

Nitrogen Water Quality Guidelines (Reformatted Guideline from 1988)

Technical Appendix

Ministry of Environment and Climate Change Strategy
Water Protection & Sustainability Branch



The Water Quality Guideline Series is a collection of British Columbia (B.C.) Ministry of Environment and Climate Change Strategy water quality guidelines. Water quality guidelines are developed to protect a variety of water values and uses: aquatic life, drinking water sources, recreation, livestock watering, irrigation, and wildlife. The Water Quality Guideline Series focuses on publishing water quality guideline technical reports and guideline summaries using the best available science to aid in the management of B.C.'s water resources. For additional information on B.C.'s approved water quality parameter specific guidelines, visit:

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Sections of this report on industrial water use, drinking water and recreation have been removed. B.C. adopts Health Canada drinking water and recreation guidelines and no longer develops or supports guidelines for industrial water use.

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1. INTRODUCTION

Nitrogen compounds are a necessary and integral part of the aquatic ecosystem since they serve as essential nutrients for photosynthetic and bacterial production. However, as with many other necessary chemical compounds, they can be harmful to man, other animals, or aquatic biota if present in sufficiently high concentrations. This report evaluates the effects of nitrogen in the aquatic environment as a toxicant, and defines the concentrations which will protect the beneficial uses of water.

Nitrogen can, under some circumstances, stimulate excessive algal growth in streams and lakes, causing environmental degradation and damaging beneficial uses of water, but this aspect (eutrophication) is not considered in this document. For details of this aspect see Water Quality Criteria for Nutrients and Algae (Nordin 1985). The emphasis here is on the aquatic toxicity of three particular nitrogen compounds.

This review deals with three major forms of nitrogen: nitrate, nitrite, and ammonia. Since the threshold effects of each are notably different, they are each dealt with in sequence within each applicable section. Ammonia is the variable to which most environmental concern has been directed. Criteria based on literature reviews of ammonia toxicity to freshwater biota have been prepared by a number of agencies: U.S. Federal Water Pollution Control Administration (1968); European Inland Fisheries Advisory Commission (1970); National Academy of Sciences and National Academy of Engineering (1973); Willingham (1976); U.S. Environmental Protection Agency (1977, 1980); National Research Council (1979); Willingham et al. (1979); Alabaster and Lloyd (1982); and Haywood (1983). The most recent and comprehensive criteria report considering aquatic life was done by the U.S. Environmental Protection Agency (1985b). All of the above references contribute to the understanding of ammonia toxicity, but many of the conclusions given here reflect the interpretation and advances of the 1985 EPA document.

In contrast to ammonia, relatively few reviews of nitrite or nitrate toxicity have been undertaken. The recent review by Lewis and Morris (1986) summarizes the toxicity to fish of nitrite. Few reports of research on nitrate toxicity exist. As a consequence, more reference to the original literature was necessary and more basic interpretation was required for nitrite and nitrate.

The Canadian Council of Resource and Environment Ministers (CCREM 1986) issued criteria for a wide range of water chemistry characteristics. The criteria proposed here are consistent with the CCREM Guidelines except as noted.

There have been some criteria proposed by other agencies for nitrogen compounds other than nitrate, nitrite or ammonia. At least three agencies designate concentrations for total or Kjeldahl nitrogen. The governments of Saskatchewan and Alberta (Saskatchewan 1975; Alberta 1977) give 1 mg/L total nitrogen as the criterion for all water uses (drinking water, aquatic life, wildlife, agriculture, recreation and aesthetics, and industrial use). The Anglian Water Authority (1982) sets values of Kjeldahl and total nitrogen for drinking water (2 or 3 mg/L Kjeldahl, 19.0 - 22.6 mg/L total N), aquatic life (75-90 mg/L total), and agriculture (85-100 mg/L for livestock watering). No rationale for the values for nitrogen is given in any of these documents, although some explanations for the criteria for ammonia, nitrate, and nitrite are included. Concentrations of total nitrogen which are high (>0.5 mg/L) may be coincident with symptoms of eutrophication, but the nitrogen fractions which should be of concern (since they are more likely to be directly related to uptake by algae) are the inorganic dissolved forms (ammonia and nitrate). Since eutrophication is outside the scope of this report, and no convincing evidence of the toxicity of total nitrogen exists, it would seem appropriate not to take into account any attempt at setting a criterion for total nitrogen. Likewise, no known criteria exist for organic nitrogen, and no discussion of the toxicity of organic nitrogen is included here.

Nitrosamines have also been the object of some study and concern; however, very little if any information exists on toxicity of nitrosamines to aquatic life. The major risk appears to be as a carcinogen rather than a toxicant. Greico et al. (1978) reported liver cancers associated with dietary doses of a nitrosamine compound. The U.S.E.P.A. (1980b) reviewed the data on nitrosamines but felt that insufficient data existed to recommend criteria.

Nitrogen compounds can affect aquatic organisms not only through their direct toxicity, but by reduction of dissolved oxygen concentrations caused by the nitrification process. This problem is also not dealt with here, but will be considered in a criterion document on dissolved oxygen. Similarly, supersaturation of nitrogen gas (N_2) in water can cause gas bubble disease in aquatic organisms, but this phenomenon will be considered in a criterion document on total dissolved gases.

All concentrations are cited as nitrogen (N). Un-ionized ammonia is clearly specified when that form is referred to, and values are given as N rather than NH_3 as is done in some cases.

2. FORMS AND TRANSFORMATIONS IN THE ENVIRONMENT: THE NITROGEN CYCLE

Nitrogen moves between a number of major forms both organic and inorganic as a consequence of environmental conditions and microbial action. The emphasis here is on inorganic nitrogen. The form in which most nitrogen exists is nitrogen gas (N_2), however important forms in the aquatic environment which are considered below are nitrate, nitrite, and ammonia, as well as nitrogen oxide gases (NO and N_2O). A schematic of the nitrogen cycle is given as Figure 1.

2.1 Processes

(a) Nitrogen fixation

Molecular nitrogen (N_2) is utilized by microorganisms and incorporated as part of their tissues, typically as NH_2 groups in organic nitrogen compounds. Most nitrogen fixation takes place in the soil by bacteria. However, in lakes and rivers and tropical seas, cyanobacteria (blue-green algae) can also fix significant amounts of nitrogen.

(b) Ammonification

During metabolism, organic nitrogen is excreted from organisms. On death of an organism, cellular breakdown begins and organic nitrogen compounds are liberated and broken down by heterotrophic bacteria in the process of ammonification or by proteolytic deamination to form ammonia (NH_4^+ and NH_3).

(c) Nitrification

Under aerobic conditions, NH_4^+ , NH_3 , NO, and NO_2 and N_2O are oxidized to nitrite (NO_2^-), a relatively short-lived intermediate, and then to nitrate (NO_3^-). Two separate groups of bacteria are involved in the conversion: from ammonia to nitrite; and nitrite to nitrate.

(d) Denitrification

Many bacteria utilize nitrite or nitrate as sources of nitrogen or hydrogen acceptors in place of oxygen. This process usually takes place under anaerobic conditions, and nitrate and nitrite are usually reduced to molecular nitrogen (N_2). Numerous species of bacteria and fungi can perform these transformations, but anaerobic or near anaerobic conditions are generally required.

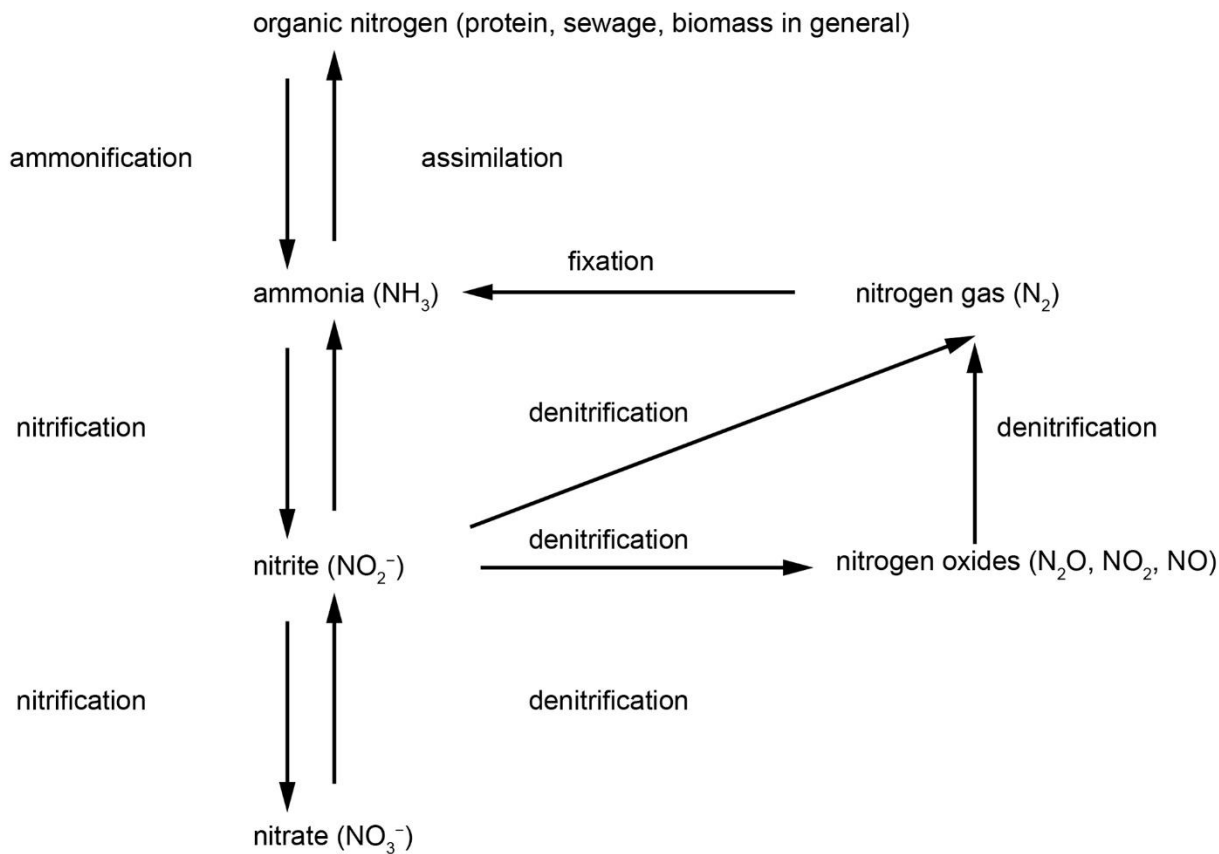


Figure 1. The nitrogen cycle

2.2 Nitrogen Fractions

2.2.1 Ammonium (NH₄⁺) and Ammonia (NH₃)

Ammonia is the most reduced inorganic nitrogen form found in water and includes molecular ammonia (un-ionized ammonia) and the ammonium ion. Ammonium and un-ionized ammonia exist in equilibrium in the environment with their relative proportions determined by environmental conditions. Increasing pH (alkaline conditions) and temperature shift the equilibrium to ammonia formation, while decreasing pH (acidic conditions) and temperature produce ammonium (Trussell 1972). The ionic strength of water can also affect ammonia ionization. At salinities of seawater, there is approximately 20% less un-ionized ammonia than in freshwater at the same temperature and pH (Bower and Bidwell 1978). Messer et al. (1984) note that a correction for ammonia ionization in hard water (up to 1600 mg/L) is required which can result in less un-ionized ammonia (10-20%) than previously calculated. The ammonium ion is a cation and is adsorbed to the cation-exchange complex of a soil, and thus is relatively immobile in soils (immobile relative to nitrate but not to other cations). Alkaline conditions promote the formation of ammonia, which is volatile, and can move from the soil to water and/or the atmosphere (Kolenbrander 1977). Both ammonium and ammonia are stable under anaerobic conditions, but under aerobic conditions they are oxidized to nitrate by bacteria (nitrification) at a rate that is directly proportional to temperature. For example, the application of ammonium fertilizers to soils will result in the oxidation of ammonium to nitrate in a few weeks or even days. Both terrestrial and aquatic plants can use ammonium as a nutrient for plant growth (Kolenbrander 1977; Forsberg 1977). Ammonia, ammonium, and its salts are very soluble in water. Ammonia plus ammonium are normally referred to as total ammonia.

2.2.2 Nitrate (NO_3^-)

The nitrate ion is an anion, and there is practically no adsorption of nitrate by soils, thus it is highly mobile in the groundwater system. Nitrate is stable under aerobic conditions, although it is utilized as a nutrient by both terrestrial and aquatic plants. Under anaerobic conditions, nitrate is reduced to nitrogen gas (mainly) or ammonia by bacteria (denitrification) via the intermediates NO_2^- , NO and N_2O (Lind 1977; Brezonik 1977). The rate of denitrification is directly proportional to temperature, and the bacteria require a soluble organic carbon energy source to perform denitrification (Kolenbrander 1977; Culp et al. 1978).

Denitrification can be a significant process in the soil-groundwater system under saturated (anaerobic) conditions if there is an adequate soluble carbon energy source. There is generally sufficient carbon in the rooting zone (down to 1 m) for denitrification, but subsoils may not have enough carbon for denitrification. Kolenbrander (1977) indicated that subsoils have a denitrification capacity of only 1-5 mg/L $\text{NO}_3\text{-N}$ (based on available carbon), and concluded that dilution is the most important process in reducing nitrate levels in subsoils.

2.2.3 Nitrite (NO_2^-)

Nitrite is generally found in only very small quantities (less than 0.005 mg/L) in well aerated surface waters. It may comprise a significant fraction of dissolved nitrogen in situations where anaerobiosis persists (stagnant groundwater, anoxic lake hypolimnia), or where the second step of denitrification is inhibited. Concentrations in surface water of greater than 0.010 mg/L can be regarded as a sign of anthropogenic contamination.

2.2.4 Nitrogenous Gases (N_2 , NO, NO_2 , N_2O and NH_3)

Nitrogen is a stable gas that comprises 78 percent of the atmosphere by volume and is slightly soluble (23 mg/L N at 0°C, 12 mg/L at 35°C at standard pressure) in water (Sawyer and McCarty 1967). Certain nitrogen-fixing terrestrial and aquatic microorganisms (e.g., blue-green algae) can utilize nitrogen gas dissolved in water as a nitrogen source.

The nitrogen oxides (NO, NO_2 , and N_2O) are oxidized to nitrate under aerobic conditions (Sienko and Plane 1966), and reduced to nitrogen gas under anaerobic conditions (Brezonik 1977). Nitrogen oxides are formed by lightning, by biological processes, or are the product of burning of fossil fuels.

Ammonia gas is also present in the atmosphere, but its concentration is generally very low.

2.2.5 Other Nitrogen Compounds

There are a variety of nitrogen compounds which are considered to be in the transition between organic and inorganic. The most important single compound is urea. Urea is the chief dissolved or soluble component of mammalian urine and is an end product of protein decomposition. Humans excrete approximately 30 grams per day and make a substantial contribution to the environment. Bacteria break the urea down to carbon dioxide and ammonia. Urea is apparently not very toxic to fish. McKee and Wolf (1963) report a 24 h LC50 of between 16 000 (no deaths) and 30 000 mg/L (all died) for creek chub which they describe as a fish of average tolerance.

Other important nitrogen forms are amines, amides and nitriles. Insufficient information is available to assess their effects on water uses.

3. OCCURRENCE IN THE ENVIRONMENT

3.1 Natural Sources

3.1.1 Ammonia

Atmospheric precipitation and dry fallout may contain significant ammonia concentrations. Rainfall washes material from the air and concentrations generally decrease with time during the precipitation event. Nitrate plus ammonia atmospheric deposition averages 0.1 g/m²/year as N over the continental U.S.A. but the Great Lakes Basin receives about 1 g/m²/year, of which 0.3 g/m²/year is in precipitation and 0.7 g/m²/year is in dry fallout (Wetzel 1983). The decomposition of nitrogenous organic material (plant or animal tissues) and soil erosion may increase ammonia concentrations in surface water (McNeely et al. 1979). Nitrogen fixation by leguminous plants or alder (*Alnus* spp.) and subsequent leachate entry into surface waters may also contribute ammonia to surface waters.

3.1.2 Nitrate

Igneous rocks and volcanic activity provide localized sources of nitrates to water. Upon complete oxidation, vegetable and animal debris and animal excrement can be significant sources. Rainwater may contain a nitrate concentration of 0.2 mg/L N (McNeely et al. 1979). Precipitation tends to scrub nitrogen compounds from the air. These compounds can be contributed by natural phenomena (lightning, gasification of ammonia from water bodies) or from man-made sources (fertilizers, burning of fossil fuels) (Martin and Goff 1972).

3.1.3 Nitrite

Since nitrite is an unstable intermediate form between nitrate and ammonia, it is generally not generated from natural sources in the form of nitrite. It may, depending on the environmental conditions, be transformed from nitrate or ammonia and its presence is an indicator of high concentrations of either of these compounds.

3.2 Anthropogenic Sources

One of the major considerations in examining nitrogen from man-made sources is the conversion between forms. For instance, an effluent with a high concentration of ammonia may result in elevated concentrations of nitrite and/or nitrate, depending on environmental conditions. There also can be difficulty in determining sources of nitrogen in some cases. In removing nitrogen from waste effluents by ammonia stripping and denitrification, additional nitrogen can be added to the atmosphere and the consequent washout by precipitation can lead to indirect increases in nitrogen in surface water (Martin and Goff 1972). This would not likely be a problem with regard to toxicity, but is a factor in eutrophication and acidification of surface waters by oxides of nitrogen.

3.2.1 Ammonia

Ammonia can originate from many industrial processes, waste treatment of sewage, and from agricultural activities and practices; There are numerous industrial processes in which ammonia is involved since it is a primary raw material and a byproduct of many others. Geadah (1985) gives an inventory of both natural and anthropogenic atmospheric sources and emissions of ammonia in Canada as of 1980. Fertilizer production is the single largest user of anhydrous ammonia. Fertilizer is produced as urea, ammonium phosphate, ammonium nitrate, and mixtures with sulphate and potassium. Ammonia is one of the starting raw materials of explosives used by the military and the construction and mining industries. Ammonia is required for making soda ash, nitric acid, nylon, plastics, lacquers, dyes, rubber and other products (Shreve and Brink 1977). Nitrogen losses from the use of ammonium nitrate-based explosives at open pit coal mines in British Columbia has been investigated by Pommen (1983). Total ammonia concentrations in a

river flowing through the minesite under investigation at times reached up to 5 mg/L N, although much of the ammonia had already been nitrified in transit through the groundwater.

The predominant form of nitrogen in the effluent of sewage treatment plants is ammonia. The concentration of ammonia in sewage which has received secondary treatment is generally 10 to 20 mg/L N although this depends somewhat on the plant operation and input quality. Some plants may have effluent with 25-30 mg/L of ammonia (as N). Septic tanks may also be a source of ammonia, either in groundwater or surface water via groundwater, and fish hatchery effluent may contain high concentrations of ammonia (0.05 to 0.5 mg/L N).

In agriculture, loss of ammonia from fertilized fields can be a problem if high rates of application are used, soil conditions are poor for retention of nitrogen, or heavy rains or over-irrigation cause losses to groundwater or surface waters. High concentrations can also occur where concentrations of farm animals occur and animal manure accumulates (e.g., feed lots, piggeries, poultry farms). Piggery wastes in the lower mainland area contain up to 300 mg/L ammonia (Gough 1986). Animal feed lot drainage can contain up to 150 mg/L ammonia (Pomeroy and Orlob 1967).

Elevated concentrations of ammonia near airports may result from the use of urea as a de-icing agent or from losses of fire retardant applied by aircraft in controlling forest fires (Remington 1986).

3.2.2 Nitrate

Nitrate is manufactured and used primarily in the form of ammonium nitrate. In this form it is used for fertilizer and to a lesser extent, explosives. Potassium nitrate is also produced in Canada and other nitrate compounds (sodium nitrate, calcium nitrate, silver nitrate, and other metal nitrates) are used in a variety of applications (oxidants in chemical processes, explosives, fireworks, matches, photography, engraving, textile dyes, food processing (processed meats), and as a raw material for manufacturing nitric acid).

In British Columbia, high levels of nitrate can be found in streams affected by mining activity where explosives use is significant. Sewage treatment plants, septic tanks, agricultural runoff from fertilized fields, feedlots, etc. can be sources of nitrate, as well as ammonia and nitrite since transformations between these forms occur.

3.2.3 Nitrite

Because of the unstable nature of nitrite, it generally is very low in concentration even if high concentrations of ammonia and nitrate are present. The second step of nitrification, the conversion of nitrite to nitrate, can be inhibited by high levels of un-ionized ammonia and nitrous acid (HNO_2), which are intermediates formed during nitrification, thus causing a buildup of nitrite (Anthonisen et al. 1976). This inhibition is most likely to occur in effluents, resulting in elevated nitrite levels in the receiving waters, which may persist for some time especially at low temperatures which retard nitrification. Sources of nitrite are generally similar to the sources cited above for ammonia and nitrate. Nitrite salts are used as corrosion inhibitors in some industries. Nitrites may also be present in freshly cropped forage or moist feeds where high concentrations of organic nitrogen are being oxidized (McNeeley et al. 1979). The most frequently encountered source of nitrite is usually sewage treatment plants. One particular problem which has received considerable attention in the recent past is nitrite in intensive fish culture facilities, particularly with water recirculation systems where bacterial nitrification is taking place.

3.3 Natural Levels in Water and Sediment

3.3.1 Ammonia

In surface waters which are not affected by waste discharges, ammonia concentrations would not be expected to exceed 0.1 mg/L N. The only exception to this would be for hypolimnia of biologically

productive lakes or deep anoxic marine waters. Anaerobic hypolimnia concentrations can approach or exceed 5 mg/L N.

In British Columbia, most reported problems of high ammonia have occurred below sewage treatment plants when low river flow conditions precluded adequate dilution. Similar situations have also been reported due to leachate from domestic landfills and drainage from explosives manufacturing plants at mines.

In some Wisconsin lakes, total ammonia concentrations (fixed plus exchangeable) in lake sediments varied from 100-500 mg/kg as N; and in interstitial waters they ranged from 3 to 12 mg/L (Keeney et al. 1970). Lake sediments in British Columbia have total nitrogen concentrations of 0.3 to 41.5 mg/kg as N dry weight (mean 10.1, n = 201) (McKean unpublished data).

The ratio of nitrate to ammonia in fresh water has been used as an indicator of the relative contributions of natural and anthropogenic sources. In areas draining calcareous sedimentary landforms, unpolluted lakes can have nitrate to ammonia nitrogen ratios of 25:1. In areas where sources of nitrate are low, the ratio may approach 1: 1; where slight or moderate sewage contamination or agricultural sources are present, ratios of 1:10 can be common (Wetzel 1983).

3.3.2 Nitrate

In surface waters, inorganic nitrogen is primarily in the form of nitrate. The concentration varies with the level of biological productivity, but in unproductive (oligotrophic) lakes and streams, nitrate would be expected to be less than 0.1 mg/L N. In eutrophic lakes, concentrations can exceed 0.2 mg/L N in some cases.

In British Columbia, unusually high concentrations of nitrate have been noted as a consequence of explosives residues from open pit coal mining (Pommen 1983). Elevated concentrations many kilometers downstream have occurred as a result of these sources (Clark and Peppin 1984). In this situation, concentrations exceeded 10 mg/L N. However, in surface waters in B.C. concentrations are rarely greater than 1 mg/L N.

High levels of nitrate can occur in groundwater. Normal background levels are less than 0.2 mg/L. Dakin (1985) states that nitrate in groundwater in a number of rural areas (Matsqui, Summerland, Kelowna, Naramata) have increased in recent years and have exceeded 10 mg/L N. These high concentrations are due to the high density of residential septic drain fields, leaching from animal waste piles, and the application of large quantities of fertilizer. Concentrations in groundwater in the Fraser Valley can exceed 40 mg/L (Gough 1980). In groundwater from the Osoyoos area Hodge (1985) found high concentrations (up to 40 mg/L) of nitrate which may originate from agricultural fertilizers.

Rainwater may contain nitrate up to 0.2 mg/L N (McNeely et al. 1979).

3.3.3 Nitrite

Nitrite is only rarely reported in ambient waters at concentrations greater than the Ministry Environmental Laboratory minimum detection limit of 0.005 mg/L. Industrial and municipal effluents are the usual source of nitrite in surface water.

4. AQUATIC LIFE (FRESHWATER, MARINE, AND ESTUARINE)

In the literature, there has been a much more detailed examination of the response to nitrate-, nitrite-, and ammonia-nitrogen by freshwater biota, particularly fish, than by marine biota. Studies concerning estuarine biota are almost totally absent. As a consequence, the data on which to base criteria are much better for freshwater than marine water. Virtually no data exist for nitrogen toxicity in estuarine

environments, so no criteria are suggested. The more stringent of freshwater and marine criteria should be used for estuaries. Freshwater and marine toxicity are discussed in separate sections below.

As noted in the introduction, relatively recent thorough reviews have been carried out of the toxicity of ammonia to aquatic life (U.S. Environmental Protection Agency 1985b) and to fish (Haywood 1983). Much of the ammonia toxicity information given below is taken from these documents. Data on toxicity of nitrate and nitrite have not recently received similarly comprehensive reviews.

4.1 Effects on Algae

4.1.1 Freshwater

(a) Nitrate

Nitrate and ammonia can both serve as sources of nutrients for algae and some aquatic plants. Very little information exists on toxicity to algae of high concentrations of nitrate. Different species have preferred ranges of nitrate at which they show optimum growth, so increased concentrations of nitrate may lead to changes in species composition.

(b) Nitrite

Nitrite can also serve as a nutrient for algae at low concentrations (14 µg/L), but it may inhibit growth at higher concentrations for some species, according to laboratory studies (Syrett 1962). However, very little information exists for this subject area.

(c) Ammonia

Little work has been done with regard to the toxicity of ammonia to algae. From this limited amount of data, it would appear that in comparison to other organisms, algae are not particularly sensitive to ammonia. Abeliovich and Azov (1976) measured carbon dioxide uptake rates for four species of freshwater algae at different concentrations of ammonia. Some depression (10 to 16%) of carbon dioxide photoassimilation rate occurred at concentrations of 0.60 mg/L ammonia (0.49 mg/L N). More severe effects (77 to 92% depression in rates) occurred at very high concentrations (38 mg/L ammonia or 31.2 mg/L N). An EC50* for one species was calculated to be 11 mg/L NH₃ (9 mg/L as N). Przytocka-Jusiak (1976) calculated an LC50 of 9.8 mg/L ammonia (8.1 mg/L as N) and an EC50 of 2.4 mg/L (2.0 mg/L as N) for *Chlorella vulgaris*. Ohmori et al. (1977) noted inhibition of nitrate uptake at ammonia concentrations of 0.17 mg/L (0.19 mg/L as N). Guseva (1947) reported that 0.4 to 0.5 mg/L ammonia was toxic to *Aphanizomenon*.

Toxicity may also be expressed as time. Lethal time (LT) is expressed in terms of an amount (e.g. 50%) of test organisms dying (e.g. LT 50).

An excellent explanation of toxicity terminology is contained in Sprague (1969).

*the terms LC50 and EC50 are used in the text to indicate toxicity. Lethal concentration (LC) is the toxicant concentration producing death of a test organism. Generally 50% lethal toxicity of a population (LC50) is used over a specified period of time (typically 96 h). Effective concentration (EC) is the toxicant concentration affecting some specified physiological response (e.g. respiration, growth, loss of equilibrium) in a given time (typically 96 h).

4.1.2 Marine Algae

(a) Nitrate

No information could be located on the toxicity of nitrate to marine algae.

(b) Nitrite

No information could be located on the toxicity of nitrite to marine algae.

(c) Ammonia

Admiraal (1977) tested ammonia toxicity for 10 species of marine diatoms. A 14 to 73% reduction in chlorophyll a was found at a concentration of 0.24 mg/L ammonia (0.2 mg/L as N) relative to controls for nine species. A tenth species was found to show a 77% reduction in chlorophyll a at a concentration of 1.2 mg/L ammonia (1.0 mg/L as N).

4.2 Effects on Invertebrates

4.2.1 Freshwater Species

(a) Nitrate

Wickens (1976) tested the response of the freshwater prawn *Macrobrachium rosenbergii* to long-term toxicity. He found a 3 to 4 week LC50 of 160 mg/L N.

(b) Nitrite

Wickens (1976) also evaluated the response of *M. rosenbergii* to nitrite and gave a 3 to 4 week LC50 of 15.4 mg/L N.

(c) Ammonia

Several studies e.g., Thurston (1984a), have been carried out on a number of species and families of invertebrates. These are reviewed by the U.S. Environmental Protection Agency (1985b).

A wide range of response is shown, but invertebrates are generally less sensitive than fish. In the EPA document, a ranking is made of the sensitivity of families of organisms reported on in the literature based on the response of individual species. The list is a useful one and a modification of Table 3 from the EPA report is shown as Table 1. It gives not only a relative ranking of sensitivities to ammonia, but also some quantification. This summary indicates that for the aquatic animals tested, fish appear to be (as a group) more sensitive than invertebrates. The four most sensitive families of animals tested were fish, although there are families of invertebrates which do show responses to relatively low concentrations of ammonia. However, in considering protection of freshwater aquatic life, the present evidence appears to indicate that fish should be the focus of concern. Salmonids have been identified as a group which are particularly sensitive, and their importance in British Columbia gives support to the use of salmonids as key organisms for setting an ammonia criterion.

4.2.2 Marine Invertebrate Species

(a) Nitrate

Average acute toxicity (48 h LC50) for seven penaeid prawn species was 3 400 mg/L N (Wickens 1976). For chronic effects, he tested a species of prawn (*Penaeus monodon*) and found there was no effect on growth at concentrations of 200 mg/L N nitrate after three to five weeks. Another species of prawn was somewhat

more sensitive showing three to four week LC50 values of 160 mg/L N. Epifanio and Srna (1975) investigated nitrate toxicity to a species of clam (*Mercenaria*) and oyster (*Crassostrea*); however, they concluded that the toxicity was so low as to make a 96 h LC50 ecologically meaningless (>20 000 mg/L N).

Table 1. Ranking of Acute Toxicity of Total Ammonia to Freshwater Fish and Invertebrate Animal Families (adapted and modified from U.S. Environmental Protection Agency 1985b)

Ranking in decreasing order of sensitivity			
Rank	Family	Family mean acute value (mg/L N) corrected for pH (see U.S.E.P.A. 1985b)	
1	Percidae (darter, perch)	0.6 (most sensitive)	fish
2	Salmonidae (trout, salmon)	0.7	fish
3	Centrarchidae (sunfish)	1.2	fish
4	Catostomidae (sucker)	1.3	fish
5	Dendrocoelidae (flatworms)	1.3	invertebrate
6	Cottidae (sculpins)	1.4	fish
7	Daphnidae (cladocerans)	1.5	invertebrate
8	Cyprinidae (carps & minnows)	1.6	fish
9	Percichthyidae (perch)	1.9	fish
10	Baetidae (mayflies)	2.0	invertebrate
11	Poeciliidae (mosquito fish)	2.1	fish
12	Perlodidae (stoneflies)	2.2	invertebrate
13	Ictaluridae (catfish)	2.4	fish
14	Tubificidae (sludge worms)	2.5	invertebrate
15	Actacidae (Crayfish)	2.9	invertebrate
16	Asellidae (Isopods)	3.2	invertebrate
17	Ephemerellidae (Mayflies)	5.1	invertebrate
18	Elmidae (Beetles)	6.8 (least sensitive)	invertebrate

(b) Nitrite

Wickens (1976) calculated a mean 48 h LC50 for seven species of prawns of 170 mg/L N. In chronic tests, he found that a concentration of 6.4 mg/L reduced growth in the one penaeid species tested (*P. monodon*) by 50% after 34 days. Epifanio and Srna (1975) tested clam (*Mercenaria*) and oyster (*Crassostrea*) tolerance to nitrite. They calculated an LC50 of 1081-2 415 mg/L N depending on the species and life stage.

(c) Ammonia

There is a large difference in the number of species of marine invertebrates in comparison to freshwater; however, much less toxicity work has been done, so less basis exists for making generalizations about ammonia toxicity to marine invertebrates. The U.S.E.P.A. (1983) ranked five representatives of marine invertebrates with respect to their sensitivity (Table 2).

There are a number of examples of short-term marine ammonia toxicity tests. Linden et al. (1979) investigated the ammonia toxicity to the copepod *Nitocra spinipes* and reported a 96 h LC50 of 1.2 mg/L N. Epifanio and Srna (1975) tested oyster (*Crassostrea*) and clam (*Mercenaria*) and reported 96 h LC50 concentrations (un-ionized ammonia) of 6.8 to 30.3 mg/L N and 2.6 to 59 mg/L N, respectively. Armstrong et al. (1978) reported LC50 values of 0.3 to 1.1 mg/L N for the prawn *Macrobrachium*, depending on the pH values.

Brown (1974) reported acute toxicity for a marine worm (*Cerebratulus*) of 1.9 mg/L N for a 106 minute LT50.

Table 2. Family and Species Mean Acute Toxicity Values to Total Ammonia (corrected for pH) (adapted and modified from U.S. Environmental Protection Agency 1985)

Ranking in decreasing order of sensitivity.			
	Family	Species	Acute Toxicity Value (mg/L NH ₃ -N)
1.	Palaemonidae	<i>Macrobrachium rosenbergii</i> (prawn)	1.2
2.	Canthocamptidae	<i>Nitocra spinipes</i> (copepod)	1.6
3.	Nephropidae	<i>Homarus americanus</i> (American Lobster)	2.1
4.	Veneridae	<i>Mercenaria mercenaria</i> (Quahog clam)	4.9
5.	Ostreidae	<i>Crassostrea virginica</i> (eastern oyster)	18.0

Very few data on the chronic effects of un-ionized ammonia on marine invertebrates exist. A three-week toxicity test with a prawn species (*Penaeus* sp.) gave an EC50 value of 0.6 mg/L N total ammonia based on reduced growth rates (Wickens 1976). A test over six weeks with another species (*Macrobrachium* sp.) showed growth reduction at 0.10 mg/L N. Armstrong et al. (1978) showed growth reduction in the same species at 0.090 mg/L N at pH 6.8. Sullivan and Ritacco (1985) reported 48 h LC50 values of 0.14-0.21 mg/L un-ionized ammonia for the larval stages of two species of the marine copepod *Acartia*, which is considerably lower than previous reports.

4.3 Effects on Fish

4.3.1 Freshwater

Considerable information exists for nitrogen toxicity to freshwater fish. Most of the data reported in the literature have been from work on acute toxicity, typically as 48 or 96 h LC50 tests. Some generalized results for ammonia toxicity to different families of freshwater fish are presented in part in section 4. 2.1. What is more important in the context of this report is to discuss specific toxicity, particularly to species that are native to B.C. and are important sportfish.

The toxicity data presented below emphasize rainbow trout (*Salmo gairdneri*) as well as cutthroat trout (*Salmo clarki*) when data are available. Rainbow trout is a widely distributed British Columbia sport fish, and is a sensitive fish species to ammonia and nitrite toxicity (U.S. Environmental Protection Agency 1976; Russo and Thurston 1977). Cutthroat trout is also a widely distributed sport fish in British Columbia. Nitrite and ammonia toxicity data were found only for fry of cutthroat trout, but toxicity data for ammonia were available for all life stages of rainbow trout, which is comparable to cutthroat trout in its susceptibility to nitrite and ammonia toxicity (Russo and Thurston 1977; Thurston et al. 1978). According to the U.S. Environmental Protection Agency (1985b) and Haywood (1985) some data exist indicating that Chinook salmon may be somewhat more sensitive to ammonia than rainbow trout based on acute toxicity data. However, the amount of toxicity data available for chinook is far less than that for rainbow trout.

Nitrite and ammonia are both toxic to salmonids, and are likely to be present in water together. No data were found on the combined toxicity of ammonia and nitrite in water. Considering the toxic mechanisms of nitrite (reduction of the oxygen carrying capacity of blood) and ammonia (gill damage) it is likely that their toxicities are additive; however, no investigation appears to have been carried out to confirm this although this should be a consideration in designating site specific objectives.

Some work has been done on the effects of other toxicants in conjunction with ammonia. In most cases reported in the literature, the toxicants investigated appear to have an effect which is simply additive. Herbert and Vandyke (1961.J) and Shemchuk (1971) investigated the effects of copper and ammonia and found the effects were additive. The U.K. Ministry of Technology (1962, 1963) found similar results with ammonia and zinc, and Herbert (1962) reported similarly for ammonia and phenol mixtures. Brown et al. (1969) found the toxicity of ammonia, zinc, and phenol to be additive. Rubin and Elmaraghy (1977) found

toxicity of nitrate and ammonia to be additive. One exception to this general finding of additive toxicity is the results of Broderius and Smith (1979) who found that ammonia and cyanide exerted a synergistic effect on toxicity. A review of mixtures of toxicants was carried out by the European Inland Fisheries Advisory Commission (1980) and can be referred to for additional details.

(a) Nitrate

Nitrate is generally considered to have a low toxicity to fish with 1-day to 7-day LC50 values ranging from 420 to 2 000 mg/L nitrate-N for various species of fish. The respective 4- and 7-day LC50 values for fingerling rainbow trout in fresh water were 1 360 and 1 060 mg/L nitrate-N (U.S. E.P.A. 1976b). For rainbow trout in hatcheries, Westin (1974) recommended a maximum allowable concentration of 56 mg/L nitrate-N (0.1 of the 7 d LC10), and a preferred concentration of 6 mg/L nitrate-N (0.01 of the 7 d LC10), or less. The preferred concentration appears to be very conservative, and the maximum allowable concentration is probably a more realistic criterion for nitrate. A variety of reports exist which discuss the toxicity of nitrate to salmonids and other species (Rubin and Elmoraghy 1977; Colt and Tchobanoglous 1976; Westin 1974; Knepp and Arkin 1973; Trama 1954). In general, they report toxicity (96 h LC50) to be very low (>1000 mg/L). One paper which reports results quite different from the above results is Kincheloe et al. (1979). They report significant effects on salmonid eggs and fry from concentrations as low as 5-10 mg/L nitrate (1-2 mg/L NO₃-N). Little work has been done previously on these early life stages and no other similar results have been reported. The authors of the paper did note that they encountered problems with fungal infections of incubating eggs; however, they did not attribute any mortalities to this problem.

An evaluation of nitrate toxicity to salmonid eggs and emergent fry was undertaken to investigate the toxicity to these early life stages, as was suggested by the results reported in the paper by Kincheloe et al. The work was carried out at the Environmental Protection Service Toxicity Laboratory in North Vancouver. Two species of eggs were used: coho (*Onchorynchus kisutch*) and rainbow trout (*Salmo gairdneri*). The eggs were exposed to 10 and 40 mg/L nitrate (as N) for 28-31 days. The results are summarized below:

Concentration		No. exposed	No. hatched	No. dead	% hatched
Control	(coho)	300	270	30	90
	(rbt)	300	282	18	94
10 mg/L	(coho)	300	265	35	88
	(rbt)	300	270	30	90
40 mg/L	(coho)	300	240	60	80
	(rbt)	300	286	14	95

The second aspect of the study was a test of emergent fry to nitrate toxicity. The concentrations used in this 96h LC50 test were twice the concentrations used in the incubations (i.e., fish incubated at the 10 mg/L concentration were exposed to 20 mg/L concentrations for 96 hr).

Concentration	Number of fish	Cumulative Mortality			
		24 hr	48 hr	72 hr	96 hr
Control	20	0	0	0	0
20 mg/L	20	0	0	0	0
80 mg/L	20	5	5	5	6

It would appear from these data that some threshold effect might be present between 40 and 80 mg/L. The 40 mg/L appears to have little if any effect on eggs or emergent fry; however, coho eggs seem to be

slightly more sensitive than rainbow trout. The 80 mg/L concentration is not acutely toxic but appears to cause about 30% toxicity in a 96 hour test. It is difficult to use these isolated data to extrapolate to general toxicity. Because of the limited number of concentrations no LC50 can be calculated and it is clear that an acutely toxic concentration would be somewhat higher. More investigation in the area of nitrate toxicity to early life stages is needed.

(b) Nitrite

Little investigation has been carried out on aquatic organisms other than fish. Beitinger and Huey (1981) reported a 96 h LC50 for crayfish (*Procambarus simulans*) of 1.9 mg/L N for nitrite. Increased chloride reduced toxicity in this situation. Wickens (1981) found a 3-4 week LC50 for juvenile prawns (*Macrobranchiurn rosenbergii*) of 15.4 mg/L N. Huey and Beitinger (1980) found a 96 h LC50 for nitrite of 1.09 mg/L N for larval salamanders (*Ambystoma texanum*).

Nitrite is highly toxic to fish. The toxic mechanism in fish is the same as in humans, with nitrite combining with hemoglobin to form methemoglobin, thus reducing the oxygen carrying capacity of the blood (Russo and Thurston 1977). In both mammals and fish, a small proportion of the hemoglobin (usually 5% or less) is present as methemoglobin (Meade and Perrone 1980). Lewis and Morris (1986) felt that even somewhat above 10%, it should not be viewed as exceptional. Nitrite in water raises the concentration of methemoglobin in response to its concentration in the water, exposure time, chloride concentration, and fish species. Fish can tolerate relatively high levels of methemoglobin. Tucker and Schwedler (1983) felt 25-30% was safe for channel catfish and Brown and McLeay (1975) reported 70% in rainbow trout and chinook salmon without mortality. Nitrite can also cause tissue damage (specifically gills) at levels of 0.060 mg/L N after a 3-week exposure for juvenile steelhead trout (Wedemeyer and Yasutake 1978). Acute bioassays for cutthroat trout fry (*Salmo clarki*) produced 96 h LC50 values of 0.5 to 0.6 mg/L nitrite (NO₂-N), and 36-day LC50 values of 0.4 mg/L nitrite-N. The maximum concentration with no mortalities after 36 days was 0.20 to 0.25 mg/L N (Thurston et al. 1978).

Acute bioassays on rainbow trout (*Salmo gairdneri*), produced 96 h LC50 values as low as 0.11 mg/L nitrite-N (Russo and Thurston 1977; Russo et al. 1981). The maximum level with no mortality after 10 days was 0.06 mg/L nitrite-N (U.S. E.P.A. 1976b).

A number of water quality characteristics appear to modify the toxicity of nitrite to fish; however, some of them are not well documented. Bicarbonate has been noted by Eddy et al. (1983), Huey et al. (1980), Bath

and Eddy (1980), and Bowser et al. (1983). Crawford and Allen found that addition of calcium sulphate reduced toxicity of chinook salmon. Calcium has been implicated by several investigators as having an effect on fish toxicity (Bowser et al. 1983, Wedemeyer and Yasutake 1978, Tomasso et al. 1980).

Nitrite toxicity appears to decrease as the pH increases, particularly at high pH (>8.6), and has some dependence on sulphate, phosphate, and nitrate concentrations (Russo et al. 1981). Huey et al. (1980) and Eddy et al (1985) found that bromide reduced the toxicity of nitrite.

The major moderating factor in the taxicity of nitrite is chloride concentration. Russo and Thurston (1977) and Russo et al. (1981) found nitrite toxicity to be markedly dependent on chloride concentration, with 10 mg/L chloride reducing the 96 h LC50 by an order of magnitude. This effect was also documented by Wedemeyer and Yasutake (1978) (who also noted a similar effect due to calcium), Crawford and Allen (1977), and Perrone and Meade (1977). There have been a number of relationships described between toxicity levels and chloride concentration. Lewis and Morris (1986) give a regression line for the data of Russo and Thurston (1977) showing that an increase of mg/L chloride increases the 96h LC50 concentration by 0.29 mg/L nitrite (as N). Similarly the data of Schwedler and Tucker (1983) combined

with the data of Tomasso et al. (1979) show that an increase of 1 mg/L chloride raises the 96h LC50 concentration by 0.37 mg/L.

Russo et al. (1981) found that fish size was not a factor in nitrite toxicity, contradicting earlier studies. Lewis and Morris (1986) feel that very small fish were less sensitive than intermediate or large fish. No data appear to be available for eggs or early stages of development.

Sublethal effects of nitrite on rainbow trout (i.e., increased methemoglobin, decreased hemoglobin) have been observed at levels of 0.015 to 0.10 mg/L N (Russo and Thurston 1977). B.C. Research (1981) concluded that 0.02 mg/L nitrite-N should be a guideline as to the maximum level acceptable for salmonids for continuous exposure in fish rearing tanks using recycled water. Wedemeyer and Yasutake (1978) tested steelhead trout for chronic response to nitrite. They found that no mortality occurred at 0.060 mg/L N for exposures up to six months. They noted some increase in methemoglobinemia as well as some gill damage. Excellent reviews of the effects of nitrite on freshwater fish can be found in European Inland Fisheries Advisory Commission (1984) and Lewis and Morris (1986).

(c) Ammonia

Ammonia in water assumes an equilibrium between the ionized (ammonium - NH_4^+) and un-ionized (ammonia - NH_3) chemical species that is principally dependent upon pH and temperature. Un-ionized ammonia is toxic to fish, while ammonium is considered non-toxic, or at least considerably less toxic (U.S. E.P.A. 1976b; Thurston et al. 1978). Un-ionized ammonia values can be calculated from total ammonia, pH, and water temperature measurements, as outlined by Trussell (1972) or Emerson et al. (1975). Un-ionized ammonia values calculated by this method are approximate because the calculations do not consider the formation of ammonia-heavy metal complexes that reduce un-ionized ammonia levels (Schaeffer et al. 1980).

With increasing levels of ammonia in the ambient environment, the ammonia excretion of most aquatic animals decreases and the ammonia level in the blood and tissue increases. This increased ammonia level can have serious effects on the physiology of the animal on a cellular, organ, and system level (Colt and Armstrong 1981).

Ammonia in water is readily oxidized to nitrite and then to nitrate under aerobic conditions. The theoretical oxygen demand for nitrification of ammonia is 4.6 mg O₂ per mg NH₃-N, and thus ammonia may reduce dissolved oxygen levels in water (American Fisheries Society 1979). Nitrite is the intermediate in the nitrification of ammonia, but is rapidly converted to nitrate, and thus is normally present only in trace amounts. However, the second step of nitrification can be inhibited by nitrous acid and un-ionized ammonia, resulting in the buildup of nitrite which is highly toxic to fish (Anthonisen et al. 1976). These concerns will be addressed via criteria for dissolved oxygen and nitrite.

Acute bioassays on cutthroat trout fry gave 96 h LC50 values of 0.4 to 0.7 mg/L un-ionized NH₃-N, and the maximum concentration with no mortality after 36 days was 0.18 mg/L un-ionized NH₃-N (Thurston et al. 1978). Toxicity of un-ionized ammonia to cutthroat trout was caused by damage to the gills, kidneys, and livers (Thurston et al. 1978). Acute bioassays on rainbow trout, which are comparable to cutthroat trout in their susceptibility to ammonia, indicate that juveniles and adults are more susceptible than fry (Thurston et al. 1978). Consequently, the acute toxicity levels for larger cutthroat trout may be lower than those levels cited above for fry.

Thurston and Russo (1983) performed acute toxicity bioassays on rainbow trout over a range of sizes from fry to adult. The 96 h LC50 concentrations ranged from 0.160 to 1.1 mg/L un-ionized ammonia-N. Sensitivity decreased as the fish developed from fry to juveniles, but increased with progressively older

fish. They also noted that results of 12 and 35 day tests were not appreciably different from the shorter duration tests.

All of the reported acute toxicity (i.e., 1- to 4-day LC50) values for salmonids (including rainbow and cutthroat trout) lie between 0.13 and 0.7 mg/L un-ionized NH₃-N (American Fisheries Society 1979; Thurston et al. 1981c; Thurston and Russo 1983). Exceptions are values of Rice and Stokes (1975), which were 0.06 to 0.08 mg/L un-ionized NH₃-N for rainbow trout (24 h LC50). Fluctuating exposure to un-ionized ammonia was found to be more toxic than constant exposure, with 96 h LC50 values as low as 0.08 mg/L (Thurston et al. 1981).

B.C. Research (1981) reviewed the literature on the sublethal effects of un-ionized ammonia on fish. The results of that review are presented in Table 3, B.C. Research concluded that for continuous exposure of salmonids, un-ionized ammonia levels should not exceed 0.006 to 0.009 mg/L N, and 0.007 mg/L N was judged to be the most suitable upper level.

Haywood (1983) reviewed the ammonia toxicity literature and recommended a maximum concentration for waters with salmonid fish of 0.002 mg/L un-ionized ammonia or 1 mg/L total ammonia.

Table 3. Sublethal Effects of Un-Ionized Ammonia on Fish

Concentration of Un-ionized Ammonia (mg/L N)	Effect on Fish	Source
0.003	Permanent gill damage to chinook salmon after continuous exposure of 6 weeks	Burrows (1960) and Trussell (1972)
0.006	Recommended as suitable upper level for continuous exposure	Mayo et al. (1972)
0.007-0.009	No effect on rainbow trout at dissolved oxygen levels above 7 mg/L in multiple reuse operation	Larmoyeux and Piper (1973)
0.025	Maximum level that fish can tolerate over a long period	Dept. of Environment-U.K. (1973)

Thurston et al. (1984b) carried out the most comprehensive chronic toxicity experiment for rainbow trout. The experiment was conducted over five years and three generations of fish. They found histological changes occurring at 0.040 mg/L un-ionized ammonia (0.033 mg/L N) in the first generation and 0.020 mg/L un-ionized ammonia (0.016 mg/L N) in the second generation at pH and temperatures averaging 7.7 and 9.3°C, respectively.

There are some data indicating toxicity at relatively low ammonia concentration. Haywood et al. (1980) noted effects at 0.035 mg/L. Rice and Bailey (1980) used 61-day tests and pink salmon fry and determined that 0.002 mg/L N un-ionized ammonia caused a reduction in growth. Many other examples of chronic toxicity to salmonids were reviewed by U.S.E.P.A. (1985b).

One difficulty in relating laboratory toxicity results to field conditions is that laboratory concentrations are generally held at a single level, whereas actual concentrations in the field usually vary with time. Very little work has been carried out to determine the effects of fluctuating concentrations on toxicity. In general, fluctuating concentrations have greater toxicity than static concentrations with the same average. Brown et al. (1969) reported acute toxicity increased (reduced survival time) when ammonia concentrations fluctuated between 1.5 and 0.5 times the 96 h LC50 at two-hour cycles but not one-hour cycles. Thurston et al. (1981a) indicated similar results, with lower LC50 concentrations realized for fish exposed to fluctuating levels of ammonia (expressed as mean values) than for fish exposed to constant concentrations. This difference did not hold for chronic exposure times (14 d and 28 d) when 6 h or 12 h cycles of fluctuation were used.

A number of factors act to modify either the calculation of, or the effect of, un-ionized ammonia in freshwater. The two major factors which determine the proportion of total ammonia which is un-ionized are temperature and pH. (Emerson et al. 1975; Thurston et al. 1979; Trussell 1972).

Temperature: The general relationship of toxicity of un-ionized ammonia has been an increase with increasing temperature (Wuhrman et al. 1947; Wuhrmann and Waker 1948; Woker 1949; Burrows 1964). Brown (1968) found higher toxicity at 3°C than 13°C, but this finding is at odds with the results from most of the literature. There are two general effects on toxicity caused by temperature. First, as the temperature changes the proportions of un-ionized and ionized ammonia change (see Emerson et al. 1975). Second, there is evidence that the toxicity itself changes with temperature. In general, the toxicity increases as the water temperature decreases (Burrows 1964, Thurston and Russo (1983)). An evaluation of previous data by Erickson (1985) resulted in his conclusion that temperature and toxicity could be described as single log-linear models.

pH: With increasing pH the proportion of un-ionized ammonia (of total ammonia) increases and, in general, the toxicity increases. As with temperature, there are two effects on toxicity caused by pH. The major effect is due to the change in proportions of un-ionized and ionized ammonia. Increases in pH cause higher amounts of un-ionized ammonia to be formed. A lesser effect is the direct effect of pH on toxicity. Most investigators have made a direct relationship between pH and toxicity response due to un-ionized ammonia; however, a number of papers have indicated that there may be other factors than un-ionized ammonia (as indicated by pH) which affect toxicity. Tabata (1962) tested the toxic response of *Daphnia* to ammonia and concluded that ionized ammonia was also a factor in the toxic response. Several other researchers (Armstrong et al. 1978; Thurston 1980; Tomasso et al. 1980; Thurston et al. 1981c) have also indicated that the effect of pH on toxicity may involve more than an alteration of the proportions of ionized and un-ionized ammonia with pH, that un-ionized ammonia may not be the only toxic component, and that ionized ammonia (NH₄⁺) may also contribute to toxicity. Erickson (1985) examined mathematical models which had been proposed to take into account both temperature and pH in affecting ammonia toxicity. He concluded that a model which assumed un-ionized ammonia and ammonium were jointly toxic was strongly supported by the data on pH dependence. However, it did not explain temperature dependence.

Total Dissolved Solids/Salinity: Messer et al. (1984) pointed out that a correction for hardness is necessary in the estimation of un-ionized ammonia. Hardness (and total dissolved solids and salinity) can affect acute toxicity. In general, increasing total dissolved solids reduces the toxicity of ammonia to rainbow trout up to salinity about 10 ‰ (ten parts per thousand) (Herbert and Shurben 1965; Harader and Allan 1983). A detailed table calculating un-ionized ammonia from pH, temperature, and total dissolved solids was compiled by Skarheim (1973). Some weaknesses in his calculation of values have been noted by Emerson et al. (1975), and most commonly used tables (Emerson et al. 1975; Thurston et al. 1974) use only pH and temperature. However, it would appear that hardness/total dissolved solids or salinity should be considered as factors when evaluations of ammonia toxicity are made.

Other Factors: dissolved oxygen (or the presence of other toxicants) can affect the concentration at which symptoms are manifested. The observations made by a number of workers indicate that higher ambient oxygen concentrations increase survival time at a given ammonia concentration (Downing and Merckens 1955; Thurston et al. 1981b). A mathematical model for the relationship between dissolved oxygen and ammonia toxicity was proposed by Thurston et al. (1981).

Carbon dioxide concentration can also affect tolerance to ammonia by fish. This phenomenon was first noted by Alabaster and Herbert (1954) and noted by other investigators since that time. Alabaster and Herbert found that an increase in carbon dioxide concentrations up to 30 mg/L decreases ammonia toxicity. The other factors influencing ammonia toxicity are pre-exposure to fluctuating concentrations. In

general, fish with some prior exposure to sublethal concentrations of ammonia are better able to stand acutely lethal concentrations. The data on fish exposure to a fluctuating (as contrasted to constant) concentration indicate that fish are more susceptible to a fluctuating concentration. Summaries of these latter two factors can be found in U.S.E.P.A. (1985b).

4.3.2 Marine Fish

(a) Nitrate

Brownell (1980) investigated the effects of nitrate concentration on larval marine fish. He reported very high acute toxicity concentrations (24 h LC50 of > 4000 mg/L N) for four fish species. For 24 h EC50 influencing feeding, the average concentration given was 778 mg/L N.

(b) Nitrite

Brownell (1980) also reported responses of larval marine fish to nitrite additions. For 24 h LC50, a mean concentration of 1870 mg/L N was given for five species. Feeding effects, measured as 24 h EC50 values, averaged 366 mg/L N. Crawford and Allen (1977) noted that chinook salmon in seawater had a much higher tolerance to nitrite than in freshwater. In freshwater, they found a 48 h LC50 of 5.8 mg/L N, but in seawater a concentration of 325 mg/L N caused only a 10% mortality. This protective effect of chloride on nitrite toxicity has also been documented by Perrone and Meade (1977); Russo et al. (1981); and Wedemeyer and Yasutake (1978). Increased calcium concentrations may also act as a protective mechanism for fish against nitrite toxicity.

(c) Ammonia

Holland et al. (1960) reported the "critical level" for chinook salmon (*Oncorhynchus tshawytscha*) to be 0.03 to 0.09 mg/L ammonia nitrogen and for coho salmon to be 0.11 mg/L ammonia N. A static test with coho salmon provided a 48 h LC50 value of 0.41 mg/L N (Katz and Pierro 1967). Brownell (1980) investigated ammonia toxicity in five species of larval marine fish and found sublethal consequences (feeding effects) at concentrations of 0.030 to 0.130 mg/L N, depending on species, and 24 h LC50 concentrations of 0.360 to 0.460 mg/L N.

Alderson (1979) reported that sublethal effects (cessation of growth) for Dover sole occurred at un-ionized ammonia concentrations of 0.38 to 0.77 mg/L N and for turbot at 0.3 to 0.9 mg/L N. He also identified levels at which little or no effect on growth was evident. These levels were 0.066 mg/L N for sole, and 0.11 mg/L N for turbot (16°C and 34 ‰ salinity). A review of ammonia toxicity to marine organisms in general, but emphasizing fish, is contained in U.S.E.P.A. (1985).

One major consideration which must be taken into account is the effect of salinity (particularly chloride) on the toxicity of ammonia. With increasing chloride concentrations, toxicity decreases dramatically (Harader and Allen 1983; Crawford and Allen 1977). Because of this, ammonia toxicity in seawater is quite different from that in freshwater. Haywood (1983) suggested criteria for marine fish based on a review of available data. He primarily used the data of Alderson (1979) and noted that it appeared that there was a regular five-fold difference between non-salmonid freshwater fish and saltwater fish for un-ionized ammonia, and a two-and-a-half-fold difference between freshwater and saltwater fish for total ammonia for maximum acceptable levels. He recommended maximum acceptable levels of 0.050 mg/L un-ionized ammonia (0.041 mg/L as N) or 2.5 mg/L total ammonia (2.0 mg/L N). In determining the proportion of un-ionized ammonia to total ammonia, the tables of Bower and Bidwell (1978) should be consulted.

4.4 Criteria from the Literature (Freshwater)

Many agencies have specified levels for various forms of nitrogen to protect aquatic life. However, the vast majority of criteria are concerned with ammonia.

4.4.1 Nitrate

No criteria could be located which specify concentrations for nitrate or nitrate plus nitrite to protect aquatic life.

4.4.2 Nitrite

The only criteria from other jurisdictions which could be located are listed below in Table 4.

Table 4. Suggested Criteria for Nitrite (as N) for Protection of Freshwater Aquatic Life

Criteria Statements	Criteria Values	Jurisdictions
For salmonid dominated waters, 95 and 99 percentiles for nitrite are 0.15 and 0.25 mg/L, respectively.	0.15 mg/L 0.25 mg/L	Anglian Water Authority (1982)
For cyprinid dominated waters, 95 and 99 percentiles for nitrite are 0.45 and 1.0 mg/L, respectively.	0.45 mg/L 1.0 mg/L	Anglian Water Authority (1982)
For salmonid hatcheries, the ratio of chloride to nitrite be maintained at 100:1. For chloride concentrations below 2 mg/L, nitrite should not exceed 0.015 mg/L.	0.015 mg/L	Sigma Environmental Consultants(1983)
For waters with salmonid fish	0.01 mg/L with chloride < 1 mg/L	E.I.F.A.C. (1984)
Protection of aquatic life	0.06 mg/L	C.C.R.E.M. 1986

4.4.3 Ammonia

The criteria from a variety of agencies are listed in Table 5.

Table 5. Criteria for Ammonia (as N) for Protection of Freshwater Aquatic Life

Criteria Statements	Criteria Values	Jurisdictions
For freshwater aquatic life (as un-ionized ammonia) = 0.02 mg/L	0.02 mg/L (un-ionized)	U.S. Environmental Protection Agency (1976b) Ontario (1978)
Acceptable limit for un-ionized ammonia: 0.02 mg/L	0.02 mg/L (un-ionized)	Manitoba (1979)
Agrees with the 0.02 mg/L NH ₃ criterion to protect freshwater salmonids as established by QCW, 1976, if not complicated by other toxicants and extreme temperatures, low D.O. or high CO ₂	0.02 mg/L (un-ionized)	American Fisheries Society (1979)
Warm-water-biota: mean concentration of un-ionized ammonia at a level 0.05 mg/L as based on a minimum of 5 samples taken over a 30-day period.	0.05 mg/L (un-ionized)	Idaho (1980)

Criteria Statements	Criteria Values	Jurisdictions
Cold-water-biota and Salmonid spawning: mean concentration of un-ionized ammonia at a level 0.04 mg/L as based on a minimum of 5 samples taken over a 30-day period if water quality characteristics are near optimal for the protected use. In all other cases the mean concentration of un-ionized ammonia is to be 0.02 mg/L based on a minimum of 5 samples taken over a 30-day period.	0.04 mg/L (un-ionized)	Idaho (1980)
	0.02 mg/L (un-ionized)	Idaho (1980)
For the protection of aquatic life, un-ionized ammonia not to exceed 20 µg/L.	0.02 mg/L (un-ionized)	Walker (1980) (I.J.C.)
Maximum acceptable concentration for cold or cool water aquatic life = 0.02 mg/L un-ionized.	0.02 mg/L (un-ionized)	Manitoba (1983)
For salmonid dominated waters, 95 and 99 percentiles for free and saline ammonia are 0.75 and 1.25 mg/L, respectively.	0.75 mg/L 1.25 mg/L (total)	Anglian Water Authority (1982)
For cyprinid dominated waters, 95 and 99 percentiles for free and saline ammonia are 1.5 and 2.5 mg/L, respectively.	1.5 mg/L 2.5 mg/L (total)	Anglian Water Authority (1982)
For salmonid dominated waters, 95 and 99 percentiles for un-ionized ammonia are 0.021 and 0.04 mg/L, respectively.	0.021 mg/L 0.04 mg/L (un-ionized)	Anglian Water Authority (1982)
For cyprinid dominated waters 95 and 99 percentiles for un-ionized ammonia (as N) are 0.021 and 0.08 mg/L, respectively.	0.021 mg/L 0.08 mg/L (un-ionized)	Anglian Water Authority (1982)
Protection of fisheries. More stringent criteria may be necessary if the pH is less than 6.5; the D.O. is less than 5 mg/L, the temperature is less than 5°C; or the sodium concentration is less than the total ammonia concentration (mg/L N)	0.02 mg/L (un-ionized)	Utah* * cited in Messer et al. (1984)
Protection of aquatic life: 0.016 mg/L un-ionized	0.016 mg/L (0.020 mg/L as NH ₃)	U.S.EPA (1973, 1976b)
Protection of aquatic life: dependent on pH and temperature	variable depending on pH and temperature	U.S. EPA (1985b)
Protection of aquatic life	0.030 (general), variable depending on pH in limited- use zones for	I.J.C. (1986)

Criteria Statements	Criteria Values	Jurisdictions
	short-term exposure.	

Table modified from Singleton and Clark (1983)

Criteria which have been proposed for protection of aquatic life have generally specified a concentration of un-ionized ammonia which was based on bioassays. The un-ionized ammonia concentrations which were recommended were calculated from total ammonia using pH and temperature relationships which have been reported from a number of sources (e.g., Trussel 1972; Thurston et al. 1974). The "single value" criterion was based on the assumption that the toxicity to fish was the same at all pH and temperatures. However, reports have been made of toxicity changing at different pH or temperature values despite the concentration of un-ionized ammonia remaining the same (Lloyd and Herbert 1960; Tabata 1962; Roseboom 1982). Szumski et al. (1982) state that fish appear to be far more tolerant to un-ionized ammonia at high pH, and thus any criterion should have some factor which compensates for pH and temperature, other than the ionization constants which govern the proportion of ionized (NH_4^+) and un-ionized ammonia (NH_3).

One mechanism which has been cited is that CO_2 excreted by the fish at their gill surfaces reduces the pH in the immediate vicinity of the gills and lowers the toxicity of ammonia. This appears to corroborate those observations which do not show correlation between un-ionized ammonia concentration and toxicity. However, other explanations are also possible.

The 1985 U.S. Environmental Protection Agency criteria document on ammonia took a very different approach which appears to take into account the factors noted above. Instead of a single value for un-ionized ammonia, the maximum allowed concentration varies with pH and temperature (U.S. Environmental Protection Agency (1985a). For example, for acute toxicity at pH 6.5 and 0°C the maximum un-ionized ammonia allowed is 0.008 mg/L N. At pH 9.0 and 20°C, 0.214 mg/L N un-ionized ammonia is acceptable. The EPA provides tabulated maximum and average concentrations for both un-ionized and total ammonia. Calculation of maximum and average concentrations through the use of equations is also possible for values which are intermediate to the tabulated pH and temperature values.

The present knowledge of ammonia toxicity indicates that although un-ionized ammonia is a major factor in the toxic response, temperature and pH modify the concentration at which toxicity is manifested. The older, single-value criterion had the inherent flaw of being over-protective for the majority of ranges of pH and temperature, but underprotective for some conditions of low pH and temperature. The most commonly used single value criterion for un-ionized ammonia was 0.020 mg/L. An advance on the single value criterion was the concept of a two-value-criteria set which specified maximum acceptable concentrations for both short term (acute) and long term (chronic exposure). The major advance and advantage of the approach the U.S.E.P.A. has taken in their 1985 ambient water quality criteria document is that presumably safe levels of exposure have been established which take into account both pH and temperature. In contrast to the single-value or two-value criteria, a set of values in tabular form can be used to evaluate un-ionized toxicity at ranges of temperature and pH normally encountered. The values of un-ionized ammonia for chronic toxicity range from 0.0007 mg/L (0.0006 mg/L N) at 0°C and pH 6.5 to 0.035 mg/L (0.029 mg/L N) at higher pH (>8) and temperatures (>15°C) for protection of salmonids. Since un-ionized ammonia cannot be measured directly but must be calculated from total ammonia concentration, temperature and pH, there is considerable advantage to using total ammonia as reference values for criteria. Criteria values for total ammonia are included in Tables 12 and 13 which are adapted from U.S. Environmental Protection Agency (1985b).

In the 1983 draft of the 1985 U.S.E.P.A. ammonia criteria; the time periods for acute and chronic toxicity were established as a maximum concentration and an average over 30 days. In the final criteria document

the time periods were modified to one-hour and four-day averages for acute and chronic exposure, respectively.

For application of criteria in this document, the maximum and 30-day method has been adopted rather than the one-hour and four-day time periods. There are a number of technical and practical reasons for using the maximum and 30-day averages.

The U.S. Environmental Protection Agency (1985b) criteria document states that the one-hour average concentration is designed to protect against acute toxicity. However, the data which are used to derive the acute criteria are based on results of LC50 testing, usually of 96 hour duration. The rationale for the one-hour time period which is presented is twofold. First, it is pointed out that the acute response of some fish to ammonia is very rapid and data are cited indicating that toxicity tests (LC50's) show only minor differences between 3-hour and 96-hour results. However, short-term toxicity can also be used to evaluate longer (96 h) exposures. The second reason put forward for the one-hour period is that it minimizes the amount of time the exposure concentrations can be above the criteria concentration without exceeding the average. Because mean concentrations are specified, concentrations which are significantly higher than the mean can exist for significant periods and cause toxicity if a shorter averaging period were not used. The shorter period minimizes this problem. For the one-hour averaging period, the EPA specifies that the criterion only applies where the maximum values are less than 1.5 times the average for that period. The CCREM Guidelines adopted the EPA average criteria as maximum values, which is unnecessarily restrictive.

The earlier version of the EPA criteria document (U.S. Environmental Protection Agency 1983) used maximum concentrations to evaluate acute toxicity. This principle is adopted here. Single concentrations provide a faster and less complex means of evaluating potential toxicity. The use of the U.S.E.P.A. values for one-hour average concentrations as maximum concentrations provides an additional safety factor of approximately 1.5, since the U.S.E.P.A. values allow for excursions in concentration 1.5 times the average over the period.

For chronic criteria, the U.S.E.P.A. (1985b) uses a four-day average concentration. This time period also represented a major departure from the earlier criteria drafts which had used a 30-day average. It was noted

earlier that the criteria for acute toxicity (measured by EPA as a one-hour average) were based on the 96 hour LC50 results from the literature. The chronic toxicity criteria are based on exposures to ammonia of typically 20 to 40 days; however, the measurement period specified is four days (96 hours). The argument which is put forward is that the short (four day) averaging period, as opposed to a longer period (e.g., 30 days) which is more reflective of the duration of the tests, is to preclude concentrations above the average from being present for too long. However, another way of preventing periods of higher concentration from affecting biota is to set limits on the concentration above the average which will be allowed. These limits can be expressed as a proportion of the average and as a proportion of samples taken. This method was adopted here for the chronic criteria concentrations.

In this report, the 30-day averaging period is used in conjunction with the following changes: concentrations between the 30-day average concentration and the maximum concentration should be limited to 20% of the samples taken in any 30-day sampling period (e.g., 1 sample in 5, 2 samples in 10 etc.), and no more than 20% of samples should exceed the 30-day average concentration by more than a factor of 1.5 times.

Table 6 gives the methods for calculating criteria concentrations for un-ionized ammonia for both maximum and 30-day averages. Tabulated values are shown as Tables 14 and 15.

4.5 Recommended Criteria

4.5.1 Freshwater Aquatic Life

(a) Nitrate

From the literature, there appears to be little evidence that any serious toxicity problems from nitrate are likely to be encountered by aquatic biota in surface water in British Columbia. From the limited data available, nitrate toxicity is not a concern with regards to fish (or other biota) unless concentrations reach 50 to 100 mg/L N. Concentrations even approaching these values have never been reported in B.C. Concentrations this high would be only expected to occur as a consequence of a major industrial discharge. They would likely be accompanied by high concentrations of other chemicals, particularly nitrite and ammonia, which would be of more concern. The proposed criteria are a maximum of 200 mg/L N (approximately half of the lowest 96 h LC50) and a 30-day average of 40 mg/L N (approximately one-tenth of the lowest 96h LC50, see section 4.3.1, and the no effect level of investigations reported on in section 4.3.1 (a)).

Table 6. Calculation of Criteria for Un-ionized Ammonia for Protection of Aquatic Life

<p>The following equations are modified from U.S.E.P.A. (1985b).</p> <p>Freshwater aquatic organisms should not be affected unacceptably if:</p> <p>(1) the concentration of un-ionized ammonia does not exceed at any time the numerical value given by $0.52/FT/FPH/2$ where:</p> $FT = 10^{0.03(20-T)}$ $FPH = 1 \quad \text{where } 8 \leq \text{pH} \leq 9$ $= \frac{1 + 10^{7.4-\text{pH}}}{1.25} \quad \text{where } 6.5 \leq \text{pH} < 8$ <p>The result is expressed as mg/L un-ionized NH_3. To convert to mg/L un-ionized $\text{NH}_3\text{-N}$, multiply by 0.822.</p> <p>(2) the 30-day average concentration of un-ionized ammonia is not exceeded. No more than 20% individual concentrations may exceed the mean by more than 150%. The 30-day average is given by $0.80/FT/FPH/\text{RATIO}$ where FPH is as above and</p> $\text{RATIO} = 16 \quad \text{where } 7.7 \leq \text{pH} < 9$ $= \frac{24 \cdot 10^{7.7-\text{pH}}}{1 + 10^{7.4-\text{pH}}} \quad \text{for } 6.5 \leq \text{pH} < 7.7$ $FT = 1.41 \quad \text{for } 15 \leq T \leq 20$ $= 10^{0.03(20-T)} \quad \text{for } 0 < T < 15$ <p>The result is expressed as mg/L un-ionized NH_3. To convert to mg/L un-ionized $\text{NH}_3\text{-N}$, multiply by 0.822.</p> <p>Criteria for un-ionized ammonia nitrogen are shown in Table 10 (maximum) and Table 11 (30-day average). Total ammonia criteria are more useful since they can be compared directly to analytical results. Table 8 and 13 are the criteria for total ammonia nitrogen (maximum and 30-day average respectively) which have been generated using the formulae for un-ionized ammonia and the relationship between un-ionized and total ammonia given by Emerson et al. (1975).</p>
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(b) Nitrite

Because of its much greater toxicity than nitrate, more investigation has been directed to nitrite. Although research on nitrite toxicity which has been done has not covered all aspects of the problem, there is enough information to formulate a criterion. Most research has been directed toward fish, so a large gap exists as to the effect of nitrite on aquatic invertebrates and other aquatic life. However, because of the importance of fish, particularly salmonids, and the understanding which does exist as to the levels of nitrite which may be harmful to native salmonids, the following criteria are proposed.

In streams (or lakes), it would appear that nitrite concentrations should not exceed 0.060 mg/L N in very soft water. Concentrations greater than this are likely to be directly toxic to salmonids. This value is intended to serve as a maximum criterion for short-term effects. However, toxicity is reduced by the presence of chloride as discussed previously, so there is an increasing scale of acceptable concentrations with corresponding chloride concentrations. For longer-term exposure of salmonids, a lower concentration is necessary. The recommended criterion for long-term exposure is 0.020 mg/L N in very soft water. This value is one which should not be exceeded as an average value over a 30-day period when at least five weekly samples have been obtained. This value is also modified when higher amounts of chloride are present. The table below gives the criteria for nitrite for British Columbia.

Table 7. Criteria for Nitrite for Protection of Freshwater Aquatic Life

chloride concentration (mg/L)	maximum nitrite concentration (mg/L as N)	30-day average (mg/L as N)
less than 2	0.060	0.020
2 - 4	0.120	0.040
- 6	0.180	0.060
6 - 8	0.240	0.080
8 - 10	0.300	0.100
greater than 10	0.600	0.200

The maximum concentration criteria (0.060 mg/L) is based on the bioassay results from the literature discussed in section 4.3.1. The U.S.E.P.A. (1976) used 0.060 as a short term (10 day) "no effect" level. It is approximately one-half of the lowest 96h LC50 to rainbow trout.

The 30-day average criterion is based primarily on three other sources which cite evidence of 0.020 mg/L as N as being the concentration at which some evidence of harm to fish occurs. These references are Russo and Thurson (1977), B.C. Research (1981), and Sigma (1983) and were discussed in Section 4.3.

As noted previously, nitrite toxicity can be reduced by the presence of chloride or calcium and also is affected by pH. There are insufficient data to quantify the effects of calcium and pH; however, for chloride Sigma (1983) and EIFAC (1984) have suggested that the allowable nitrite be linked to ambient chloride concentrations. Sigma suggested a ratio of 100:1 of chloride to nitrite N for chronic exposure: 0.020 mg/L NO₂-N where chloride concentrations were less than 2 mg/L. Thus, for example, for long-term exposure at a chloride concentration of 10 mg/L the criterion would be 0.100 mg/L. Maximum concentrations (acute exposure) above 0.060 mg/L should correspond to chloride concentration in a ratio of 30:1 chloride to nitrite N. The criteria proposed by EIFAC for salmonids are slightly different and specify an average nitrite N concentration of 0.01 mg/L at 1 mg/L chloride, 0.05 at 5 mg/L chloride, 0.09 at 10 mg/L chloride and 0.12 at 20 mg/L. Values for 95th percentile concentrations are also given based on a ratio of 1:3 between average and 95th percentile (e.g., 0.01 average and 0.03 for 95th percentile).

The C.C.R.E.M. (1986) Guidelines specify a maximum of 0.06 mg/L for all chloride concentrations. The recommended criteria vary with chloride concentration to reflect the marked influence of chloride on

nitrite toxicity, and average criteria have also been recommended to provide adequate protection to the salmonids prevalent in British Columbia, particularly at low chloride concentrations.

(c) Ammonia

Criteria to protect aquatic life against ammonia toxicity in British Columbia are given in Tables 12 and 13. Total ammonia is given first since evaluation of environmental conditions is simplified by keying on it rather than the un-ionized form. Un-ionized ammonia criteria are supplied in Tables 14 and 15 since they may be useful for comparative purposes.

Criteria Application

A protocol is required to calculate average concentrations for 30-day averages, and evaluate the averages against the criteria or objectives. For many water quality characteristics, calculating mean values is straightforward; however, for the calculation of a single criterion value of total ammonia, measurements of simultaneous pH and temperature are required. The calculation of a mean total ammonia and comparison to a criterion is proposed to be made as follows. A simplified sequence of the protocol is given in Table 12.

Table 8. Maximum Concentration of Total Ammonia Nitrogen for Protection of Aquatic Life (mg/L-N)

pH	Temp.										
	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
6.5	27.7	28.3	27.9	27.5	27.2	26.8	26.5	26.2	26.0	25.7	25.5
6.6	27.9	27.5	27.2	26.8	26.4	26.1	25.8	25.5	25.2	25.0	24.7
6.7	26.9	26.5	26.2	25.9	25.5	25.2	24.9	24.6	24.4	24.1	23.9
6.8	25.8	25.5	25.1	24.8	24.5	24.2	23.9	23.6	23.4	23.1	22.9
6.9	24.6	24.2	23.9	23.6	23.3	23.0	22.7	22.5	22.2	22.0	21.8
7.0	23.2	22.8	22.5	22.2	21.9	21.6	21.4	21.1	20.9	20.7	20.5
7.1	21.6	21.3	20.9	20.7	20.4	20.2	19.9	19.7	19.5	19.3	19.1
7.2	19.9	19.6	19.3	19.0	18.8	18.6	18.3	18.1	17.9	17.8	17.6
7.3	18.1	17.8	17.5	17.3	17.1	16.9	16.7	16.5	16.3	16.2	16.0
7.4	16.2	16	15.7	15.5	15.3	15.2	15.0	14.8	14.7	14.5	14.4
7.5	14.4	14.1	14	13.8	13.6	13.4	13.3	13.1	13.0	12.9	12.7
7.6	12.6	12.4	12.2	12.0	11.9	11.7	11.6	11.5	11.4	11.3	11.2
7.7	10.8	10.7	10.5	10.4	10.3	10.1	10.0	9.92	9.83	9.73	9.65
7.8	9.26	9.12	8.98	8.88	8.77	8.67	8.57	8.48	8.40	8.32	8.25
7.9	7.82	7.71	7.6	7.51	7.42	7.33	7.25	7.17	7.10	7.04	6.98
8.0	6.55	6.46	6.37	6.29	6.22	6.14	6.08	6.02	5.96	5.91	5.86
8.1	5.21	5.14	5.07	5.01	4.95	4.90	4.84	4.80	4.75	4.71	4.67
8.2	4.15	4.09	4.04	3.99	3.95	3.90	3.86	3.83	3.80	3.76	3.74
8.3	3.31	3.27	3.22	3.19	3.15	3.12	3.09	3.06	3.03	3.01	2.99
8.4	2.64	2.61	2.57	2.54	2.52	2.49	2.47	2.45	2.43	2.41	2.40
8.5	2.11	2.08	2.06	2.03	2.01	1.99	1.98	1.96	1.95	1.94	1.93
8.6	1.69	1.67	1.65	1.63	1.61	1.60	1.59	1.58	1.57	1.56	1.55
8.7	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.27	1.26	1.26	1.25
8.8	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.03	1.02	1.02	1.02
8.9	0.871	0.863	0.856	0.849	0.844	0.839	0.836	0.833	0.832	0.831	0.831
9.0	0.703	0.697	0.692	0.688	0.685	0.682	0.681	0.681	0.680	0.681	0.682

pH	11.0	12.0	13.0	14.0	15.0	16.0	17.0	18.0	19.0	20.0
6.5	25.2	25.0	24.8	24.6	24.5	24.3	24.2	24.0	23.9	23.8
6.6	24.5	24.3	24.1	23.9	23.8	24.6	23.5	23.3	23.3	23.2
6.7	23.7	23.5	23.3	23.1	23.0	22.8	22.7	22.6	22.5	22.4
6.8	22.7	22.5	22.3	22.2	22.0	21.9	21.8	21.7	21.6	21.5
6.9	21.6	21.4	21.3	21.1	21.0	20.8	20.7	20.6	20.5	20.4
7.0	20.3	20.2	20.0	19.9	19.7	19.6	19.5	19.4	19.3	19.2
7.1	18.9	18.8	18.7	18.5	18.4	18.3	18.2	18.1	18.0	17.9
7.2	17.4	17.3	17.2	17.1	16.9	16.8	16.8	16.7	16.6	16.5
7.3	15.9	15.7	15.6	15.5	15.4	15.3	15.2	15.2	15.1	15.1
7.4	14.2	14.1	14.0	13.9	13.9	13.8	13.7	13.6	13.6	13.5
7.5	12.6	12.5	12.4	12.4	12.3	12.2	12.2	12.1	12.1	12.0
7.6	11.1	11.0	10.9	10.8	10.8	10.7	10.7	10.6	10.6	10.5
7.7	9.57	9.50	9.43	9.37	9.31	9.26	9.22	9.81	9.15	9.12
7.8	8.18	8.12	8.07	8.02	7.97	7.93	7.90	7.87	7.84	7.82
7.9	6.92	6.88	6.83	6.79	6.75	6.72	6.69	6.67	6.65	6.64
8.0	5.81	5.78	5.74	5.71	5.68	5.66	5.64	5.62	5.61	5.60
8.1	4.64	4.61	4.59	4.56	4.54	4.53	4.51	4.50	4.49	4.49
8.2	3.71	3.69	3.67	3.65	3.64	3.63	3.62	3.61	3.61	3.61
8.3	2.97	2.96	2.94	2.93	2.92	2.92	2.91	2.91	2.91	2.91
8.4	2.38	2.37	2.36	2.36	2.35	2.35	2.35	2.35	2.35	2.36
8.5	1.92	1.91	1.91	1.90	1.90	1.90	1.90	1.90	1.91	1.92
8.6	1.55	1.54	1.54	1.54	1.54	1.54	1.55	1.55	1.56	1.57
8.7	1.25	1.25	1.25	1.25	1.25	1.26	1.26	1.27	1.28	1.29
8.8	1.02	1.02	1.02	1.02	1.03	1.03	1.04	1.05	1.06	1.07
8.9	0.832	0.834	0.838	0.842	0.847	0.853	0.861	0.870	0.880	0.891
9.0	0.684	0.688	0.692	0.698	0.704	0.711	0.720	0.729	0.740	0.752

Table 9. Average 30-day Concentration of Total Ammonia Nitrogen for Protection of Aquatic Life (mg/L-N)

pH	Temp.										
	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
6.5	2.08	2.05	2.02	1.99	1.97	1.94	1.92	1.90	1.88	1.86	1.84
6.6	2.08	2.05	2.02	1.99	1.97	1.94	1.92	1.90	1.88	1.86	1.84
6.7	2.08	2.05	2.02	1.99	1.97	1.94	1.92	1.90	1.88	1.86	1.84
6.8	2.08	2.05	2.02	1.99	1.96	1.94	1.92	1.90	1.88	1.86	1.84
6.9	2.08	2.05	2.02	1.99	1.97	1.94	1.92	1.90	1.88	1.86	1.84
7.0	2.08	2.05	2.02	1.99	1.97	1.94	1.92	1.90	1.88	1.86	1.84
7.1	2.08	2.05	2.02	1.99	1.97	1.94	1.92	1.90	1.88	1.86	1.84
7.2	2.08	2.05	2.02	1.99	1.96	1.95	1.92	1.90	1.88	1.86	1.85
7.3	2.08	2.05	2.02	1.99	1.97	1.95	1.92	1.90	1.88	1.86	1.85
7.4	2.08	2.05	2.02	2.00	1.97	1.95	1.92	1.90	1.88	1.87	1.85
7.5	2.08	2.05	2.02	2.00	1.97	1.95	1.93	1.91	1.88	1.87	1.85
7.6	2.09	2.05	2.03	2.00	1.97	1.95	1.93	1.91	1.89	1.87	1.85
7.7	2.09	2.05	2.03	2.00	1.98	1.95	1.93	1.91	1.89	1.87	1.86
7.8	1.78	1.75	1.73	1.71	1.69	1.67	1.65	1.63	1.62	1.60	1.59
7.9	1.50	1.48	1.46	1.44	1.43	1.41	1.39	1.38	1.36	1.35	1.34
8.0	1.26	1.24	1.23	1.21	1.20	1.18	1.17	1.16	1.15	1.14	1.13
8.1	1.00	0.989	0.976	0.963	0.952	0.942	0.932	0.922	0.914	0.906	0.899
8.2	0.799	0.788	0.111	0.768	0.759	0.751	0.743	0.736	0.730	0.724	0.718
8.3	0.636	0.628	0.620	0.613	0.606	0.599	0.594	0.588	0.583	0.579	0.575
8.4	0.508	0.501	0.495	0.489	0.484	0.479	0.475	0.471	0.467	0.464	0.461
8.5	0.405	0.400	0.396	0.381	0.387	0.384	0.380	0.377	0.375	0.372	0.370
8.6	0.324	0.320	0.317	0.313	0.310	0.308	0.305	0.303	0.301	0.300	0.298
8.7	0.260	0.257	0.254	0.251	0.249	0.247	0.212	0.244	0.243	0.242	0.241
8.8	0.208	0.206	0.204	0.202	0.201	0.200	0.198	0.197	0.197	0.196	0.196
8.9	0.168	0.166	0.165	0.163	0.162	0.161	0.161	0.160	0.160	0.160	0.160
9.0	0.135	0.134	0.133	0.132	0.132	0.131	0.131	0.131	0.131	0.131	0.131

pH	11.0	12.0	13.0	14.0	15.0	16.0	17.0	18.0	19.0	20.0
6.5	1.82	1.81	1.80	1.78	1.77	1.64	1.52	1.41	1.31	1.22
6.6	1.82	1.81	1.80	1.78	1.77	1.64	1.52	1.41	1.31	1.22
6.7	1.83	1.81	1.80	1.78	1.77	1.64	1.52	1.41	1.31	1.22
6.8	1.83	1.81	1.80	1.78	1.77	1.64	1.52	1.42	1.32	1.22
6.9	1.82	1.81	1.80	1.78	1.77	1.64	1.53	1.42	1.32	1.22
7.0	1.83	1.81	1.80	1.79	1.77	1.64	1.53	1.42	1.32	1.22
7.1	1.83	1.81	1.80	1.79	1.77	1.65	1.53	1.42	1.32	1.23
7.2	1.83	1.81	1.80	1.79	1.78	1.65	1.53	1.42	1.32	1.23
7.3	1.83	1.82	1.80	1.79	1.78	1.65	1.53	1.42	1.32	1.23
7.4	1.83	1.82	1.80	1.79	1.78	1.65	1.53	1.42	1.32	1.23
7.5	1.83	1.82	1.81	1.80	1.78	1.66	1.54	1.43	1.33	1.23
7.6	1.84	1.82	1.81	1.80	1.79	1.66	1.54	1.43	1.33	1.24
7.7	1.84	1.83	1.81	1.80	1.79	1.66	1.54	1.44	1.34	1.24
7.8	1.57	1.56	1.55	1.54	1.53	1.42	1.32	1.23	1.14	1.07
7.9	1.33	1.32	1.31	1.31	1.30	1.21	1.12	1.04	0.970	0.904
8.0	1.12	1.11	1.10	1.10	1.09	1.02	0.944	0.878	0.818	0.762
8.1	0.893	0.887	0.882	0.878	0.874	0.812	0.756	0.704	0.655	0.611
8.2	0.714	0.709	0.706	0.703	0.100	0.651	0.606	0.565	0.527	0.491
8.3	0.571	0.568	0.566	0.564	0.562	0.523	0.487	0.455	0.424	0.396
8.4	0.458	0.456	0.455	0.453	0.452	0.421	0.393	0.367	0.343	0.321
8.5	0.369	0.367	0.366	0.366	0.365	0.341	0.318	0.298	0.278	0.261
8.6	0.297	0.297	0.296	0.296	0.296	0.277	0.259	0.242	0.227	0.213
8.7	0.241	0.240	0.240	0.241	0.241	0.226	0.212	0.198	0.186	0.175
8.8	0.196	0.196	0.196	0.197	0.198	0.185	0.174	0.164	0.154	0.145
8.9	0.160	0.161	0.161	0.162	0.163	0.153	0.144	0.136	0.128	0.121
9.0	0.132	0.132	0.133	0.134	0.135	0.128	0.121	0.114	0.108	0.102

Table 10. Maximum Concentration of Un-ionized Ammonia Nitrogen, for Protection of Aquatic Life (mg/L-N)

pH	Temp.										
	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
6.5	0.008	0.008	0.009	0.009	0.010	0.011	0.011	0.015	0.013	0.014	0.015
6.6	0.009	0.010	0.011	0.011	0.012	0.013	0.014	0.015	0.016	0.017	0.018
6.7	0.011	0.012	0.013	0.014	0.015	0.016	0.017	0.018	0.020	0.021	0.022
6.8	0.014	0.015	0.016	0.017	0.018	0.019	0.020	0.022	0.023	0.025	0.027
6.9	0.016	0.017	0.019	0.020	0.021	0.023	0.024	0.026	0.028	0.030	0.032
7.0	0.019	0.021	0.022	0.024	0.025	0.021	0.029	0.031	0.033	0.036	0.038
7.1	0.022	0.024	0.026	0.028	0.030	0.032	0.034	0.036	0.039	0.042	0.045
7.2	0.026	0.028	0.030	0.032	0.034	0.037	0.039	0.042	0.045	0.048	0.052
7.3	0.030	0.032	0.034	0.037	0.039	0.042	0.045	0.085	0.052	0.055	0.060
7.4	0.034	0.036	0.039	0.041	0.044	0.047	0.051	0.054	0.058	0.063	0.067
7.5	0.037	0.040	0.043	0.046	0.049	0.053	0.057	0.061	0.065	0.010	0.075
7.6	0.041	0.044	0.047	0.051	0.054	0.058	0.062	0.067	0.071	0.077	0.082
7.7	0.045	0.048	0.051	0.055	0.059	0.063	0.068	0.072	0.078	0.083	0.089
7.8	0.048	0.052	0.055	0.059	0.063	0.068	0.073	0.078	0.083	0.089	0.096
7.9	0.051	0.055	0.059	0.063	0.067	0.072	0.077	0.083	0.089	0.095	0.102
8.0	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.1	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.2	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.3	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.4	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.5	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.6	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.7	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.8	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
8.9	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
9.0	0.054	0.058	0.062	0.066	0.071	0.076	0.081	0.087	0.093	0.100	0.107
pH	11.0	12.0	13.0	14.0	15.0	16.0	17.0	18.0	19.0	20.0	
6.5	0.016	0.017	0.018	0.020	0.021	0.023	0.024	0.026	0.028	0.030	
6.6	0.020	0.021	0.023	0.024	0.026	0.028	0.030	0.032	0.034	0.037	
6.7	0.024	0.026	0.027	0.029	0.032	0.034	0.036	0.039	0.041	0.044	
6.8	0.029	0.031	0.033	0.035	0.038	0.041	0.044	0.047	0.050	0.054	
6.9	0.034	0.037	0.040	0.042	0.046	0.049	0.052	0.056	0.060	0.064	
7.0	0.041	0.044	0.047	0.050	0.054	0.058	0.062	0.066	0.071	0.076	
7.1	0.048	0.051	0.055	0.059	0.063	0.068	0.073	0.078	0.083	0.089	
7.2	0.056	0.059	0.064	0.068	0.073	0.078	0.084	0.090	0.096	0.103	
7.3	0.064	0.068	0.073	0.078	0.084	0.090	0.096	0.103	0.110	0.118	
7.4	0.072	0.011	0.082	0.088	0.095	0.101	0.109	0.116	0.125	0.134	
7.5	0.080	0.086	0.092	0.098	0.105	0.113	0.121	0.130	0.139	0.149	
7.6	0.088	0.094	0.101	0.108	0.116	0.124	0.133	0.143	0.153	0.164	
7.7	0.096	0.102	0.110	0.118	0.126	0.135	0.145	0.155	0.166	0.178	
7.8	0.103	0.110	0.118	0.126	0.135	0.145	0.155	0.167	0.178	0.191	
7.9	0.109	0.117	0.125	0.134	0.144	0.154	0.165	0.177	0.189	0.203	
8.0	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	
8.1	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	
8.2	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	
8.3	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	
8.4	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	
8.5	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	
8.6	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	
8.7	0.115	0.123	0.132	0.141	0.151	00.162	0.174	0.186	0.200	0.214	
8.8	0.115	0.123	0.132	0.141	0.151	162.000	0.174	0.186	0.200	0.214	
8.9	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	
9.0	0.115	0.123	0.132	0.141	0.151	0.162	0.174	0.186	0.200	0.214	

Table 11. Average 30-day Concentration of Un-ionized Ammonia for Protection of Aquatic Life (mg/L-N)

pH	Temp.										
	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
6.5	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
6.6	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002
6.7	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.002	0.002	0.002
6.8	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
6.9	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
7.0	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003
7.1	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.004	0.004
7.2	0.002	0.003	0.003	0.003	0.003	0.004	0.004	0.004	0.004	0.005	0.006
7.3	0.003	0.003	0.004	0.004	0.004	0.005	0.005	0.006	0.006	0.007	0.007
7.4	0.004	0.005	0.005	0.005	0.005	0.006	0.007	0.007	0.007	0.008	0.008
7.5	0.006	0.006	0.007	0.007	0.007	0.007	0.008	0.009	0.009	0.010	0.011
7.6	0.007	0.007	0.008	0.008	0.008	0.010	0.011	0.011	0.011	0.012	0.014
7.7	0.008	0.009	0.010	0.011	0.011	0.012	0.013	0.014	0.014	0.016	0.017
7.8	0.009	0.010	0.011	0.012	0.012	0.013	0.014	0.015	0.015	0.017	0.018
7.9	0.010	0.011	0.012	0.012	0.012	0.014	0.015	0.016	0.016	0.018	0.020
8.0	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.1	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.2	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.3	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.4	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.5	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.6	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.7	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.8	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
8.9	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
9.0	0.011	0.011	0.012	0.012	0.012	0.015	0.016	0.016	0.016	0.019	0.021
pH	11.0	12.0	13.0	14.0	15.0	16.0	17.0	18.0	19.0	20.0	
6.5	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	
6.6	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	
6.7	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	
6.8	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.003	0.003	
6.9	0.003	0.003	0.003	0.003	0.004	0.004	0.004	0.004	0.004	0.004	
7.0	0.003	0.004	0.004	0.004	0.005	0.005	0.005	0.005	0.005	0.005	
7.1	0.005	0.005	0.005	0.006	0.006	0.006	0.006	0.006	0.006	0.006	
7.2	0.006	0.007	0.007	0.007	0.007	0.008	0.008	0.008	0.008	0.008	
7.3	0.007	0.008	0.008	0.009	0.010	0.010	0.010	0.010	0.010	0.010	
7.4	0.009	0.010	0.011	0.012	0.012	0.012	0.012	0.012	0.012	0.012	
7.5	0.012	0.012	0.013	0.014	0.016	0.015	0.015	0.015	0.015	0.015	
7.6	0.015	0.016	0.016	0.018	0.019	0.019	0.019	0.019	0.019	0.019	
7.7	0.018	0.020	0.021	0.023	0.024	0.024	0.024	0.024	0.024	0.024	
7.8	0.020	0.021	0.023	0.025	0.026	0.026	0.026	0.026	0.026	0.026	
7.9	0.021	0.022	0.024	0.025	0.028	0.028	0.028	0.028	0.028	0.028	
8.0	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.1	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.2	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.3	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.4	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.5	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.6	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.7	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.8	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
8.9	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	
9.0	0.022	0.024	0.025	0.027	0.029	0.029	0.029	0.029	0.029	0.029	

Table 12. Comparison of Ambient Concentrations to Criteria

calculate average 30-day criterion value (lab pH and field temperature)	for each pH (lab) and temperature (field) of individual samples, locate 30-day criterion values
↓	↓
calculate mean field concentration	compare individual sample results to corresponding criteria
↓	↓
Does mean field concentration exceed mean criterion?	No more than 20% of individual sample results should exceed the criterion by 1.5 times (150%)

When the results of the water chemistry analysis are compiled, the total ammonia as well as the field temperature and laboratory pH* are used. The procedure for checking results against criteria uses two steps. First, the mean ammonia value for field results for the 30-day period is determined as an average of all the samples. It is then compared to the mean criteria which is an average of the values from the Table obtained by using the temperature and pH of the individual field samples. Second, a comparison is made between the individual field values and the individual criteria to determine if more than 20% of the individual results exceed 1.5 times the average criterion value.

The comparison of individual field results to individual criteria is done to ensure that an excessive number of high concentrations does not occur in any sampling set. The occurrence of some high concentrations with some low concentrations could result in the average criteria for the period being met; however, the occurrence of high concentrations can result in toxicity if concentrations were high enough and persisted long enough. What is suggested here is that only 20% or less of individual samples should be allowed to exceed a level of 1.5 times the criterion value. For example, if this restriction were not included, in a 10 sample set many of the samples (even a majority) could exceed 150% of the criterion value, as long as the average of the set was below the average criterion value. However, with this proposal only two samples could exceed 150% of the criterion value. More than two values exceeding 150% of the average criterion

*laboratory pH is recommended over the field pH, since it corresponds with the time the analysis is done. Field pH, while seemingly a simple procedure, is very difficult to measure accurately and consistently. Field pH can be used if there is strong assurance of the accuracy of the measurement and if some evidence exists that the pH changes between the sample collection and sample analysis.

would mean that the criteria were not met even if the averaged measured concentration were less than the average criterion value.

The comparison of field sample results to criteria/objective concentrations could also be made with un-ionized ammonia as the criterion or objective value. Averaging field results values and comparing these to the appropriate table values is done in the same manner as above, except for the extra step of calculating un-ionized ammonia using for instance Emerson et al. (1975). Virtually all toxicity data are reported as un-ionized ammonia so these tables provide a means of relating to the existing literature on ammonia toxicity.

Two examples of evaluating field data against criteria are given as illustration in Table 13.

4.5.2 Marine Aquatic Life

The criteria which are proposed apply to fish since the data they were derived from originate almost exclusively from bioassay work on fish species. Effects on other groups of organisms are relatively poorly documented.

(a) Nitrate

The little information which exists indicates that nitrate has a very low toxicity to marine fish (>500 mg/L N for sublethal effects). In the absence of detailed information and the very low apparent risk, no criterion is recommended.

(b) Nitrite

The toxicity of nitrite in seawater has not received very much attention from researchers. The investigations which have been done appear to indicate that the toxicity of nitrite, which is very high in freshwater, is greatly reduced in seawater. This may be due to the reduction in toxicity caused by chloride and calcium. Toxic concentrations may be two orders of magnitude higher than in freshwater. Thus, it would appear that at present the apparent risk associated with nitrite in seawater is very low. Only where a very large discharge is made to a confined marine system is a problem likely to occur. Consequently, because of the lack of information and the low apparent risk, no marine nitrite criteria are recommended.

Table 13. Two Examples of Checking Ammonia Criteria

Example 1. Five samples taken over 30-day period				
pH	temperature °C	measured total ammonia N	30-d criterion	ratio of measured NH ₃ to criterion
7.9	14	1.21	1.31	0.92
8.1	16	1.32	0.812	1.63
8.0	17	0.93	0.944	0.96
8.0	15	0.80	1.09	0.73
8.1	15	<u>0.71</u>	<u>0.874</u>	0.81
		0.994 (mean)	1.006 (mean of above)	

- measured average concentration (0.994) is less than mean criterion (1.006) - only one measured value (1.32) is greater than 150% of criterion for that pH and temperature.
- conclusion: average ambient concentration is considered within criterion.

Example 2.

pH	temperature °C	measured total ammonia mg/L	30-d criterion mg/L	ratio of measured NH ₃ to criterion
7.1	18	0.24	1.418	0.17
7.2	17	2.30	1.529	1.50
7.2	18	2.21	1.420	1.56
7.2	17	2.51	1.529	1.64
7.4	16	0.41	1.651	0.08
		1.48 (mean)	1.509 (mean of above)	

- measured average concentration (1.48) is less than mean criterion (1.509)
- but three measured values exceed 150% of criteria for same pH and temperature
- conclusion: the criterion is considered to be exceeded.

(c) Ammonia

Ammonia does pose the potential for toxicity at relatively low concentrations in seawater. Very little work has been done on the toxicity of ammonia to the many groups of marine invertebrates. However, some evaluation has been done on the toxicity of un-ionized ammonia to several fish species (Haywood 1983). On the basis of this work, a criterion of 0,041 mg/L N of un-ionized ammonia or 2.5 mg/L total ammonia was proposed as a maximum acceptable concentration. The U.S. Environmental Protection Agency (1973) felt a concentration of 0.01 mg/L un-ionized ammonia presented minimal risk to marine biota and concentrations of greater than 0.11 mg/L presented a hazard, For British Columbia, a criterion of 2.5 mg/L total ammonia N is proposed as a maximum and a criterion of 1.0 mg/L total ammonia is proposed for a long term average (30-d). Because the criteria are based on a limited amount of technical data, and since no other agencies have set marine criteria for ammonia, these criteria may be subject to early revision as more information becomes available. The proposed criteria will provide at least a point of reference for the wide range of concentrations which might be encountered. The absence of criteria would allow no means of even roughly evaluating a situation without reference to the literature and time-consuming searching. For calculating un-ionized ammonia from total ammonia, temperature, pH, and salinity the tables in Bower and Bidwell (1978) should be referred to.

The U.S. Environmental Protection Agency (1985b) concluded that insufficient data existed to set marine criteria for aquatic life; however, it would seem advantageous to make a first step by proposing values. Haywood (1983) felt there was justification for suggesting criteria for marine fish, His evaluation of the data and his criterion of 0.050 mg/L un-ionized ammonia (as NH₃) was used as the basis of the criterion suggested here. The values at least can be used as a basis for future work. There are no CCREM Guidelines for marine aquatic life. The single concentration type criteria are used because insufficient information is available to provide more detailed criteria such as has been prepared for ammonia in fresh water.

4.5.3 Estuarine Aquatic Life

Virtually no data exist for nitrogen toxicity in estuarine waters and consequently no criteria are proposed. The more stringent of the freshwater and marine criteria should be used for estuaries.

4.5.4 Analytical Methods

There are several considerations to be made regarding analysis of samples which contain the forms of nitrogen discussed here. The actual analytical methods do not appear to be a problem since there are several methods which have gained general acceptance and are used routinely by water chemistry laboratories (see American Public Health Association et al. 1980; McQuaker 1976; Stainton et al. 1977; Stephens and Brandstaetter 1983).

The different analytical methods and laboratory adaptations of them do show variance in the detection limits of different fractions. The lowest criterion for nitrate is sufficiently high (10 mg/L) so as not to present any problems with detection limits. For nitrite and ammonia, levels of toxicity can be closer to the typical detection limits used by many laboratories, but in most cases no problems exist and there is no need for development of new methods to allow lower detection limits. For nitrite, the long-term criterion for freshwater aquatic life is 0.020 mg/L N. The Environmental Laboratory (B.C. Ministry of Environment and Parks) detection limit for nitrite is 0.005 mg/L and many other laboratories have routine detection limits which are lower (e.g., 0.001 mg/L, Dept. of Fisheries and Oceans; Stephens and Brandstaetter 1983). For ammonia, the lowest criterion is 0.1 mg/L total ammonia (long-term freshwater aquatic life, pH 9). The routine detection limit for the B.C. Environmental Laboratory is 0.005 mg/L total ammonia nitrogen and this provides an adequate detection limit.

A second consideration, and a more important one, is sampling and handling procedures which minimize any change in concentration between the time of sampling and the time of analysis. Because transformations between nitrate, nitrite, dissolved ammonia, organic nitrogen, and ammonia gas can occur, it is imperative that these transformations be minimized if correct interpretations of ambient conditions are to be made. Since most of the changes from one form to another are a consequence of bacteriological metabolism, one means of maintaining concentrations in the sample is to field-filter with an appropriate membrane filter (e.g., 0.45 µm) as soon as possible (<2 h from time of sampling). In conveying the sample between the sampling location and the laboratory, the standard handling procedures of cold storage (4°C) and darkness should be observed. Freezing the sample can also reduce the transformations taking place. The B.C. Environmental Lab requires analysis within 72 hours of sampling and recommends cool, dark handling or freezing samples for storage and shipping. Standard Methods (American Public Health Association et al. 1985) recommends prompt analysis or acidification to pH 1.5 - 2.0 with sulphuric acid for both ammonia and nitrate. For nitrate, refrigeration or freezing is recommended. Preservatives are also suggested for nitrate and nitrite to prevent biological conversion; however, the recommended chemical (40 mg mercuric chloride per litre) has the disadvantage of being hazardous to health as well as contaminating samples to be analysed for mercury.

A technique for preserving nitrite samples in particular seems to be an outstanding need.

In evaluating a situation in regard to the 30-day criteria, it is important that sufficient samples be obtained to make calculation of an average statistically useful.

5. OTHER WATER USE CATEGORIES

There are other water use categories for which less information exists; for these, criteria are more difficult to set. The information with regard to these water uses is reviewed below.

5.1 Agriculture

No criteria have been established for ammonia. However, for nitrate (or nitrate plus nitrite) several agencies have established guidelines (Table 14).

Table 14. Criteria for Nitrate plus Nitrite (as N), for Agriculture

Criteria Statements	Criteria Values	Jurisdictions
(i) Irrigation		
Acceptable limit = 20-30 mg/L depending on the classification.	20-30 mg/L	Manitoba (1979)
(ii) Livestock		
Recommended that nitrate plus nitrites < 100 ppm in livestock drinking water	100 mg/L	U.S.E.P.A. (1973)
Permissible level for livestock	20 mg/L	Ontario (1973)
Desirable level for livestock ≤ 10 mg/L	10 mg/L	Ontario (1973)
Acceptable limit ≤ 100 mg/L	100 mg/L	Manitoba (1979)
Acceptable limit ≤ 100 mg/L	100 mg/L	Hart (1974)

Table adopted from Singleton and Clark (1983)

Criteria have also been established by some agencies for nitrite in livestock watering sources (Table 15).

Table 15. Criteria for Nitrite (as N) for Agriculture

Criteria Statements	Criteria Values	Jurisdictions
Recommended level 10 ppm in livestock drinking water	10 mg/L	U.S.E.P.A. (1973)
Acceptable limit 10 mg/L 95th and 99th percentiles for	10 mg/L	Manitoba (1979)
nitrite in water for livestock are 8.5 and 10 mg/L, respectively.	8.5 mg/L 10 mg/L	Anglian Water Authority (1982)

For waters used as a source of livestock drinking water, it would appear that there is justification for establishing criteria for both nitrate and nitrite. The recommended criteria for livestock watering are a maximum of 100 mg/L nitrate-N or nitrate plus nitrite-N and a maximum of 10 mg/L nitrite-N. Some agencies appear to have specified lower concentrations; however, the information on the effects of high nitrate or nitrite on farm animals is limited and the 100/10 mg/L criteria for nitrate/nitrite are proposed.

Similarly, there appears to be only one nitrate criterion set for irrigation water by another jurisdiction. The value suggested is <20-30 mg/L N (Manitoba 1979) which would be extremely unusual to encounter in B.C surface waters. The irrigation criterion is also dependent on the soil type, the irrigation rate, and other factors. In light of the lack of knowledge as well as these high levels, no criteria are suggested for nitrate, nitrite, or ammonia for irrigation. Several spray irrigation projects presently irrigate with municipal waste water (Osoyoos, Cranbrook, Vernon). The nitrate concentrations are greater than 20 mg/L N and there are very high levels of nitrite and ammonia in comparison to any surface water, without any apparent adverse effect on soils or crops. The problem of nitrogen content in irrigation water appears to be a very minor one.

5.2 Wildlife

Only one jurisdiction has specified criteria for nitrogen for wildlife. Manitoba (1979) gives a maximum acceptable concentration of nitrate plus nitrite of 100 mg/L N and 10 mg/L N of nitrite-N. These are the same criteria that Manitoba has specified for livestock watering, and as outlined in Section 5.1.

The most appropriate criteria would appear to be the same as were proposed for drinking water for livestock. Thus, for nitrate or nitrate plus nitrite, and for nitrite the criteria recommended here for wildlife are 100 mg/L N nitrate and/or 10 mg/L N nitrite, respectively.

6. RESEARCH AND DEVELOPMENT NEEDS

Much of the basis for water quality criteria is laboratory toxicity work. The major problem with this approach is the tenuous link between the laboratory toxicity levels and the toxicity which occurs in nature. There has been little effort to calibrate laboratory results with field results. Laboratory studies attempt to control as many of the environmental characteristics as possible to gain an understanding of concentration - toxicity relationships. The weakness of this is that, in the field, a species will be faced with a suite of biotic and abiotic variables which may substantially change the toxicity (Brinkhurst 1985). To evaluate the data on which the criteria are based, field toxicity calibration is necessary and should be a priority for future research.

Additional investigation of the mechanism of toxicity of un-ionized ammonia and the factors which govern the toxicity of ammonia is required, especially in saltwater.

Additional investigation of the toxicity of ammonia to saltwater invertebrates is needed.

Additional investigation of the chronic/sublethal effects of nitrate and nitrite to aquatic organisms is needed,

The effects of the combined toxicity of ammonia and nitrite, and their toxicity in the presence of other toxicants require further investigation.

There should be additional work done to describe the toxicity of nitrate, nitrite and ammonia to early life stages of fish such as eggs and newly emerged fry.

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