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Ambient Water Quality Criteria for Silver

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Summary

This document is one in a series that establishes ambient water quality criteria for British Columbia. It includes an overview which is followed by the main body of the report. This document sets criteria for silver to protect freshwater and marine aquatic life.

Criteria were not set for human, livestock or wildlife drinking water, recreational waters, irrigation water or industrial water uses, since, either suitable data documenting the effects of silver for these uses were lacking, or the criteria would have been about 1000 times higher than the aquatic life criteria and therefore redundant.

Silver is most toxic to microscopic organisms or larval forms of aquatic animals. There is no evidence that silver is naturally transformed to a hazardous biologically-available form (such as mercury into methyl mercury). Ionic silver is more toxic to aquatic organisms than silver compounds. Thiosulphate-complexed silver breaks down to silver sulphide which is less toxic than the silver ion. Silver criteria are summarized in the chapter on Recommended Criteria. A more detailed discussion of the criteria is presented in the main body of the report.

Preface

Establishing the Criteria

The Ministry of Environment, Lands and Parks is developing ambient water quality criteria for British Columbia. This work has two goals:

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

The criteria represent safe conditions or safe levels of a substance, and are set to protect various water uses. A criterion 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 criteria are applied province-wide, but they are use-specific, and are being developed for these water uses:

- raw drinking water, public water supply and food processing *
- aquatic life and wildlife
- agriculture (livestock watering and irrigation)
- recreation and aesthetics **
- industrial water supplies

** The criteria 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.*

*** Criteria relating to public health at bathing beaches will be the same as those used by the Ministry of Health, which regulates their use.*

The criteria are established after considering the scientific literature, 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 is not always conclusive because it is usually based on laboratory work that, at best, only approximates field conditions. To compensate for this uncertainty, and applying the "precautionary principle", the criteria have built-in safety factors that are conservative, but reflect the natural background in the province. The criteria are subject to review and revision as new information becomes available or as other circumstances dictate.

Using the Criteria to Set Objectives

The criteria are used to set ambient water quality objectives for specific waterbodies. The objectives are also 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 criteria. However, when natural background levels exceed the criteria, the objectives could be less stringent than the criteria. In rare instances—for example, if the resource is unusually valuable or of special provincial significance—the safety factor could be increased by using objectives that are more stringent than the criteria. Another approach in special cases would be to develop site-specific objectives by conducting toxicity experiments in the field. However, because this approach is costly and time consuming, it is seldom used.

Neither the criteria 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 which 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.

Introduction

Silver Toxicity

A natural or man-made chemical present in the environment does not always lead to human or animal exposure. Exposure requires contact with substances containing the chemical. Exposure itself is not necessarily harmful; several other factors determine whether contact leads to harmful effects and the type and severity of these effects. These factors include the dose (how much), the duration (how long), the timing (when in the life cycle), the route of exposure (injection, inhalation, ingestion, contact) and individual characteristics and lifestyles (sex, age, health, habits, fitness, genetic predisposition).

Populations that are unusually susceptible to toxic effects from silver are those with dietary deficiencies of vitamin E or selenium, or those with genetically-based deficiencies in the metabolism of these essential nutrients. Those populations with damaged livers and those exposed to very high selenium levels in their diet are also at higher risk. Some people may exhibit an allergic response to silver.

Silver Speciation

Most toxicological studies have been conducted with silver in the free, elemental or 0 oxidation state, and with the +1 monovalent silver ion. The rarer +2 and +3 oxidation states have not been studied adequately. The majority of silver resulting from photo-processing occurs in an insoluble form. Theoretical calculations of organic and inorganic silver complexes indicate that, due to the low solubility of silver sulphide and the high affinity of silver for sulphide, little free silver would occur at equilibrium, in effluents or surface waters that contained any sulphide.

Bioassays have demonstrated that, although 'free' silver caused the death of fathead minnows at relatively low silver concentrations, silver thiosulphate and silver sulphide salts had no effect at over 1000 times the 'free' silver concentration.

The Aquatic Ecosystem Objectives Committee of IJC agrees that 'free' silver is a better measure of toxicity than total silver, The committee does not recommend the adoption of an objective based on 'free' silver for the following reasons:

- near an effluent, silver may not yet be in equilibrium with all the available complexing agents.
- sulphide, which is the only reactant likely to reduce silver adequately, is readily oxidized to sulphate when oxygen is available. The half-life of sulphide is about 50 hours but oxidation rates may be increased five-fold by metals such as calcium. Sulphide has not been found, even at very low detection limits, in the Great Lakes.
- weaker organic complexing agents for silver still permit 'free' silver to exist at concentrations near the objective level.
- the method presented by Kodak for measuring silver ion activity is not adequate for low environmental concentrations; there are difficulties with reproducibility, dependability and comparability. The method is only reliable at levels of 'free' silver higher than the criteria.

Until a reliable method is developed to measure 'free' silver at concentrations below 0.1 micrograms per litre, silver objectives should be expressed as total silver. This level is the routine total or dissolved silver detection limit for water samples analyzed in labs used by the British Columbia Ministry of Environment for analysis of ambient water samples.

Recommended Criteria

The following criteria are based on information presented in the technical appendix, and are summarized in the tables below. The Canadian Council of Ministers of the Environment (CCME) is considering similar guidelines for silver.

Aquatic Life

Summary Table

Recommended Criteria for the Protection of Marine and Freshwater Aquatic Life

Environment	Criteria as total Silver	Conditions
fresh water	0.05 µg/L as a 30-day mean	hardness < or = 100 mg/L
	0.1 µg/L maximum	hardness < or = 100 mg/L
	1.5 µg/L as a 30-day mean	hardness > 100 mg/L
	3.0 µg/L maximum	hardness > 100 mg/L
marine water	1.5 µg/L as a 30-day mean	open coast and estuaries
	3.0 µg/L maximum	open coast and estuaries

Drinking Water and Food Processing Industries

For human, laboratory animal, wildlife and livestock drinking water, and for food processing industries where water is incorporated into the product, no silver criterion appears to be necessary. The aquatic life criteria are more than adequate for any such uses. The level used by Health and Welfare Canada in 1987, and by Australia in 1992, for human drinking water was 50 µg/L. Health and Welfare Canada deleted silver from the 1989 Guidelines for Canadian Drinking Water Quality as the value was very conservative and had no defensible, scientific basis.

Recreation and Aesthetics

Silver is not volatile, has no offensive odour and does not cause any colour or other visual effects in water, therefore it is not a concern for aesthetics. For recreation, levels of concern would be at least as high as, or higher, than the drinking water criterion. Therefore, no silver criterion appears to be necessary for these uses of the water. The aquatic life criteria are more than adequate for any such uses.

Industrial

Industries, such as solid state electronics and photofinishing, which may have stringent silver requirements, may need to reduce silver concentrations in-house to levels suitable for their processes.

Application of Criteria for Aquatic Life

Silver is a disinfectant for non-spore forming bacteria at concentrations about 1000 times lower than the levels at which it is toxic to mammalian life. This extreme mammalian-to-bacterial toxicity differential is the definition of an oligodynamic material. The low concentration necessary for oligodynamic activity allows silver or one of its insoluble salts to be used indefinitely in contact with sterile liquids without silver levels building up to concentrations harmful to people.

The biological effects of silver are apparently due to reversible bonds with enzymes and other active molecules on the surface of cells. Due to its sulphydryl binding propensity, biologically-available silver disrupts membranes, disables proteins and inhibits enzymes. The ionic form of silver is necessary for biological activity and the lipid phase of the membrane appears to be important in adsorbing silver ions to living cells. The active sites on enzymes which are affected by silver are apparently the electron-rich functional groups such as–SH groups.

Silver combines with plasma proteins, is removed by the liver and over 90% is eliminated in the bile; most of this in the feces with very little in the urine. That silver which is not excreted is deposited in the skin and mucous tissues. Tissue deposition of silver results from precipitation of insoluble salts such as silver chloride and silver phosphate. These may be transformed to soluble silver sulphide albuminates and bind with amino or carboxyl groups in proteins and nucleic acids. They may also be oxidized to metallic silver by ascorbic acid or catecholamines.

Argyria, silver deposition, occurs in all organs. Common deposition sites for people who have no history of therapeutic use are the liver, skin, pancreas, adrenals, glomeruli of the kidney, brain, bone marrow, walls of the blood vessels, thyroid, mesenteric glands, choroid plexus, spleen and testes. Generalized argyria is indicated by slate-gray skin and hair colouring, silver finger nails, a blue halo around the cornea and in the conjunctiva of the eye, disturbance of dark adaptation and turbidity of the anterior lens capsule. The tissue content and distribution pattern of silver deposition is a function of the intake route, quantity and chemical form.

The discoloured skin in argyric patients exposed to ultraviolet radiation is likely caused by photoreduction of silver chloride to metallic silver, which is then oxidized to black silver sulphide and bound by tissues. If the diet is high in selenium, the silver sulphide is converted to silver selenide which may result in higher silver deposition rates than with silver sulphide.

Silver is tightly bound by sewage sludge and elevated levels of silver are often associated with sewage outfalls receiving minimal treatment. In the absence of sewage, silver associates with iron oxides and humic substances. The relative bioavailability of either silver-inorganic complexes or silver-organic complexes appears to depend on the individual compounds. Silver-inorganic complexes are probably the most common in the marine environment. Silver-chlorides are generally not bioavailable except for silver chloride. Silver-iron oxides or silver-magnesium complexes in sediments increase the availability to bottom feeding organisms. Activated sludge organisms may bioaccumulate silver at 100 times the concentration in the effluent.

Silver has low toxicity to vertebrate animals and is eliminated rapidly when ingested orally. It is not a cumulative toxin. Since surface waters in Canada generally contain low levels of silver and there are few data on chronic silver toxicity to animals, no criteria seem to be justified at this time for wildlife, livestock or laboratory animal drinking water. Wildlife, free range and confined livestock and laboratory animals can safely drink water which meets the aquatic life criteria.

Maximum and 30-day average criteria have been set despite the paucity of data for marine fish since fish are not sensitive to silver at concentrations over 10 times the levels that affect most invertebrates and algae. Criteria are set to protect the most sensitive lifestage of the most sensitive species. The literature indicates that the most sensitive organisms are phytoplankton and the embryonic and larval stages of invertebrates. Since the sensitivity of invertebrates and phytoplankton to silver is much greater than that of fish, and because a great deal of literature is available concerning their sensitivities, the requirements for marine fish data were considered to be superfluous and were waived.

The life stage, size of the organisms, length of time of exposure, species sensitivity and salinity all contribute to the variation in toxicity reported in the literature. The relative proportion of the free silver+ ion to the total silver content in the oceans is a function of the salinity. In the ocean, most of the silver at any one time is present as chloride complexes; of these complexes only the mono-chloro complex silver chloride is biologically available. At a salinity of 25 parts per thousand, which is almost the natural concentration in the sea, only about 1 part in 16 000 parts of the silver would exist as the free ion.

This lack of free silver ion is generally not accounted for in the literature where most values are given as total silver and the actual toxic forms of the silver would be a considerably smaller value. This factor accounts for much of the wide variation in toxicity values reported in the literature, for while salinity is generally reported, it is rarely considered as a factor affecting toxicity. The total silver measurements reflect the worst-case scenario, which should be considered when setting any water quality criteria in order to protect the most sensitive life stages of the most sensitive species. This worst-case scenario is particularly important for estuaries, where salinity can fluctuate quite dramatically.

Silver is one of the most toxic of the heavy metals to freshwater micro-organisms. Water hardness, length of exposure, size of the organism and life stage of the organism all affect the toxicity values. Reports of the validity of static versus flow-through tests within the literature are variable; however static tests with renewal of test water appear to be as accurate as flow-through bioassays. Invertebrates and embryos of fish are generally much more sensitive than juvenile and adult fish.

The effect of speciation on the acute and chronic toxicity of silver was compared using the fathead minnow as the test organism. Silver sulfide, silver thiosulfate and silver chloride were compared to the silver ion, added as silver nitrate. The tests were flow-through in soft water at 25¡C. Silver chloride was found to be 300 times less toxic, silver sulfide was 15,000 times less toxic, and silver thiosulfate was 17,500 times less toxic than silver nitrate.

Most existing silver criteria, objectives or regulated amounts are not based on the free ionic monovalent ion, which is acutely toxic to aquatic life. Instead they are based on total silver which includes the metal, complexes and precipitates, all of which are very much less toxic than the monovalent ion. Thus, these existing regulations and criteria are often overprotective. A method of measuring the biologically-available forms of silver is needed so that the criteria and the risk are correlated.

Regulations should reflect the appropriate risk but the problem is that there is no monovalent ion specific measurement. In addition, some non biologically-available silver may be in forms that are in equilibrium with monovalent silver and thus much of the silver pool becomes ultimately available as the monovalent silver is taken up. Benthic organisms will take up some insoluble forms of silver as they graze, and thus more than just the monovalent form is available to them. Therefore, total silver is recommended.

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