Water Quality

Ambient Water Quality Guidelines for Chlorate

Environmental Quality Branch
Ministry of Environment

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

Approved: _____

Assistant Deputy Minister: _____

CIP Information Summary

This document is one in a series that establishes ambient water quality guidelines for British Columbia. The guidelines represent safe conditions or levels of a variable, which have province-wide application and are set to protect various water uses. This report sets guidelines for chlorate to protect marine and freshwater algae and drinking water for humans, wildlife and livestock. Guidelines were not set for other uses due to the low sensitivity of other organisms to chlorate, presently known ambient and effluent levels, and lack of good data. The Canadian Council of Ministers of the Environment (CCME) has not set a guideline for chlorate.

A major use of the guidelines is to set site-specific ambient water quality objectives. These objectives are the guidelines, adopted or modified to meet specific local conditions, applied to a particular body of water to protect the most sensitive designated water use. The guidelines and objectives do not have legal standing, but are used in the preparation of Waste Management Permits, Orders or Approvals, which do have legal standing.

Microorganisms can adapt their metabolic processes to use virtually any source of carbon, including chlorate, for growth. There is evidence for anaerobic bacterial degradation of chlorate in nature. If the organisms have never been exposed to chlorate, there will be an initial adaptation period but once the adaptive phase is over and a large microbial population has been established, breakdown of chlorate is rapid. Subsequent additions of chlorate to the environment would be quickly degraded, if the concentrations were not excessive.

The guidelines to protect wildlife, freshwater life, marine life, livestock and source human drinking water are summarized in Table 1.

Table 1. Summary of Chlorate Guidelines

Water Uses	Guidelines
Raw Drinking Water	2.4 milligrams/L
Wildlife and Livestock	3 milligrams/L
Freshwater Aquatic Life	30 milligrams/L
Marine Aquatic Life	5 micrograms/L

Preface

Establishing the Guidelines

The Ministry of Environment is developing ambient water quality guidelines for British Columbia. This work has two goals:

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

The guidelines represent safe conditions or safe levels of a substance, and are set to protect various water uses. A guideline is defined as "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 applied province-wide, but they are use-specific, and are being developed for the following:

- raw drinking water, public water supply and food processing[1]
- recreation and aesthetics[2]
- aquatic life and wildlife, and
- agriculture (livestock watering and irrigation)

The guidelines are established after considering the scientific literature, guidelines and criteria from other jurisdictions and environmental conditions in British Columbia. The scientific literature provides information about the effects of toxicants on various life forms. This information may not be conclusive since it is usually based on laboratory work that only approximates field conditions. To compensate for

this uncertainty, the guidelines have built-in safety factors that are conservative, but reflect natural background conditions in the province.

The guidelines are subject to review and revision, as new information becomes available or as other circumstances dictate. The working guidelines in this document are established using the best readily available published data.

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[1] The guidelines apply to an 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.

[2] Guidelines relating to public health at bathing beaches will be the same as those developed by the Ministry of Health, which regulates the recreation and aesthetic water use.

Using the Guidelines to Set Objectives

Water quality guidelines are used to set ambient water quality objectives for specific waterbodies. The objectives are based on present and future uses, waste discharges, hydrology, limnology, oceanography, and on existing background water quality.

In most cases, the objectives will be the same as the guidelines. However, when natural background levels exceed the guidelines, the objectives could be less stringent than the guidelines. In rare instances, for example, if the resource is unusually valuable or of special provincial significance, using objectives that are more stringent than the guidelines could increase the safety factor. Another approach in special cases would be to develop site-specific guidelines by conducting toxicity experiments in the field. This approach is costly and time consuming, and is seldom used.

Neither the guidelines nor the objectives derived from them have any legal standing. Objectives can be used to calculate waste discharge limits. These limits are outlined in waste management permits that do have legal standing. Objectives are not usually incorporated as conditions of a permit. Objectives are also used in the preparation of waste management orders and approvals. These documents also have legal standing.

Since there are an endless number of substituted phenols possible, all with somewhat different toxicity thresholds to individual species, and it is not practical to determine guidelines for each phenol, we recommend a site-effluent-and-species-specific determination for any given situation. This means that one should determine what species are present in the receiving water, choose several that are most likely to be very sensitive, amphibian tadpoles and salmonid fry are normally the species of choice, and carry out bioassays using a typical effluent mixture of phenols. The water quality objective developed for the local situation should be 0.05 of the LC50 determined by the assay in order to account for any more sensitive species and for atypical, more toxic, effluent mixtures.

Introduction

Chlorate has been used historically as a herbicide to kill all terrestrial plants except mosses. The only other major source of chlorate input to the environment is pulp mill effluent where chlorine dioxide is used for bleaching. Minor amounts of chlorate are also produced when chlorine dioxide is used to disinfect drinking water. Chlorate toxicity is linked to nitrate concentrations and aerobic conditions. The most sensitive species to chlorate are marine brown algae, the kelps, i.e. *Macrocystis* and *Fucus*, which are vital components of the coastal ecosystem. Most other species are relatively insensitive. Brown algae are ubiquitous along coastal BC, are dominant components of the ecosystem and are the preferred sites for herring to spawn.

The chlorate anion is not directly toxic; the mechanism of chlorate toxicity in plants is indirect. In simple terms an enzyme system in plants, evolved to reduce nitrate, also reduces chlorate to a toxic intermediate product, apparently chlorite or hypochlorite. These reduction products of chlorate inactivate the nitrate reductase system. The nitrate reductase enzyme system in plants is an inducible enzyme system that requires a certain minimum threshold level of nitrate in order to become activated. It then reduces nitrate to nitrite and ultimately to ammonium, the preferred form of nitrogen for use by the plant. If there is sufficient nitrate in the growth medium, the nitrate reductase system is activated and takes up chlorate, reducing it to the toxic chlorite.

Generally, in BC, nitrate levels are low in large rivers and coastal marine waters which tend to be nitrogen-limited systems; rarely would there be enough nitrate available to tie up all the active sites in the nitrate reductase enzyme system. Often there will not even be enough nitrate to induce the enzyme system to activity. Chlorate is not very toxic in ammonium-based systems.

There is no evidence of chlorate being mutagenic, carcinogenic or teratogenic. Chlorate is readily biodegraded by microorganisms under anaerobic conditions. There is no tendency for chlorate to accumulate or bioconcentrate in organisms and it is not magnified in the food chain.

Chlorate can be removed from bleach plant effluents by reduction with sulphur dioxide but this is an incomplete process and consumes large quantities of chemicals. Anaerobic bacteria can remove chlorate from kraft bleach effluent with less than one-hour retention time.

1. Recommended Guidelines

1. Drinking Water

It is recommended that the total concentration of chlorate in drinking water should not exceed 2.4 mg/L to protect 5-kg infants.

Rationale:
This guideline is designed to protect 5-kg infants since they drink more water in proportion to their body

weight than adults do. The maximum daily intake rate from all sources is 1 mg/kg body weight. Water consumption is assumed to be 1.5 L/d, the normally accepted drinking water consumption rate for average people in north temperate climates. The lowest doses reported as fatal in humans are 2 g in small children and 5 g in adults or about 100 mg/kg. Applying a factor of 0.01 to derive a no observed effect level (NOEL) from the acute fatally toxic threshold gives a guideline of 1 mg/kg. This entire intake is not in the water since there must be some allowance reserved for intake from food and other sources. In the table below consumption ratio of about 70% in the water and 30% from other sources is assumed.

Table 2. Body Weight and Safe Chlorate Concentration in the Drinking Water

weight in kg	5	10	20	30	50	70	90
[chlorate] mg/L	2.4	4.8	9.6	14.4	24.0	33.6	43.2

The calculation is 1 mg/kg X 5 kg = 5 mg/ 1.5 L/d = 3.4 mg/L X 0.7 = 2.38 mg/L (rounded to 2.4 mg/L for 5 Kg infants). This leads to overprotection for adults who are heavier but tend to drink about the same amount of water.

Doses in excess of 100 mg/kg, 7 grams for a 70-kg adult human or 500 mg for a 5-kg baby, are generally fatal, although doses of this magnitude are unlikely from ambient exposures.

2. Aquatic Life

2.1 Freshwater

To protect freshwater aquatic life from adverse effects, the concentration of chlorate should not exceed 30 mg/L in the water column.

Rationale:
Chlorate appears to be non-toxic (LC_{50} is greater than 100 mg/L) to freshwater life. Five species of insects were exposed for 10 days to chlorate up to 100.0 mg/L. The 48-hour LC_{50} for *Daphnia magna* was estimated at 3162 mg/L. For freshwater algae the lowest effect level, an LOEC for growth inhibition in *Chlorella vulgaris*, was 334 mg/L chlorate at 28 mg/L nitrate. The lowest effect level, a 24-hour LC_{50} to an aquatic invertebrate (the water flea, *Daphnia magna*) was 880 mg/L of chlorate. The lowest effect level, a 96-hour LC50 to a freshwater fish, (larval cherry salmon, *O. masou*) was 863 mg/L of chlorate at an unspecified nitrate level.

For freshwater life a guideline is proposed to protect the most sensitive species, which appear to be green algae. The recommended guideline is 30 mg/L of chlorate ion (37 mg/L sodium chlorate), based

on applying a LOEL to NOEL factor of 0.1 results to the LOEL of 334 mg/L, resulting after rounding in a guideline of 30 mg/L.

2.2 Marine

To protect marine aquatic life from adverse effects, the concentration of chlorate should not exceed 5 µg/L in the water column.

Rationale:
For marine life, the guideline is set to protect the most sensitive species, brown algae. These include the kelps (*Macrocystis*) and *Fucus* (bladder wrack). This guideline is based on the NOEC of 5 µg/L chlorate from a six-month chronic study on the growth of *Fucus vesiculosus*. The LOEC for chlorate from this study was 15 µg/L and the EC50 was 100 µg/L. The NOEC was accepted as the guideline since the reported values from these studies confirm the standard 20:1 ratio of EC50 (or LC50) to NOEC that is generally applied in deriving guidelines.

3. Wildlife and Livestock

To protect wildlife and livestock from adverse effects, the average concentration of chlorate should not exceed 3 mg/L.

Rationale:
The recommended guideline was designed to protect dogs. Applying the safety factor of 0.01 to an LD_{50} of 500 mg/kg gives a guideline of 5 mg/kg. At 5 mg/kg chlorate and 80 mL/kg water intake the chlorate concentration in the water should not exceed 62.5 mg/L for an adult animal. The chlorate level to protect neonate animals becomes 4.166 mg/L if the same ratio (1:15) of chlorate intake for neonate animals to adult animals is used as was used in humans. When the same water to food source ratio as was applied for humans (70% in water and 30% in food) is used, the guideline becomes 3 mg/L. This is close to the 2.4 mg/L proposed for human drinking water.

4. Irrigation, Recreation and Industrial Uses

No guidelines are set for these water uses.

Rationale:
Chlorate is used as a herbicide at concentrations over 20 gram/L. In fresh water situations the worst case situation would be a pulp mill discharging 100 mg/L of chlorate into a river with a minimal dilution of 20:1 for a final concentration of 5 mg/L. This should not affect plant growth. There is no evidence, given the mode of action of chlorate, to suspect that they would have any effect on recreational activities at the

expected concentrations in fresh or marine waters. There are no known literature guidelines or documented effects on irrigation, recreation or industrial uses and none are anticipated at the maximum expected concentrations.