Aluminum Water Quality Guidelines - Wildlife, Livestock Watering, and Irrigation (Reformatted Guideline from 1988)

Ministry of Water, Land and Resource Stewardship Water Protection & Sustainability Branch





No. WQG-09-2

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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Document citation:

British Columbia Ministry of Environment and Parks 1988. Water quality criteria for aluminum. Water management branch (reformatted in 2023).

Original Author:

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Notes on Reformatted Version:

Sections of this report on aquatic life, industrial water use, drinking water and recreation have been removed and all remaining text are from the original 1988 document. Freshwater aquatic life, drinking water and recreation guidelines can be found in separate documents on the B.C. water quality guidelines website. B.C. no longer develops or supports guidelines for industrial water use.

Cover Photograph:

Location: Bulkley River, B.C.

Acknowledgements

The following individuals are acknowledged for their valuable assistance with the preparation and/or critical review of this report:

- Dr. R.J. Buchanan, Mr. R.J. Rocchini, Mr. L.W. Pommen, Mr. W. Bailey, Mr. D.W. Roberts, and Mr. R.A. Fairservice of the Water Management Branch.
- Dr. M.J.R. Clark, Mr. R.J. Crozier, Mr. M. Macfarlane, Mr. B. Moore, Mr D. Wetter, and Mr. B.D. Wilkes of the Waste Management Branch.

Dr. J.H. Smith of the Ministry of Health.

- Mr. R. Puls of the Ministry of Agriculture and Food. Dr. M.C. Taylor and Mr. B. Kelso of Environment Canada.
- Dr. M. Havas of the Institute for Environmental Studies, University of Toronto.
- Dr. C.M. Neville of the Ontario Ministry of the Environment.

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1. INTRODUCTION

Aluminum is widely distributed in the environment and has been long known as a toxicant to plants growing in acidic soils. Recently, attention has focused on the role of aluminum both as a key toxic factor in aquatic acidification phenomena and as a pathogenic factor in human diseases, notably Alzheimer's syndrome.

The purpose of this document is to develop water quality criteria for aluminum appropriate to British Columbia for various water uses, including drinking water, aquatic life, wildlife, livestock watering, irrigation, recreation and aesthetics, and industrial water supplies. Literature was reviewed pertaining to the sources of aluminum, its speciation, transformations and accumulation in the environment, the effect on human health, and the toxicological effects on aquatic biota. Much of the recent literature is devoted to the toxic effects of aluminum on aquatic organisms as related to acidic precipitation, and therefore a large portion of this document focuses on aquatic life effects.

Standards, objectives, criteria, and accompanying rationales from other jurisdictions were reviewed and their suitability for the formulation of defensible criteria for British Columbia waters was considered. Criteria are recommended to protect water users from aluminum originating from anthropogenic sources. Research needs in the field of aluminum toxicity are identified.

2. OCCURRENCE IN THE ENVIRONMENT

2.1 Natural Sources

Aluminum is the third most ubiquitous element in the earth's crust and the most abundant metal (Hunter et al., 1980). Although it is a constituent of all soils, plants, and animals, it is too reactive to persist in nature in the elemental form. In the lithosphere, it is never found as a pure metal but rather in combination with oxygen and silicon as complex and insoluble aluminosilicate minerals (Freeman and Everhart, 1971), which are abundant in igneous, metamorphic, and sedimentary rocks (Gunn and Keller, 1984).

As a result of natural weathering processes, aluminum becomes enriched in soils as stable secondary mineral forms such as impure aluminum silicates or clays, aluminum hydroxides or bauxite alumina (as the trihydrate gibbsite Al(OH)₃, or the monohydrate boehmite AlOOH). Other aluminum-containing minerals including feldspar, mica, amphibole, garnet, cryolite, zeolite, alunite, dawsonite, and corundum may also be present in soils. The clays, however, are the most common of all the sedimentary aluminum-bearing minerals that natural waters come into contact with (Freeman and Everhart, 1971; Hem, 1970).

Since aluminum is so abundant and widely distributed, most natural waters have ample opportunity to dissolve it. However, because of the insolubility of the parent materials, the concentration of dissolved aluminum in natural waters is normally <1 mg/L (Freeman and Everhart, 1971; Hem, 1970). The exceptions are waters of low and high pH or waters high in organics in which soil-bound aluminum becomes more soluble. Naturally acidified surface waters with a pH <4, including bog lakes, volcanic drainage, thermal and saline springs, and shale deposit runoff may contain up to several hundred or even several thousand mg/L of aluminum (Hem, 1970; Burrows and Hem, 1977). High aluminum concentrations can also occur in acidic groundwater.

Aluminum is mobilized not only from the rocks and soils of watersheds', but also from lake sediments (Schindler et al., 1980) and stream sediments (Hall et al., 1980; Hall and Likens, 1984) under acidic conditions. The increase in aluminum concentration may be the result of solubility changes, the

dissolution of aluminum hydroxide compounds, cation exchange on sediment exchange sites, or some combination of these mechanisms (Hall and Likens, 1984).

From a compilation of water quality data for 314 different sites from around the world, Burrows and Hem (1977) concluded that:

- 1) Acid waters consistently contain much more soluble aluminum than neutral or alkaline waters.
- 2) Highly saline waters contain higher levels of aluminum than fresh waters.
- 3) Hot waters tend to contain more aluminum than cold waters.
- 4) Moving waters contain more aluminum than quiescent waters.

The atmosphere also makes natural contributions of aluminum to watersheds in the form of dustfall and precipitation. Atmospheric aluminum levels in Canada (S.E. Ontario) have been recorded to be 0.04-0.39 μ g/m³, and aluminum concentrations in snow and rain have been 0.07-1.3 mg/L and 0.5-1.12 mg/L, respectively (Sorenson et al., 1974).

2.2 Anthropogenic Sources

2.2.1 Aluminum Water Treatment

Aluminum sulphate compounds, called alum as a group, are introduced commonly to water supplies for the removal (by flocculation) of suspended solids, color bodies, and microorganisms, for pH adjustment, and for dechlorination purposes (Sorenson et al., 1974; NAS/NAE, 1980; McKee and Wolf, 1963). Alum has also been used to precipitate phosphorus in highly eutrophic lakes (Lamb and Bailey, 1981). Alum is a double sulphate of aluminum and sodium, potassium, or ammonium (e.g., KAI(SO₄)₂). In water, alum is positively charged and attracts negatively charged impurities, forming an aggregate or floe sufficiently heavy to settle out and be removed. Alum may also act as a disinfectant: some studies have suggested that alum has bacteriostatic properties and is capable of inactivating polio and hepatitis viruses (Sorenson et al., 1974; McKee and Wolf, 1963).

Although the aim of alum treatment is to leave as little aluminum as possible in the drinking water, some small residue of aluminum as suspended aluminum hydroxide particles always remains (McNeely et al., 1979; Hem, 1970; Sorenson et al., 1974). Levels of aluminum above 0.3 mg/Lin the final water usually reflect faults in the coagulation, sedimentation, or filtration stages of treatment signalling the need for corrective measures (WHO, 1984). A survey of drinking waters performed by the U.S. EPA found that the median aluminum level in alum coagulated water was 0.11 mg/L (range of 0.01-2.7 mg/L) (AWWA, 1986). In British Columbia, the settled floc or alum sludge created during alum treatment is usually disposed of on land, and is not directly discharged to receiving waters.

2.2.2 *Effluent Discharge*

Effluent from industrial operations such as paper mills, aluminum manufacturing, anodizing plants, canneries, textile mills, tanneries, and metal cleaning plants may contain high levels of aluminum. Various manufacturing processes can use a wide range of aluminum compounds:

Aluminum chloride	-	dyes, catalysts, disinfectants, cosmetics (deodorants), pape making, refining operations
Aluminum nitrate	-	tanning and finishing leather, dyes, incandescent filaments, fabri printing
Aluminum-ammonium sulphate	-	dyes, fabric printing, food additives, coagulants

Aluminum oxide (alumina)	-	abrasives, paint filler, paper manufacturing, dyes, dispersing agent in food and drugs
Aluminum-calcium silicate	-	in vanilla powders
Sodium silicoaluminate	-	additive to seasonings, salt, sugar, baking powder
Aluminum stearate	-	component of defoaming agents
Sodium-aluminum sulphate	-	coagulant, bleaching agent in flour (Sorenson et al., 1974; McKee and Wolf, 1963; Decker and Menendez, 1974)
Aluminum metal (Al)	-	explosives, paint

This list also indicates the variety of aluminum compounds consumed by humans and directed ultimately to municipal discharges. Other pathways of aluminum into municipal effluent include aluminum cookware, containers, piping, foil packaging, toothpastes, pharmaceuticals (e.g., antacids), and dental amalgams. The natural aluminum content of some foods can be quite high, and according to Sorenson et al. (1974) it far exceeds the amount that is added by processing, packaging, or is included in aluminum-containing additives. In one study of the water quality of the Roanoke River, Virginia, it was found that sewage treatment plants were the most significant anthropogenic contributors of aluminum to the river, followed by a landfill site and a railroad yard (Sorenson et al., 1974). The exact sources of the aluminum were not determined. Treatment of municipal effluent with alum, to reduce the phosphorus level, can produce a discharge of residual aluminum.

2.2.3 Distribution Systems

Metallic aluminum is used in many water distribution systems in the form of piping, screens, fittings, and tanks. Its resistance to dissolution or corrosion by most waters is equal to or better than most metals. Industries requiring high-purity water prefer vessels made of aluminum rather than other metals (Sorenson et al., 1974). Corrosion of aluminum results in the formation of an impervious film of oxide or hydroxide precipitate, which provides protection to the metal between pH 4.5 and 8.5. In both acidic and basic solutions, however, the oxide coating may dissolve exposing the underlying metal, thereby increasing the concentration of soluble aluminum in water. Corrosion rates also depend on the purity of the aluminum, the flow rate of the solution, and the presence of chloride, sulphate, and metals of different electrochemical potential (especially copper). Aluminum corrosion is of concern in fish hatcheries with water supplies that are not circumneutral and that make extensive use of metallic aluminum (Sigma Environmental Consultants Ltd., 1983).

2.2.4 Mining

Man-induced exposure of geologic formations (e.g., mining activities, reservoir impoundments) may cause increases in the aluminum content of natural waters. Coal mining formations with high sulphur content and consequent acidic drainage can contribute to levels of aluminum toxic to aquatic life (Sorenson et al., 1974). The explosives used in mining also contain powdered aluminum as a fuel-sensitizer (Pommen, 1983). The reaction between ammonium nitrate and aluminum during detonation produces aluminum oxide, which is generally insoluble. However, as a result of misfires (i.e., no detonation) and the presence of acidic drainage, elevated aluminum levels could be expected, although this would be minor compared to the contribution from exposed soils.

2.2.5 Acid Rain

Anthropogenic acid precipitation and deposition have been found to be responsible for elevated levels of aluminum in both surface waters and groundwaters. These increased aluminum concentrations are related not to atmospheric loadings of aluminum, but rather to the mobilization of aluminum from the

surrounding terrestrial soils and lake and stream sediments at lower pH levels (Hall et al., 1980; Fisher et al., 1968; Baker and Schofield, 1982). Data from the Adirondack lakes have shown that aluminum concentrations in acidified lakes are 10-50 times higher than concentrations in nearby circumneutral waters (Cronan and Schofield, 1979). Similar patterns have been described for lakes in Canada, Norway, Sweden, Scotland, and Germany (Hall and Likens, 1984; Schofield and Trojnar, 1980). The dramatic increase in the aluminum cation may result from solubility changes (Cronan et al., 1978) and/or cation exchange (Hall and Likens, 1984).

Pulses of high aluminum concentrations may occur during spring snowmelt as the acidic deposits stored in the snowpack are released causing severe pH depressions (Schofield, 1977; CRREM, 1987). Johannessen and Henriksen (1978) determined that 50-80% of acidic materials stored in the snowpack are released with the first 30% of meltwater. The resulting rapid increases in aluminum levels during snowmelt or rain on snow events can cause aquatic life mortality at much lower concentrations than can chronic exposure to gradually increased concentrations (Haines, 1981).

Elevated levels of aluminum in waters may be toxic to the aquatic community at pH levels not physiologically harmful, and thus aluminum is considered a primary factor in explaining the disappearance of aquatic life in waters acidified by man (Schofield and Trojnar, 1980; Baker and Schofield, 1982; Havas and Hutchinson, 1982).

2.3 Natural Levels in Water and Sediment

As indicated previously in Section 2.1, dissolved aluminum concentrations in near-neutral natural fresh waters are generally low. Dissolved aluminum levels can increase in acidic/alkaline solutions as a result of solubility changes, or due to the presence of various inorganic complexing agents. Total aluminum concentrations can be high (>1 mg/L), but in near-neutral waters this usually represents high levels of aluminosilicate material or organically complexed/adsorbed aluminum (Hem, 1970; Burrows and Hem, 1977).

Background aluminum data^{*} for British Columbia rivers, streams, and lakes were extracted from three data sets:

- SEAM data (System for Environmental Assessment and Management) included lakes and rivers with a pH range of 5.7-9.0. Total aluminum (n = 1340) ranged from detection level, 0.02 mg/L, to 7.6 mg/L with a median of 0.05 mg/L and a 90th percentile of 0.61 mg/L. Dissolved aluminum (n=598) ranged from 0.02 to 0.9 mg/L with a median of 0.03 mg/L and a 90th percentile of 0.08 mg/L. Five percent (31 of 598) of the dissolved measurements exceeded 0.1 mg/L. Of a total of 99 sites in the dissolved aluminum data set, 13 sites had measurements exceeding 0.1 mg/L.
- 2) EQUIS data (Environmental Quality Information System; pre-1985) and data from consultants and other government agencies were summarized. This data set included rivers and streams (n = 710) with a pH range of 5-9.1. Total aluminum ranged from <0.005 to 10.4 mg/L and the overall median was 0.130 mg/L. Dissolved aluminum ranged from <0.005 to 0.82 mg/L with an overall median of 0.03 mg/L.
- Lake data were extracted from the Resource Quality Section lake classification file. Total aluminum for the 369 lake samples in this data set ranged from <0.02 to 1.0 mg/L. Dissolved aluminum was not measured.

There were 197 surface samples which averaged 0.052 mg/L (range 0.02-0.64 mg/L) and had a median of 0.03 mg/L and a 90th percentile of 0.09 mg/L. Bottom samples (n = 172) averaged 0.07 mg/L (range 0.02-1.0 mg/L) and had a median of 0.03 mg/L and a 90th percentile of 0.13 mg/L.

^{*} excluding sites downstream from effluent discharges, acid mine drainage, and contaminated groundwater.

There were 26 samples with pH <6.5 (4.9-6.4). Total aluminum in these samples ranged from 0.02 to 0.35 mg/L and the median and 90th percentile values were 0.1 mg/L and 0.31 mg/L, respectively.

Total aluminum levels were also determined for sediment samples from the same series of lakes. Background total aluminum levels in lake sediments averaged 19 mg/g (range 0.12-941 mg/g). Mean total aluminum in stream sediments from 25 streams across British Columbia ranged from 16.2 to 44 m g/g (Environment Canada, Environment Protection data).

Natural aluminum levels in salt water are very low (0.002-0.154 mg/L; Washington-British Columbia coast [Joyner, 1964, as cited in Burrows and Hem, 1977]).

3. FORMS AND TRANSFORMATIONS IN THE ENVIRONMENT

The chemistry of aluminum in water is complicated, but can be characterized by three important properties:

- 1. Its hydroxides are amphoteric (i.e., readily soluble in both acidic and basic solutions).
- 2. It forms stable soluble complexes with other substances present in the water.
- 3. It tends to polymerize over time.

As a result, the species and concentration of aluminum in natural waters depend on the pH and the types of complexing ligands present in the receiving waters and, to a lesser extent, on the temperature and duration of exposure to the water (Hunter et al., 1980; Burrows and Hem, 1977). The resultant speciation of aluminum has a substantial effect on aluminum toxicity.

3.1 Monomeric (Inorganic) Complex Ions

All aluminum in solution is a result of mineral weathering. Under the action of water or an acidic soil solution, granitic and similar aluminosilicate minerals release basic cations into solution. This hydrolytic disintegration follows the sequence of bonding strengths of the different ions constituting the mineral lattice: first the alkaline earths and akali metals are released, and eventually the trivalent aluminum ion (e.g., for the sodium feldspar component of granite:

$$NaAlSi_{3}O_{8} + 4H_{2}O + 4H^{+} \rightarrow Na^{+} + Al^{3+} + 3Si(OH)_{4}).$$

Aluminum in aqueous solution does not exist as the free, simple cation AI^{3+} , but rather as the monomeric hydrated complex ion $AI (H_2O)_6^{3+}$ (hexaquaaluminum). The AI^{3+} ion and its water ligands are bound closely together and behave like a single, large ion (although for convenience, the water ligands are usually omitted in formulae). The AI^{3+} ion hydrolyses to various monomeric aluminum hydroxides according to the following reactions:

$$\begin{split} \mathsf{AI}(\mathsf{H}_2\mathsf{O})_6^{3^+} + \mathsf{H}_2\mathsf{O} &\to \mathsf{AI}(\mathsf{OH})(\mathsf{H}_2\mathsf{O})_5^{2^+} + \mathsf{H}_3\mathsf{O}^+ \\ \mathsf{AI}(\mathsf{OH})(\mathsf{H}_2\mathsf{O})_5^{2^+} + \mathsf{H}_2\mathsf{O} &\to \mathsf{AI}(\mathsf{OH})_2(\mathsf{H}_2\mathsf{O})_4^+ + \mathsf{H}_3\mathsf{O}^+ \\ \mathsf{AI}(\mathsf{OH})_2 \ (\mathsf{H}_2\mathsf{O})_4^+ + \mathsf{H}_2\mathsf{O} &\to \mathsf{AI}(\mathsf{OH})_3(\mathsf{H}_2\mathsf{O})_3^0 + \mathsf{H}_3\mathsf{O}^+ \\ \mathsf{AI}(\mathsf{OH})_3 \ (\mathsf{H}_2\mathsf{O})_3^0 + \mathsf{H}_2\mathsf{O} &\to \mathsf{AI}(\mathsf{OH})_4(\mathsf{H}_2\mathsf{O})_2^- + \mathsf{H}_3\mathsf{O}^+ \end{split} (\text{Bohn et al., 1979; Voigt, 1980). \end{split}$$

Successive hydrolysis reactions are associated with solutions of successively higher pH. The solubility of these monomeric aluminum hydroxide species is strongly pH dependent. Figure 3.1b shows the amphoteric nature of aluminum in solution: minimal solubility at pH 6, increasing with changes in pH. Figure 3.1a shows a version of the distribution of these monomeric hydroxy aluminum species with pH, and it also illustrates the relative contribution of the various species to dissolved aluminum (in waters containing hydroxide species). Aluminum speciation is complicated between pH 4 and pH 7, but relatively

simple above pH 8 and below pH 4. The Al^{3 +} ion predominates below pH 5, AlOH²⁺ between pH 5 and pH 5.4, Al(OH)₂⁺ between pH 5.4 and pH 5.9, Al(OH)₃⁰ between pH 5.9 and pH 6.1, and Al(OH)₄⁻ (aluminate ion) above pH 6.1. The aluminate ion represents the apparent limit for hydrolysis of Al³⁺; the species Al(OH)₅²⁻ and Al(OH)₆³⁻ have not been reported.



Figure 3.1. (A) Percent composition of total aluminum for the soluble aluminum species as a function of pH and (B) Equilibrium solubility of microcrystalline gibbsite at 25°C (from Playle, 1985).

Aluminum also forms strong coordinate bonds with inorganic ligands other than water and hydroxide. The most important of these in descending order are the fluoride, sulphate, and phosphate ions. Thus, in aqueous aluminum solutions, there may be many dissolved aluminum species present (Hem, 1968). The forms and extent of aluminum complexing in solutions containing both fluoride and sulphate and the effects of pH on complexing are shown by Hem (1968) using graphs. These inorganic complexes are pH-dependent and act to increase the solubility of aluminum (Hem, 1970).

Although fluoride is a minor constituent of most natural waters (generally <0.1 mg/L), its strong complexing action has considerable influence on the forms of dissolved aluminum present (Hem, 1968). Six stable aluminum fluoride complexes are known (Burrows and Hem, 1977), although AIF_2^+ and AIF_2^+ are

the major species (in waters containing <1.0 mg/L fluoride) (Hem, 1970). Fluoride complexes are the predominant form of aluminum solute species in water with pH <6, when more than 0.1 mg/L fluoride is present. At higher pH (>6), fluoride plays less of a role as hydroxy complexes form preferentially (Andelman and Miller, 1986). If fluoride levels are high enough (in excess of aluminum), the AlOH²⁺ species becomes an insignificant part of the total aqueous aluminum species. Driscoll et al. (1980) determined that aluminum fluoride complexes were the dominant inorganic form of Al, comprising 25 percent of total measured Al in acidified Adirondack lakes and streams. Al³⁺ and Al hydroxide complexes were less significant fractions of the total aluminum (10 and 12 percent respectively). Gunn and Keller also reported that fluoride complexes were the predominant form of inorganic aluminum in an acidified lake in Ontario (Gunn and Keller, 1984).

Sulphate ions have a much weaker complexing effect than fluoride ions, and they play a lesser role in the aquatic environment. The two major forms are $Al(SO_4)^+$ and $Al(SO_4)_2^-$. However, $Al(SO_4)^+$ may predominate in below neutral pH solutions with high sulphate concentrations, not normally encountered in natural waters, but possible in acid mine drainage, sulfur springs, and acidic, volcanic lakes. For example, if the total sulphate level is 500 mg/L, 90 percent of the total aluminum would be complexed (Hem, 1968). Sulphate can also complex in combination with the hydroxide ligand, e.g., $Al_8(OH)_{10}(SO_4)_5^{4+}$ (Burrows and Hem, 1977). In acidified Adirondack lakes and streams, levels of aluminum complexed with sulphate were very low (1%) and were generally insignificant.

Aluminum phosphate complexes (e.g., AIPO₄•2H₂O) have low solubilities and tend to precipitate and settle out. This property is used in water treatment (i.e., alum addition) to reduce phosphate concentrations. Al³⁺ and Fe³⁺ are important in controlling aqueous phosphate concentrations in acid waters and in forming a reservoir of P in the bottom sediments (Bailey and Stokes, 1985; Boyd, 1979). Aluminum phosphate interactions are pH dependent with maximum complexation occurring at pH 6.0; complexation decreases as pH is lowered or raised from pH 6.0 (Nalewajko and Paul, 1985). Thus, as acidified waters are neutralized, aluminum phosphate interactions intensify and accelerate the oligotrophication of the waterbody. The control of phosphate availability by aluminum may be an important mechanism controlling primary productivity. Experiments by Nalewajko and Paul (1985) have demonstrated that precipitation of phosphate can be substantial when aluminum is added at concentrations existing in many waterbodies. Soluble aluminum phosphate complexes have been reported (Hem, 1970), but are poorly understood and may not exist (Andelman and Miller, 1986). They would be expected only in very acidic or very alkaline waters (from solubility diagrams [Bailey and Stokes, 1985]).

3.2 Polymeric (Inorganic) Complex Ions

Aluminum speciation in solutions changes with time. The hydrolysis of Al^{3+} between pH 4.5 and 6.5 is complicated by the polymerization of the hydrolysis products over time (complications not shown in Figures 3.1a and 3.1b). In soils and waters, the monomeric aluminum hydroxide, $Al(OH)_2^+$, tends to polymerize into large units of colloidal size with the structural pattern of $Al(OH)_3$, This polymer is believed to be an unstable intermediate, which upon aging can precipitate into more stable products: 1) as crystalline gibbsite, or 2) in the presence of dissolved silica, can precipitate as copolymer, layer-type clay minerals (Hem, 1970; Hem, 1968). Polymerization is a relatively slow process: the particle size and the amount of precipitate is dependent on the aging period (Hunter et al., 1980), not pH. During aging, this polymerization releases H⁺ ions with a resultant decrease in the pH of the aluminum solution (Spry et al., 1981), Driscoll et al. (1980) found that on the average 15 percent of the total aluminum measured in acidified Adirondack lakes and streams was comprised of colloidal and polymeric aluminum.

3.3 Organic Monomeric Complex Ions

Aluminum also forms soluble complexes with various organic chelates (or polydentate ligands) (Bohn et al., 1979) derived from watershed soils including: humic and fulvic acids from litter decay and a mixture of polyphenols, sugars, and organic acids from canopy drip (Burrows and Hem, 1977). These chelating agents facilitate the extraction (weathering) of aluminum from parent materials, and the resulting organo-Al complexes are transported by water movement through the soil profile (Voigt, 1980). These may end up in surface waters or be deposited in lower soil horizons as acidity decreases with depth causing precipitation of the complexes. The remobilization of these soil aluminum accumulations by strong mineral acids from anthropogenic sources (i.e., acid rain) has been determined as the cause of the high concentrations of aluminum in acidified lakes (Fisher et al., 1968; Abrahamsen et al., 1976; Cronan and Schofield, 1979; Driscoll et al., 1980; Schofield and Trojnar, 1980).

Driscoll et al. (1980) determined that the predominant form of aluminum in Adirondack surface waters (37 percent) was aluminum complexed with dissolved organic ligands. Johnson et al. (1984) found that in the headwater stream of Jamieson Creek (near Vancouver, B.C.), which is acidified by organic acids, dissolved aluminum is present almost entirely in the form of organo-aluminum complexes. The concentration of these complexes has been found to be independent of pH, but correlated with dissolved organic carbon (DOC) concentrations (Driscoll, 1980; Campbell et al., 1984). Waters with high levels of dissolved organics have higher concentrations of aluminum complexed with organic ligands and reduced concentrations of the more toxic inorganic monomeric aluminum forms.

4. WILDLIFE

4.1 Effects

The toxic effects of aluminum on wildlife have not been addressed adequately in the existing literature. Nyholm (1981) suggested that biomagnification of aluminum through invertebrate prey items may have been the cause of breeding failure among nesting passerine birds near acidified lakes in Sweden. The effect of aluminum on calcium and phosphorus metabolism was suggested as a cause of defective eggshells, although this is inconclusive due to possible body burdens of PCBs and DDT which would confound these observations.

The toxic effects of aluminum on prey items lower on the food chain have the potential to impact the feeding and ultimately the survival of wildlife. Evidence for this comes from a study of Dipper birds, *Cinclus cinclus*, which were absent from streams with >0.1 mg/L aluminum (Ormerod et al., 1986, as cited in Havas and Jaworski, 1986). Abundance and biomass of invertebrate and fish prey were lower in the streams, presumably as a result of aluminum toxicity. Although unstudied to date, similar effects could be expected in small mammal populations dependent on aquatic production.

Since the toxic effects of aluminum on livestock are likely similar for wildlife, refer to the discussion of the toxic effects of aluminum on livestock (Section 5).

4.2 Criteria from the Literature

Criteria, specifically designed for the protection of wildlife, have not been developed by other jurisdictions. Most waters available for use by wildlife will usually be inhabited by aquatic life, and thus the criteria for the more sensitive aquatic life would apply. However, for the uncommon situation where aquatic life is either absent or not considered an important resource, the aquatic life criteria would be over-restrictive for wildlife protection and a separate level of protection is desirable.

4.3 Recommended Criterion

The concentration of total aluminum in waters frequented by wildlife should not exceed 5 mg/L at any time.

4.4 Rationale

The criterion for the protection of wildlife from waterborne aluminum is the same as that specified for livestock watering. The basis for the use of the livestock criterion for wildlife protection is the likelihood that the safe concentration of aluminum for both groups of animals is similar. The rationale for the livestock watering criterion is presented in Section 5.

In the practical sense, wildlife will almost always be protected by the aquatic life criteria because, in the case of multi-use waters, the criteria for the most sensitive water use will apply.

5. LIVESTOCK WATERING

5.1 Effects

There are few data available from the literature to indicate the levels at which aluminum in drinking water is harmful to domestic livestock. No harmful effects were observed when aluminum sulphate was fed to sheep and cows at 15 000 mg/kg of diet (Bailey, 1977), or when AlCl₃ was fed to cattle at 1200 mg/kg (Valdivia et al., 1978). A level of 4000 mg Al/kg of diet caused phosphorus deficiency in chicks (Deobald and Elvehjem, 1935, as cited in U.S. EPA, 1973). The N.A.S. (NAS/NAE, 1980) summary of mineral tolerance data for domestic animals suggests that aluminum in the diet at concentrations below 500 mg/kg does not harm poultry, but concentrations >500 mg/kg could be harmful. Most edible grasses contain approximately 15-20 mg Al/kg (U.S. EPA, 1973).

5.2 Criteria from the Literature

Aluminum criteria from other jurisdictions, specifically designed for the protection of livestock watering, are all set at 5 mg/L (Table 5.1). There are insufficient data, at present, to specify separate criteria for the different kinds of domestic livestock (e.g., ruminants, poultry).

Criteria Statements	Criteria Values	Jurisdiction/ Reference	Date
Maximum concentration	5.0mg/L	Ontario	
		Ministry of the	1978
		Environment	
95 percentile range	5.0mg/L	Britain	
		Anglian Water	1982
		Authority	
Maximum concentration	5.0mg/L	Canada	1987
		CCREM	

Table 5.1. Aluminum Criteria for Livestock Watering

5.3 Recommended Criterion

The concentration of total aluminum in livestock drinking water should not exceed 5 mg/L at any time.

5.4 Rationale

The criterion recommended in this document for the protection of livestock is the same as that adopted by the U.S. EPA (U.S. EPA, 1973), Ontario (Ontario Ministry of the Environment, 1978), Canada (CRREM, 1987), and Britain (Anglian Water Authority, 1982). None of these jurisdictions provided a detailed rationale explaining how this level was chosen. This level appears to be conservative and at present there are insufficient data to justify a change in this level of protection. The following analysis of aluminum intake using sheep as the example illustrates the level of protection provided by this criterion.

Assuming a dry food intake for sheep of 1 kg/d and an average aluminum concentration of 20 mg/kg in the grass eaten, then the average aluminum intake via food would be 20 mg/d. Consumption of the daily water requirement for sheep (4-15 L [NAS, 1974]) containing the criterion level of 5 mg Al/L would result in an additional 20-75 mg Al/ct. Given these assumptions, the total daily oral intake of aluminum for sheep would be 40-95 mg/d. If the average adult sheep weighs 50 kg, this daily intake of aluminum would result in a maximum body concentration of 1.9 mg/kg, which is approximately 50 times lower than the concentration (100 mg/kg) that was shown to produce sublethal effects in mice (Sorenson et al., 1974).

In a practical sense, levels of >5 mg/L aluminum are uncommon in British Columbia, and for the majority of cases the more stringent criteria for the protection of aquatic life and drinking water will apply to waters being used by livestock.

6. IRRIGATION WATERS

6.1 Effects

Aluminum is very abundant in most soils with typical concentrations in mineral soils ranging from 10 000 to 300 000 μ g/g and averaging 10 percent by weight (Bowen, 1979). However, aluminum is normally present in plants in relatively low concentrations as a result of its low bioavailability. Higher levels of availability are dependent on several factors, the most important of which is low pH. Acidic soils with high concentrations of available aluminum can be found in many locations: where there has been heavy cropping or use of nitrogen fertilizers, in acid mine tailing sites, and acidic forest soils. Aluminum toxicity is considered to be one of the main causes of nonproductivity in acid soils (U.S. EPA, 1973).

The essentiality of aluminum to plant life is unproven, although its toxic effects on growth and productivity have been long recognized by agronomists and plant ecologists. Different strains or species of plant show varying tolerance to aluminum in soils or nutrient solutions. Leaves of the tea plant and various South American plants growing on leached acid soils may accumulate aluminum in concentrations exceeding 10 000 mg/kg (Hutchinson, 1983). Early work (Hutchinson, 1983) classified a number of crops according to their aluminum sensitivity: those whose growth was depressed by 2 mg/L aluminum in a nutrient solution were termed sensitive (lettuce, beets, timothy, barley, carrot); those depressed by 2-7 mg/L aluminum were described as of medium sensitivity (radish, sorghum, cabbage, oats, and rye); and those affected by >14 mg/L aluminum were termed aluminum-resistant (corn, turnip and red top grass). High soil aluminum levels have also been implicated in the die-off of beech and spruce forests in Germany (Ulrich et al., 1980).

Acidified soils near a smelter in Sudbury, Ontario, contained 51-99 μ g/g of water extractable aluminum, which was toxic to several plant species during bioassays (Whitby and Hutchinson, 1974). Aluminum levels as low as 2 mg/L in the soil solution were found to inhibit root growth of several crop species that were tested.

The phytotoxicity of aluminum is not well understood and the effects of aluminum are not easily recognized, with no distinct leaf symptoms. Aluminum toxicity may resemble phosphorus deficiency with

stunting, late maturity, small leaves, and purple coloring; or it may resemble calcium deficiency as shown by curling of young leaves and petiole collapse (Kramer et al., 1981). Aluminum generally affects the root system first, rather than the shoots, where it accumulates in the protoplasm of living cells and especially in the nucleus (Hutchinson, 1983). The intensity of the phytotoxicity to root growth has been shown to be highly correlated with Al^{3+} activity, but not with total aluminum in the soil solution (Hue et al., 1986; Pavan et al., 1982). Hue et al. (1986) reported that relative taproot length of the cotton plant decreased by 51% with $AlCl_3$ at a concentration of 0.1 mg/L. Adams and Lund (1966) also reported that monomeric aluminum levels were progressively more toxic to cotton taproots at levels >0.04 mg/L. Soybean root elongation was observed to be reduced severely with aluminum concentrations of ≥0.27 mg/L.

Organic acids in soils act to protect root growth from aluminum toxicity by forming insoluble organoaluminum complexes. According to Hue et al. (1986) organic acids can be classified according to their ability to alleviate the phytotoxicity of aluminum: strong (citric, oxalic, tartaric), moderate (maleic, malonic, salicylic), and weak (succinic, lactic, formic, acetic, and phthalic). It appears that their aluminum detoxifying capacities are highly correlated with the relative positions on the main carbon chain of OH and COOH groups. Cultivated soils usually have a lower abundance of organic acids compared to natural forest soils, and hence they would likely be more susceptible to high aluminum levels in irrigation waters. Other factors which have been shown to reduce aluminum toxicity in soils include phosphate, calcium, ionic strength, and the sulfate adsorption capacity (Havas and Jaworski, 1986).

The mechanism of aluminum phytotoxicity is not presently known, although changes in various physiological processes appear important and have been summarized from the above references as follows:

- inhibition of root cell division.
- creation of abnormal, polynucleated root cells.
- inhibition of ATPase (adenosine tri phosphatase) activity needed for cation transport.
- disruption of phosphorus distribution and nitrate uptake.
- changes in the uptake and/or translocation of calcium.
- interference with cellular water relations.

Geneticists have studied the heritability of plant aluminum tolerance (Havas and Jaworski, 1986), suggesting the possibility of producing aluminum-tolerant cultivar strains at some time in the future.

6.2 Criteria from the Literature

Criteria to protect crops from detrimental effects of aluminum in irrigation waters have been compiled from other jurisdictions (Table 6.1). Existing criteria range from 5 mg/L for long-term, continuous use to 20 mg/L for use on fine-textured, neutral to alkaline soils for up to 20 years (U.S. EPA, 1973; Ontario Ministry of the Environment, 1978; CRREM, 1987). Manitoba (Manitoba Department of Environment and Workplace Safety and Health, 1983) and Australia (Hart, 1974) have adopted maximum concentrations from the U.S. EPA document (U.S. EPA, 1973) of 20 mg/L and 5.0 mg/L, respectively. The Anglian Water Authority (1982) has favoured a 95 percentile of 3.3 mg/L for spray irrigation of field crops (no rationale provided).

The U.S. EPA (1973) formulated the two-part criteria (5 and 20 mg/L) presently in use by several jurisdictions. It is not clearly stated whether these values are for total or dissolved aluminum. These criteria were not derived from toxicity data, but on the basis of the amount of limestone required to buffer soil acidity and prevent the accumulation or development of soluble aluminum. At an irrigation rate of 37 000 m³ per acre per year (3 acre feet), the calcium carbonate equivalent of the 5 mg/L concentration for 100 years would be 11.5 tonnes per acre; the 20 mg/L concentration for 20 years would be equivalent to

9 tonnes of calcium carbonate per acre. In most irrigated soils, these amounts of limestone would not have to be added because most soils have sufficient buffering capacity to neutralize the aluminum salts. In acid soils, that are near the pH where limestone should be used, the aluminum added in the water would contribute these quantities to the lime requirements.

Criteria Statements	Criteria Values	Jurisdiction/ Reference	Date
Maximum acceptable concentration for total aluminum	20.0 mg/L	Manitoba Department of Environment and Workplace Safety and Health	1983
Recommended maximum concentrations are 5.0 mg/L for continuous use on all soils and 20 mg/L for use on fine-textured, neutral to alkaline soils for up to 20 years.	5.0 mg/L and 20 mg/L	U.S. EPA	1973
As above for U.S. EPA (1973)	5.0 mg/L and 20 mg/L	ONTARIO Ministry of the Environment	1978
A derived working level for aluminum in irrigation water of 5 mg/L is recommended	5.0 mg/L	AUSTRALIA Hart	1974
95 percentile range for spray irrigation of field crops	3.3 mg/L	BRITAIN Anglian Water Authority	1982
Total aluminum should not exceed 5.0 mg/L for continuous use on all soils, or 20 mg/L for use up to 20 years on neutral to alkaline fine- textured soils	5.0 mg/L and 20 mg/L	Canada CCREM	1987

6.3 Recommended Criterion

The concentration of total aluminum in irrigation waters for continuous use on all soils should not exceed 5 mg/L at any time.

6.4 Rationale

The toxicity values reported in the literature relate to experimental nutrient solutions. Because of the significant ability of soil organics and other soil characteristics to ameliorate aluminum toxicity in presently unquantified ways, these values cannot be used directly to determine criteria numbers for irrigation waters. Until more is known about the interactions of aluminum with hardness, DOC, and pH in soils and the levels of aluminum required to cause toxic responses in various cultivars, we follow the maximum guideline for continuous use recommended by U.S. EPA (1973) and CCREM (1987). The input of irrigation waters containing aluminum in some situations may be less important for plant growth than the application of low pH irrigation waters with the capacity to mobilize the large reservoir of aluminum already present in the soil. The need for a pH criterion for irrigation waters to protect plants from aluminum toxicity is being addressed in a separate report on pH criteria (C. McKean, personal communication).

7. RESEARCH AND DEVELOPMENT NEEDS

The following areas of research require further development to broaden our understanding of aluminum toxicity and to refine the recommended criteria.

- 1. The development of a standardized fractionation method for the routine measurement of the biologically available inorganic monomeric aluminum form.
- 2. Improvement in the minimum detectable concentration for dissolved aluminum by the Provincial Environmental Laboratory to levels below the criteria levels recommended in this document.
- 3. More research regarding the acute and chronic toxicity of low levels of aluminum (<0.1 mg/L) to aquatic life at pH 6-8.5.
- 4. In view of the paucity of data on the effects of aluminum to marine organisms native to British Columbia, toxicological studies should be conducted using, as a first priority, the economically important marine organisms such as: the five Pacific salmon species; the harvested shellfish food organisms (e.g., mussels, clams, oysters, crabs, shrimp); and the important components of the kelp and littoral macrophyte communities.
- 5. The elucidation of quantified relationships between aluminum toxicity and the mitigating effects of organic/inorganic complexing ligands and calcium.
- 6. A better understanding of the toxic effects of aluminum to livestock and wildlife species, including the potential for biomagnification.
- 7. The effects of temperature and fluctuating aluminum levels on toxicity.
- 8. Research into the toxic effects of aluminum on sportsfish species important in British Columbia but not studied elsewhere (e.g., Dolly Varden char, cutthroat trout, Arctic grayling, Mountain whitefish).

Recommendations for research needs pertaining to aqueous aluminum have recently been outlined by Havas and Jaworski (1986) and are repeated here:

- 1. Development of a recommended procedure for determining aluminum speciation in aqueous solutions (this should include interlaboratory comparisons to verify the methodology).
- 2. Improvement of input thermodynamic data for computer-assisted models used for calculating aqueous concentrations of aluminum species under different environmental conditions.
- 3. Investigation of abiotic factors (pH, calcium, phosphate, fluoride, organic ligands) affecting aluminum availability in soil and water as well as implications for the health of plants and animals.
- 4. Investigation of possible synergistic or antagonistic effects of other metals (e.g., iron, zinc, manganese, copper, nickel, cadmium) on aluminum toxicity.
- 5. Elucidation of the mechanisms of the physiological and biochemical responses of aquatic organisms to aluminum.
- 6. Studies on the effects of aluminum on indicator organisms as well as on sensitive life-cycle stages (germination, fertilization, hatching, molting, etc.).
- 7. Determination of whether exposure to aluminum of people at risk affects the progress of certain diseases and determination of whether removal of aluminum from affected individuals changes the course of these diseases.
- 8. Development of a cell model for aluminum interaction and transport.

8. PERSONAL COMMUNICATION

Bailey, W. Public Health Engineering Section, Water Management Branch, Victoria. September, 1986.

McKean, C. Resource Quality Section, Water Management Branch, Victoria. June, 1986.

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