

# Cyanide 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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## 1. INTRODUCTION

The toxicity of cyanide to humans and to other organisms is well known and, because of the occurrence of cyanide in the aquatic environment, has become a concern to the water-use categories addressed in this document. These water-use categories include drinking water, aquatic life, wildlife, livestock watering, irrigation, recreation and aesthetics, and industrial water supplies. Where applicable, or where sufficient information exists, criteria are recommended to protect water uses from cyanide originating from anthropogenic sources. Standards, objectives, criteria, and accompanying rationales from other jurisdictions are reviewed and their suitability for British Columbia waters are considered.

Because of the extensive amount of literature on cyanide, a large portion of the information used in this document has been extracted from a few recent reviews documenting the numerous toxicological studies pertaining to this contaminant. The purpose of this document was not to re-review the extensive amount of original literature already addressed in recent publications, but instead, to focus on the most applicable information which could be used to develop defensible criteria for British Columbia waters.

## 2. FORMS AND TRANSFORMATIONS IN THE ENVIRONMENT

### 2.1 Chemical Groups

Cyanide is a chemical group composed of nitrogen triply bonded to carbon ( $-C\equiv N$ ), and exists in a variety of inorganic and organic forms in the aquatic environment. The form of cyanide in water is largely dependent upon pH, but is also influenced by temperature, dissolved oxygen, salinity, and the presence of other ions (Inland Waters Directorate, 1979). Some of the more common forms of cyanide which are known to exist in the aquatic environment are described below.

- (i) CYANIDE ION refers to the single free anion  $CN^-$ , which chemically behaves similarly to the halide ions ( $Cl^-$ ,  $Fl^-$ ,  $Br^-$ ,  $I^-$ ).
- (ii) MOLECULAR CYANIDE refers to cyanide in the form of the uncharged, undissociated molecule, HCN. Its other common names are molecular HCN, hydrocyanic acid, hydrogen cyanide, and prussic acid. Under normal temperature and pressure, HCN is a gas (boiling point of  $26^\circ C$ ). HCN is infinitely soluble in water but, because of its volatility, tends to vapourize into the atmosphere.
- (iii) FREE CYANIDE refers to the sum of molecular cyanide and the cyanide ion ( $HCN+CN^-$ ) in aqueous solution. The equilibrium between the two forms is dependent mainly upon pH and, to a lesser degree, upon temperature. The equilibrium shifts in favour of HCN as the pH or temperature of the aqueous media decreases according to the equation,  $CN^- + H_2O = HCN + OH^-$ . At  $10^\circ C$  and pH 8.5, the proportion of HCN is 92%, and increases to 99% at pH 6.0. At  $4^\circ C$  and pH 8.5, the proportion of HCN is 94%. Therefore, under normal environmental conditions, free cyanide in natural waters would be mostly in the form of HCN.

SIMPLE CYANIDES refer to compounds represented by the formula  $A(CN)_x$  where A is an alkali or a metal (e.g.  $NaCN$ ,  $Pb(CN)_2$  and  $Zn(CN)_2$ ) and x depicts the number of attached cyano groups (APHA, 1980).

The alkali cyanides such as potassium cyanide (KCN) and sodium cyanide (NaCN) are very soluble in water and readily hydrolyze to form HCN under normal environmental conditions.

- (iv) COMPLEX CYANIDES are also referred to as metalocyanides due to the complexing of cyanide with metals such as nickel, silver, copper, cobalt, iron, mercury, zinc and cadmium. The complex cyanides normally can be represented by the formula  $A_yM(CN)_x$  (e.g.,  $K_3Fe(CN)_6$ ), where A represents are

alkali or metal present  $y$  times,  $M$  represents the heavy metal, and  $x$  the number of CN groups;  $x$  is equal to the valence of  $A$  taken  $y$  times plus that of the heavy metal (APHA, 1980). Initial dissociation of these alkali-metallic, complex cyanides yields an anion that is the radical  $M(CN)_x^{y-}$ . This may dissociate to some extent, depending on several factors, with the liberation of  $CN^-$  and consequent formation of HCN (APHA, 1980). The rate of formation of HCN from these complexes is largely dependent upon pH. In the case of ferro- and ferricyanide complexes, the cyanide ion is liberated by exposure of the solution to visible or ultraviolet light, and tends towards the formation of HCN at lower pH. Ultraviolet light also accelerates the dissociation of the cyanide ion from chromium and cobalt complexes in water (Leduc et al., 1982).

- (v) ORGANOCYANIDES are also called nitriles and refer to organic compounds containing one or more  $CN$  groups. Some organocyanides such as the cyanohydrins can decompose to form HCN, while others such as acrylonitrile and acetonitrile can be degraded to their respective acids (acrylic and acetic acid) and ammonia by microorganisms. Cyanogenic compounds produced naturally by some plants can also be decomposed by microorganisms to form HCN (see Section 3.1).
- (vi) CYANATES are compounds which contain the  $OCN^-$  group and are formed when a strong oxidizing agent such as  $Cl_2$  or  $Br_2$  is introduced to an alkaline solution containing free cyanide or some simple cyanides. Alkaline chlorination is often used to treat wastewaters contaminated with cyanide, cyanide being far less toxic than HCN. Cyanates eventually can be oxidized to carbon dioxide and nitrogen gas if free chlorine is present.
- (vii) THIOCYANATES are compounds which contain the  $SCN^-$  group; these compounds form complexes with numerous elements. Thiocyanate is considerably less toxic than HCN. During chronic exposure of humans to cyanide, thiocyanate is formed by enzymatic activity in the body and excreted in the urine.

## 2.2 Analytical Techniques Performed at the B.C. Provincial Environmental Laboratory

### (A) Strong-Acid Dissociable Cyanide

Definition - this method determines the so-called "total" cyanide which includes the cyanide ion, HCN, simple cyanides, and complex cyanides such as ferri- and ferrocyanide after hydrochloric acid-hydroxylamine hydrochloride digestion-distillation. (Note: this method does not measure thiocyanate, cyanate, and cobalt- and gold-cyanide complexes).

Sample Preparation - unfiltered and field preserved to pH 12 with 10 N NaOH.

Analytical Methods - reflux-distillation of the sample in the presence of hydrochloric acid and hydroxylamine hydrochloride converts simple and most complex cyanides such as ferri- and ferrocyanide into HCN (known exceptions are cobalt- and gold-cyanide complexes) which is absorbed in a solution of sodium hydroxide. The resulting cyanide in the sodium hydroxide solution is then converted to cyanogen chloride (CNCl) by reaction with chloramine-T at pH less than 8. The CNCl, on addition of pyridine-barbituric acid reagent, forms a red-blue complex which is measured colourimetrically at 578 nm.

Minimum Detectable Concentration - 5  $\mu\text{g/L}$

Interferences - Oxidizing agents such as chlorine may oxidize the cyanides during storage and sample analysis. If oxidizing agents are present, add sodium arsenite (0.1 g/L) or oxalic acid (2 g/L) until a potassium iodide starch test gives no response (no blue colour formation).

- Sulphides distill over into the absorbing solution and adversely affect the colour development. Sulphides may also convert the cyanide to thiocyanate during storage, especially at the high pH used for preservation.

(a) High concentrations of sulphide should be removed as soon as possible after sample collection and prior to sample distillation. Sulphide is removed by treating the alkaline sample with small increments of powdered lead carbonate. Black lead sulphide precipitates in samples containing sulphides. Repeat this operation until precipitation is complete. Filter immediately.

(b) Low concentrations of sulphide may be removed during sample distillation by placing a glass wool plug saturated with lead acetate in the tube leading to the absorbing solution. If carry-over of sulphide occurs into the absorbing solution, add cadmium nitrate solution to precipitate the sulphide. Filter immediately.

#### (B) Weak-Acid Dissociable Cyanide

Definition - this method measures free, simple, and weak-acid dissociable metal cyanides such as zinc- and cadmium-cyanide complexes, but does not measure the more stable cyanide complexes such as ferri- and ferrocyanide, cobalt- or gold-cyanide complexes, thiocyanate, or cyanate.

Sample Preparation - unfiltered and field preserved to pH 12 with 10 N NaOH.

Analytical Methods - distillation of the sample in the presence of acetate buffer (pH 4.5) converts free, simple, and weak-acid dissociable cyanides into HCN, which is then absorbed into a solution of ammoniacal nickel chloride. The resulting tetracyanonickelate complex is then measured colourimetrically at 267 nm and 284 nm.

Minimum Detectable Concentration - 5 µg/L.

Interferences - there are no known interferences.

#### (C) Thiocyanate

Sample Preparation - Unpreserved, kept cool, and Laboratory filtered.

Analytical Method - ion chromatography. Minimum Detectable Concentration - 100 µg/L

Interferences - there are no known interferences.

#### (D) Cyanate

Sample Preparation - Unpreserved, kept cool, and Laboratory filtered.

Analytical Method - ion chromatography. Minimum Detectable Concentration - 100 µg/L

Interferences - there are no known interferences.

### **2.3 Analytical Techniques Performed at The Federal Environmental Protection Service Chemistry Laboratory of Environment Canada**

#### (A) Total Cyanide

Definition - interpreted to mean “total recoverable cyanide”, and is identical to the “strong-acid dissociable cyanide” method used at the B.C. Provincial Environmental Laboratory (Section 2.2(A)), except that the minimum detectable concentration is 20 µg/L.

#### (B) Weak-Acid Dissociable Cyanide



Definition - identical to the “weak-acid dissociable cyanide” method used at the B.C. Provincial Environmental Laboratory (Section 2.2(B)), except that the minimum detectable concentration is 20 µg/L.

## **2.4 Analytical Techniques Performed at the Federal Inland Waters Directorate Water Quality Laboratory of Environmental Canada**

### **(A) Complex Cyanides**

Definition - this method essentially measures total cyanide which includes the cyanide ion, HCN, simple cyanides, and complex cyanides such as ferri- and ferrocyanide, and cobalt-cyanide complexes. This method also measures thiocyanate, but it does not measure cyanate.

Sample Preparation - field preserved by the addition of sufficient NaOH to raise the pH to 11.

Analytical Methods - Complex cyanides are converted to hydrocyanic acid (HCN) by irradiation with ultraviolet light. After irradiation the sample is distilled from a phosphoric acid medium into a phosphate buffer solution (pH 5.2). The cyanide in the buffer solution is converted to cyanogen chloride (CNCl) by reaction with chloramine-T. The CNCl then forms a red complex on addition of the pyridine-barbituric acid reagent and the absorbance is measured at 580 nm.

Minimum Detectable Concentration - 0.5 µg/L.

Interferences - Oxidizing materials, such as oxygen, ozone, chlorine, etc., when present may oxidize both the free and some complex cyanides resulting in lower cyanide values.

- Sulphides give a positive interference and should be removed before analysis.
- Some organic cyanide compounds such as nitriles are decomposed under test conditions.
- Other interfering substances are removed during the distillation step.

### **(B) Simple Cyanides**

Definition - this method may also be termed weak acid dissociable cyanide as it measures free, simple, and weak-acid dissociable metal cyanides such as zinc- and cadmium-cyanide complexes, but does not measure the more stable cyanide complexes such as ferri- and ferrocyanide, cobalt-, or gold-cyanide complexes, thiocyanate, or cyanate.

Sample Preparation - field preserved by the addition of sufficient NaOH to raise the pH to 11.

Analytical Methods - the method is the same as that used for complex cyanides except that the ultraviolet irradiation step is omitted.

Minimum Detectable Concentration - 0.5 µg/L.

Interferences - as noted for the “complex cyanides” analytical technique.

## **3. OCCURRENCE IN THE ENVIRONMENT**

### **3.1 Natural Sources**

Cyanide is ubiquitous in the environment and can be produced naturally by many species of plants, as well as by some species of fungi, algae and bacteria. Over 1 000 species of plants are able to synthesize cyanogenic glycosides such as amygdalin, which is found in the seeds of cherries, plums, peaches, apricots,

apples, and pears (U.S. EPA, 1980). High levels of cyanide are also found in the edible portion of some plants such as the bitter almond (2.5 mg/g), some lima beans (3.0 mg/g) and the cassava (1.2 mg/g) (Montgomery, 1969, as cited in Health and Welfare, Canada, 1978b). Decomposition of cyanogenic glycosides by microorganisms can liberate free cyanide to the environment. According to Leduc et al. (1982), the ecological significance of these naturally occurring organocyanides as a source of cyanide to surface waters is not known. However, it is believed that naturally occurring cyanides are not dangerous to man, except in cases of unusual diet, for example, eating large numbers of apricot seeds.

### 3.2 Anthropogenic Sources

Waste effluents from several industrial processes, which include gas works, coke ovens, gas scrubbing in steel plants, aluminum smelters, metal cleaning, electroplating, chemical plants, and petroleum refineries, may provide significant contributions of cyanide to surface waters. Another major source of cyanide to the aquatic environment in British Columbia is the gold mining and milling industry where cyanide is frequently used to extract gold from the ore. A large number of dead or dying hatchery steelhead (*Salmo gairdneri*) smolts were documented in spring, 1982, when cyanide-contaminated effluent was discharged from a gold mine tailings pond to the Coquihalla River via Ladner Creek near Hope, B.C. (Ptolmey, 1985). The actual number of fish killed is not known. This example demonstrates the impact that cyanide-contaminated wastes can have on aquatic biota.

### 3.3 Natural Levels in Water and Sediment

Although cyanide is ubiquitous in the environment, cyanide compounds are generally found in natural waters in only small amounts (Inland Waters Directorate, 1979). The persistence of cyanide in water is highly variable, and is dependent upon the chemical form, the concentration, and the nature of other constituents in the water (U.S. EPA, 1976). For example, in waters where HCN is formed from compounds containing cyanide, the HCN, because of its volatility, tends to escape from the water column and into the atmosphere. In addition, low concentrations of cyanide can be readily degraded by microorganisms and by animal metabolism (U.S. EPA, 1980). This biodegradation can prevent the accumulation of cyanide in the water column and in the sediment.

Cyanide in freshwater, expressed as total cyanide, has been measured in the rural and wilderness areas of Canada and Germany. Although background levels reported in the literature for Canada are surprisingly high, with values of 30 to 60 µg/L not uncommon, it may well be that these values reflect poor analytical methodology rather than the environmental levels. The highest levels were recorded during low flow in small to medium-sized rivers, and during or after freshet in large rivers (Prairie Provinces Water Board, 1978, as cited in Leduc et al., 1982). In Germany, mean annual levels of total cyanide were 3 and 20 µg/L for rural and industrial watersheds, respectively. For wilderness areas, total cyanide concentrations averaged between 0.7 and 2 µg/L, with the highest concentration (5 µg/L) occurring in fall and winter. In large rivers, the highest concentrations occurred in summer (Krutz, 1981, as cited in Leduc et al., 1982). A survey of 2 595 water samples in the United States found no samples exceeding a cyanide concentration of 8 µg/L (U.S. EPA, 1980).

For British Columbia, Clark (1978) prepared a statistical overview of water quality analyses for the years 1965 to 1976. For strong-acid dissociable cyanide, the 90th percentile for stream (1 849 measurements), lake (361 measurements), and marine (22 measurements) waters were 10, 40, and < 10 µg/L, respectively. The minimum detectable concentration (MDC) for cyanide during this period was 10 µg/L. These levels are not necessarily representative of background levels in British Columbia because cyanide is usually only monitored at locations likely to be contaminated by cyanide-containing wastes. Drinnan and Clark (1980)

reported that cyanide in all 155 measurements taken from the Lower Fraser River between 1970 and 1978 were below the MDC of 10 µg/L. A few samples had a MDC of 100 µg/L.

Samples collected by the Environmental Protection Service in watersheds unaffected by cyanide releases generally were less than the detection limit of 30 µg/L. Even in the streams draining the Endako Mine site, where cyanide is used in the process, all samples were less than the detection limit except for one seepage stream from the toe of the tailings dam. Samples collected in Ladner Creek and the Coquihalla River above Carolin Mines contained usually less than 0.5 µg/L using the Inland Waters Directorate's ultraviolet irradiation analytical technique (Section 2.4(A)) for complex cyanides (Environmental Protection Service, 1985).

Leduc et al. (1982) state that because of different or improper analytical techniques used to measure total cyanide, and because of different methods used to record and interpret data, Canadian background levels of total cyanide cannot be established at this time. Furthermore, the toxicological significance of these levels to aquatic biota cannot be determined because the chemical species of cyanide are not known.

According to Leduc et al. (1982), no data pertaining to the action of free cyanide in the bottom sediments of natural aquatic ecosystems were available. Murmann and Koutz (1972, as cited in Leduc et al., 1982) demonstrated that the cyanide ion is only weakly adsorbed and retained in soils. Tests indicated that cyanide salts introduced to soils were either biologically degraded to form nitrates, or complexed by trace metals.

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

##### 4.1 Effects on Algae

Few data were available regarding the effects of cyanide on algae. According to the U.S. EPA (1973), algae appear to be more tolerant than animals to the effects of cyanide, but recent evidence indicates that sensitivity to cyanide appears to vary depending upon the algal species tested.

##### 4.1.1 *Freshwater Algae*

The U.S. EPA (1973) reported some unpublished data on the toxicity of cyanide to two species of diatoms at different temperatures in hard and soft water. The toxicity was found to increase with increased temperature for *Nitzschia linearis* in soft water, but in hard water an increase in toxicity to *Navicula seminulum* with increased temperature was not obvious, as indicated by the cyanide concentration (as CN) which caused a 50 percent reduction in population growth as follows:

<i>Nitzschia linearis</i> in soft water (44 mg/L Ca+Mg as CaCO <sub>3</sub> )		<i>Navicula seminulum</i> in hard water (170 mg/L Ca+Mg as CaCO <sub>3</sub> )	
CN (µg/L)	Temperature (°C)	CN (µg/L)	Temperature (°C)
920	22.2	360	22.2
300	27.7	490	27.7
280	30.0	420	30.0

Fitzgerald et al. (1952, as cited in U.S. EPA, 1985) reported a 90 percent mortality of the blue-green alga *Microcystis aeruginosa* when exposed to a free cyanide concentration of 7 790 µg/L, but the U.S. EPA (1985) reported incipient inhibition of cell propagation for the same species by a free cyanide

concentration (as CN) of 75 µg/L. The U.S. EPA (1985) also reported incipient inhibition of cell propagation for the green alga *Scenedesmus quadricauda* exposed to a free cyanide concentration (as CN) of 30 µg/L.

#### **4.1.2 Marine Algae**

The U.S. EPA (1985) reported the results of tests performed on three marine species exposed to cyanide. One study (Webster and Hackett, 1965, as cited in U.S. EPA, 1985) found that respiration of the species *Prototheca zopfii* was inhibited by a free cyanide concentration (as CN) of 3 000 µg/L. Nelson and Tolbert (1970, as cited in U.S. EPA, 1985) noted enzyme inhibition in *Chlorella pyrenoidosa* at 30 000 µg/L. However, there appears to be some confusion in the U.S. EPA (1985) document in that these two species are believed by this author to be freshwater species of algae, and therefore these data should not be extrapolated to the marine situation. Nevertheless, Steele and Thursby (1983, as cited in U.S. EPA, 1985) reported that one marine species of red algae, *Champia parvula*, was particularly sensitive to the effects of free cyanide, which inhibited reproduction and growth between 5 and 20 µg/L (as CN).

## **4.2 Effects on Aquatic Macrophytes**

Few data were available regarding the effect of cyanide on aquatic macrophytes. Two studies reported by the U.S. EPA (1985) indicated that aquatic macrophytes may be quite tolerant to cyanide. Kondo and Tsudzukl (1980, as cited in U.S. EPA, 1985) reported decreased potassium uptake in duckweed (*Lemna gibba*) at a concentration of 26 000 µg/L (as CN). Stanley (1974, as cited in U.S. EPA, 1985) reported that the 32-day EC50 (affecting root weight) for Eurasian milfoil (*Myriophyllum spicatum*) was 22 400 µg/L (as CN).

## **4.3 Effects on Invertebrates**

There is a paucity of data pertaining to the effects of cyanide on invertebrates, especially in the area of chronic toxicity.

### **4.3.1 Freshwater Invertebrates**

Dowden and Bennett (1965) reported that the 96 h LC50's for water fleas (*Daphnia magna*) and snail eggs (*Lymnaea* sp.) exposed to potassium cyanide were 400 and 130 000 µg/L (as CN), respectively. Cairns et al. (1978, as cited in U.S. EPA, 1985) reported that the 48 h LC50's for *Daphnia pulex* at 5, 10, 15, and 25°C were 330, 330, 180, and 1 µg/L (as CN), respectively. Other tests using *Daphnia* sp. indicated that the LC50 was usually about 100 µg/L or more.

Cairns and Scheier (1958, as cited in U.S. EPA, 1973) reported that the 96 h LC50's for the pond snail (*Physa heterostropha*) exposed to potassium cyanide under low (2 mg/L) and normal (5.9 mg/L) dissolved oxygen concentrations were 480 and 1080 µg/L (as CN) respectively, whereas Patrick et al. (1968) reported a 96 h LC50 of 432 µg/L cyanide (as CN) for the pond snail under normal dissolved oxygen conditions. Leduc et al. (1982) suggest that the combined effect of decreased oxygen and cyanide would vary with the concentration of cyanide. At high concentrations of cyanide, the effect of low oxygen is expected to be minimal because cytochrome oxidase is inhibited. At low oxygen concentrations and low cyanide concentrations the ventilation rate of an organism would increase, which would accelerate the uptake of HCN. Leduc et al. (1982) expect that additive effects of oxygen reduction and cyanide intoxication would occur under certain exposure regimes for organisms incapable of sustained anaerobic metabolism.

Oseid and Smith (1979, as cited in Leduc et al., 1982) performed chronic toxicity tests by exposing isopods (*Asellus communis*) and scuds (*Gammarus pseudolimnaeus*) to cyanide for 98 to 115 days. The highest no-effect level for isopods was between 28 and 38 µg/L CN. Scuds were more sensitive to cyanide, which seriously affected survival and reproduction at concentrations of 50 and 15 µg/L CN, respectively. However, when these two species were tested together in the same aquarium at sublethal cyanide levels,

the competitive advantage shifted from the normally more aggressive scuds to the isopods because of the greater tolerance of isopods to cyanide.

#### **4.3.2 Marine Invertebrates**

Few data were available regarding the effects of cyanide on marine invertebrates, but recent evidence indicates that the early life stage of at least one species is very sensitive to the effects of cyanide. The U.S. EPA (1985) reported that the most sensitive marine invertebrate tested was the rock crab (*Cancer irroratus*). LC50's of 4.2 and 5.7 µg/L free cyanide (as CN) were reported for the larval stage of this species. The exposure period was not reported. Other marine invertebrates tested include the adult oyster (*Crassostrea* sp.) and the opossum shrimp (*Mysidopsis bahia*). The oyster appeared to be more tolerant to cyanide as feeding (ciliary activity) was reduced after 10 minutes on exposure to 150 µg/L cyanide (as CN), but total inhibition of ciliary activity did not occur until after 3 hours at 30 000 µg/L (U.S. EPA, 1985). Life cycle tests using the opossum shrimp demonstrated no adverse effects on growth or survival at concentrations less than 50 µg/L (as CN), but mortality of this species occurred at 113 µg/L (U.S. EPA, 1985).

### **4.4 Effects on Fish**

The majority of information pertaining to the effects of cyanide on aquatic life has focussed upon fish. Because of the extensive amount of literature on this subject, the information presented here will focus upon species native to British Columbia fresh and coastal marine waters. Where pertinent data are not available on local species, toxicological data on non-native species are included.

#### **4.4.1 Acute Toxicity**

The toxicological mode of action of cyanide on fish is similar to that for humans, except that HCN uptake in fish is primarily through the gills, which renders fish much more susceptible than humans to the effects of cyanide in water. The Inland Waters Directorate (1979) reported that cyanide levels greater than 200 µg/L are rapidly fatal to most fish species, and concentrations as low as 10 µg/L have been reported to cause adverse effects. The U.S. EPA (1985) reports that the toxicity of cyanide varies with the life stage and species of fish, and that embryos, sac fry, and warmwater fish tend to be the most tolerant. Free cyanide concentrations between 50 and 200 µg/L are fatal to juveniles of most species. Salmonids are reported to be the most sensitive family of fishes to the effects of cyanide. Kovacs and Leduc (1982) exposed juvenile rainbow trout (*Salmo gairdneri*) to HCN at three different temperatures in flow-through bioassays. The 96 h LC50's for trout acclimated and tested at 6, 12, and 18°C were 27, 40, and 65 µg/L (as CN), respectively. This same study reported that the highest cyanide concentration with no mortality to juvenile rainbow trout over 96 hours was 17 µg/L CN at 6°C. Smith et al. (1978) exposed different life stages of the brook trout (*Salvelinus fontinalis*) to HCN in flow-through bioassays. Sac fry were more tolerant to cyanide than the juveniles or swim-up fry. 96 h LC50's for juveniles, swim-up fry, and sac fry ranged from 52 to 143 µg/L, 54.4 to 104 µg/L, and 105 to 507 µg/L (as CN), respectively.

A number of researchers have investigated the potential toxicity of iron-cyanide complexes on exposure to ultraviolet or simulated sunlight. As outlined in Section 2.1(v), iron-cyanide complexes, on exposure to ultraviolet light, dissociate to form highly toxic HCN by photolysis. Broderius and Smith (1980) demonstrated the rapid photodecomposition of iron-cyanides and formation of HCN, and concluded that this photochemical reaction may be of toxicological importance under certain environmental conditions. For example, in clear shallow waters subjected to significant amounts of sunlight the loss of HCN due to natural removal mechanisms (volatilization, oxidation, and biological degradation) is thought to be considerably slower than HCN formation by photolysis of iron-cyanides at mid-day and near the surface (Broderius and Smith, 1980). Meyn et al. (1984) studied the acute toxicity of ferro- and ferri- cyanide to

rainbow trout under dark and simulated sunlight conditions. These compounds were more toxic on exposure to light and toxicity increased with increasing light intensity. Also, a bioassay test performed recently at the North Vancouver Federal Bioassay Laboratory provided further evidence of HCN toxicity induced by the photolytic reaction of cyanide complexes (Clark, personal communication, 1983). A water sample suspected of cyanide contamination from a mining operation was found to be non-toxic to fish after 96 hours of exposure. However, when the same water was exposed to ultraviolet light, all the fish died within minutes.

Further testing of rainbow trout exposed to potassium ferrocyanide under dark (blacked out) conditions, under normal laboratory lighting, and under simulated summer sunlight confirmed this photolytically-induced toxicity. The 96 h LC50's were 500 000 µg/L and 5 000 µg/L, and the 5 h LC50 was 250 µg/L (as nominal concentrations of  $\text{Fe}(\text{CN})_6$ ), respectively (Horvath et al., 1986, in preparation). Assuming maximum dissociation of the ferrocyanide complex (85% as reported by Broderius and Smith, 1980), these concentrations, reported as CN equivalents, are approximately 313 000, 3 130, and 156 µg/L, respectively. Similar tests using *Daphnia magna* gave 48 h LC50's of 191 000 µg/L when tested in complete darkness, 10 600 µg/L when tested under normal laboratory lighting, and a 2 h LC50 of 163 µg/L (as CN equivalents and assuming 85% dissociation of ferrocyanide) when tested under natural summer sunlight (Horvath et al., 1986, in preparation).

The Canadian Environmental Protection Service recently investigated the occurrence of photolysis under natural conditions in cyanide-contaminated waters downstream from a mine in British Columbia (Ferguson, 1985). The study indicated that up to 28 percent of the iron-cyanide originally present in the wastewater may have been converted by photolysis to free cyanide at the creek mouth, 6 km downstream from the discharge. Theoretical calculations indicated that substantially higher concentrations of free cyanide may have been present at other locations in the creek compared to levels measured at the mouth. Ferguson (1985) concluded that the photolysis of iron-cyanide complexes is an environmental concern at some gold mines and, in those cases, the quantity of iron-cyanide complexes released to the receiving waters should be restricted.

The acute toxicities of thiocyanate (CNS) and cyanate (CNO) have been investigated recently by the Environmental Protection Service in Canada. The 96 h LC50's of these compounds were usually several orders of magnitude higher (lower toxicity) than for free cyanide, but other researchers have shown the acute toxicity of these two compounds to vary widely.

Parker (1983) exposed fingerling rainbow trout to potassium thiocyanate (KCNS) at different levels of pH and hardness. In soft water (20 mg/L  $\text{CaCO}_3$ ) and neutral pH the 96 h LC50 was 255 000 µg/L (as CNS), and toxicity increased at lower pH and higher hardness. The 96 h LC50's ranged from 147 000 µg/L (as CNS) at a water hardness of 250 mg/L (as  $\text{CaCO}_3$ ) to 267 000 µg/L (as CNS) at a hardness of 20 mg/L (as  $\text{CaCO}_3$ ). The 96 h LC50's at constant hardness (20 mg/L  $\text{CaCO}_3$ ) and pH 5.0, 7.0, and 8.5 were 161 000, 260 000, and 228 000 µg/L (as CNS), respectively. Heming et al. (1985) reported that concentrations as low as 8 000 µg/L (as CNS) caused mortality among rainbow trout exposed for 96 hours, and then stressed. However, the lowest (most toxic) 96 h LC50 reported by Speyer and Raymond (1984) for stressed rainbow trout was 158 000 µg/L (as CNS) at 5°C and pH 6.0. Tests performed recently at the Federal Environmental Protection Service Bioassay Laboratory in North Vancouver, indicate that photolysis of thiocyanate by sunlight is negligible (van Aggelen, 1985).

Parker and Doe (1983) exposed fingerling rainbow trout to potassium cyanate (KCNO) in soft water (hardness of 20 mg/L  $\text{CaCO}_3$ ) at neutral pH. The 96 h LC50's ranged from 28 000 to 36 000 µg/L (as CNO). These results were 6 to 8 times lower (more toxic) than those reported in an earlier study by Speyer (1981, as cited in Parker and Doe, 1983). The difference between the results of the two studies was suggested to be due to the higher water hardness (250 to 275 mg/L  $\text{CaCO}_3$ ) of the earlier study, but this was not

confirmed. In a more recent study, Speyer and Raymond (1984) reported that the lowest 96 h LC50 for rainbow trout was 7 300 µg/L (as CNO) at 5°C, pH 6.0, and water hardness of 75 mg/L (asCaCO<sub>3</sub>). The formation of ammonia was suggested to have increased the toxicity of the test solution.

#### **4.4.2 Chronic Toxicity**

Chronic exposure of fish to sublethal levels of cyanide has produced a number of effects which may affect their ability to survive in nature. Chronic exposure to sublethal levels of cyanide has been shown to cause cell damage, and to interfere with respiration, growth, reproduction, early life stag development, swimming ability, and osmotic and ionic regulation. Evidence of these effects are presented in the following sections.

##### **(a) Histopathological Effects**

Histological examination revealed extensive liver tissue damage in rainbow trout exposed to 9.6 µg/L CN after 9 days (Dixon and Leduc, 1981, as cited in Leduc et al., 1982). The extent of tissue damage increased with the concentration.

##### **(b) Respiration**

Dixon and Leduc (1981, as cited in Leduc et al., 1982) reported an increased respiration rate in juvenile rainbow trout pre-exposed to 9.6 µg/L CN for 18 days. About four days after removal from the contaminated water, the respiration rates of these fish levelled off, but at higher levels than the controls. Leduc et al. (1982) suggest that this stabilization at higher respiration rates may be indicative of permanent damage in the form of reduced metabolic efficiency in fish. Carter (1962, as cited in U.S. EPA, 1985) noted that oxygen uptake by juvenile brown trout (*Salmo trutta*) was inhibited in 25 µg/L free cyanide (as CN) after 5 hours.

##### **(c) Growth**

Studies investigating the effects of cyanide on fish growth have been performed by a number of researchers. Negilski (1973, as cited in Leduc et al., 1982) noted that juvenile chinook salmon (*Oncorhynchus tshawytscha*) grew faster than controls when exposed to 9.6 µg/L CN, whereas growth was reduced in fish exposed to 19 µg/L. Leduc (1966, as cited in Leduc et al., 1982) exposed coho salmon (*Oncorhynchus kisutch*) at 16°C and cichlids (tropical fish) at 25°C to 9.6 to 96 µg/L CN, and noted that growth was initially enhanced at lower cyanide concentrations, but inhibited at higher levels. This pattern reversed with time whereby fish in lower concentrations showed a marked drop in weight gain and fish in the higher concentrations grew better. Dixon and Leduc (1981, as cited in Leduc et al., 1982) reported reduced weight gain in juvenile rainbow trout exposed to 19 and 29 µg/L CN for 18 days at 12°C.

Sublethal tests performed on juvenile rainbow trout demonstrated that a concentration of 4.8 µg/L CN caused a greater reduction in growth at 6°C than at 12 or 18 °C (Kovacs and Leduc, 1982). This study also found that a CN concentration of 9.6 µg/L reduced dry weight gain by 18 percent. This reduction in dry weight gain was attributed to the reduction in fat content, which ranged between 40 and 75 percent at 6°C, 20 and 80 percent at 12°C, and 12 and 50 percent at 18°C. The study concluded that at sublethal levels, cyanide was more potent at lower temperatures.

McCracken and Leduc (1980, as cited in Leduc et al., 1982) found that growth was reduced in larger juvenile rainbow trout, whereas growth was enhanced in smaller juveniles at a concentration of 9.6 µg/L CN. They attributed this observation to the different metabolic rates of the different sized fish. Based on the results of growth studies, these researchers calculated the energy consumption of fish

exposed to cyanide. They estimated the energy required for metabolism in the absence of cyanide to be 32.5 calories/g/day, whereas chronic exposure to 9.6 µg/L CN would increase the energy requirement to 115.8 calories/g/day. The greater energy requirement of chronically-exposed fish in the presence of sublethal cyanide levels for prolonged periods could result in starvation where food is scarce.

#### (d) Reproduction and Early Development

Chronic exposure to sublethal levels of cyanide has been shown to cause abnormalities in the reproduction process in fish. Leduc et al. (1982) suggest that cyanide may impair the formation of gametes in adult fish, Lesniak<sup>50</sup> noted abnormal oocyte development in yearling rainbow trout exposed to a concentration of 9.6 µg/L free cyanide (as CN) after 20 days. Ruby et al. (1979, as cited in U.S. EPA, 1985) noted a 13 percent reduction in sperm development in juvenile rainbow trout exposed to the same concentration after 18 days. Histological examinations by Lesniak and Ruby (1982) revealed that exposure of yearling rainbow trout to 9.6 µg/L CN for 15 to 20 days could seriously reduce oocyte maturation. Koenst et al. (1977, as cited in U.S. EPA, 1985) reported a 50 percent reduction in egg production of juvenile brook trout after 144 days exposure to 26 µg/L CN. Adult brook trout exposed to 62 and 72 µg/L CN spawned successfully, but none of the eggs survived early development stages. Leduc (1978, as cited in Leduc et al., 1982) noted a 15 percent reduction in the hatching success of Atlantic salmon (*Salmo salar*) eggs exposed to 9.6 µg/L CN, and hatching success decreased with increasing HCN concentrations to a 40% reduction at 96 µg/L as CN.

#### (e) Swimming Ability

Studies have shown that chronic exposure of fish to sublethal cyanide levels can affect swimming ability, and that performance decreases with decreasing temperature. Kovacs and Leduc (1982) reported reductions in performance of juvenile rainbow trout of 26 percent at 43 µg/L CN and 18°C, 71 percent at 29 µg/L and 12°C, and 90 percent at 14 µg/L and 6°C. Neil (1957, as cited in U.S. EPA, 1985) noted that brook trout suffered a 75 percent reduction in swimming endurance in 10 µg/L free cyanide (as CN) after 25.5 minutes. Broderius (1970, as cited in Leduc et al., 1982) found that, on return of cyanide-exposed fish to cyanide-free water, full recovery of swimming performance was not achieved after 15 to 20 days, which indicates the possibility of permanent impairment of this activity.

#### (f) Osmotic and Ionic Regulation

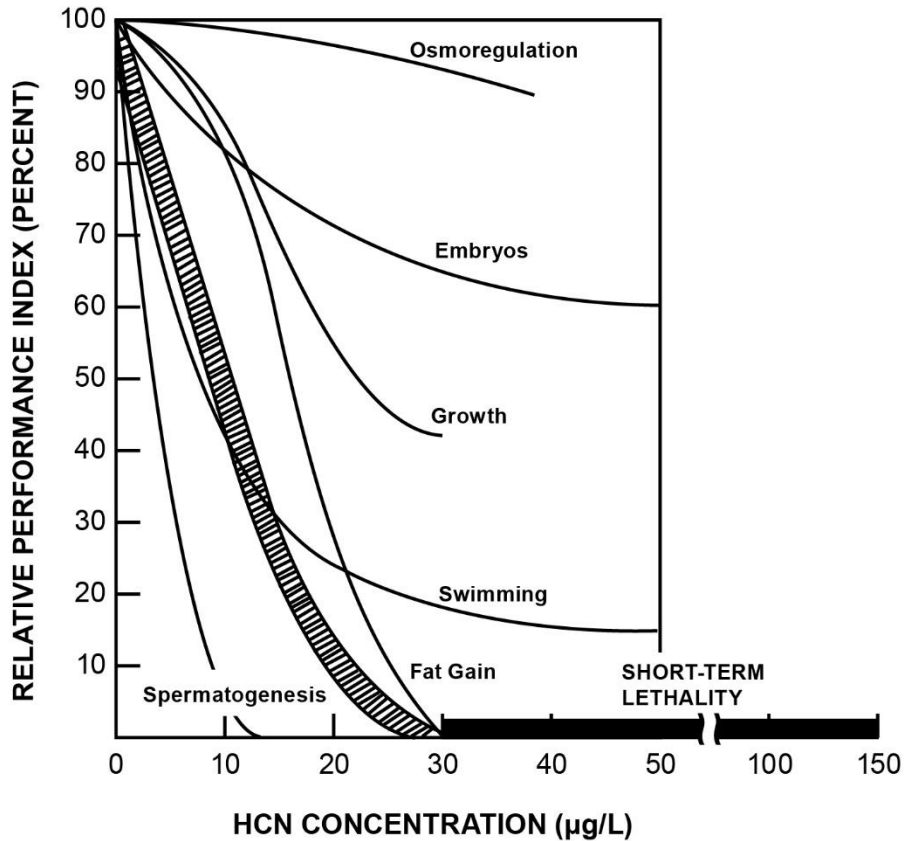
Exposure to cyanide affects the ability of fish to regulate body water content and the ionic content of plasma. Leduc and Chan (1975, as cited in Leduc et al., 1982) performed experiments where rainbow trout were transferred from cyanide-contaminated freshwater to cyanide-free saltwater (salinity of 18.9 parts per thousand) after 28 days, and then back to cyanide-free freshwater. Compared to control fish the cyanide-exposed fish were less capable of adjusting to the changes. Leduc et al. (1982) suggested that this inability to adjust was related to the increased metabolic energy expended due to the exposure to cyanide. Leduc et al. (1982) predicted that tolerance of fish to cyanide may be less in seawater than in freshwater because the metabolic expenditure for osmotic and ionic regulation is greater in seawater. Broderius (1973, as cited in Leduc et al., 1982) compared the toxicity of cyanide to the threespine stickleback (*Gasterosteus aculeatus*) in various salinities, and noted that the acute taxi city increased with increasing salinity.

#### (g) Summary of Combined Sublethal Effects on Fish

In an attempt to determine the overall significance of the effects of chronic exposure to sublethal doses of cyanide to fish, Leduc (1977, as cited in Leduc et al., 1982) plotted the performance of various



functions of fish exposed to cyanide, and from these curves calculated a “Relative Performance Index” shown as the dark shaded curve in Figure 1. This curve indicates a 50 percent reduction in the relative performance of fish continuously exposed to 10 µg/L HCN\* for 20 to 30 days at 10 to 13°C. Leduc et al. (1982) concluded that cyanide in the concentration range of 3 to 5 µg/L HCN would result in relatively minimum impairment of freshwater fish based upon this “Relative Performance Index”.



(Note: CN = 0.96 HCN)

(from Leduc, 1977)

Figure 1. A Summary of the Combined Sublethal Effects of HCN on Fish

#### 4.4.3 Multiple Toxicity

The occurrence of multiple toxic effects of cyanide mixed with other contaminants has been reviewed by Leduc et al. (1982). The toxic mechanism of these mixtures to fish is poorly understood. Some additive models have been tested in an attempt to predict the toxicity of cyanide mixed with various contaminants. However, in most cases the additive models failed to explain the experimental results. For example, Broderius and Smith (1979) predicted about 20 percent mortality of fish in a chromium-HCN mixture using additive models designed by Anderson and Weber (1977, as cited in Leduc et al., 1982). The actual

\*NOTE: CN = 0.96 HCN

mortality was 50 percent. Similarly, zinc-HCN and ammonia-HCN mixtures killed about 50 percent of the fish compared to a predicted mortality of <1 percent. These results suggest that synergistic (greater than additive) mechanisms are involved at acutely lethal concentrations.

On the other hand, sublethal concentrations of cyanide mixed with other contaminants produced antagonistic, additive, or synergistic responses, depending on the contaminants involved. Sublethal concentrations of cyanide mixed with chromium or zinc reduced dry-weight gain in fish to levels which were similar to cyanide tested alone (antagonism). A sublethal ammonia-HCN mixture reduced dry-weight gain more than predicted (synergism). Negilski (1973, as cited in Leduc et al., 1982) demonstrated that sublethal mixtures of cyanide, pentachlorophenol, and zinc produced a greater than additive (synergistic) effect on growth and production of juvenile chinook salmon. In another study, Speyer (1975, as cited in Leduc et al., 1982) found that the response addition model successfully predicted growth changes of rainbow trout exposed to sublethal arsenic-HCN mixtures.

The above results indicate that the toxicity of cyanide in combination with other contaminants is influenced by the contaminants which are present in the mixture and by their respective concentrations. Thus, the inconsistency of these results rules out the use of any existing models to develop defensible, universal, quantitative criteria which protect aquatic life from the combined toxicity of cyanide mixed with other contaminants.

An extensive review of the literature on the combined effects of mixtures of toxicants on freshwater aquatic life was carried out by the European Inland Fisheries Advisory Commission (EIFAC) (1980), and Alabaster and Lloyd (1982). They concluded that because concentrations lower than the EIFAC recommended values for individual toxicants, commonly occurring in sewage and industrial wastes, do not appear to contribute to the toxicity of mixtures of toxicants, there is no need to adjust these values downward in such situations. However, neither the EIFAC (1980) nor Alabaster and Lloyd (1982) have recommended criteria for cyanide at this time.

We recommend that situations of multiple toxicity involving cyanide be considered on a site-specific basis. Where the contaminants involved have been studied in the literature, these studies can serve as a guide to appropriate modifications to the criteria for the contaminants. Where the contaminants involved have not been studied, then acute and/or chronic bioassays should be performed on sensitive local species and the results compared with an additive toxicity model using the concentrations of contaminants in the water. In many situations it may be advisable to perform such bioassays under sunlight or simulated sunlight. These bioassays should indicate whether synergistic, antagonistic, or additive toxicity mechanisms are involved. If synergistic or additive effects are found, then the criteria presented in this document may have to be lowered to provide the appropriate protection to aquatic life in the area.

#### **4.5 Criteria from the Literature**

Criteria, objectives, and standards to protect aquatic life from cyanide have been compiled from a number of jurisdictions and tabulated in Tables 2 and 3. The maximum acceptable levels to protect freshwater aquatic life from the long-term effects of cyanide are fairly consistent at about 5 µg/L CN.

Between 1980 and 1985, the U.S. EPA has considered averaging periods of 24 hours, 30 days, and 4 days for criteria to address chronic effects, and a maximum instantaneous, a 4-day maximum in a 30-day period, and a one-hour average concentration to address acute effects (Table 1). The most recent (1985) approach bases the criterion for acute effects on a one-hour average concentration, and the chronic effects on a 4-day average concentration. These were chosen over its previous 1983 draft criteria. These proposed a maximum concentration, which could persist for up to 96 hours of cumulative events to address acute effects, and a 30-day average to address chronic effects. The main reason for these changes

was, in the case of chronic toxicity, that a shorter averaging period (4 days instead of 30 days) would limit the duration and magnitude of concentrations above the chronic criterion concentration caused by fluctuations in concentrations. Recent evidence has shown that fluctuating concentrations of some contaminants are more toxic than a continuous concentration even though the average is the same. For acute toxicity, the change from a 96-hour maximum concentration to a one-hour average concentration was considered appropriate by the U.S. EPA because high concentrations of some materials can cause death in one to three hours.

Table 1. Cyanide Criteria for Freshwater Aquatic Life

Criteria Statements	Criteria Values	Jurisdiction	Date
Once a 96 h LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of free cyanide (CN <sup>-</sup> ) safe to aquatic life in that water can be estimated by multiplying the 96 h LC50 by an application factor of 0.05; but no concentration greater than 5 µg/L is recommended at any time or place.	5 µg/L	U.S. EPA	1972
It is recommended that the derived working level for cyanide in water supporting aquatic life be 0.1 of the 96 h LC50 value determined using the water in question and the most sensitive species in the locality as test organisms.	0.1 times the 96 h LC50	Australia	1974
Max. concentration for total cyanide = 10 µg/L.	10 µg/L	Saskatchewan Alberta	1975 1977
Total cyanide criterion for freshwater aquatic life is 5.0 µg/L	5 µg/L	U.S. EPA	1976
Concentrations of free cyanide in unfiltered water samples should not exceed 5 µg/L for the protection of aquatic life.	5 µg/L	Ontario	1979
The 5 µg/L total cyanide concentration limit (U.S. EPA, 1976) should be replaced with a 5 µg/L free cyanide limit or, more preferably, with a 5µg/L molecular HCN concentration limit.	5 µg/L	American Fisheries Society	1979
Concentrations of free cyanide in unfiltered water samples should not exceed 5 µg/L for the protection of aquatic life.	5 µg/L	International Joint Commission	1980
For protection of freshwater aquatic life the maximum 24-hour average for free cyanide (HCN + CN <sup>-</sup> ) is 3.5 µg/L or the maximum at any time should not exceed 52 µg/L.	3.5 and 52 µg/L	U.S. EPA	1980
For salmonid and cyprinid dominated waters the 95 and 99 percentiles for cyanide are 10 and 15 µg/L, respectively.	10 and 15 µg/L	England	1982
Maximum acceptable concentration to protect freshwater aquatic life is 3.5 µg/L free cyanide (sum of HCN and CN <sup>-</sup> , expressed as CN).	3.5 µg/L	Manitoba	1983
To protect freshwater aquatic life and its uses, in each 30 consecutive days: a) the average concentration of free cyanide (the sum of cyanide present as HCN+CN <sup>-</sup> , expressed as CN) should not exceed 4.2 µg/L; b) the	4.2 and 22 µg/L	U.S. EPA (Draft)	183

Criteria Statements	Criteria Values	Jurisdiction	Date
maximum concentration should not exceed 22 µg/L; and (c) the concentration may be between 4.2 and 22 µg/L for up to 96 hours.			
Freshwater aquatic organisms and their uses should not be affected unacceptably if the 4-day average concentration of cyanide does not exceed 5.2 µg/L more than once every 3 years on the average and if the 1-hour average concentration does not exceed 22 µg/L more than once every 3 years on the average. The criteria should be applied in terms of total cyanide until an EPA approved analytical technique for free cyanide is developed.	5.2 and 22 µg/L	U.S. EPA	1985

Table 2. Cyanide Criteria for Marine Aquatic Life

Criteria Statements	Criteria Values	Jurisdiction	Date
As guideline in the absence of data for marine organisms the panel recommends that an application factor of 0.1 be applied to marine 96 h LC50 data for the appropriate organisms most sensitive to cyanide. On the basis of data available at this time it is suggested that concentrations of cyanide equal to or exceeding 10 µg/L constitute a hazard in the marine environment, and levels less than 5 µg/L present minimal risk of deleterious effects.	5 µg/L	U.S. EPA	1972
Total cyanide criterion for marine aquatic life = 5 µg/L.	5 µg/	U.S. EPA	1976
The 5 µg/L total cyanide criterion level recommended by the U.S. EPA should be replaced with a 5 µg/L free cyanide limit or, more preferably, with a 5 µg/L molecular HCN limit.	5 µg/	American Fisheries Society	1979
For protection of marine aquatic life: acute toxicity = 30 µg/L free cyanide, chronic toxicity = 2.0 µg/L free cyanide provided the acute-chronic ratio for salt water organisms is similar to that for freshwater organisms.	30 µg/L and 2.0 µg/L	U.S. EPA	1980
To protect saltwater aquatic life and its uses, in each 30 consecutive days: a) the average concentration of free cyanide (the sum of cyanide present as HCN and CN <sup>-</sup> , expressed as CN) should not exceed 0.57 µg/L; b) the maximum concentration should not exceed 1.0 µg/L; and c) the concentration may be between 0.57 and 1.0 µg/L for up to 96 hours.	0.57 µg/L and 1.0 µg/L	U.S. EPA (Draft)	1983
Saltwater aquatic organisms and their uses should not be affected unacceptably if the 1-hour average concentration of cyanide does not exceed 1.0 µg/L more than once every 3 years on the average. The criteria should be applied in terms of total cyanide until an EPA approved analytical technique for free cyanide is developed.	1.0 µg/L	U.S. EPA	1985

The U.S. EPA criteria were derived using a system developed by Stephan et al. (1985), and are intended to protect at least 95 percent of a group of diverse species, unless an affected species is economically, recreationally, or socially important. In this case, the criteria are based on the sensitive important species. The system used to develop the U.S. EPA criterion protecting aquatic life from acute toxicity is based upon the "Final Acute Value" (geometric mean of genus mean acute values). In the case of an important sensitive species, the criterion is based upon the "Species Mean Acute Value" which becomes the "Final Acute Value". The "Final Acute Value" is divided by a safety factor of two to determine the criterion level to protect aquatic life from short-term effects. The U.S. EPA freshwater criterion is based on the "Species Mean Acute Value" for rainbow trout (44.73 µg/L), which becomes the "Final Acute Value"; and  $44.73 \div 2$ , rounded off, gives the criterion level of 22 µg/L CN for the protection of aquatic life from the short-term effects of cyanide.

The U.S. EPA (1985) criterion to protect saltwater organisms (Table 2) from the acute effects of cyanide is calculated by the same method as the freshwater acute criterion. The saltwater "Final Acute Value" calculated from the "Genus Mean Acute Values" was 2.03 µg/L. Half this value gives the criterion level of 1.0 µg/L CN to protect marine organisms from the short-term effects of cyanide. This level suggests that marine aquatic life is more sensitive to cyanide than freshwater life, which is in agreement with Leduc et al. (1982). They rationalized that saltwater organisms are probably more sensitive to cyanide than freshwater organisms because the metabolic expenditure of osmotic and ionic regulation is greater for organisms in saltwater (Leduc et al., 1982).

The U.S. EPA (1985) 4-day average criterion level to protect freshwater organisms from the chronic effects of cyanide is derived by dividing the "Final Acute Value" by the geometric mean of the acute-chronic ratios (inverse of the application factor) for sensitive organisms. For the protection of freshwater organisms the cyanide criterion is 5.2 µg/L CN.

The U.S. EPA (1985) marine criterion for chronic effects is the same as that specified for acute effects because the acute value (1.0 µg/L, based on toxicity to the larvae of the sensitive rock crab) was considered a better indication of chronic sensitivity than would be obtained by dividing the acute value by an acute-chronic ratio, as was done for the freshwater chronic criterion. The use of an acute-chronic ratio would include data for more tolerant species, and thus result in a higher criterion.

The U.S. EPA (1985) has introduced a new concept to their most recent aquatic life criteria. They permit the criteria to be exceeded an average of once every three years. The reasoning behind this concept is based on the U.S. EPA's best scientific judgement that three years is the average amount of time it would take an unstressed system to recover from a pollution event (Stephan et al., 1985).

The criteria, objectives, and standards from other jurisdictions usually specify a free cyanide criterion because HCN is the primary toxic form of cyanide. Other forms of cyanide are often omitted from the criteria because they are several orders of magnitude less toxic than HCN, or because the cyanide ion is strongly complexed with another chemical group, thus preventing dissociation and the subsequent formation of highly toxic HCN in natural waters. Furthermore, most acute and chronic toxicity tests upon which criteria were developed have been based upon the determination of free cyanide. Most criteria appear either to dismiss the iron-cyanide complexes, which can dissociate on exposure to sunlight, as insignificant contributors to toxicity, or to advocate that the presence of these complexes should be considered on a site-specific basis. In their literature review on cyanide, Leduc et al. (1982) concluded that although free cyanide should be considered the primary indicator of immediate toxic effects, those compounds that generate free cyanide under given environmental circumstances should also be considered. The U.S. EPA (1985) also states that the importance of release of cyanide from metalocyanide complexes by photolysis should receive consideration on a site-specific basis if the national criterion is possibly unacceptable.

The U.S. EPA (1985) believes that a measurement of free cyanide would provide a more scientifically correct basis upon which to establish criteria for cyanide. However, until an EPA approved analytical technique can be developed for free cyanide, the agency recommends that the criteria should be applied in terms of total cyanide.

Doudoroff (1977) and Broderius (1981), both specialists in the field of cyanide toxicology, have maintained consistently that free cyanide, and especially HCN, is the form by which criteria should be specified because it is the primary toxic form. Broderius (1981) has developed an analytical technique to measure free cyanide and HCN in aqueous solutions. However, some individuals involved with the chemistry of cyanide have expressed concern over certain aspects of free cyanide determination. Ingles (Environmental Protection Service, 1985) questions its use for regulatory purposes because of concerns with sample preservation and analytical problems. According to Maynard (1982, as cited in Sneddon, 1983), at the Can Test Laboratory in Vancouver, analysis for free cyanide in waters containing *mine* wastes is virtually impossible because of the many substances in mine wastes which can interfere with the analysis. A report by the Analytical Sub Group of the Gold Processor's Working Group (Barkley et al., 1982) assessed a number of analytical techniques for measuring cyanide in gold process effluents, for regulatory purposes. Based upon the accuracy and reproducibility of results through the round-robin testing of cyanide-spiked samples among a number of laboratories across Canada, the committee recommended that total (strong-acid dissociable) cyanide and weak-acid dissociable cyanide are the most appropriate techniques and that both should be measured.

#### **4.6 Recommended Criteria**

Criteria to protect aquatic life from cyanide in fresh, estuarine, and coastal marine waters of British Columbia are based partially upon the most recent criteria developed by the U.S. EPA (1985). These criteria are designed to address both the long-term sublethal effects and short-term acute effects of cyanide to aquatic life.

##### **4.6.1 Freshwater Aquatic Life**

- (a) In a 30-day period the average concentration (based on a minimum of 5 weekly samples) of weak-acid dissociable cyanide (expressed as CN) in unfiltered samples should not exceed 5 µg/L; and
- (b) the maximum concentration should not exceed 10 µg/L at any time.

##### **4.6.2 Marine and Estuarine Aquatic Life**

The maximum concentration of weak-acid dissociable cyanide (expressed as CN) in unfiltered samples should not exceed 1 µg/L at any time.

Note: For details of monitoring strategy, see Application of Criteria.

##### **4.6.3 Cyanate and Thiocyanate**

Cyanate and thiocyanate are much less toxic than cyanide.

The lowest concentration of thiocyanate (as CNS) reported to cause mortality to rainbow trout exposed for 96 hours was 8.0 mg/L. Other tests have indicated that the 96 h LC50 of thiocyanate to rainbow trout was greater than 150 mg/L.

The lowest concentration of cyanate (as CNO) reported to cause mortality to rainbow trout exposed for 96 hours was 7.3 mg/L. Other tests have indicated that the 96 h LC50 of cyanate to rainbow trout was usually greater than 20 mg/L.

The available data are too few and too variable to allow the recommending of defensible criteria for these two compounds at this time.

#### **4.6.4 Application of Criteria**

The criteria recommended here apply when cyanide is acting alone. Situations of multiple toxicity (Section 4.4.3) involving cyanide should be considered on a site-specific basis. Where the contaminants involved have been studied in the literature, these studies can serve as a guide to appropriate modifications to the criteria for the contaminants. Where the contaminants involved have not been studied, then acute and/or chronic bioassays should be performed on sensitive local species and the results compared with an additive toxicity model, using the concentrations of contaminants in the water. In situations where iron-cyanide compounds are suspected of being present, it may be advisable to perform such bioassays under sunlight or simulated sunlight. These bioassays should indicate whether synergistic, antagonistic, or additive toxicity mechanisms are involved. If synergistic or additive effects are found, then the criteria presented in this document may have to be lowered to provide the appropriate protection to aquatic life in the area.

The criterion recommended for marine aquatic life is below the limit detectable by the Provincial Environmental Laboratory. The minimum detectable concentration for weak-acid dissociable cyanide is 5 µg/L at this time and, until the detection limit can be improved, measurements reported as < 5 µg/L (as CN) will be considered acceptable. However, calculated receiving water cyanide concentrations should not exceed the recommended criterion or site-specific objective at appropriate locations in the waterbody.

Any cyanide concentration which exceeds the 30-day average criterion should serve as an alert signal to increase the sampling frequency. When this occurs at least 5 weekly samples should be taken during the next 30 days so that a 30-day average concentration can be determined. This increased monitoring frequency should be continued until each of 5 consecutive samples are below the 30-day average criterion level.

When testing fresh and marine receiving waters to check if aquatic life criteria are being met, measurements of strong-acid dissociable cyanide should also be made. If the values for strong-acid dissociable cyanide exceed the criteria expressed as weak-acid dissociable cyanide, then further sampling should be carried out even if weak-acid dissociable cyanide criteria are being met. The sampling should be repeated hourly, or as frequently as possible, at the same site and additional samples should be taken from sites further from the source, preferably during bright sunlight (between 1100 and 1400 hours). Such tests will check whether the possible photolysis of iron-cyanide complexes has produced free cyanide at levels which may be unacceptable. In cases where sampling sites are located a considerable distance from the suspected source, then the sampling time frame should be extended to allow the water, which had been exposed during peak sunlight hours, to reach that site. Samples should be kept in the dark (i.e., out of sunlight) immediately after collection and during transport to the laboratory.

Cyanate and thiocyanate should also be measured when these compounds are known to be discharged.

#### **4.6.5 Rationale**

The criteria recommended in this document for the protection of marine, estuarine, and freshwater aquatic life in British Columbia have been based partially upon the most recent U.S. EPA (1985) criteria, which address both chronic and acute toxicity. Certain aspects of the U.S. EPA criteria have been modified to provide a more appropriate level of protection to aquatic life in British Columbia.

The U.S. EPA (1985) has taken into account the most recent research data pertaining to acute and chronic toxicity, and the criteria were derived using a system developed by Stephan et al. (1985), which is described briefly in Section 4.5.

#### (a) Freshwater Aquatic Life

The U.S. EPA (1985) cyanide criterion level of 5.2 µg/L CN for the protection of freshwater aquatic life from chronic effects is closely comparable to criteria established by other jurisdictions. Furthermore, a recent thorough review of cyanide toxicity data by Leduc et al. (1982) concluded that cyanide in the concentration range of 3 to 5 µg/L HCN\* (2.9 to 4.8 µg/L as CN) would result in relatively minor impairment of freshwater fish based upon the “Relative Performance Index” (Section 4.4.2(g)) calculated from sublethal toxicity data.

The cyanide criterion level of 22 µg/L CN as a one-hour average is considered, by the U.S. EPA (1985), to provide adequate protection for freshwater aquatic life from acute effects. This level is based upon 96 h LC50's performed on various species of fish and invertebrates. The lowest 96 h LC50 which has been recorded for freshwater organisms (except for one questionably low value for *Daphnia*) was 27 µg/L CN for juvenile rainbow trout at 6°C (Kovacs and Leduc, 1982). However, this same study reported that the highest cyanide concentration with no mortality to juvenile rainbow trout over 96 hours was 17 µg/L CN at 6°C. Since 6°C was the coldest temperature tested in this study, and since toxicity was shown to increase with decreased temperature at relatively low, slowly lethal HCN concentrations, it is not unreasonable to presume that lower HCN concentrations may be lethal to juvenile rainbow trout in water colder than 6°C. Thus the U.S. EPA criterion level of 22 µg/L (as CN) may permit the mortality of rainbow trout in British Columbia waters which are frequently colder than 6°C. We therefore recommend a maximum cyanide level of 10 µg/L CN for short-term exposures. The 10 µg/L value is supported by much of the material in Sections 4.1 to 4.4 and also provides a safety factor of about two for acute toxicity.

#### (b) Marine and Estuarine Aquatic Life

The U.S. EPA (1985) saltwater criterion was derived by basically the same system as the freshwater criteria, except that the acute value (1.0 µg/L, based on toxicity to the larvae of the sensitive rock crab) was considered a better indication of chronic sensitivity than would be obtained by dividing this acute value by an acute-chronic ratio. However, the marine criterion is somewhat more questionable than the freshwater criteria because the level has been based upon fewer tests and fewer organisms. The marine criterion is considerably lower than those established for freshwater, but there is evidence that organisms in saltwater are less tolerant than organisms in freshwater (Broderius, 1973, as cited in Leduc et al., 1982; Doudoroff, 1976). For example, LC50's (exposure period not specified) for the rock crab were 4.2 and 5.7 µg/L (CN), and a cyanide concentration of 11 µg/L (CN) stopped sexual reproduction and reduced growth in the red alga *Champia parvula*. Furthermore, Leduc et al. (1982). have suggested that organisms in saltwater are likely to be more sensitive to cyanide than organisms in freshwater because the metabolic expenditure of energy by organisms in saltwater is greater (Section 4.4.2(f)). Since the U.S. EPA has been the only agency to develop a cyanide criterion for marine waters, and since the criterion level takes into account the most recent research data, this level has been adopted by the British Columbia Ministry of Environment to protect aquatic life in the estuarine and marine coastal waters of British Columbia.

This criterion was based on toxicity tests performed on a crab species which is not indigenous to B.C. waters, and therefore may be overprotective. Nevertheless, until acute and chronic toxicity tests are

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\*NOTE: CN = 0.96 HCN



performed on local sensitive species, there is no justification to specify a level higher than the criterion recommended here.

#### (c) Averaging Periods

In the past, a single criterion maximum value, often based on a somewhat arbitrary application factor, could have been over-restrictive for many situations. The goal of the Ministry is to provide a balance between acceptable levels of protection against acute and chronic effects, without being over-restrictive, and the practical application of the criteria in terms of monitoring requirements. Therefore various averaging periods, considered by the U.S. EPA over the past five years, were reviewed (Section 4.5). The most recent U.S. EPA concept (one-hour average and a 4-day average) was rejected as being impractical. The U.S. EPA criteria would require very frequent monitoring to obtain average values over such short averaging periods. Such frequent monitoring would be extremely expensive, and therefore impractical. Instead, the recommended criteria are expressed in terms of a maximum concentration and a 30-day average concentration. Although this approach is similar to that which was rejected by the U.S. EPA on the basis of duration and magnitude of fluctuating concentrations (see Section 4.5), this concern has been addressed by recommending a lower acute criterion (10 µg/L) than that (22 µg/L) recommended by the U.S. EPA (1985). Furthermore, the acute criterion, specified here as a maximum concentration, is more restrictive than the U.S. EPA's one-hour average acute criterion. This is because, by definition, a maximum concentration places an upper limit on a concentration permitted at any time, whereas an average does not. Therefore the recommended criteria, expressed in terms of a maximum concentration and a 30-day average concentration, will prevent excessive fluctuations over the 30-day average concentrations while still addressing both the acute and chronic effects of cyanide.

The new U.S. EPA (1985) concept of permitting the criteria for aquatic life to be exceeded an average of once every three years (see Section 4.5) was not adopted. This concept could result in a situation whereby a water body is condemned to a perpetual state of recovery, and it would defeat the entire purpose of criteria.

#### (d) Forms of Cyanide to be Measured

Based on the discussion of potential toxicity due to the photolysis of iron-cyanide complexes by sunlight (Section 4.4.1), a dual sampling concept has been recommended. The criteria apply in terms of weak-acid dissociable cyanide, but strong-acid dissociable cyanide is also measured to indicate the potential toxicity that may occur from the photodecomposition of iron-cyanide complexes. This approach allows the criteria to apply in terms of the immediate toxic forms of cyanide so that the criteria are not over-restrictive, while at the same time a check is kept on potentially toxic iron-cyanide complexes. As outlined in the "Application of Criteria" (Section 4.6.4), a provision has been made to intensify monitoring on a site-specific basis when strong-acid dissociable cyanide measurements exceed the 30-day average criterion. This ensures that the photodecomposition of iron-cyanide complexes has not produced free cyanide at levels which may be unacceptable.

As noted above, the criteria have been specified in terms of weak-acid dissociable cyanide. Although "free cyanide" has been recommended by the U.S. EPA and other researchers as the appropriate form to be measured, concerns have been expressed regarding problems with sample preservation and analysis of free cyanide (see Section 4.5). Weak-acid dissociable cyanide is considered a more reasonable estimate of the toxic components than total cyanide, is not subject to interferences by other compounds during analysis, and can be measured on a routine basis by the B.C. Provincial Environmental Laboratory. Thus, weak-acid dissociable cyanide was chosen as the most appropriate form in which to specify the criteria at the present time.

Under some conditions, weak-acid dissociable cyanide can overestimate free cyanide, but does not underestimate it. Therefore this analytical technique provides an inherent safety factor against situations such as pH fluctuations in natural waters. While a minor reduction in pH will not cause much change in the HCN/CN<sup>-</sup> equilibrium in natural waters, it can increase the dissociation of metal-cyanide complexes, which significantly increases toxicity. For example, Doudoroff (1976) noted that a reduction in pH from 7.8 to 7.4 corresponded to a 10- to 13-fold increase in toxicity of the tetracyanonickelate complex, and was due to the dissociation of the complex and formation of highly toxic HCN. Furthermore, Lloyd and Herbert (1960) observed that carbon dioxide released naturally by fish at the gill surface will reduce local pH levels. Therefore, by recommending the determination of weak-acid dissociable cyanide (digested at pH 4.5) for British Columbia waters, we ensure that potential toxicants subject to dissociation by minor pH fluctuations are not excluded from the measurement.

Thiocyanate and cyanate are not measured by the analytical techniques for weak-acid or strong-acid dissociable cyanide and therefore are not included in the criteria. These two compounds are considerably less toxic than free cyanide and they do not dissociate to form free cyanide, to any significant extent, under normal environmental conditions. Separate criteria for thiocyanate and cyanate have not been recommended at this time because the available acute toxicity data are too variable, and there is very little known about sublethal or chronic effects to form scientifically defensible criteria. Instead, a short summary of known toxicities of these compounds has been included to provide some idea of the range of concentrations which may be harmful. More research on the acute and chronic toxicity of these compounds is needed before meaningful criteria can be recommended. Where these compounds are known to be discharged, it is recommended that they be measured in separate samples to obtain some idea of concentrations that may occur in B.C waters. The data may be useful in developing criteria for these compounds at some future time.

## **5. OTHER WATER USE CATEGORIES**

No cyanide criteria exist which have been designed specifically for the protection of other water-use categories including wildlife, livestock watering, irrigation, recreation and aesthetics, and industry (other than food processing). Because very little information was available pertaining to the effects of cyanide to water-users in these categories, it would be inappropriate to recommend criteria for these categories at this time. Aquatic life is probably the most sensitive of all water uses, and must be protected in nearly all waters. Thus adequate protection for the water uses for which criteria are not available will probably be provided.

The acute toxicological mode of action of cyanide appears to be similar for most animals (i.e., a respiratory poison), and oral consumption of water is the only major uptake mechanism for water-users in the categories of wildlife, livestock watering, and primary contact recreation (i.e., swimming, diving, etc.). Thus, the drinking water criterion level of 200 µg/L strong-acid dissociable cyanide (expressed as CN) probably would provide adequate protection. McKee and Wolf (1963) reported that water contaminated with 99 000 µg/L CN was fatal to cows and ducks. They also reported toxic and lethal doses of cyanide to cows (375 555 to 885 920 µg CN), sheep (38 520 to 96 300 µg CN), dogs (29 000 to 38 520 µg CN) and horses (375 555 µg CN). Therefore, assuming the water consumed contains 200 µg/L CN, these animals would have to consume massive volumes of water (relative to their body size) over a short period of time to achieve toxic or lethal doses. For example, a dog would have to consume 145 litres of water to achieve the toxic dosage of 29 000 µg CN. Therefore the drinking water criterion for humans would probably provide adequate protection for livestock and wildlife. However, a level such as this only can be considered a guideline as considerable research is necessary before defensible criteria can be recommended.

One aspect of cyanide toxicity that deserves mention is the absorption of cyanide through the skin. The U.S. EPA related one case whereby a worker spilled liquid HCN over his hand and collapsed in unconsciousness after five minutes. It was assumed that absorption through the skin occurred because the worker was wearing a fresh air respirator which prevented the inhalation of any gas. The toxicological significance of this accident to humans involved in primary recreational activities or to other animals immersed in cyanide-contaminated water is not known, but concentrations high enough to cause such an effect are unlikely in a waterbody, given the dilution normally available.

The effects of cyanide-contaminated water used to irrigate vegetation are not known. In terms of cyanide mobility in soil, Murmann and Koutz (1972, as cited in Leduc et al., 1982) demonstrated that cyanide was either biologically decomposed or complexed with trace metals within a short distance. Therefore vegetation with shallow roots may be more susceptible to cyanide than deep-rooted vegetation. Also, there is no information regarding the effects of cyanide-contaminated water on exposed plant surfaces irrigated by sprinklers. However, because of the volatile nature of HCN, sprinkler irrigation would accelerate volatilization so that high concentrations of HCN reaching exposed plant surfaces are unlikely. Also, many plants contain naturally high levels of organic cyanide compounds (Section 3.1), and therefore may not be affected by cyanide. These considerations are purely speculative and research on these aspects are necessary before defensible criteria can be recommended.

## **6. RESEARCH AND DEVELOPMENT NEEDS**

(Listed in approximate order or priority)

- The minimum detectable concentration for weak-acid dissociable cyanide should be improved to levels below the criteria levels recommended in this document.
- The toxicity of cyanide to fish at cyanide concentrations <10 µg/L and low temperature needs to be evaluated.
- More research regarding the acute and chronic toxicity of thiocyanate and cyanate to aquatic life is needed to assist in developing criteria for these contaminants.
- A better understanding of the fate of all forms of cyanide in the receiving environment is needed.
- A better understanding of the toxicity of cyanide mixed with other contaminants is needed to determine the relationships and to develop protocol (e.g., cyanide analytical techniques, acute and chronic bioassay test procedures).
- In view of the paucity of data on the effects of cyanide to marine organisms, more toxicological studies using marine organisms should be performed.
- The toxicological significance and stability of particulate (<0.45 µm) metalocyanide complexes need to be investigated.
- Research is necessary regarding the effects of cyanide on water-use categories other than drinking water and aquatic life so that meaningful criteria can be developed to protect these uses.

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