



Water Quality

Water Quality Criteria for Cyanide

Overview Report

Prepared pursuant to Section 2(e) of the
Environment Management Act, 1981

Original signed by B. Marr
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Environment
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Tables

Table 1: Summary of Water Quality Criteria

Water Use	Strong-acid Dissociable Cyanide Plus Thiocyanate µg/L (as CN)	Strong-acid Dissociable Cyanide µg/L (as CN)	Weak-acid Dissociable Cyanide µg/L (as CN)
Raw Drinking Water - includes food processing water (maximum at any time)	200 µg/L	Not applicable	Not applicable
Freshwater Aquatic Life (30- day average)	Not applicable	None proposed	less than or equal to 5 µg/L
Freshwater Aquatic Life (maximum at any time)	Not applicable	None proposed	10 µg/L
Marine and Estuarine Aquatic Life (maximum at any time)	Not applicable	None proposed	1 µg/L

1. All characteristics apply to unfiltered water.

2. The average is calculated from at least 5 weekly samples taken in a period of 30 days.

3. Measure strong-acid dissociable cyanide in addition to weak-acid dissociable cyanide. If tests show that strong-acid dissociable cyanide is greater than the criteria for weak-acid dissociable cyanide, further sampling of the receiving water is recommended at the same site during bright sunlight, and from sites further from the cyanide source.

4. If it can be shown for a particular water supply, that treatment methods (chlorination, ozonation or ultraviolet irradiation) do not produce free cyanide or cyanogen chloride from the dissociation of thyocyanate, then the criterion should apply only to strong-acid dissociable cyanide.

Preface

THE MINISTRY OF ENVIRONMENT, LANDS AND PARKS (now called Ministry of Water, Land and Air Protection) develops province-wide ambient water quality guidelines for variables that are important in the surface waters of British Columbia. This work has the following goals:

1. to provide guidelines for the evaluation of data on water, sediment, and biota
2. to provide guidelines for the establishment of site-specific ambient water quality objectives

Ambient water quality objectives for specific waterbodies will be based on the guidelines and also consider present and future uses, waste discharges, hydrology/limnology/oceanography, and existing background water quality. The process for establishing water quality objectives is more fully outlined in *Principles for Preparing Water Quality Objectives in British Columbia*, copies of which are available from Water Quality Section of the Water Management Branch.

Neither guidelines nor objectives which are derived from them, have any legal standing. The objectives, however, can be used to calculate allowable limits or levels for contaminants in waste discharges. These limits are set out in waste management permits and thus have legal standing. The objectives are not usually incorporated as conditions of the permit.

The definition adopted for a guideline is:

A maximum and/or a minimum value for a physical, chemical or biological characteristic of water, sediment or biota, which should not be exceeded to prevent specified detrimental effects from occurring to a water use, including aquatic life, under specified environmental conditions.

The guidelines are province-wide in application, are use-specific, and are developed for some or all of the following specific water uses:

- Raw drinking, public water supply and food processing
- Aquatic life and wildlife
- Agriculture (livestock watering and irrigation)
- Recreation and aesthetics
- Industrial (water supplies)

The guidelines are set after considering the scientific literature, guidelines from other jurisdictions, and general conditions in British Columbia. The scientific literature gives information on the effects of toxicants on various life forms. This information is not always conclusive because it is usually based on laboratory work which, at best, only approximates actual field conditions. To compensate for this uncertainty, guidelines have built-in safety factors which are conservative but reflect natural background conditions in the province.

The site-specific water quality objectives are, in most cases, the same as guidelines. However, in some cases, such as when natural background levels exceed the guidelines, the objectives could be less stringent than the guidelines. In relatively rare instances, for example if the resource is unusually valuable or of special provincial significance, the safety factor could be increased by using objectives which are more stringent than the guidelines. Another approach in such special cases is to develop site-specific guidelines by carrying out toxicity experiments in the field. This approach is costly and time-consuming and therefore seldom used.

Guidelines are subject to review and revision as new information becomes available, or as other circumstances dictate.

The guidelines apply to the ambient raw water source before it is diverted or treated for domestic use.

The Ministry of Health regulates the quality of water for domestic use after it is treated and delivered by a water purveyor.

Guidelines relating to public health at bathing beaches are the same as those used by the Ministry of Health which regulates the recreation and aesthetic use.

Recommended Guidelines

These criteria are based on a detailed analysis given in a technical document.

The terms strong-acid dissociable and weak-acid dissociable cyanide refer to the analytical methods of the Provincial Environmental Laboratory. The strong-acid dissociable cyanide includes free cyanide, simple cyanides and complex metal cyanides (excluding cobalt and gold complexes). The weak-acid

dissociable cyanide includes only free cyanide, simple cyanides and weak-acid dissociable metalocyanides such as zinc- and cadmium-cyanide complexes. Neither method measures cyanate, thiocyanate, or cyanogen chloride. See Application of Criteria for details of these analyses.

RAW DRINKING WATER (includes food processing water)

In raw drinking water, strong-acid dissociable cyanide plus thiocyanate (expressed as CN) should not exceed 200 µg/L in an unfiltered sample.

Note: If it can be shown for a particular water supply that treatment methods (chlorination, ozonation, or ultraviolet irradiation) do not produce free cyanide or cyanogen chloride from the dissociation of thiocyanate, then the criterion should apply only to strong-acid dissociable cyanide.

AQUATIC LIFE

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
(b) the maximum concentration should not exceed 10 µg/L at any time.***

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.

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.

OTHER WATER-USE CATEGORIES

There is insufficient information to allow the recommending of criteria for other water-use categories. The drinking water criterion is suggested as a guideline for other water-use categories which include wildlife, agriculture, recreation, and industry (other than food processing).

Application of the Guidelines

The aquatic life criteria recommended here apply when cyanide is acting alone. If other contaminants are present with cyanide, the criteria may have to be modified to account for antagonistic, additive, or synergistic effects, depending on the contaminants involved.

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 less than 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.

DETAILS OF ANALYSES

The analytical techniques reported here are those currently being used by the Provincial Environmental Laboratory, and may be subject to change as new techniques are developed. Any other techniques should be assessed to determine if they are comparable to those currently being used.

(A) Strong-acid Dissociable Cyanide

Sample Preparation — unfiltered and field preserved to pH 12 with 10N 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 are 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 Concentrations — 5 µg/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 distil 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

Sample Preparation — unfiltered and field preserved to pH 12 with ION 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 Concentrations — 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.