, however, all these processes are considered to happen at very slow rates[141].
Mode of action/ toxicity	DDT insecticide primarily affects the peripheral nervous system of animals. The currently accepted hypothesis is that the DDT prevents the deactivation of sodium gates of the axon after activation[321] physiological effects, and selectivity. The structural requirements for toxicity are assessed, and structure-activity relationships are considered for each subclass. Lipophilicity is important for all the groups because it facilitates delivery of these neurotoxicants to the site of action in the nerve. Steric factors including molecular volume, shape, and isomeric configuration greatly influence toxicity. Electronic parameters also have been demonstrated to affect biological activity in some of the groups of insecticides, e.g., Hammett's sigma and Taft's sigma * as indicators of electronegativity. New synthetic pyrethroids continue to be developed, with varied structures and different physicochemical and biological properties. The leakage of charged sodium ions through the neuron membrane results in repetitive firing of the neuron[321]physiological effects, and selectivity. The structural requirements for toxicity are assessed, and structure-activity relationships are considered for each subclass. Lipophilicity is important for all the groups because it facilitates delivery of these neurotoxicants to the site of action in the nerve. Steric factors including molecular volume, shape, and isomeric configuration greatly influence toxicity. Electronic parameters also have been demonstrated to affect biological activity in some of the groups of insecticides, e.g., Hammett's sigma and Taft's sigma * as indicators of electroneg- ativity. New synthetic pyrethroids continue to be developed, with varied structures and different physico- chemical and biological properties. The average acute toxicity for different taxa range for DDT as rated by the Pesticide Action Network ranged from moderately toxic in molluscs, nematodes and zoo plankton to very highly toxic in crustaceans, fish and phytoplankton[319]. Average LC_{50} dosages for fish range from 0.53 µg/L to over almost 9 mg/L (median value of 13 µg/L)[319]. LC_{50} doses for crustaceans were between 0.5 µg/L and 600 µg/L[319]. At lower doses, DDT and it metabolites are known to cause changes in behaviour, growth, mortality, development, reproduction in animals[319]. Biomagnification of these compounds can lead to these problems being expressed more in animals higher in the food chain which are often exposed to higher doasges[324]. Of particular note, DDE has been indicated in the lowered the reproductive rate in many birds caused eggshell thinning and embryo deaths[328].

<table>
<tr><td>Natural occurrence in South African waters</td><td colspan="3">DDT in not a naturally occurring chemical and therefore has no natural levels of occurrence within South African waters. DDT is currently, however, still being used in South Africa to control malaria mosquitos in some areas and as such is expected to occur within the environment[318].

DDT is often found in marine top predators, however, levels tend to be highest in marine predators from the temperate fringe of the northern hemisphere[329]long term surveys. Therefore the results from several surveys must be combined and this causes arctifactual variation due to differences in the sampling and analytical techniques used and in the biological characteristics of the individuals sampled. Moreover, information is not homogeneously distributed in either space or in time. Most research is concentrated in western Europe, northern America and certain areas of Asia, while it is extremely limited or non-existent in Africa and most regions of the southern hemisphere. Marine mammals from the temperate fringe of the northern hemisphere, particularly fish-eating species which inhabit the mid-latitudes of Europe and North America, show the greatest organochlorine loads; noteworthy are the extremely high levels found in the Mediterranean Sea and certain locations on the western coasts of the United States. Concentrations in the tropical and equatorial fringe of the northern hemisphere and throughout the southern hemisphere appear to be low or extremely low. However, the lowest concentrations were found in the polar regions of both hemispheres. During recent decades, concentrations have tended to decrease in the regions where pollution was initially high but they have increased in regions located far from the pollution source as a consequence of at- mospheric transport and redistribution. It is expected that the Arctic and, to a lesser extent, the Antarctic, will become major sinks for organochlorines in the future. Effort should be devoted to both assessment of organochlorine trends in the now highly-polluted populations of the temperate fringe of the northern hemi- sphere and to the implementation of long-term monitoring of marine mammal populations inhabiting polar regions."</td></tr>
<tr><td>Measurement in seawater</td><td colspan="3">The most common method of measuring levels of DDT in water is by gas chromatography with electron capture detection. The limits of detection are 60 ng/l for p,p'DDT, 10 ng/l for p,p'DDE and 2.5 ng/l for p,p'DDD [327].</td></tr>
<tr><td rowspan="10">Guideline levels adopted in other jurisdictions (µg/L)</td><td></td><td>Natural Environment</td><td>Mariculture</td></tr>
<tr><td>EPA 1980[330]</td><td>DDT: 0.13 (Acute); 0.001 Chronic)</td><td></td></tr>
<tr><td>EPA 2015[45]</td><td>DDT:</td><td>DDT: 0.00003[A]
DDE: 0.000018[A]
DDD: 0.00012[A]</td></tr>
<tr><td>EPA Oregon 2013[194]</td><td>DDT: 0.13 (Acute); 0.001 Chronic)</td><td></td></tr>
<tr><td>EPA Florida 2015[18]</td><td>DDT: 0.001 (Acute);
0.00059(Chronic)</td><td>DDT: 0.001 (Acute)[B];
DDT: 0.00059(Chronic)[B]</td></tr>
<tr><td>EPA South Carolina 2014[16]</td><td>DDT: 0.13 (Acute); 0.001 (Chronic)</td><td>DDT: 0.00022[C]
DDE: 0.00022[C] DDD:0.00031[C]</td></tr>
<tr><td>EPA North Carolina 2016[11]</td><td>DDT: 0.001 (Chronic)</td><td></td></tr>
<tr><td>European Union 2013[14]</td><td></td><td></td></tr>
<tr><td>BCLME 2006[4]</td><td>DDT: 0.001</td><td>DDT: 0.001[B]</td></tr>
<tr><td>WIOR 2009[5]</td><td>DDT: 0.001</td><td>DDT: 0.001[B]</td></tr>
</table>

A Protection of human health, consumption of water and organisms
B Protection of mariculture organism health
C Protection of human health, consumption of organisms only

4.6.3 Endosulfan

Constituent	Endosulfan ($C_9H_6Cl_6\ O_3\ S$) Including Endosulfan alpha, Endosulfan beta and Endosulfan sulphate			
	Endosulfan	Endosulfan alpha	Endosulfan beta	Endosulfan sulphate
IUPAC Names	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro- 6,9-methano-2,4,3-benzodioxathiepine-3-oxide			
CAS RN	115-29-7	959-98-8	33213-65-9	1031-07-8
Category	Toxic substances; Organic constituents; Organic pesticides; Organochlorine compounds			
Description	Endosulfan is a broad spectrum organochlorine pesticide. There are two isomers of the endosulfan, α and β (also known as endo and exo, or I and II). Endosulfan sulphate is a product of oxidation of endosulfan. While all three forms exist and have separate CAS numbers, the name endosulfan refers to all three forms. Technical grade endosulfan is a mixture of the two biologically active isomers (α and β) in approximately 2:1 to 7:3 ratios[331]. Endosulfan has been used as a pesticide since the 1950s, however, it is now listed as a chemical banned under the Stockholm Convention of Persistent Organic Pollutants and its use is being phased out world-wide. Endosulfan is harmful to aquaculture organism and human health. Endosulfan does not cause tainting.			
Recommended Guidelines for endosulfan as total endosulfan (µg/L)	**Natural Environment and Mariculture** 00.0005 (Chronic)			
Notes for guidelines	Guideline values for endosulfan and its isomers were not derived separately for the countries considered in this review. Although it is possible to analytically separate these isomers, such methods are currently not readily available.			
Sources	Endosulfan is available as an emulsifiable concentrate, water dispersible powder, dispersion, dust or granules. It has been used both in residential and agricultural applications. The chemical is directly applied to vegetation, however, can end up in in watercourses and in the ocean through spillage, spray-drift, leaching and run-off, as well as bioaccumulation in animals. In South Africa, endosulfan has been used extensively in the past on vegetable, fruit and grain crops. Endosulfan was a registered pesticide within South Africa and had maximum residue levels set between 0.01-0.05 for most crops on which it was used[332]. In 1970, the use of endosulfan on fodder crops was suspended in South Africa[318]. In 2012, endosulfan was banned globally under the Stockholm Convention of Persistent Organic Pollutants. The Rotterdam Convention (formally, the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade) is a multilateral treaty to promote shared responsibilities in relation to importation of hazardous chemicals. South Africa, being a signatory, has called for sales and use of the chemical to be terminated from the 31st April 2012.			
Environmental fate and behaviour	Endosulfan is a hydrophobic, nonpolar molecule with low water solubility. The **β** isomer generally has a lower solubility than the **α** isomer or endosulfan sulphate (**α** isomer 0.164 ppm; **β** isomer 0.07 ppm; endosulfan sulphate 0.117 ppm[333]). The **α** isomer has the lowest melting point at 108-110°C (c.f. **β** isomer 207-208°C; endosulfan sulphate 198-201°C[333]). Both isomers have intermediate to high volatility under field conditions and have the potential to volatilise from water or moist soil surfaces[331]. The half-life of combined residues of endosulfan can range from 6 months to 9 years[334] and approximately 1 month in water at pH 7[335]. As is the case with many organochlorine pesticides, potential for bioaccumulation of endosulfan along the food chain is high given that it has a low octanol-water partitioning coefficient (K_{ow}) value of 3.55[331]. Like other organic pesticides, endosulfan has high lipid solubility and accumulates in fatty tissue of animals. Endosulfan is non-ionic and therefore will not dissociate within the band of pH values found in the environment[320]. In the environment, endosulfan most commonly breaks down into endosulfan sulphate. Others include endosulfan diol, endosulfan hydrycarboxylic acid and endosulfan lactone[320]. Both the isomers and the endosulfan are reported to depurate quickly within aquatic invertebrates and fish (depuration half-lives of 2.9-5.9 days[336].			

Mode of action/toxicity	Endosulfan primarily affects animals through impairing the function of GABA (gamma amino butyric acid) which is an inhibitory neurotransmitter in the central nervous system[320,321]. This neurotoxicity can lead to convulsions, respiratory failure and death in some animals[322]. At lower concentrations, endosulfan is known to be an endocrine disruptor and can exhibit oestrogenic properties, bind to progesterone receptors and inhibit testicular synthesis of androgens[333,337–340]. These effects can alter sex ratios, and affect the long-term viability of populations as well as induce chronic illness and death[322]. The short-term toxicity estimates for marine/estuarine fish ranges from 0.1 μg/L to 0.38 μg/L of the active ingredient. The lowest observed long-term effect concentrations for growth in estuarine/marine fish was 0.6 μg/L and 1.3 μg/L for survival[320]. Marine and estuarine invertebrates exposed to endosulfan have a variable response with responses from different species of oysters varying by an order of magnitude[320]. The LC_{50} values for selected crustaceans range from 0.03-176 μg/L in seagrass ecotones; 0.13-478 μg/L in mangrove systems and 10- >30 μg/L in coral reefs[5]. Sea grass also showed a reduction in photosynthetic processes on exposure to 50 μg/L[5].
Natural occurrence in South African waters	Endosulfan is not naturally occurring and therefore has no natural levels of occurrence within South African waters. Endosulfan has, however, been used agriculturally in South Africa and some studies present data for levels within marine and estuarine environments[320]. Average concentration of total endosulfan in an agriculturally impacted estuary near apple, pear and plum orchards) in the Western Cape was found to be 0.033 μg/L, with a 90th percentile value of 0.158 μg/L[341]. These values exceeded measurements from other estuaries worldwide[341]. No marine values have, however, been measured within South Africa.

Guideline levels adopted in other jurisdictions (μg/L)		**Natural Environment**	**Mariculture**
	ANZECC 2000[3]	Total: 0.0005-0.05[A]	Total: 0.001[C]
	CCME 2010[320]	Total: 0.009 (Acute); 0.002 (Chronic)	
	EPA 1980[330]	Total: 0.034 (Acute); 0.0087 (Chronic)	
	EPA 2015[45]	Alpha : 30[D] Beta : 40[D] Sulfate : 40[D]	
	EPA California 2013[6]	Total: 0.009-0.027[B]	
	EPA Florida 2015[18]	Total: 0.0087 (Acute)	Total: 0.0087 (Acute)[C]
	EPA South Carolina 2014[16]	Total: 0.034 (Acute); 0.0087 (Chronic)	Total: 89[E]
	EPA North Carolina 2016[11]	Total: 0.009 (Chronic)	
	European Union 2013[14]	Total: 0.0005 (Chronic); 0.004 (Acute)	
	WIOR 2009[5]	Total: 0.003 (Acute)	Total: 0.003 (Acute)[C]

A Values for alternative levels of protection (% species). Alternative levels include 80% = 0.05 μg/L, 90% = 0.02 μg/L, 95% = 0.01 μg/L and 99% = 0.0005 μg/L.

B Values for alternative measurements. Alternative measurements include 6-month average = 0.009 μg/L, Daily maximum = 0.018 μg/L, Instantaneous maximum = 0.027 μg/L.

C Protection of mariculture organism health.

D Protection of human health, consumption of water and organisms.

E Protection of human health, consumption of organisms only.

4.6.4 Polyaromatic hydrocarbons

<table>
<tr><td>Constituent</td><td colspan="2">Polyaromatic hydrocarbons (PAHs)</td></tr>
<tr><td>CAS RN
Chemical grouping</td><td colspan="2">Various (Table 10 and Table 11)
Organic compounds</td></tr>
<tr><td>Category</td><td colspan="2">Toxic substances; Organic constituents; Hydrocarbons; Polyaromatic hydrocarbons</td></tr>
<tr><td>Description</td><td colspan="2">Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that contain two or more benzene rings in their structure. PAHs are usually coloured crystalline solids with high melting and boiling points, low vapour pressures and low water solubilities. Commonly occurring PAHs include:
• acenaphthalene
• acenaphthene
• anthracene
• benzo(a)anthracene
• benzo(b)fluoranthene
• benzo(k)fluoranthene
• benzo(a)pyrene
• benzo(g,h,i)perylene
• chrysene
• dibenzo(a,h)anthracene
• fluoranthene
• fluorene
• indeno(1,2,3-cd)pyrene
• naphthalene
• phenanthrene
• pyrene
All PAHs are considered potentially harmful to aquaculture organism and human health. Only acenaphthene and naphthalene are tainting substances.</td></tr>
<tr><td rowspan="10">Recommended guidelines for PAHs (µg/L)</td><td></td><td>**Natural environment and Mariculture**</td></tr>
<tr><td>Acenaphtene</td><td>20 (Chronic)</td></tr>
<tr><td>Anthracene</td><td>0.1 (Chronic)</td></tr>
<tr><td>Benzo*(a)*pyrene</td><td>0.00017 (Chronic)</td></tr>
<tr><td>Benzo*(b)*fluor-anthene</td><td rowspan="4">Benzo(a)pyrene serves as a marker for these PAHs.</td></tr>
<tr><td>Benzo-(ghi)perylene</td></tr>
<tr><td>Benzo(k)fluor-anthene</td></tr>
<tr><td>Indeno1,2,3-(cd)Pyrene</td></tr>
<tr><td>Fluoranthene</td><td>0.0063 (Chronic)</td></tr>
<tr><td>Naphthalene</td><td>2 (Chronic)</td></tr>
<tr><td>Source</td><td colspan="2">PAHs are ubiquitous in terrestrial, atmospheric, and aquatic environment, originating from forest fires, volcanoes and possibly production by some plants. PAHs originate from incomplete combustion of organic material (natural/anthropogenic), diagenesis and biosynthesis. PAHs of natural origin are, however, produced at very low rates[342] when compared to those originating from anthropogenic sources. Their widespread occurrence results largely from formation and release during the incomplete combustion of coal, oil, petrol and wood, but they are also components of petroleum and its products[343]. PAHs reach the marine environment via sewage discharges, stormwater run-off, industrial discharges, oil spillages and deposition from the atmosphere[91].</td></tr>
</table>

Environmental fate and behaviour	PAHs easily adsorb to sediment substrates due to their hydrophobic nature and low water solubility[343]. The hydrogeologic conditions of the aquatic system together with the affinity of PAHs for sorption to sediment substrates play an important role in PAH transport and distribution[141]. Adsorption efficiency depends on the molecular weight and octanol-water partitioning coefficient (K_{ow}) (e.g. benzo(a)pyrene = 88%, fluorine = 13%, Pyrene = 20%)[344]. Adsorption efficiency decreases in the presence of dissolved organics such as humic acids[345]. PAHs with higher molecular weight readily undergo photodegradation[346], which can chemically transform PAHs, resulting in more carcinogenic and toxic compounds[347,348]. It is unclear though whether adsorption to particles reduces photodegradation[349]. PAHs with lower molecular weight are removed from aquatic systems via volatilisation[349]. For example, naphthalene has the highest vapour pressure of all PAHs and volatilisation from aquatic environments is likely to be the most important removal mechanism for this compound[141]. Acenaphthene, anthracene, fluorine, and phenanthrene have moderate volatility[350], while volatilisation is insignificant for PAHs with two or more aromatic rings[351]. Biodegradation by various microorganisms (bacteria, fungi and certain algae), which live in soils, in sediment substrate, or are suspended in the water column removes PAHs from bottom sediments and the water column[352]. Biodegradation of PAHs is depends on the number of aromatic rings and type of ring fusion[349]. Many two- and three-ringed PAHs including naphthalene, phenanthrene and anthracene are readily biodegraded. Higher molecular weight compounds, such as pyrene and benzo(a) pyrene, degrade more slowly though[349]. PAHs can be biotransformed to nontoxic and harmless end products. Animal mixed-function oxygenase (MFO) enzyme systems are responsible for biotransformation of PAHs. Intermediate products are known to be toxic, carcinogenic and and/or mutagenic (e.g. derivatives of trans-dihydrodiols, phenols and quinones)[353]. PAHs are also absorbed by aquatic organisms from the water column (pelagic organisms) and from bottom sediments (benthic organisms)[349]. PAHs are bioaccumulated as a result of uptake from water, sediment and food. Uptake by aquatic organisms depends on physical and chemical properties of the PAH (e.g. molecular weight, octanol-water partition coefficient etc.), environmental variables (e.g. suspended matter, dissolved organic matter, bioavailability, temperature, presence of other contaminants, biodegradation etc.), and biological factors (e.g. PAH metabolism and depuration rates, feeding characteristics of organisms, fat content of tissue, life stage etc.)[354]. Bioconcentration varies according to species, PAH compounds, within species and over time[343]. The potential for bioaccumulation and bioconcentration is influenced by the ability of organism to metabolise PAHs. For example, algae and molluscs metabolise PAHs slowly and exhibit highest bioconcentration rates. By contrast, fish and many crustaceans metabolise PAHs rapidly and generally display lower whole body residues[343].
Mode of action/ toxicity	PAHs are absorbed by aquatic organisms from the water column (pelagic organisms) and from bottom sediments (benthic organisms). However, dissolved PAHs are taken up more efficiently and pelagic organisms may be at higher risk in a high intensity exposure situation than benthic organisms[349]. Lower molecular weight PAHs can be acutely toxic to aquatic organisms. The major concern is that some PAHs form carcinogenically-active metabolites (e.g. benzo[a]pyrene). PAH concentrations in sediments have also been linked with liver neoplasms and other abnormalities in bottom-dwelling fish[355]. Elevated PAH concentrations may therefore pose a threat to aquatic organisms and potentially also to human consumers of fish and shellfish[356].
Natural occurrence in South African waters	PAHs are ubiquitous environmental contaminants. Although they can be formed naturally (e.g. forest fires), their predominant source is anthropogenic emissions, and the highest concentrations of PAH are generally found around urban centres. Concentrations of PAHs in the aquatic environment are generally highest in sediment, intermediate in biota and lowest in the water column[91]. Information on occurrence of PAHs in South African coastal waters is currently not available.
Guideline levels adopted in other jurisdictions	Mariculture guideline values/standards have been developed for sixteen PAHs (Table 10 and Table 11). Most of these guideline values protect Protection of human health and ensure palatability of the mariculture products (i.e. organoleptic effects or tainting). Standards developed for the protection aquaculture organisms are identical to those applicable to the natural environment (EPA Florida 2015[18], BCLME[4], WIOR[5]).

Table 7: Natural environment guidelines/criteria/standards for the most common polyaromatic hydrocarbons adopted in other jurisdictions shown in µg/L. The molar mass (g/mol) and Octanol-water partition coefficient (K_{OW} in logL/kg) are important characteristics of the chemical, which have been shown to influence toxicity.

				Natural Environment						
PAH Compound IUPAC name	**CAS Number**	**Molar mass (g/ mol)**	**K_{ow} (logL/kg)**	**CCME 1999[349]**	**ANZECC 2000[3]**	**EPA Florida 2015[18]**	**EPA NC 2016[11]**	**European Union**	**BCLME 2006[4]**	**WIOR 2009[5]**
Total PAHs*	N/A	N/A	N/A			0.031 (Chronic)				
Acenaphtene	83-32-9	154.21	3.9				20 (Chronic)			
Acenaphthalene	208-96-8	152.2	Not available			See total PAH				
Anthracene	120-12-7	178.23	4.3					0.1 (Acute) 0.1 (Chronic)	0.4 (Acute)	0.4 (Acute)
Benz(a)anthracene	56-55-3	228.29	5.61			See total PAH				
Benzo(a)pyrene	50-32-8	252.32	6.0			See total PAH		0.00017 (Chronic); 0.0027 (Acute)	0.4 (Chronic)	0.4 (Chronic)
Benzo(b) fluor-anthene	205-99-2	252.3093	6.6			See total PAH		0.017 (Acute); **		
Benzo(g,h,i)-perylene	191-24-2	276.3307	7			See total PAH		0.00082 (Acute) **		
Benzo(k) fluor-	207-08-9	252.32	6.8			See total PAH		0.017 (Acute) **		
Chrysene	218-01-9	228.29	5.73			See total PAH				
Dibenz(a,h) Anthracene	53-70-3	278.35	6.75			See total PAH				
Fluoranthene	206-44-0	202.26	5.5				0.22 (Chronic)	0.0063 (Chronic); 0.12 (Acute)	1.7 (Chronic)	1.7 (Chronic)
Indeno1,2,3-(cd)Pyrene	193-39-5	276.34	5.97			See total PAH		**		
Naphthalene	91-20-3	128.17	3.6	1.4 (Chronic)	50-120[A]		52 (Chronic)	2 (Chronic); 130 (Acute)	70 (Chronic)	70 (Chronic)
Phenanthrene	85-01-8	178.23	4.5			See total PAH			4 (Acute)	4 (Acute)

*Total of: Acenaphthylene; Benzo(a)anthracene; Benzo(a)pyrene; Benzo(b)fluoran-thene; Benzo-(ghi)perylene; Benzo(k)fluoranthene; Chrysene; Dibenzo- (a,h)anthracene; Indeno(1,2,3-cd)pyrene; and Phenanthrene.

** Benzo(a)pyrene can be considered as a marker for other benzo PAHs and chronic toxicity guidelines are not required for Benzo(b) fluor-anthene, Benzo(g,h,i)-perylene, Benzo(k)fluor-anthene, and Indeno1,2,3-(cd)Pyrene as a result (European Union 2013[14]).

A Values for alternative levels of protection (% species). Alternative levels include 80% = 120 µg/L, 90% =90 µg/L, 95% = 70 µg/L and 99% = 50 µg/L.

Table 8: Mariculture guidelines/criteria/standards for the most common polyaromatic hydrocarbons adopted in otherjurisdictions shown in µg/L. The molar mass (g/mol) and Octanol-water partition coefficient (K_{ow} in LogL/kg) are important characteristics of the chemical, which have been shown to influence toxicity.

PAH Compound IUPAC name	CAS Number	Molar mass (g/mol)	K_{ow} (logL/kg)	Mariculture					
				ANZECC 200[03]	EPA 2015[45]	EPA Florida 2015[18]	EPA – South Carolina 2014[16]	BCLME 2006[4]	WIOR 2009[5]
Total PAHs*	N/A	N/A	N/A	-	-	0.031 (Chronic)[A]	-	-	-
Acenaphtene	83-32-9	154.21	3.9	20 [B]	20[C] 90 [D]	<2700 (Acute) [B]	990 [E] 20 [C]	20 [C]	20 [C]
Acenaphtha-lene	208-96-8	152.2	Not availa-ble			See total PAH [A]			
Anthracene	120-12-7	178.23	4.54	-	400 [D]	<110 000 (Acute) [B]	40 000 [E]	0.4 [A]	0.4[V]
Benz(a)anthra-cene	56-55-3	228.29	5.61	-	0.0013 [D]	See total PAH [A]	0.018 [E]	-	-
Benzo(a) pyrene	50-32-8	252.32	6.0	-	0.00013 [D]	See total PAH [A]	0.018 [E]	0.4 (Chronic) [A]	0.4 (Chronic) [A]
Benzo(b) fluor-anthene	205-99-2	252.3093	6.6	-	0.0013 [D]	See total PAH [A]	0.018 [E]	-	-
Benzo-(ghi) perylene	192-24-2	276.3307	6.63	-	-	See total PAH [A]	-	-	-
Benzo(k) fluor-anthene	207-08-9	252.32	6.8	-	0.013 [D]	See total PAH [A]	0.018 [E]	-	-
Chrysene	218-01-9	228.29	5.73	-	0.13 [D]	See total PAH [A]	0.018[E]	-	-
Dibenz(a,h) Anthracene	53-70-3	278.35	6.75	-	0.00013 [D]	See total PAH [A]	0.018 [E]	-	-
Fluoranthene	206-44-0	202.26	5.5	-	20 [D]	<370 (Acute)[B]	140 [E]	1.7 (Chronic) [A]	1.7 (Chronic) [A]
Fluorene	86-73-7	166.22	4.4	-	70[D]	<14 000 (Acute)[B]	5300 [E]	-	-
Indeno1,2,3-(cd)Pyrene	193-39-5	276.34	5.97	-	-	See total PAH [A]	0.018 [E]	-	-
Naphthalene	91-20-3	128.17	3.6	1000[B]	-	-	-	1000C 70 (Chronic) [A]	1000C 70 (Chronic) [A]
Phenanthrene	85-01-8	178.23	4.5	-	-	See total PAH [A]	-	4 (Acute) [A]	4 (Acute) [A]
Pyrene	129-00-0	202.25	4.88	-	-	<11 000[B]	4000 [E]	-	-

*Total of: Acenaphthylene; Benzo(a)anthracene; Benzo(a)pyrene; Benzo(b)fluoran-thene; Benzo-(ghi)perylene; Benzo(k)fluoranthene; Chrysene; Dibenzo- (a,h)anthracene; Indeno(1,2,3-cd)pyrene; and Phenanthrene.

** Benzo(a)pyrene can be considered as a marker for other benzo PAHs and chronic toxicity guidelines are not required for Benzo(b) fluor-anthene, Benzo(g,h,i)-perylene and Benzo(k)fluor-anthene as a result (European Union 2013[14]).

A	Protection of mariculture organism health
B	Human consumption (not specified whether Protection of human health or organoleptic effect)
C	Organoleptic effects (not toxic to humans)
D	Protection of human health, for consumption of organisms and water
E	Protection of human health, for consumption of organisms only

4.6.5 Chlorophenols

Constituent	Chlorophenols
CAS RN	Various (Table 7 and Table 8)
Chemical grouping	Organic compounds
Category	Toxic substances; Organic constituents; Chlorinated organics; Chlorophenols
Description	A chlorophenol is any organochloride of phenol that contains one or more covalently bonded chlorine atoms. There are five basic types of chlorophenols (mono- to pentachlorophenol) and 19 different chlorophenols in total when positional isomerism is taken into account. Chlorophenols are produced by electrophilic halogenation of phenol with chlorine. Most chlorophenols are solid at room temperature. They have a strong, medicinal taste and smell. Chlorophenols are commonly used as pesticides, herbicides, and disinfectants. The list of 19 chlorophenols includes: • Monochlorophenol (3 positional isomers) o 2-Chlorophenol o 3-Chlorophenol o 4-Chlorophenol • Dichlorophenol (6 positional isomers) o 2,3-Dichlorophenol o 2,4-Dichlorophenol o 2,5 Dichlorophenol o 2,6 Dichlorophenol o 3,4 Dichlorophenol o 3,5 Dichlorophenol • Trichlorophenol (6 positional isomers) o 2,3,4-Trichlorophenol o 2,3,5-Trichlorophenol o 2,3,6-Trichlorophenol o 2,4,5-Trichlorophenol o 2,4,6-Trichlorophenol o 3,4,5-Trichlorophenol • Tetrachlorophenol (3 positional isomers) o 2,3,4,5-Tetrachlorophenol o 2,3,4,6-Tetrachlorophenol o 2,3,5,6-Tetrachlorophenol • Pentachlorophenol (1 positional isomer) All chlorophenols are considered potentially harmful to aquaculture organism and human health. Guidelines/standards based on toxicity endpoints have not been derived for all chlorophenols at the time of writing. Chlophenols are tainting substances.

Recommended guidelines for Chlorophenols		**Natural environment**	**Mariculture**
	2-Chlorophenol	-	0.1[A]
	3-Chlorophenol	-	0.1[A]
	4-Chlorophenol	-	0.1[A]
	2,3-Dichlorophenol	-	0.04[A]
	2,4-Dichlorophenol	0.42 (Chronic)	0.42 (Chronic)
	2,5-Dichlorophenol	-	0.5[A]
	2,6-Dichlorophenol	-	0.2[A]
	3,4-Dichlorophenol	-	0.3[A]
	2,3,5-Trichlorophenol	-	1[A]
	2,4,5-Trichlorophenol	-	1[A]
	2,4,6-Trichlorophenol	6.5 (Chronic)	1[A]
	2,3,4,6-Tetrachlorophenol	-	0.1[A]
	Pentachlorophenol	0.4 (Chronic)	0.4 (Chronic)
Notes for guidelines	A Organoleptic effects (not toxic to humans)		
Source	Chlorophenols are anthropogenically produced[357] and are ubiquitous contaminants in terrestrial, atmospheric, and aquatic environments[358]. Chlorophenols are used as intermediates in manufacturing agricultural chemicals, pharmaceuticals, biocides, and dyes[359]. Sources of chlorophenols also include industries that produce textiles, leather products, domestic preservatives, and petrochemical industries[360]. Chlorophenols also originate from the degradation of other pesticides containing chlorobenzenes[361] and chlorinated cyclohexanes[362]. The majority (85%) of known environmental releases of three chlorophenols (2-Chlorophenol, 2,4-Dichlorophenol, and 2,4,6-Trichlorophenol) were to surface water[363]. The principal point source of water pollution by chlorophenols is industrial waste discharge and the leaching of chlorophenols from landfills. Sewage treatment plants and drinking water treatment, which can result in the chlorination of phenol, also contribute to point source pollution[364]. The primary nonpoint source pollution of chlorophenols comes from the application of pesticides that are made from chlorophenols and the chlorination of waste water containing phenol. Chlorophenols enter the atmosphere through volatilization, with mono- and dichlorophenols being the most volatile (See Environmental fate and behaviour section for details). Chlorophenols reach the marine environment via industrial waste, runoff from agricultural fields treated with pesticide and insecticide, or by degradation of complex chlorinated hydrocarbons[359].		

Environmental fate and behaviour	Once released to the environment, chlorophenols are subject to a series of physical, chemical, and biological transformations. Sorption, volatilization, degradation, and leaching are the primary processes governing their fate and transport. The environmental fate and transport of chlorophenols are controlled by their physical and chemical properties and environmental conditions. All chlorophenols are solids at room temperature except for 2-Chlorophenol, which is a liquid. As the number of chlorine molecules increase, the vapour pressure and water solubility of chlorophenols decrease and the boiling point increases. Therefore, chlorination increases the tendency of the chlorophenols to partition into sediments and lipids and to bioconcentrate[365]. Higher vapour pressure of monochlorophenols (due to lower number of chlorine molecules) suggests that these compounds are most likely to be found in the atmosphere. Once vaporised, the compounds will not partition into the particulate phase[366]. The octanol water partition coefficients (pK_a and $\log K_{ow}$) are other important properties which detemine the transport and partitioning of chemicals. The lower chlorophenols (monochlorophenols) have higher pK_a coefficients (7.42-8.49 note values are temperature dependent), which means that in natural waters these compounds exist primarily as undissociated compounds (i.e. intact). Conversely, tetrachlorophenols have lower pKa values (5.48-6.96) and compounds are present predominantly in the dissociated form (i.e. ionised)[367]. The degree to which chlorophenol compounds ionise increases with increasing pH (Table 7 and Table 8) and have a tendency to partition into sediments. It should be noted however, that other factors than the $\log K_{ow}$ (e.g. the concentration of organic particles and the presence of hydrogen peroxide) also influence the adsorption rate of chemical compounds[367,368]. Bioconcentration values (and log octanol/water partitioning coefficients indicate that chlorophenols bioaccumulate in aquatic organisms[369]. Monochlorophenols are unlikely to biomagnify within aquatic food chains[370]. No information on biomagnification potential of higher chlorophenols could be obtained. Both direct photolysis and the reaction of chlorophenols with hydroxyl radicals and singlet oxygen produced by ultraviolet radiation may be important processes of chlorophenol degradation near the water surface and results in dechlorination[371]. Compared to microbial degradation, photolysis is the dominant transformation process for 2,4-Dichlorophenol and 2,4,5-Trichlorophenol, with the rate of photolysis decreasing with molecule size. Unlike the polychlorinated phenols, microbial degradation was the primary transformation process for 4-Chlorophenol[372]. Although as a group chlorophenols are poorly biodegradable and persistent in the environment, several studies have shown that aerobic and anaerobic degradation of chlorophenol congeners is possible[373–376]. The position of, rather than the number of chlorine atoms, is more important in determining the biodegradation of chlorophenols. Compounds containing chlorine in the meta positions show greater resistance to microbial attack[377].
Mode of action/toxicity	The noxious influence of chlorophenols and their derivatives on the biological organisms may lead to acute cytotoxicity, histopathological changes, mutagenicity, and cancer. Chlorophenol derivatives include catechol, chlorocatechols, guaiacol, chloroguaiacols, and syringol[378]. The International Agency for Research on Cancers categorised Pentachlorophenol, 2,3,4,6-Tetrachlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, and 2,4-dichlorophenol as chemicals for which sufficient evidence of car- cinogenicity in animals and inadequate evidence of carcinogenicity in humans have been established (Category 2B)[379,380]. Oral exposure to chlorophenol-contaminated food and water is the main route of exposure to the general human population. Water contaminated through chlorination is most likely to contain lower chlorinated phenols, while higher chlorinated phenols are more likely to be found in fish[363].
Natural occurrence in South African waters	Chlorophenols are man-made and are ubiquitous environmental contaminants. Pentachloro-phenol and 2,4,6-Trichlorophenol are used in several industrial processes and therefore often lead to wastewater contamination[358]. Information on occurrence of chlorophenols in South African coastal waters is limited to the Isipingo Estuary in KwaZulu Natal (published in 1996). It was found that the above-mentioned chlorophenol types ranged from 0.1-27µg/L[381].
Guideline levels adopted in other jurisdictions	Mariculture guideline values/standards have been developed for thirteen of the above-listed chlorophenols (Table 7 and Table 8). Most of these guideline values are for protection of human health and ensure palatability of the mariculture products (i.e. organoleptic effects or tainting). Standards for the Protection of mariculture organism health have only been developed for 2,4,6-Trichlorophenol and pentachlorophenol. These standards are in force in Florida and are identical to those for the natural environment (EPA Florida 2015[18]).

Table 9: Natural environment guidelines/criteria/standards for the most common chlorophenols adopted in other jurisdictions shown in µg/L. The CAS number, molar mass (g/mol) and Octanol-water partition (K_{ow} in LogL/kg) are important characteristics of the chemical, which have been shown to influence toxicity

PAH Compound IUPAC name	CAS Number	Molar mass (g/ mol)	K_{ow} (logL/ kg)*	Natural Environment					
				ANZECC 2000[03]	EPA 19952[14]	EPA Florida 2015[18]	EPA – South Carolina 2014[16]	European Union 2013[14]	UK 2014[17]
2,4-Dichlorophenol	120-83-2	162.997	2.88						6 (Acute) 0.24 (Chronic)
2,4,6-Trichlorophenol	88-06-2	197.439	3.48			6.5 (Chronic)			
Pentachlorophenol	87-86-5	266.323	4.69	11-55[A]	13 (Acute) 7.9 (Chronic)	7.9 (Acute)	13 (Acute) 7.9 (Chronic)	1 (Acute) 0.4 (Chronic)	

Table 10: Marine guidelines guidelines/criteria/standards for the most common chlorophenols adopted in other jurisdictions shown in µg/L. The CAS number, molar mass (g/mol) and Octanol-water partition (K_{ow} in LogL/kg) are important characteristics of the chemical, which have been shown to influence toxicity

PAH Compound IUPAC name	CAS Number	Molar mass (g/ mol)	K_{ow} (logL/ kg)*	Mariculture					
				ANZECC 20003	EPA 1986; 201545	EPA Florida 201518	EPA – South Carolina 201416	BCLME 20064	WIOR 20095
2-Chlorophenol	95-57-8	128.56	2.15	0.1-15[A]	0.1[A]; 800[B]	<400 (Acute)[E]	-	1[A]	1[A]
3-Chlorophenol	108-43-0	128.56	2.5	-	0.1[A]	-	0.1[A]	1[A]	1[A]
4-Chlorophenol	106-48-9	128.56	2.39	0.1[A]	0.1[A]	-	0.1[A]	10[A]	10[A]
2,3-Dichlorophenol	576-24-9	162.997	3.26	-	0.04[A]	-	0.04[A]	0.04[A]	0.04[A]
2,4-Dichlorophenol	120-83-2	162.997	2.88	0.1-14[A]	0.3[A]; 60[B]	<790 (Acute)[E]	0.3[A]; 290[D]	1[A]	1[A]
2,5-Dichlorophenol	583-78-8	162.997	3.06	20[A]	0.5[A]		0.5[A]	23[A]	23[A]
2,6-Dichlorophenol	87-65-0	162.997	2.88	30[A]	0.2[A]		0.2[A]	35[A]	35[A]
3,4-Dichlorophenol	95-77-2	162.997	Not available	0.3[A]	0.3[A]		0.3[A]	0.3[A]	0.3[A]
2,3,5-Trichlorophenol	933-78-8	197.439	Not available	1[A]	-		-	1[A]	1[A]
2,4,5-Trichlorophenol	95-95-4	197.439	3.72	-	1[A]; 600[B]		1[A]; 3600[D]	1[A]	1[A]
2,4,6-Trichlorophenol	88-06-2	197.439	3.48	2[A]	2[A]; 2.8[A]	6.5 (Chronic)[C]	1[A]; 2.4[D]	3[A]	3[A]

PAH Compound IUPAC name	**CAS Number**	**Molar mass (g/ mol)**	**K_{ow} (logL/ kg)***	**Mariculture**					
				ANZECC 2000[3]	**EPA 1986; 2015[45]**	**EPA Florida 2015[18]**	**EPA – South Carolina 2014[16]**	**BCLME 2006[4]**	**WIOR 2009[5]**
2,3,4,6-Tetrachloro-phenol	58-90-2	231.881	4.45	0.1 [A]	1 [A]		-	1 [A]	1 [A]
Pentachloro-phenol	87-86-5	266.323	4.69	30 [A]	30 [A];0.04 [B]	7.9 (Acute) [C]	30[A]; 3 [D]	30 [A]	30 [A]

*Note that the K_{ow} (logL/kg) vary depending on the literature consulted. These numbers serve to show that the K_{ow} increases with higher chlorophenols but should not be used as definite reference values.

A Organoleptic effects (not toxic to humans)
B Protection of human health, for consumption of organisms and water
C Protection of mariculture organism health
D Protection of human health, for consumption of organisms only
E Protection of human health, unknown whether water or organisms

4.6.6 Polychlorinated biphenyls (PCBs)

Constituent	Polychlorinated biphenyls (PCBs)
CAS RN	1336-36-3 (Category, individual CAS numbers have been assigned to 209 PCB congeners).
Chemical grouping	Organic compounds
Category	Toxic substances; Organic constituents; Chlorinated organics; Polychlorinated biphenyls
Description	Polychlorinated biphenyls (PCBs) are a group of synthetic organic chemicals consisting of carbon, hydrogen and chlorine atoms (chlorinated hydrocarbons). 209 PCB congeners have been identified, each representing a unique chemical compound in the PCB category[382]. The number of chlorine atoms and their location in a PCB molecule determine many of its physical and chemical properties[141]. Individual PCBs vary widely in their physical, chemical and biological properties depending on the degree of chlorination[141]. PCBs have no known taste or smell, and range in consistency from an oil to a waxy solid[382]. Due to their non-flammability, chemical stability, high boiling point and electrical insulating properties, PCBs were manufactured from 1929 until environmental toxicity and persistence of these compounds was recognised and manufacturing was banned in 1979 in the USA[383]. Many other countries, including South Africa, followed suit by becoming a signatory to the Stockholm Convention on Persistent Organic Pollutants (effective from May 2004). PCBs were mainly produced in the northern hemisphere and used in hundreds of industrial and commercial applications including[382]: • Electrical, heat transfer and hydraulic equipment • Plasticizers in paints, plastics and rubber products • Pigments, dyes and carbonless copy paper • Other industrial applications PCBs are harmful to aquaculture organism and human health. PCBs do not cause tainting.
Recommended guidelines for poly-chlorinated biphenyls (µg/L)	**Natural Environment and Mariculture** 0.000045 (Chronic)

Source	PCBs are anthropogenically produced[383] and are ubiquitous contaminants in terrestrial, atmospheric, and aquatic environments[384]. Although no longer commercially produced, PCBs may be present in products and materials produced before the Stockholm Convention on Persistent Organic Pollutants came into effect. Products that may contain PCBs include[383]: • Transformers and capacitors; • Electrical equipment including voltage regulators, switches, re-closers, bushings, and electromagnets; • Oil used in motors and hydraulic systems; • Old electrical devices or appliances containing PCB capacitors; • Fluorescent light ballasts; • Cable insulation; • Thermal insulation material including fiberglass, felt, foam, and cork; • Adhesives and tapes; • Oil-based paint; • Caulking; • Plastics; and • Carbonless copy paper; • Floor finish; Consequently, PCBs can still be released into the environment from: • Poorly maintained hazardous waste sites that contain PCBs; • Illegal or improper dumping of PCB wastes; • Leaks or releases from electrical transformers containing PCBs; • Disposal of PCB-containing consumer products into municipal or other landfills not designed to handle hazardous waste; and • Burning of PCB-containing wastes in municipal and industrial incinerators. PCBs do not readily break down and can remain for long periods cycling between air, water and soil[141]. PCBs can be carried long distances and have been found in snow and sea water in areas far from where they were released into the environment (including Antarctica[384]). Coastal sediments and open ocean water are major sinks of PCBs[384]. Ensuring safe disposal of PCB-containing products is of paramount importance in reducing the rate of PCB releases into the environment.
Environmental fate and behaviour	Photolysis may result in destruction of heavier PCBs. PCBs are however stable to oxidation and hydrolysis (basic and acidic) [383,385]. The combination of low water solubility and high octanol/water partition coefficient (2.8-7.4) means that PCBs have a tendency for adsorption to sediments. Adsorption is the major non-destructive process affecting PCBs after introduction to the aquatic environment and increases with the degree of chlorination and with the organic content of the absorbent[386] Volatilisation and transport as an aerosol, falling as dust or rain, is the probable cause of the ubiquitous distribution of PCBs. The more highly chlorinated compounds are less volatile than the lighter ones andthe presence of suspended solids tends to reduce volatilisation as PCB compounds are strongly adsorbed, thereby reducing their concentration in solution. [141] PCBs are strongly partitioned into biota with generally very high bioconcentration factors of up to 10^6. The potential for bioaccumulation of PCBs is greater for heavier congeners, which have a greater octanol/water partition coefficient and are more resistant to biodegradation[387]. PCBs are persistent in the environment and have been categorised as Persistent Organic Pollutants (POPs). Biotransformation/Biodegradation is the only proven mode of destruction of PCBs with fewer than 4-chlorines per molecule[141].

<table>
<tr><td>Mode of action/ toxicity</td><td colspan="3">PCBs constitute a group of persistent environmental chemicals. Due to their hydrophobic nature and resistance towards metabolism, these chemicals have been found in fatty tissues of animals and humans. PCBs can cause dermal toxicity, immunotoxicity, carcinogenicity, and adverse effects on reproduction, development, and endocrine functions[388]fish, and wildlife risk assessment. Based on existing literature data, TEFs were (re.
PCB is taken up by marine organisms through
• ingestion of PCB containing food
• ingestion of polluted water
• unintentional ingestion of plastic particles which either contain PCBs or to which PCBs have been adsorbed[389].
Marine organisms bioaccumulate PCBs and people who ingest mariculture products grown in polluted waters are likely to be exposed to these toxic substances.</td></tr>
<tr><td>Natural occurrence in South African waters</td><td colspan="3">PCBs are man-made, ubiquitous environmental contaminants. No information on occurrence of PCBs in South African coastal waters could be found.</td></tr>
<tr><td rowspan="8">Guideline levels adopted in other jurisdictions (µg/L)</td><td></td><td>Natural environment</td><td>Mariculture</td></tr>
<tr><td>EPA 2002[45]</td><td></td><td>0.000064[A]</td></tr>
<tr><td>EPA (Unknown Year)[214]</td><td>0.03</td><td></td></tr>
<tr><td>EPA Florida 2015[18]</td><td>0.03 (Acute);
0.000045 (Chronic)</td><td>0.03 (Acute);
0.000045 (Chronic)[B]</td></tr>
<tr><td>EPA South Carolina 2014[16]</td><td></td><td>0.000064[C]</td></tr>
<tr><td>EPA North Carolina 2016[11]</td><td>0.001</td><td></td></tr>
<tr><td>BCLME 2006[4]</td><td>0.3 (Acute)</td><td>0.3 (Acute)[B]</td></tr>
<tr><td>WIOR 2009[5]</td><td>0.3 (Acute)</td><td>0.3 (Acute)[B]</td></tr>
</table>

A Protection of human health, consumption of water and organism.
B Protection of mariculture organism health.
C Protection of human health, consumption of organisms only.

4.6.7 Tributyltin

Constituent	Tributyltin
IUPAC Names CAS RN	Tributyltin compounds 36643-28-4
Category	Toxic substances; Organic constituents; Organotin compounds
Description	Tributyltin (TBT) compounds belong to the chemical group organotins. Organotins include many compounds characterised by the presence of a carbon-tin bond (e.g. butyltins, phenyltins, cyclohexyltins, methyltins). The physical and chemical properties of organotins vary widely according to the numbers and types of organic and inorganic moieties bonded to the tin atom[390]. There is a lack of toxicity data on most organotin compounds and discussion in literature is usually restricted to the three groups, methyltins, butyltins and phenyltins. Only TBT compounds are discussed as no water quality guideline values for any organotin other than TBT compounds are available. TBT compounds are organic derivatives of tetravalent tin[391] and include tributyltin oxide, tributyltin benzoate; tributyltin chloride, tributyltin fluoride, tributyltin linoleate, tributyltin methacrylate, and tributyltin naphthenate. Tributyltin is harmful to aquaculture organism and human health. Tributyltin does not cause tainting.
Recommended Guidelines for tributyltin Measured as tributyltin cation (µg/L)	**Natural Environment and Mariculture**
	0.0002 (Chronic)
Note for guideline	The tributyltin cation is representative of the sum of all tributyltin compounds.
Source	Tributyltin compounds have been registered as[391]. • a molluscicide; • antifoulants on boats, ships, quays, buoys, crab pots, fish nets and cages; • a wood preservatives; • a slimicide on masonry; • a disinfectant; and • a biocides for cooling systems, power station cooling towers, pulp and paper mills, breweries, leather processing and textile mills. High levels of TBT in water, sediment, and biota have been found close to pleasure boating activities, especially in or near marinas, boat yards and dry docks. In the proximity of pleasure boating (especially marinas), TBT levels have been found to reach 1.58 ug/L in seawater, 26 300 µg/kg in coastal sediments, 6.39 mg/kg in bivalves, 1.92 mg/kg in gastropods, and 11 mg/kg in fish[391]. Algicidal concentrations of TBT range from less than 1.5 to 1 000 µg/L[391].

<table>
<tr>
<td>Environmental fate and behaviour</td>
<td>
The solubility of TBT in water is low, varying from less than 1.0 mg/L to greater than 100 mg/L abd varies according to the pH, temperature and anions present in the water (which determine speciation). In seawater and under normal conditions, TBT exists as three species (hydroxide, chloride, and carbonate), which remain in equilibrium. At pH values less than 7.0, the predominant forms are $BuSnOH_2^+$ and $Bu_3 SnCl$, while at a pH of 8, they are $Bu_3 SnCl$, $Bu_3 SnOH$ and $Bu_3 SnCO_3^-$, and at pH values above 10, Bu_3SnOH, and $Bu_3 SnCO_3^-$ predominate391.

As a result of its low water solubility and lipophylic character, TBT adsorbs readily onto particles. The degree of adsorption of TBT onto particles depends on the salinity, nature and size of particles in suspension, amount of suspended matter, temperature, and the presence of dissolved organic matter[391].

Progressive disappearance of adsorbed TBT is not due to desorption but to degradation. The degradation of TBT involves the splitting of the carbon-tin bond. This can result from various mechanisms occurring simultaneously in the environment including physico-chemical mechanisms (hydrolysis and photodegradation) and biological mechanisms (degradation by micro-organisms and metabolism by higher organisms)[391]. Inorganic tin is the end product of organotin degradation in the aquatic environment.

Inorganic tin is accepted to be relatively non-toxic, probably because the metal does not react and the oxides are insoluble at normal pH levels. However, inorganic tin has the potential to be methylated, producing mono-, di-, tri-, and tetramethyltin compounds that were not previously introduced to the area[392].

TBT bioaccumulates in organisms because of its solubility in fat. Bioconcentration factors up to 7 000 have been reported in laboratory investigations with molluscs and fish, and higher values have been reported in field studies[391]. It is known that TBT degradation rates in sediments are slower than in the water column, particularly in anaerobic conditions[391].
</td>
</tr>
<tr>
<td>Mode of action/ toxicity</td>
<td>
TBT may elicit vastly different responses in marine organisms because of large interspecific disparities in toxicokinetics[393]bioconcentration factor (BCF. Typical problems associated with tributyltin include:
• general growth deficiencies;
• lowered reproduction;
• shell deformation;
• mortalities; and
• abnormalities in movement.
</td>
</tr>
<tr>
<td>Natural occurrence in South African waters</td>
<td>TBT is not a natural component of seawater[390].</td>
</tr>
<tr>
<td>Guideline levels adopted in other jurisdictions (µg/L)</td>
<td>
<table>
<tr><th></th><th>Natural environment</th><th>Mariculture</th></tr>
<tr><td>CCME 1999[394]</td><td>0.001 (Chronic)</td><td></td></tr>
<tr><td>ANZECC 2000[3]</td><td>0.0004-0.05[A]</td><td><0.01[C]</td></tr>
<tr><td>EPA 2004[395]</td><td>0.42 (Acute); 0.0074 (Chronic)</td><td></td></tr>
<tr><td>EPA Oregon 2013[194]</td><td>0.37 (Acute); 0.01 (Chronic)</td><td></td></tr>
<tr><td>EPA South Carolina 2014[16]</td><td>0.37 (Acute); 0.01 (Chronic)</td><td></td></tr>
<tr><td>EPA North Carolina 2016[11]</td><td>0.007 (Chronic)[B]</td><td></td></tr>
<tr><td>European Union 2013[14]</td><td>0.0015 (Acute); 0.0002 (Chronic)</td><td></td></tr>
</table>
</td>
</tr>
</table>

A Values for alternative levels of protection (% species). Alternative levels include 80% = 0.05 µg/L, 90% = 0.02 µg/L, 95% = 0.006 µg/L and 99% = 0.0004 µg/L.

B Note that the standard for North Carolina is applied to the sum of trialkyltin and tributyltin.

C Protection of mariculture organism health.

4.7 Human pathogens – Microbiological indicators

4.7.1 Faecal indicators - Faecal coliform

Constituent	Faecal coliform	
IUPAC Names CAS RN	N/A N/A	
Category	Human pathogens, microbial indicator organisms, faecal indicator	
Description	Human pathogens are microbiological organisms which may cause disease or other health problems in man (mainly gastrointestinal problems). In terms of marine waters, this can either be through contact or ingestion of water containing these organisms (this aspect is covered in the recreational water quality guidelines), or through the consumption of seafood, which has been cultured in contaminated waters. Generally, human pathogens can be divided into three broad groups including bacteria, viruses and protozoan parasites[48]. There are many microbiological species that are considered human pathogens. Measuring the amount of each species present in water and comparing those to water quality guideline limits would be impossible to implement. Consequently, microbial indicator organisms (i.e. micro-organisms that may not pose a major human health risk, but that are indicative of the presence of human pathogens) are generally used to indicate the presence human pathogens (please refer to Section 0 for more detail on different indicator types). Faecal coliforms are one type of faecal indicator (others include E. Coli and enterococci) and refer to a group of bacteria commonly found in the faeces of man and warm-blooded animals. Depending on the amount present, faecal coliform can predict whether mariculture organisms grown in polluted waters are likely to be safe for human consumption. Some human diseases associated with polluted seawater are caused by viruses. By definition, faecal coliform analysis should also provide an indication of the exposure risk to enteric viruses and parasitic protozoa when sewage is the source of these pathogens. Certain shortcomings of using faecal coliforms to indicate virological quality have been shown however, which might be attributed to the following[53]: • viruses are only excreted by infected individuals and coliform bacteria by almost all humans and warm-blooded animals; • viruses are excreted for relatively short periods, while coliform bacteria are excreted fairly consistently; • the structure, composition, morphology and size of viruses differ fundamentally from those of bacteria, which implies that behaviour and survival in water differ extensively. Despite the shortcomings described with regards to the detection of viruses, faecal coliforms are, in the context mariculture organism consumption, currently considered the most appropriate faecal indicator type to detect faecal pollution from warm-blooded animals[22,15].	
Recommended guideline	**Natural Environment**	**Mariculture**
	N/A	**Faecal coliform -** Most Probable Number (MPN) or Membrane Filter (MF) counts (reported as colony-forming units (cfu)) shall not exceed a median value of 14 MPN/MF with not more than 10% of the samples exceeding 43 for MPN or 31 for MF, nor exceed 800 MPN/ MF on any one day.

Notes on guideline	The Most Probable Number (MPN) method is does not exactly measure the number of coliforms present in a sample, but it does give an estimate, based on the turbidity of a sample, and can determine whether or not water is below a specified safety threshold. The MPN is determined using the multiple tube fermentation method and a statistical estimation is derived from the analysis of multiple samples (i.e. usually the result is represented as the 95% confidence limit). This method is suitable when measuring water quality in turbid areas. The Membrane Filter (MF) Technique offers the advantage of isolating and counting discrete colonies of bacteria, whereas the MPN procedure only indicates the presence or absence of an approximate number or organisms. Results of the MF Technique are often expressed as colony-forming units (CFU) method represents the actual count of bacterial colonies produced in controlled lab conditions. The assumption is that each colony represents a founder. It is important to note that, unless these methods are used to isolate a species (e.g. *E. coli*), the results are not comparable and care should be taken that the correct method is applied when analysing water quality to ensure correct interpretation of results[84]. To determine the percentage of samples exceeding the criteria when there are both MPN and MF samples for a waterbody, the percent shall be calculated as 100*(nmpn+nmf)/N, where nmpn is the number of MPN samples greater than 43, nmf is the number of MF samples greater than 31, and N is the total number of MPN and MF samples.
Sources	Major sources of faecal contamination in marine waters include[49]: • sewage discharges; • bathers themselves, especially at densely populated beaches; • septic tank seepage; • stormwater run-off; • contaminated river run-off.
Environmental fate and behaviour	The survival of faecal coliforms in the marine environment is dependent on a variety of variables including temperature, exposure to ultraviolet light irradiation in sunlight, salinity, osmotic shock, microbiological antagonism, adsorption to solids and sediments and ingestion by molluscs. The rate of bacterial die-off in the marine environment is usually expressed in T90 values, which is the time required for the bacterial density to decrease by 90 %. The T values are usually larger during day time compared to night time, primarily 90 as a result of higher ultraviolet light irradiation during the day[396]. Faecal coliforms generally do not readily replicate in the water environment.
Mode of action/ toxicity	Faecal coliform serve as indicators for faecal pollution, which can be associated with the presence of harmful bacteria or viruses in affected waters. Consumers of seafood grown in polluted waters can experience gastrointestinal problems of varying degrees.
Natural occurrence in South African waters	Faecal coliforms do not occur naturally in South African coastal waters.

Mariculture guidelines adopted in other jurisdictions	ANZECC 2000[3]	The median **faecal coliform** bacterial concentration should not exceed 14 MPN/100 mL, with no more than 10% of the samples exceeding 43 MPN/100 mL.
	EPA 1986[15]	The median **faecal coliform** bacterial concentration should not exceed 14 MPN per 100 mL with not more than 10 percent of samples exceeding 43 MPN per 100 mL.
	EPA California 2013[6]	The median **total coliform** density shall not exceed 70 per 100 mL, and not more than 10 percent of the samples shall exceed 230 per 100 mL.
	EPA Florida 2015[18]	MPN or MF counts shall not exceed a median value of 14 with not more than 10% of the samples exceeding 43 (for MPN) or 31 (for MF), nor exceed 800 on any one day. To determine the percentage of samples exceeding the criteria when there are both MPN and MF samples for a waterbody, the percent shall be calculated as 100*(nmpn+nmf)/N, where nmpn is the number of MPN samples greater than 43, nmf is the number of MF samples greater than 31, and N is the total number of MPN and MF samples.
	EPA South Carolina 2014[16]	**Faecal coliform** - Monthly Geometric mean = 14MPN per 100 ml; Daily Max = 43 MPN per 100 ml.
	EPA North Carolina 2016[11]	**Faecal coliform** group not to exceed a median MF of 14/100 ml and not more than 10 percent of the samples shall exceed an MF count of 43/100 ml in those areas most probably exposed to faecal contamination during the most unfavourable hydrographic pollution conditions.
	BCLME 2006[4]	**Faecal coliform** - Median concentrations should not exceed 14 Most Probable Number (MPN) per 100 ml with not more than 10% of the samples exceeding 43 MPN per 100 ml for a 5-tube, 3- dilution method.
	WIOR 2009[5]	**Faecal coliform** - Median concentrations should not exceed 14 Most Probable Number (MPN) per 100 ml with not more than 10% of the samples exceeding 43 MPN per 100 ml for a 5-tube, 3- dilution method.

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