



Canadian Water Quality Guidelines for the Protection of Aquatic Life

ALUMINIUM

Aluminium (Al; CAS # 7429-90-5; molecular weight 26.98) is a silvery-white, pliable metal usually found in compounds as Al^{3+} (WHO 1997). It is the most abundant metal in the earth's crust, and the third most common element (Sparling and Lowe 1996). Aluminium is very light (density = $2.70 \text{ g}\cdot\text{cm}^{-3}$), capable of being hammered, cast, drawn out, machined, and moulded, and is therefore easily formed into many shapes (Frank *et al.* 1985, as cited in WHO 1997). Aluminium is found in a variety of minerals, usually combined with elements such as silicon, oxygen, phosphates, fluorine, and hydroxides, to name a few (Lide 1991, as cited in WHO 1997; Frank *et al.* 1985; Hudson *et al.* 1985).

With an annual production in excess of two million tonnes, Canada ranks third in the world in total aluminium metal production. The top primary aluminium producers in Canada are located in Quebec, except for Alcan's Kitimat smelter in British Columbia, and include Alcan Aluminium Limited, Canadian Reynolds Metals Company Limited, Aluminerie de Becancour Inc. (A.B.I), Aluminerie Luralco Inc., and Aluminerie Alouette Inc. (A.A.I) (Aluminium Association of Canada 1993). Alcan now owns and operates thirteen aluminium smelters with an annual rated capacity of 1589 kilotonnes/year including 1118 kilotonnes from its seven Canadian aluminium smelters (Alcan Aluminium Ltd. 1998). Canadian Reynolds Metals Company Limited, A.B.I, Aluminerie Luralco Inc., and A.A.I have annual production capacities for primary aluminium of 400, 360, 215, and 215 kilotonnes, respectively (Aluminium Association of Canada 1993).

Aluminium metal has many desirable characteristics for the manufacturing of consumer products (Lide 1991, as cited in WHO 1997; Sax and Lewis 1987). It is used extensively in the making of containers in the food and beverage industry. It has high electrical conductivity, is resistant to corrosion, is light, and recyclable (Aluminium Association Inc. 1998a,b; WHO 1997). Aluminium metal is used as a design material for building and construction; for rod, cable and wire products in the electrical industry; for the production of metal alloys; and for components in the transportation industry (e.g., automobiles and aircraft). Other aluminium products include jewellery, road signs, cooking utensils, foil for

household and commercial packaging, decorations, and corrosion-resistant chemical equipment (Aluminium Association of Canada 1993; ATSDR 1992, as cited in WHO 1997). Several aluminium salts have been identified as being of particular concern to the Canadian environment (Germain *et al.* 1999). These salts include aluminium chloride, aluminium sulphate and aluminium nitrate. Aluminium chloride is used in its anhydrous form in the manufacture of rubbers and lubricants. In its hydrated form it can be used for wood preservation, the manufacture of cosmetics and deodorants, or as a disinfectant in slaughterhouses. Aluminium sulphate (alum) is used in many water treatment plants in Canada as a coagulant to help remove nutrients (*i.e.*, phosphorus) from water and help prevent or reduce eutrophication (Germain *et al.* 1999; Health Canada 1994; Lamb and Bailey 1981). Aluminium polymers (*i.e.*, poly-aluminium sulphate and poly-aluminium chloride) may also be used

Table 1. Water quality guidelines for inorganic monomeric aluminium for the protection of freshwater life

pH	Guideline value ($\mu\text{g}\cdot\text{L}^{-1}$)
5.0	29.48
5.5	4.64
6.0	0.73
6.1	0.50
6.5	1.30
7.0	4.26

Table 2. Interim water quality guidelines for total aluminium ($\mu\text{g}\cdot\text{L}^{-1}$) for the protection of freshwater life

pH	DOC ($\text{mg}\cdot\text{L}^{-1}$)				
	0.5	2.5	5	7.5	10
5.2	84	87	120	154	201
5.6	98	116	149	193	252
6.0	92	108	137	178	232
6.4	74	82	97	121	156
>6.4	74	82	97	121	156

See text for derivation equation. A safety factor was not used in the development of the total aluminium guideline.

Marine Guidelines are not recommended at this time.

in water treatment. Aluminium sulphate is also used as a mordant in dyeing, in the leather industry, in the paper industry, in fire-proofing and waterproofing textiles, and in antiperspirants and pesticides among other uses. Aluminium nitrate is used in antiperspirants, as a corrosion inhibitor, as a chemical reagent and in the leather tanning industry (Germain *et al.* 1999).

The study of the environmental chemistry of aluminium has been restricted by the inability to differentiate between aqueous and particulate Al, and between inorganic and organic forms of aqueous Al (Driscoll and Postek 1996; Driscoll and Schecher 1990). Measurements of aluminium in water are made using a wide variety of analytical methods, with varying extraction periods and digestion procedures. This makes it difficult to compare Al values between studies due to the uncertainty between measured values using different methods, and the type of aluminium reported by the authors (e.g., total aluminium (Al_{tot}), inorganic monomeric aluminium (Al_{im}), organic monomeric aluminium (Al_{om}), and dissolved aluminium (Al_d)). For the purposes of these guidelines total aluminium represents all of the forms of dissolved and undissolved aluminium in water and is often determined in non-filtered samples (Driscoll and Schecher 1990). Al_{tot} is the most commonly reported form due to the low cost and ease of analysis of samples (Germain *et al.* 1999). Monomeric aluminium comprises a single ion of aluminium (Al^{3+}) that most often is linked to other compounds as a ligand, that is either organic or inorganic. Dissolved aluminium is commonly defined as the fraction of aluminium present in a sample filtered through a 0.45 μm membrane (Germain *et al.* 1999). Colloidal aluminium, aluminium bound with soluble organic ligands, and monomeric aluminium are constituents of the dissolved aluminium fraction.

Analytical methods have been developed to determine the concentration of aluminium in many environmental samples (Bloom and Erich 1996). A thorough review of the common methods for determining aluminium in water is described in 'Standard Methods for the Examination of Water and Wastewater' (APHA *et al.* 1995). The most common methods include the graphite furnace atomic emission spectrometric method (detection limit 0.003 $mg \cdot L^{-1}$), the inductively coupled plasma atomic emission spectrometric method (detection limit 0.04 $mg \cdot L^{-1}$), and many UV-visible spectrophotometry methods that involve reacting aluminium with a specific reagent (e.g., catechol method).

The fate and behaviour of aluminium in the environment is very complex. Aluminium speciation and solubility are affected by a wide variety of environmental

parameters including pH, temperature, dissolved organic carbon (DOC), and numerous ligands (e.g., F). Of primary importance to understanding aluminium fate and behaviour are its interactions with pH (Berntssen *et al.* 1997; DeLonay *et al.* 1993; Howells *et al.* 1990; OMOE 1988; Schindler 1988; Hutchinson and Sprague 1987; Burton and Allen 1986; Campbell and Stokes 1985; Clark and Hall 1985; Clark and LaZerte 1985; Baker and Schofield 1982) and dissolved organic carbon (DOC) (Kullberg *et al.* 1993; Simonin *et al.* 1993; Peterson *et al.* 1989; Hutchinson and Sprague 1987; Lacroix and Townsend 1987; Parkhurst 1987).

Both the solubility and speciation of aluminium are pH dependent (Driscoll and Postek 1996; Howells *et al.* 1990; Spry and Wiener, 1991). Aluminium is a strongly hydrolyzing metal and is relatively insoluble in the neutral pH range (6.0 - 8.0). In the presence of complexing ligands and under acidic and alkaline conditions (pH <6 or >8), aluminium solubility is enhanced. At low pH values, dissolved Al is present in the aquo form (Al^{3+}). Hydrolysis occurs as pH rises resulting in a series of less soluble hydroxide complexes (e.g., $Al(OH)^{2+}$, $Al(OH)_2^+$). Aluminium solubility is at a minimum near pH 6.5 at 20°C and then increases as the anion, $Al(OH)_4^-$ begins to form at higher pH (Witters *et al.* 1996; Driscoll and Schecher 1990; Howells *et al.* 1990). Ambient temperature will also have an impact on aluminium speciation and hence solubility in the environment (Lydersen *et al.* 1990). At low temperature (2°C), aluminium species are expected to remain in their most toxic form (Al_{im}) at a higher pH than would occur at higher temperature (20°C) (Howells *et al.* 1990; Lydersen *et al.* 1990). Thus at 2°C and pH < 5.7, aluminium is primarily present in the form Al^{+3} and $Al(OH)^{+2}$. In the pH range 5.7 - 6.7, aluminium hydroxide species dominate, including $Al(OH)^{+2}$ and $Al(OH)_2^+$. In this range, aluminium solubility is low and availability to aquatic biota should also be low. At pH >6.7, $Al(OH)_4^-$ becomes the dominant species (Howells *et al.* 1990). This shift in speciation due to temperature can have an impact on the toxicity of aluminium to aquatic organisms (Howells *et al.* 1990).

Dissolved organic carbon (DOC) is defined as the chemically reactive organic fraction of the organic carbon pool dissolved in water that passes through a 0.45 μm glass fibre filter (Rand *et al.* 1995). Dissolved organic carbon originates in the terrestrial ecosystem as by-products of biodegradation and chemical agents in the cycling of nutrients and natural weathering (Kullberg *et al.* 1993). In natural waters, DOC is comprised of a number of organic compounds the majority of which are humic acids (~50-75%) (Kullberg *et al.* 1993). Humic

substances are ubiquitous components of freshwater and their concentrations vary widely (Hutchinson and Sprague 1987). DOC concentrations range from 1-4 mg·L⁻¹ in oligotrophic and mesotrophic lakes, 2-10 mg·L⁻¹ in large rivers, 3-34 mg·L⁻¹ in eutrophic lakes, and 20-50 mg·L⁻¹ in dystrophic lakes (Rand *et al.* 1995). The Ontario Acid Sensitivity Database contains water chemistry data for about 6000 Ontario lakes (Neary *et al.* 1990, in Spry and Weiner 1991). Those Ontario lakes with pH above 5.3 typically had DOC levels greater than 1 mg·L⁻¹, and DOC concentrations in most were considerably higher. DOC will complex aluminium in water forming organo-aluminium complexes and reducing concentrations of monomeric forms of aluminium (Parent *et al.* 1996; Farag *et al.* 1993; Howells *et al.* 1990). At pH 4.5, 1 mg·L⁻¹ of DOC can complex approximately 0.025 mg·L⁻¹ of aluminium with its complexing capacity increasing as pH increases (OMOE 1988).

There are two general types of ligands that can form strong complexes with aluminium in solution. Inorganic ligands include anions such as sulphate (SO₄²⁻), fluoride (F⁻), phosphates (PO₃³⁻), bicarbonates (HCO₃⁻), or hydroxides (OH⁻), among others. Organic ligands include oxalic, humic or fulvic acids (Sparling and Lowe 1996; Driscoll *et al.* 1980). The relative concentrations of the inorganic or organic ligands will determine which type of ligand is formed in solution.

Several recent review documents have further information on the behaviour and toxicity of aluminium in the aquatic environment (Phippen and Horvath 1998; Roy 1998; Valcin 1998; WHO 1997; Sparling and Lowe 1996; Howells *et al.* 1990).

Aluminium in the aquatic environment comes from both natural and anthropogenic sources. The National Pollutant Release Inventory (NPRI) summary report for 1996 reports total on-site industrial aluminium releases for Canada of 52.4 tonnes, with 18.7 tonnes released to the air, 12.8 tonnes into water, and 17.3 tonnes to land (NPRI 1996). As aluminium makes up roughly 8.1% of the earth's crust, the amount of aluminium found naturally in the environment exceeds aluminium from anthropogenic sources (Lantzy and Mackenzie 1979, as cited in WHO 1997). Direct anthropogenic releases that impact the aquatic environment include soil-derived dusts from activities such as farming, mining, and coal combustion where aluminium is highly concentrated (WHO 1997; Havas and Jaworski 1986). Wind and water erosion from agricultural lands is a particularly important source of aluminium in the aquatic environment (WHO 1997). Aluminium can be transported in the form of

particulates in the atmosphere and deposited through both wet and dry deposition. Aluminium concentrations in precipitation are usually low (< 2 mg·L⁻¹) but can be increased markedly when influenced by industrial sources (e.g., ore smelting, coal combustion) or natural particulate sources (e.g., soil transport) (Havas and Jaworski 1986). Aluminium may be indirectly mobilised or made more bioavailable due to emissions of acidifying substances such as nitrogen oxides and sulphur dioxide to the atmosphere. These substances when deposited as acid rain lower environmental pH thereby making aluminium more soluble and altering aluminium speciation.

Between 1990 and 1996 aluminium levels in water were measured in Canada near industries using and releasing aluminium salts and other forms of aluminium. In Manitoba, mean extractable aluminium levels ranged from 0.232 mg·L⁻¹ in South Indian Lake to 0.547 mg·L⁻¹ in the Burntwood River, and average dissolved aluminium measured in the Burntwood River was 0.06 mg·L⁻¹. In Saskatchewan, the average mean levels of total aluminium ranged from 0.32 mg·L⁻¹ in the South Saskatchewan River to 2.15 mg·L⁻¹ in the North Saskatchewan River. In Ontario, total aluminium levels were highest in Kaministiquia River near Thunder Bay with concentrations reaching up to 13 mg·L⁻¹, and the highest mean total aluminium levels reached 1.3 mg·L⁻¹ in the Wabigoon River, downstream of Dryden. Lower levels of total aluminium in Ontario were measured in Lake Superior with a maximum concentration of 0.002 mg·L⁻¹. Dissolved aluminium levels ranged from 0.44 to 0.058 mg·L⁻¹ in the St. Clair River. In Quebec, mean total aluminium levels ranged from 0.07 in the St. Maurice River to 0.59 mg·L⁻¹ in the St. Lawrence River (Germain *et al.* 1999).

Water Quality Guideline Derivation

The Canadian water quality guidelines for aluminium were developed based upon CCME protocol (CCME 1991) and are provided for both Al_{im} and Al_{tot}. Many studies have demonstrated that Al_{im} is the most toxic form of aluminium (Parkhurst *et al.* 1990; Holtze and Hutchinson 1989; Baker and Schofield 1982; Driscoll *et al.* 1980) and that it is the best predictor of aluminium toxicity over a wide range of water quality conditions (Parkhurst *et al.* 1990; Gundersen *et al.* 1994; Clark and Hall 1985; Driscoll *et al.* 1980). In a field study, Baldigo and Murdoch (1997) used regression analysis to examine the effects of fluctuating chemical conditions to brook trout (*Salvelinus fontinalis*) in four Catskill Mountain streams. The regression analysis suggested that brook trout mortality was related to (in order of importance)

Al_{im} , pH, DOC, calcium, and chloride in stream water. Mean or median Al_{im} concentrations accounted for 76-85% of the variability in brook trout mortality. A similar study by Parkhurst *et al.* (1990) examined the effect of pH, Al_{tot} , Al_{im} , DOC, fluoride ion, and temperature on brook trout. The authors determined that the order of significance of these factors to brook trout fry survival in acidic solutions was Al_{im} , pH, DOC, F, and temperature. Al_{im} reportedly had a much greater effect on the survival of brook trout than pH.

Calcium (Ca^{2+}) can have a major impact on the toxicity of aluminium to some aquatic organisms (Cleveland *et al.* 1991; Brown 1983). Calcium has a known ability to reduce the permeability of biological membranes thereby reducing the loss of plasma ions due to both pH and the presence of metal ions, including Al (Freda and McDonald 1990; Sadler and Lynam 1988). Calcium acts at the level of the biological membrane, and specific responses will vary depending upon the organism (e.g., fish, invertebrates, plants). This guideline derivation did not use calcium as a contributing parameter because dose-response correlations were unavailable to be considered in the model relationship.

The impact of temperature on aluminium speciation has been addressed by separating the Al_{im} and Al_{tot} guidelines into pH ranges based on the speciation of aluminium at 2°C (Lydersen *et al.* 1990; Howells *et al.* 1990). Al_{im} , the most toxic form, is expected to be dominant over a broader pH range at 2°C than at 20°C.

Guideline for inorganic monomeric aluminium

The guidelines for Al_{im} are based on the data presented in Figure 1. A first regression of guideline values is derived for pH values from 5.0 to 6.1. Data used to derive the guideline come from the studies of Buckler *et al.* (1995)

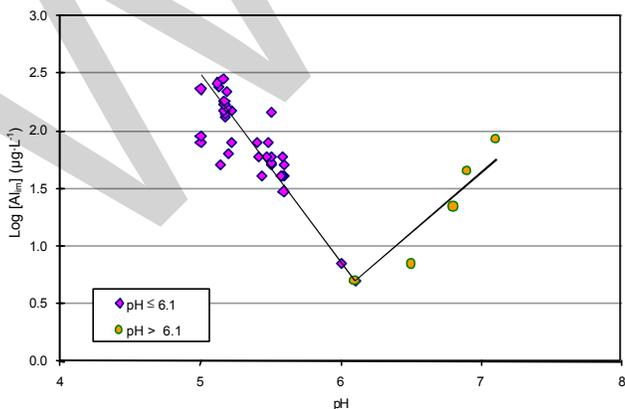


Figure 1. Selected water quality guidelines for inorganic monomeric aluminium. A safety factor of 0.1 has to be applied to the Al_{im} value obtained from the regression lines. 4

on Atlantic salmon (*Salmo salar*); Parent and Campbell (1994) on a green algae (*Chlorella pyreïnoidosa*), Baker and Schofield (1982) on brook trout (*Salvelinus fontinalis*) and white sucker (*Catostomus commersoni*). A second regression of guideline values is derived for pH values from 6.1 to 7.1. Data used to derive the guideline come from the study of Helliwell *et al.* (1983) on *C. pyreïnoidosa*. Regression lines intercept at pH value 6.1, the lowest observed effect concentration (EC_{50} at Al_{im} concentration of $5 \mu g \cdot L^{-1}$; Helliwell *et al.* 1983). The combined regression lines follow the shape of the aluminium solubility curve (microcrystalline gibbsite) (OMOE 1988). Guideline regression equations for Al_{im} are:

$$pH \leq 6.1: \text{Log } [Al_{im}] = -1.6061 * pH + 10.5 \quad (r^2=0.7) \quad 1)$$

$$pH > 6.1: \text{Log } [Al_{im}] = 1.0327 * pH - 5.6 \quad (r^2=0.9) \quad 2)$$

A safety factor of 0.1 is applied to the calculated Al_{im} guideline values. Data on background concentrations of Al_{im} in Canada were sparse and no conclusion could be drawn regarding the need for a safety factor as for total aluminium (see below). No Al_{im} guideline was developed for freshwater in the range below pH 5.0 and above pH 7.1 because there are no data for aquatic organisms exposed to Al_{im} in these ranges. At pH greater than 7.1, it is recommended to use the guideline for Al_{tot} .

Guideline for total aluminium

The data requirements for the development of a full Al_{tot} water quality guideline for aquatic life have not technically been met due to the lack of one chronic invertebrate study as outlined in CCME (1991). Several authors (Vuori 1996; OMOE 1988; Havas 1985) have noted the general lack of invertebrate data. The data available to derive the guideline includes a large number of fish species, aquatic plant data and includes amphibian data. Amphibians tend to be very sensitive to aluminium concentrations (Sparling and Lowe 1996; Freda 1991; Albers and Prouty 1987). According to CCME (1991) protocol, enough data is available for the development of an interim Al_{tot} guideline.

The toxicity of Al_{tot} is strongly influenced by pH and concentrations of dissolved organic carbon (Buckler *et al.* 1995; Wilson *et al.* 1994; DeLonay *et al.* 1993; Parkhurst *et al.* 1990; Palmer *et al.* 1988; Sadler and Lynam 1988; Parkhurst 1987; Baker and Schofield 1982). To take account of these variables in the derivation of guidelines for Al_{tot} , a multiple regression

analysis was performed based on the data from Parkhurst (1987). The dependent variable was 21 day survival of juvenile brook trout transformed into logits and transformed again by adding 10 to eliminate negative numbers:

$$\text{transformed logits} = \ln(p / (1-p)) + 10$$

3)

where p is the proportion of alevins surviving to 21 days. The independent variables were pH, DOC and Al_{tot} concentrations. In the regression analysis, total aluminium concentrations were log transformed, and power terms were added for log total aluminium and pH because these variables had non-linear relationships with survival. The analysis was performed in SAS[®] using PROC REG. Using the method of maximum likelihood, equation 4 was obtained:

$$\text{logit } Y = -63.16 + 26.17 * pH - 2.299 * pH^2 + 2.648 * \log Al - 1.583 * (\log Al)^2 + 0.249 * DOC$$

4)

Calculation details are provided following the reference section. All variables in the equation were significant ($p < 0.05$). The correlation coefficient was 0.71. Using this equation, the concentrations of total aluminium causing 25% greater mortality than caused by pH and DOC alone were estimated for a number of pH and DOC combinations. Because the model is based on chronic exposure data involving an early life stage of brook trout, the estimated LC_{25} s are considered to be chronic endpoints in this case because the sensitivity of the trout declined rapidly with age, lethality was the most sensitive response measured, and the IC_{25} has been considered in some cases to approximate the no observed effect concentration (see USEPA 1994). The protocol (CCME 1991) uses a safety factor of 10 on a chronic endpoint. However, there was concern that the resulting guideline

would have been lower than natural background. To evaluate this, monitoring data on total aluminium water concentrations in non-industrialised areas were obtained from all regions in Canada (Caux *et al.* 2000). A common database of 75,000 data points was screened (post 1985 only) and compiled. The data were collected from as many Canadian "geological provinces" as possible (Wheeler *et al.* 1996). In total, 11 of the 13 geological provinces were represented. A frequency concentration plot for total aluminium demonstrated that the number of sites for which the concentration of total aluminium falls at or below $252 \mu\text{g}\cdot\text{L}^{-1}$ was 80% ($n=1196$). The matrix for the proposed effects-based total aluminium guideline (pH and DOC dependent) in the absence of 10-fold safety factor, ranged from 61 to $252 \mu\text{g}\cdot\text{L}^{-1}$, a perfect overlap for this proportion. In this case, a weight of evidence approach integrating effects thresholds, water chemistry relationships and background concentrations support a water quality guideline for total aluminium without the need of a safety factor.

Implementation Considerations

At the site-specific level, in most Canadian geological provinces, there are proportionally only a few sites that have background concentrations of Al_{tot} below $61 \mu\text{g}\cdot\text{L}^{-1}$. For these sites, if they are deemed ecologically sensitive, a site background concentration could be used as a site-specific objective value. Although natural levels of substances may have an adverse effect on certain organisms, defensible management options should consider the contribution of natural processes in order to focus on the sites and chemicals that are primarily influenced by human activities.

It is recognised that situations outside of the range of pH and DOC concentrations presented in Table 2 occur in the Canadian environment, and in fact, that the CWQG for pH alone is from 6.5 to 9.0 (CCME 1999). Parkhurst (1987), however, did not include treatments with pH higher than 6.5 or DOC concentrations higher than $10 \text{ mg}\cdot\text{L}^{-1}$. Hence it is recommended that the most conservative total aluminium guideline closest to the pH and DOC conditions in the water body of interest be applied (*i.e.*, $74 \mu\text{g}\cdot\text{L}^{-1}$). Users of the guideline should also be aware that rapid increases in pH, such as in mixing zones, may precipitate aluminium and result in over-saturated solutions that may be acutely lethal to aquatic life.

It is recommended that the choice of guideline, either Al_{im} or Al_{tot} be based on the management goal and best professional judgement, on a case-by-case basis. The

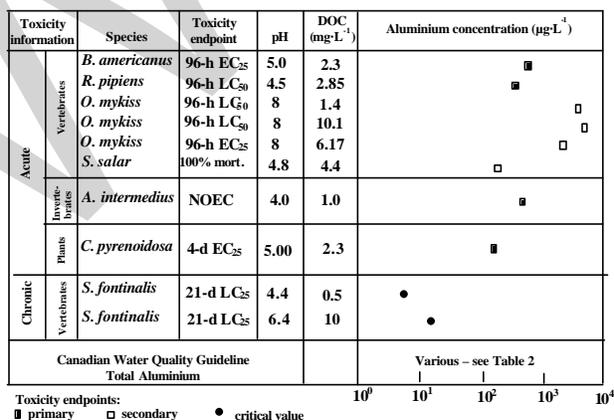


Figure 2. Selected freshwater toxicity data for total aluminium.

guideline for Al_{im} contains a safety factor and is based on the putative toxic fraction, whereas the Al_{tot} guideline may be more practical, takes natural background concentrations into account and may be more useful for non-equilibrium conditions. In addition, highly coloured, low-pH lakes (dystrophic lakes) may need to be considered on a site-specific basis. Jurisdictions may choose to develop site-specific water quality objectives as outlined in CCME 1991.

The guidelines set a high standard for the protection of aquatic life across Canada. Their use may require consideration of local conditions. The guidelines may be updated as new information becomes available.

Review of toxicity to freshwater Life

Aluminium in the aquatic environment can have a major impact on aquatic life. Acid precipitation has been implicated in the loss of fish populations from acid-sensitive waters through the mobilisation of aluminium (Buckler *et al.* 1995; Wilson *et al.* 1994; DeLonay *et al.* 1993; Palmer *et al.* 1988; Sadler and Lynam 1988; Baker and Schofield 1982). Heavy rain and snowmelt can also impact on the concentrations of aluminium in the aquatic environment by leaching large quantities of aluminium from watershed soils (Mount *et al.* 1990; Gunn and Noakes 1987). The short-term changes in aluminium concentrations caused by these events can have severe effects on aquatic biota.

Aquatic plants are able to tolerate higher levels of aluminium than aquatic invertebrates, amphibians, or fish (Sparling and Lowe 1996; Butcher 1987). As pH decreases, Ca^{2+} , metal ions (e.g., Fe) and phosphorus may interact with Al thereby negatively impacting plant growth (Hörnström *et al.* 1984). Sprenger and McIntosh (1989) observed that aqueous Al concentrations are negatively correlated with pH, thus plants that grow in acidic conditions are often aluminium tolerant. Aluminium toxicity in invertebrates is primarily due to the disruption of ion regulation and the loss of Na^+ . Aluminium is known to be more toxic to invertebrates at pH 5.1 to 5.8 than at higher pH (Hörnström *et al.* 1984). Freda (1991) reviewed the toxicity of aluminium to nine species of amphibians at different life stages. Three possible amphibian toxicity types were suggested based on the interaction of aluminium with pH. Type I indicated that toxicity is negatively related to pH; Type II toxicity is positively related to pH; and, Type III, aluminium ameliorates acid toxicity. Amphibians may be at elevated risk from Al under acidic conditions, but H^+ is also toxic and it can be difficult to distinguish between

these two factors. Fish species are sensitive to aluminium concentrations. Key factors in aluminium sensitivity for fish are, species, life stage, and form of aluminium. Salmonids are more sensitive to the toxic effects of aluminium than are warm water fish species (Spry and Wiener 1991; Roy 1998; Valcin 1998). Several studies have reported that juveniles tend to be the most sensitive life stage while embryos are the least sensitive in fish (Roy 1998; Rosseland *et al.* 1992; Baker and Schofield 1982). Fish species have been found to be equally sensitive to three forms of aqueous monomeric Al (*i.e.*, Al^{3+} , $Al(OH)^{2+}$, and $Al(OH)_2^+$) (Sparling and Lowe 1996). The mechanism of aluminium toxicity in fish tends to revolve around ionoregulatory and osmoregulatory dysfunction and various respiratory problems related to aluminium precipitation on the gills (Phippen and Horvath 1998). Aluminium binding to the gill epithelium and intracellularly within lamellar epithelial cells is a prerequisite to acute toxicity (Phippen and Horvath 1998). Visible signs of aluminium toxicity in fish include coughing response, hyperventilation, and excessive mucous clogging of the gills (Lewis *et al.* 1990).

When critically reviewing the scientific literature on aluminium toxicity, over-saturated aluminium solutions can be a major hurdle in the appropriate interpretation of laboratory toxicity tests (Roy 1998; Spry and Wiener 1991). Over-saturated solutions can be very toxic if the aluminium precipitates and adheres to gill tissues potentially causing asphyxiation (Spry and Wiener 1991). Lower toxicity may also be exhibited if the solution has been allowed to age thereby causing the formation of large polymers of aluminium and amorphous aluminium that do not interact with gill tissue (Freda 1991; Spry and Wiener 1991). Based on the solubility product for microcrystalline gibbsite, media containing more than $18.9 \mu\text{g}\cdot\text{L}^{-1}$ of inorganic Al at pH 6 and 20°C are considered over-saturated (Parent and Campbell 1994). The aqueous chemistry of aluminium becomes very complex and unpredictable under these conditions. In the natural environment, over-saturated solutions of aluminium rarely occur, particularly in low pH waters (Hutchinson *et al.* 1987, 1989; Tipping *et al.* 1988; LaZerte 1984). Situations where over-saturated aluminium solutions could occur in the environment include neutral pH watersheds receiving inputs of aluminium sulphate from municipal wastewater treatment or from the production of pulp and paper products (Roy 1998). Studies that report toxic effects based on over-saturation of the exposure solution were not considered acceptable for guideline derivation. Similarly, studies that did not use proper controls, statistics and

standardised methodologies were not selected for guideline derivation.

Inorganic monomeric aluminium

There are few studies available on the toxicity of Al_{im} to aquatic biota. In particular, studies on plants and invertebrates are rare. This is likely the result of the difficulty in finding accurate and precise analytical methods to determine the concentrations of Al_{im} in solution (Driscoll and Postek 1996; Driscoll and Schecher 1990). Additionally, the toxicity of Al_{im} to aquatic organisms can be difficult to quantify at low pH due to the inherent toxicity of the H^+ ion (Baldigo and Murdoch 1997; Atland and Barlup 1996; Parkhurst *et al.* 1990). In nature, species sensitive to low pH toxicity would not be expected to inhabit aquatic systems where acidic conditions predominate. For the purposes on this guideline, only those studies that report the toxic effects of Al_{im} relative to proper controls at the same exposure pH are reported.

Aquatic Plants

Parent and Campbell (1994) exposed the unicellular green algae (*Chlorella pyrenoidosa*) to Al_{im} to observe biological responses at various pH levels. Algal growth inhibition was minor at pH 4.3-4.6. The EC_{30} s for algal growth were calculated to range from 7-800 $\mu g \cdot L^{-1}$ for pH 6.0-5.0. The most sensitive EC_{30} was reported at pH 6.0 and 7 $\mu g \cdot L^{-1}$ Al_{im} . Toxicity was extremely dependent on pH in this range. Both Parent and Campbell (1994) and Parker *et al.* (1989, in Lydersen *et al.* 1990) have suggested that poly-nuclear hydroxyl aluminium species may have pronounced phytotoxic effects. These Al species are expected to be present at pH ranging from 5 – 7 depending upon temperature and other physical chemical factors (e.g., ligands).

Invertebrates

Mackie (1989) exposed five benthic invertebrates to six levels of Al_{im} ranging from 0-400 $\mu g \cdot L^{-1}$ and pH ranging from 4-5.5. The test species included the shredder, *Hyalella azteca*, the scraper, *Amnicola limosa*, the predator, *Enallagma sp.*, and the bivalves *Pisidium cassertanum* and *Pisidium compressum*. The invertebrates were exposed, in static test systems, to Al_{im} for 96-h to determine the LC_{50} at each exposure concentration. Insufficient mortality was observed to calculate LC_{50} values at the concentrations tested.

Khengarot and Ray (1989) examined the toxicity of various metals as ions (Al^{3+}) and the correlation to their physicochemical properties to the water flea, *Daphnia magna*. Static bioassay tests at 13°C, were used to determine the toxicity of the test metals. The 24-h EC_{50} and 48-h EC_{50} were reported as 85.9 $mg \cdot L^{-1}$ and 59.6 $mg \cdot L^{-1}$, respectively.

Amphibians

Clark and LaZerte (1985) examined the effects of pH and aluminium on eggs and tadpoles of American toad (*Bufo americanus*) and wood frog (*Rana sylvatica*). They found that at low pH (*i.e.*, 4.14), hatching success for eggs of both species were significantly reduced. Reproductive success at pH 4.32 with the addition of 9.2 $\mu g \cdot L^{-1}$ Al_{im} was reduced in the American toad. With the addition of up to 200 $\mu g \cdot L^{-1}$ of Al_{im} at pH 4.75, there was no change in hatching success. Below pH 4.75, aluminium was found to augment toxicity due to pH. Similar results have been reported for other amphibian species at different life stages (Freda 1991; Saber and Dunson 1979; Gosner and Black 1957). The sensitive endpoint at 9.2 $\mu g \cdot L^{-1}$ was not selected for guideline development due to the presence of large effects due to pH alone in the bioassay. The authors concluded that toxic response was not dependent on aluminium speciation (Clark and LaZerte 1985).

Fish

Mount *et al.* (1988) exposed brook trout (*Salvelinus fontinalis*) to monomeric aluminium in low calcium (0.5 $mg \cdot L^{-1}$) and low pH (4.97 ± 0.02) conditions. Aluminium was reported as both inorganic and total monomeric. The lowest observed effect concentration (LOEC) for growth was reported as 47 $\mu g \cdot L^{-1}$ Al_{im} . Total monomeric aluminium was 169 $\mu g \cdot L^{-1}$. The observed effects ranged from reduced growth and survival to physiological abnormalities. The authors observed that raising the calcium concentrations or lowering the aluminium concentration alleviated the observed adverse responses.

Holtz and Hutchinson (1989) exposed fish species at various life stages to solutions with low pH (ranging from pH 4.5 to 6.0) and concentrations of Al_{im} . Survival of lake whitefish (*Coregonus clupeaformis*) swim-up fry was found to be the most sensitive endpoint with a reported LOEC of 28 $\mu g \cdot L^{-1}$ at pH 5.1. The LOEC for survival in smallmouth bass (*Micropterus dolomieu*) swim-up fry at pH 5.1 was 144 $\mu g \cdot L^{-1}$ and at pH 5.4, >58 $\mu g \cdot L^{-1}$. At pH 5.97, common shiner (*Notropis cornutus*)

eggs exhibited 90.7% mortality at an Al_{im} concentration of $17 \mu\text{g}\cdot\text{L}^{-1}$. This sensitive endpoint was not selected for guideline derivation. The authors suggested that the toxicity reported at this sensitive endpoint was due to aluminium over-saturation. The authors measured colloidal and polymeric aluminium in the test solutions and determined that these were less important than acidity and Al_{im} concentrations to fish survival.

Roy and Campbell (1995) exposed juvenile Atlantic salmon (*Salmo salar*) to concentrations of aluminium (as Al_{im}) and aluminium and zinc mixtures over a wide pH range. The most sensitive response to Al_{im} alone, occurred at pH 5.24. The reported LC_{50} was $51.2 \mu\text{g}\cdot\text{L}^{-1}$ ($1.9 \mu\text{mol}$). The authors found that the LC_{50} s tended to be lower in the aluminium and zinc mixture bioassays than with just aluminium alone. Aluminium acted as a gill irritant that stimulated mucus production in the salmon. Zinc readily binds to gill mucus and can cause a rapid influx of metal ions through the gill tissue resulting in a toxic response.

Total aluminium

There is a great deal of toxicity data available that examines the impact of total aluminium on aquatic biota. A large number of these studies expose biota to aluminium concentrations in artificial exposure solutions where maximum speciation of aluminium will occur and no organic matter is present to complex aluminium. It has been demonstrated that DOC has a large impact on aluminium toxicity by complexing monomeric aluminium (Parent *et al.* 1996; Farag *et al.* 1993; Howells *et al.* 1990). It has also been shown that as DOC concentrations increase in solution, Al toxicity tends to be reduced (Parkhurst 1987; Gunn and Noakes 1987; Burton and Allan 1986). Dissolved organic carbon is a constituent of all natural waters though concentrations vary (Peterson *et al.* 1989). Due to the impact of DOC on aluminium toxicity, only those studies with measurable DOC as part of the exposure solution are selected for use in deriving the Al_{tot} water quality guideline for aquatic life.

Aquatic Plants

Parent *et al.* (1996) examined the impact of aluminium to the green alga, *C. pyrenoidosa* in the presence of dissolved organic carbon. The DOC concentrations ranged from 1.2 - $11 \text{mg}\cdot\text{L}^{-1}$. Total monomeric aluminium concentrations were determined using atomic absorption spectrophotometry with electrothermal atomisation. At pH 5.0, $167 \mu\text{g}\cdot\text{L}^{-1}$ of total monomeric aluminium and no

DOC resulted in a 30% decrease in growth of green alga over 96 hours relative to the control. When $2.3 \text{mg}\cdot\text{L}^{-1}$ of DOC and $189 \mu\text{g}\cdot\text{L}^{-1}$ Al_{tot} was added to solution at pH 5.0, growth was reduced by 25% relative to controls.

Hörnström *et al.* (1995) examined the effect of aluminium at various pH ranges and at two humus concentrations on the phytoplankton *Monoraphidium griffithii* and *Monoraphidium dybowskii*. At pH 4.8 and humus concentration $0.2 \text{mg Pt}\cdot\text{L}^{-1}$ a 70% growth reduction was observed relative to controls at $200 \mu\text{g}\cdot\text{L}^{-1}$ in *M. dybowskii*. Humic concentrations are often measured by comparing samples to standard reference solutions of platinum. The humic concentration is then reported in platinum units ($\text{mg Pt}\cdot\text{L}^{-1}$). At pH 6.8 and humus concentration $27 \text{mg Pt}\cdot\text{L}^{-1}$, growth reduction was observed at $300 \mu\text{g}\cdot\text{L}^{-1}$ aluminium in *M. dybowskii*. *M. griffithii* exhibited 82% reduction in growth relative to controls when exposed to $100 \mu\text{g}\cdot\text{L}^{-1}$ aluminium at pH 4.8 and humus concentration of $0.2 \text{mg Pt}\cdot\text{L}^{-1}$. At $27 \text{mg Pt}\cdot\text{L}^{-1}$, *M. griffithii* exposed to $300 \mu\text{g}\cdot\text{L}^{-1}$ at pH 4.8 and 6.8 exhibited 35% and 50% growth reduction, respectively.

Amphibians

Freda *et al.* (1990) exposed *R. pipiens* embryos and *B. americanus* tadpoles to levels of aluminium in order to examine the impact of organic complexation on toxicity. Aluminium was measured using spectrophotometry and the catechol-violet method. The test organisms were exposed to various pH and DOC levels with the DOC being derived from natural pond waters. A series of pond water dilutions were used to vary the DOC concentration in the bioassays. The 96-h LC_{50} for *B. americanus* tadpoles at a pH of 4.5 and DOC concentration of $2.85 \text{mg}\cdot\text{L}^{-1}$ was $627 \mu\text{g}\cdot\text{L}^{-1}$ total aluminium. Increasing the DOC content to $11.4 \text{mg}\cdot\text{L}^{-1}$ caused an increase in the LC_{50} to $> 2000 \mu\text{g}\cdot\text{L}^{-1}$. *R. pipiens* embryos exhibited a similar reaction to increasing DOC concentrations. In 100% artificial soft water at pH 4.8 and with no DOC, an LC_{50} of $471 \mu\text{g}\cdot\text{L}^{-1}$ was reported. The LC_{50} s increased markedly (>856 - $>1018 \mu\text{g}\cdot\text{L}^{-1}$) upon addition of DOC in the form of various pond water dilutions at the same pH.

Freda and McDonald (1990) demonstrated the effects of aluminium to leopard frog (*R. pipiens*) over a wide range of pH and low DOC. *R. pipiens* were exposed in a static system rather than flow through in order to better mimic conditions in ephemeral breeding ponds that have no inflow or outflow of water. The authors observed that at very low pH (pH 4.2-4.4) aluminium ameliorated the ef-

ffects of pH on frog embryos and permitted hatching. Between pH 4.6-4.8 aluminium was found to be extremely toxic with mortality being significantly increased at 500 $\mu\text{g}\cdot\text{L}^{-1}$. All tests contained a DOC concentration of 1.0 $\text{mg}\cdot\text{L}^{-1}$. The reported 96-h $\text{LC}_{50\text{s}}$ for Al_{tot} at 4.6 and 4.8 were 811 and 403 $\mu\text{g}\cdot\text{L}^{-1}$, respectively. At pH 4.4, 4.6, and 4.8 the lowest concentration of Al tested (250 $\mu\text{g}\cdot\text{L}^{-1}$) caused either mortality or abnormal development in pre-stage 25 tadpoles.

It has been suggested that amphibian species most at risk to aluminium toxicity are those that inhabit small temporary or ephemeral ponds that receive most of their water from spring runoff and snow melt (Sparling and Lowe 1996). Albers and Prouty (1987) reported that embryonic survival in spotted salamander *Ambystoma maculatum* was negatively correlated with the concentration of aluminium in temporary ponds. Aluminium levels and acidity in these waters are particularly high and exposure occurs during early life stages when amphibians tend to be the most sensitive. Larger species that inhabit lakes and permanent ponds may be less at risk from episodic events but can still be affected by chronic acidification and accompanying elevated Al. In a study to determine the effects of a range of Al_{tot} (250-1000 $\mu\text{g}\cdot\text{L}^{-1}$) on leopard frog *R. pipiens* embryos at pH 4.8, Freda (1991) reported that DOC exceeding 5.7 $\text{mg}\cdot\text{L}^{-1}$ complexed most of the Al present, decreasing labile Al.

Invertebrates

Aluminium tends to be non-toxic to invertebrates at levels commonly found in circumneutral water. Ambient levels of Al in water at circumneutral pH are usually less than 1 $\text{mg}\cdot\text{L}^{-1}$ and more typically around 500 $\mu\text{g}\cdot\text{L}^{-1}$ (Wren and Stephenson 1991; Havas and Likens 1985).

Burton and Allan (1986) examined the effect of temperature, pH, DOC, and aluminium concentrations on various stream invertebrates. They observed that the addition of 500 $\mu\text{g}\cdot\text{L}^{-1}$ aluminium to water at 15°C, pH 4.0 and DOC 42-47 $\text{mg}\cdot\text{L}^{-1}$ had no effect on mortality on the isopod, *Asellus intermedius*, stonefly, *Nemoura sp.*, and the snail *Pycnopsyche guttifer* relative to a control with no aluminium. At 2°C and with 500 $\text{mg}\cdot\text{L}^{-1}$ Al_{tot} , significant increased mortality was observed in the stonefly and isopod. Mortality increased when the experiment was repeated at very low DOC levels. The authors observed that the removal of organic matter from the exposure solution resulted in a 94-98% shift of aluminium from organic to inorganic aluminium forms.

Fish

Gundersen *et al.* (1994) exposed rainbow trout (*Oncorhynchus mykiss*) to acute and subacute combinations of Al, DOC (as humic acid) and pH. Fish were exposed in a continuous flow through exposure system. Aluminium concentrations were measured by absorbance spectrophotometry using the catechol method. In the acute test, humic acid concentrations ranged from 1.4- 10.1 $\text{mg}\cdot\text{L}^{-1}$ and pH was weakly alkaline at 7.97-8.56. The 96-h $\text{LC}_{50\text{s}}$ were 3.75, 5.43, 4.60, and 5.22 $\text{mg}\cdot\text{L}^{-1}$ at humic acid concentrations of 1.4, 2.6, 6.6, and 10.1 $\text{mg}\cdot\text{L}^{-1}$, respectively. Mortality (25%) was reported at pH 8.03, humic acid concentration of 6.17 $\text{mg}\cdot\text{L}^{-1}$ and a total aluminium concentration of 2.1 $\text{mg}\cdot\text{L}^{-1}$. At the same pH, higher humic acid concentration (9.57 $\text{mg}\cdot\text{L}^{-1}$) and similar Al_{tot} (1.9 $\text{mg}\cdot\text{L}^{-1}$) mortality was 5%. The authors found that the humic acid protected against aluminium induced mortality.

American flagfish (*Jordanella floridae*) were used to determine the toxicity of metal mixtures (Al/Cu/Zn) and the impact of humic substances on this toxicity (Hutchinson and Sprague 1987). The authors observed that aluminium toxicity is reduced by complexation with humic substances though the level of toxicity to flagfish was not specifically quantified. Also, total organic carbon was more closely associated with changes in trace metal lethality than changes associated with water hardness.

Peterson *et al.* (1989) examined the impact of aluminium to Atlantic salmon (*S. salar*) in the presence of dissolved organic carbon. DOC was isolated from natural stream waters in Nova Scotia and diluted to achieve exposure concentrations. At pH 4.8 and DOC concentration of 4.4 $\text{mg}\cdot\text{L}^{-1}$ Atlantic salmon alevins exhibited 100% mortality at 200 $\mu\text{g}\cdot\text{L}^{-1}$ (7.4 μm). At pH 4.8 and 6.8 $\text{mg}\cdot\text{L}^{-1}$ DOC, 100% salmon mortality was also exhibited at 210 $\mu\text{g}\cdot\text{L}^{-1}$ (7.8 μm). The authors suggested that acidic fractions of DOC (i.e., humic acids) are more effective in providing protection to salmon as they contain carboxyl and hydroxyl functional groups that form strong complexes with Al.

Parkhurst *et al.* (1990) examined the effect of aluminium on brook trout (*S. fontinalis*) with variable water quality parameters (e.g. pH, DOC, F and temperature). The authors used a flow-through system and reported measured as well as nominal parameter concentrations in

each bioassay. A multivariate analysis was used to determine which of the parameters were most important to brook trout survival under a wide range of exposure conditions. The authors reported that DOC accounted for 6% of the variability in survival for brook trout. Parkhurst (1987) reported the effect of aluminium on brook trout exposed to Al_{tot} . Temperature, DOC, and fluoride concentrations were varied. Nominal Al_{tot} concentrations in the bioassays ranged from 0–1000 $\mu\text{g}\cdot\text{L}^{-1}$ while measured DOC concentrations ranged from 0.6–9.1 $\text{mg}\cdot\text{L}^{-1}$. Measured values for all parameters were reported. The authors observed that DOC alone had no impact on brook trout survival. Addition of DOC to the various Al_{tot} bioassays reduced toxicity. At pH 5.3 with 11 $\mu\text{g}\cdot\text{L}^{-1}$, 21-d survival was 72% with 0.5 $\text{mg}\cdot\text{L}^{-1}$ of DOC. Survival increased substantially with the addition of 5.5 $\text{mg}\cdot\text{L}^{-1}$ DOC to 94%. At 127 $\mu\text{g}\cdot\text{L}^{-1}$, Al_{tot} toxicity was virtually eliminated with DOC addition at pH 4.8, 5.1, and 5.4.

Marine Life

Aluminium is not expected to be toxic in the natural marine environment due to the high concentrations of clay particles in marine waters and relatively constant pH of approximately 8.2 (WHO 1997). Clay particles tend to bind rapidly with aluminium forming large colloids thus removing aluminium from the water column. At pH 8.2, aluminium would be predominately in the anionic form $AlOH_4^-$, and would be rapidly removed from marine waters through the formation of polymers and colloids (WHO 1997; Howells *et al.* 1990).

No water quality guidelines for aluminium for marine life will be developed at this time.

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Calculation procedure for Total aluminium Guideline

Use this procedure to calculate (interpolate) intermediate concentrations in Table 2 if desired.

1. calculate the modelled survival of aluminium controls (i.e. $[Al]=0$) by:
 - deleting the aluminium terms from equation 4
 - substituting the pH and DOC of interest
 - calculating transformed logit y
 - substitute transformed logit y in equation 1 and solve for “ p ”, the proportion surviving
2. calculate the LC25 relative to the control survival (i.e. 0.75 p)
3. calculate the logit of the LC25 using equation 1
4. substitute this value for logit y in equation 4 and solve for aluminium concentration. This is the guideline aluminium concentration for that pH and DOC.

Do not extrapolate outside the range of the table (pH 5.2 to 6.4, DOC 0.5 to 10) because the modelled control survival becomes unacceptably low, and/or the effects of higher DOC are unknown. A computation spreadsheet is available by email from ceqg-rcqe@ec.gc.ca

Reference listing:

Canadian Council of Ministers of the Environment. 2003. Canadian water quality guidelines for the protection of aquatic life: Aluminium. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

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