

Draft
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AMBIENT AQUATIC LIFE WATER QUALITY CRITERIA FOR
ALUMINUM

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NOTICES

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FOREWORD

Section 304(a)(1) of the Clean Water Act of 1977 (P.L. 95-217) requires the Administrator of the Environmental Protection Agency to publish water quality criteria that accurately reflect the latest scientific knowledge on the kind and extent of all identifiable effects on health and welfare that might be expected from the presence of pollutants in any body of water, including ground water. This document is a revision of proposed criteria based upon a consideration of comments received from other Federal agencies, State agencies, special interest groups, and individual scientists. Criteria contained in this document replace any previously published EPA aquatic life criteria for the same pollutant(s).

The term "water quality criteria" is used in two sections of the Clean Water Act, section 304(a)(1) and section 303(c)(2). The term has a different program impact in each section. In section 304, the term represents a non-regulatory, scientific assessment of ecological effects. Criteria presented in this document are such scientific assessments. If water quality criteria associated with specific stream uses are adopted by a State as water quality standards under section 303, they become enforceable maximum acceptable pollutant concentrations in ambient waters within that State. Water quality criteria adopted in State water quality standards could have the same numerical values as criteria developed under section 304. However, in many situations States might want to adjust water quality criteria developed under section 304 to reflect local environmental conditions and human exposure patterns before incorporation into water quality standards. It is not until their adoption as part of State water quality standards that criteria become regulatory.

Guidelines to assist States in the modification of criteria presented in this document, in the development of water quality standards, and in other water-related programs of this Agency, have been developed by EPA.

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Introduction*

The aquatic toxicology of aluminum is complex because of three chemical characteristics. First, it is amphoteric with minimum solubility at a pH of about 5.5. Solubility increases as pH increases and as pH decreases. Second, a variety of ions form soluble complexes with aluminum. Third, it polymerizes in the presence of hydroxide to form a visible whitish colored precipitate. Detailed explanations of the behavior of aluminum in natural waters are presented by Hem (1968), Hem and Robertson (1967), and Robertson and Hem (1969). This document addresses the toxicity of aluminum to freshwater** aquatic organisms in waters with a pH from 6.5 to 9.0, because the water quality criterion for pH (U.S. EPA 1976) states that a pH range of 6.5 to 9.0 appears to adequately protect freshwater fishes and bottom dwelling invertebrate fish food organisms from effects of hydrogen ion. The polymerization, hydrolysis, and solubility of aluminum are all markedly affected by pH. At pH greater than 6.5, aluminum occurs predominantly in the forms of monomeric, dimeric, and polymeric hydroxides, and complexes with sulphates, phosphates, humic acids, and less common anions.

The toxic forms of aluminum are thought to be the soluble inorganic forms. Driscoll et al. (1980) worked with postlarvae of brook trout and white suckers under slightly acidic conditions and concluded that only inorganic forms of aluminum were toxic. Hunter et al. (1980) found that toxicity of aluminum was directly related to the concentration of the

*An understanding of the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al. 1985), hereafter referred to as the Guidelines, is necessary in order to understand the following text, tables, and calculations.

**EPA feels that the need for a saltwater criterion is not great enough to warrant devoting resources to it.

soluble (able to pass through a 0.45 μm membrane filter) portion. Seip et al. (1984) stated that "simple hydroxides $\text{Al}(\text{OH})^{+2}$ and $\text{Al}(\text{OH})_2^+$ are regarded as the most dangerous forms while organically bound aluminum and polymeric forms are less toxic or essentially harmless." Freeman and Everhart (1971) found that, in alkaline conditions, toxicity to rainbow trout increased with increasing pH, indicating that soluble aluminum is the toxic form.

In a study of the toxicity of "labile" aluminum to the green alga Chlorella pyrenoidosa, Helliwell et al. (1983) found that maximum toxicity occurred in the pH range of 5.8 to 6.2. This is the pH range of minimum solubility of aluminum and maximum concentration of $\text{Al}(\text{OH})_2^+$. They found that the toxicity of aluminum decreased as pH increased or decreased from about 6.0, and they speculated that the monovalent hydroxide is the most toxic form.

In dilute aluminum solutions, formation of particles and the large polynuclear complexes known as flocs is primarily a function of the organic acid and hydroxyl ion concentration (Snodgrass et al. 1984). Time for particle formation varies from < 1 min. to several days (Snodgrass et al. 1984) depending upon the source of aluminum, the pH, and the presence of electrolytes and organic acids.

When particles form aggregates large enough to become visible, the floc is whitish in color and tends to settle. Mats have been reported blanketing a stream bed (Hunter et al. 1980). Laboratory studies conducted at alkaline pHs have reported flocs in the exposure chambers (Brooke et al. 1985; Call 1984; Lamb and Bailey 1981; Zarini et al. 1983). The flocs had no known effects on toxicity to most aquatic species but did impede the swimming ability of Daphnia magna. D. magna were noticed to have "fibers" of flocculated aluminum trailing from their

carapaces. Midges were impeded in their movements and perhaps feeding, ultimately resulting in death (Lamb and Bailey 1981).

Aluminum flocs might coprecipitate nutrients, suspended material, and microorganisms. Phosphorus removal from water has been observed in laboratory studies (Matheson 1975; Minzoni 1984; Peterson et al. 1974) and in a lake (Knapp and Soltero 1983). Clay turbidity has been removed from pond waters using aluminum sulfate (Boyd 1979). Unz and Davis (1975) speculated that aluminum flocs may coalesce bacteria and concentrate organic matter in effluents, thus assisting the biological adsorption of nutrients. Aluminum sulfate was used to flocculate algae from water (McGarry 1970; Minzoni 1984; Zarini et al. 1983). Bottom dwelling species or certain life stages of other species that are associated with the bottom might be impacted by the aluminum floc or its coprecipitates.

Because of the variety of forms of aluminum (Hem 1968; Hem and Robertson 1967; Robertson and Hem 1969) and lack of definitive information about their relative toxicities, no available analytical measurement is known to be ideal for expressing aquatic life criteria for aluminum. Previous aquatic life criteria for metals (U.S. EPA 1980) were expressed in terms of the total recoverable measurements (U.S. EPA 1983a), but newer criteria for metals have been expressed in terms of the acid-soluble measurement (U.S. EPA 1985a). Acid-soluble aluminum (operationally defined as the aluminum that passes through a 0.45 μm membrane filter after the sample is acidified to pH = 1.5 to 2.0 with nitric acid) is probably the best measurement at the present for the following reasons:

1. This measurement is compatible with nearly all available data concerning toxicity of aluminum to aquatic organisms. Few test results were rejected just because it was likely that they would have been substantially

different if they had been reported in terms of acid-soluble aluminum. For example, results reported in terms of labile aluminum (Helliwell et al. 1983) were not used.

2. On samples of ambient water, measurement of acid-soluble aluminum will probably measure all forms of aluminum that are toxic to aquatic life or can be readily converted to toxic forms under natural conditions. In addition, this measurement probably will not measure several forms, such as aluminum that is occluded in minerals, clays, and sand or is strongly sorbed to particulate matter, that are not toxic and are not likely to become toxic under natural conditions. Although this measurement (and many others) will measure soluble complexed forms of aluminum, such as the EDTA complex of aluminum, that probably have low toxicities to aquatic life, concentrations of these forms probably are negligible in most ambient water.
3. Although water quality criteria apply to ambient water, the measurement used to express criteria is likely to be used to measure aluminum in aqueous effluents. Measurement of acid-soluble aluminum probably will be applicable to effluents because it will measure precipitates, such as carbonate and hydroxide precipitates of aluminum, that might exist in an effluent and dissolve when the effluent is diluted with receiving water. If desired, dilution of effluent with receiving water before measurement of acid-soluble aluminum might be used to determine whether the receiving water can decrease the concentration of acid-soluble aluminum because of sorption.
4. The acid-soluble measurement is probably useful for most metals, thus minimizing the number of samples and procedures that are necessary.
5. The acid-soluble measurement does not require filtration at the time of collection, as does the dissolved measurement.

6. The only treatment required at the time of collection is preservation by acidification to pH = 1.5 to 2.0, similar to that required for the total recoverable measurement.
7. Durations of 10 minutes to 24 hours between acidification and filtration of most samples of ambient water probably will not affect the result substantially.
8. The carbonate system has a much higher buffer capacity from pH = 1.5 to 2.0 than it does from pH = 4 to 9 (Weber and Stumm 1963).
9. Differences in pH within the range of 1.5 to 2.0 probably will not affect the result substantially.
10. The acid-soluble measurement does not require a digestion step, as does the total recoverable measurement.
11. After acidification and filtration of the sample to isolate the acid-soluble aluminum, the analysis can be performed using either atomic absorption spectrophotometric or ICP-atomic emission spectrometric analysis (U.S. EPA 1983a), as with the total recoverable measurement.

Thus, expressing aquatic life criteria for aluminum in terms of the acid-soluble measurement has both toxicological and practical advantages. On the other hand, because no measurement is known to be ideal for expressing aquatic life criteria for aluminum or for measuring aluminum in ambient water or aqueous effluents, measurement of both acid-soluble aluminum and total recoverable aluminum in ambient water or effluent or both might be useful. For example, there might be cause for concern if total recoverable aluminum is much above an applicable limit, even though acid-soluble aluminum is below the limit.

Unless otherwise noted, all concentrations reported herein are expected to be essentially equivalent to acid-soluble aluminum concentrations. All concentrations are expressed as aluminum, not as the chemical tested.

Whenever adequately justified, a national criterion may be replaced by a site-specific criterion (U.S. EPA 1983b), which may include not only site-specific criterion concentrations (U.S. EPA 1983c), but also site-specific durations of averaging periods and site-specific frequencies of allowed excursions (U.S. EPA 1985b). The latest literature search for information for this document was conducted in February, 1985; some newer information was also used.

Acute Toxicity to Aquatic Animals

An extensive review of the literature on the toxicity of aluminum to aquatic organisms was published by Burrows (1977), but most of the studies were conducted at pH less than 6.5. Durations of exposures reported in the literature varied and test endpoints were diverse.

The earliest study of the toxicity of aluminum to fish was performed by Thomas (1915) using mummichogs acclimated to fresh water. His report lacked detail and it is unclear whether the aluminum sulfate was anhydrous or hydrated. If the anhydrous form was used, 100% mortality of the mummichog occurred in 1.5 and 5 days at 2,200 and 1,100 $\mu\text{g/L}$, respectively. The pH was not reported and could have been depressed by the aluminum salt present at the lethal test concentrations. More recent tests with fish showing similar sensitivities to aluminum were conducted with brook trout with a 4-day LC_{50} of 3,600 $\mu\text{g/L}$ (Decker and Menendez 1974), rainbow trout with a 3-day LC_{50} of 5,200 $\mu\text{g/L}$ (Freeman and Everhart 1971), and common carp with a 2-day LC_{50} of 4,000 $\mu\text{g/L}$ (Muramoto 1981). Other fish species were less sensitive to aluminum.

The effect of pH on aluminum toxicity has been studied by several investigators. In a study of the median time to death of rainbow trout, Freeman and Everhart (1971) found an increase in aluminum toxicity as pH increased from 6.8 to 8.99. Hunter et al. (1980) observed the same

relationship with rainbow trout over a pH range of 7.0 to 9.0. However, the opposite relationship resulted in a study with rainbow trout by Call (1984) and in studies with the fathead minnow by Boyd (1979), Call (1984), and Kimball (Manuscript). The studies by Freeman and Everhart (1971), Hunter et al. (1980), and Kimball (Manuscript) were all flow-through or daily renewal of test solutions and showed the highest toxicities, whereas the other tests were static tests. The chemical forms of aluminum might have been different due to the time the aluminum was in solution and was able to form precipitate, thus becoming less available to organisms.

Acute toxicity of aluminum to invertebrate species occurred in about the same range of concentrations as to fish. A 48-h EC50 of 3,690 $\mu\text{g/L}$ for Ceriodaphnia sp. (Call 1984) was the lowest reported acute value, whereas the EC50s with Daphnia magna ranged from 3,900 to 38,200 $\mu\text{g/L}$. The highest LC50 was 55,500 $\mu\text{g/L}$ in a test with a snail (Call 1984). No pH-dependent trends were evident due to an insufficient number of tests with any species.

Species Mean Acute Values (Table 1) were calculated as geometric means of the available acute values, and then Genus Mean Acute Values (Table 3) were calculated as geometric means of the available freshwater Species Mean Acute Values. Because data are available for only one species in each genus, the species and genus mean acute values are identical. Several species tested were not exposed to aluminum concentrations high enough to allow calculation of an LC50. Although these were ranked in Table 3 according to the highest concentration used in the test, this does not imply a true ranking of sensitivities. Measured acute values are available for the four most sensitive genera. The freshwater Final Acute Value for aluminum was calculated to be 1,894 $\mu\text{g/L}$ using the procedure described in the Guidelines and the Genus Mean Acute Values in Table 3.

Chronic Toxicity to Aquatic Animals

Chronic toxicity values have been determined for aluminum with two freshwater species (Table 2). Daphnia magna had a chronic value of 1,388 µg/L after 28 days of exposure to aluminum sulfate (Kimball, Manuscript). This value was based upon survival of the adult. Reproduction was impaired at 2,840 µg/L. Biesinger and Christensen (1972) obtained a 21-day LC50 of 1,400 µg/L with D. magna, and they found 16% reproductive impairment at 320 µg/L (Table 5), but the concentration of aluminum was not measured in the test solutions.

Fathead minnows (Kimball, Manuscript) differed significantly in weight and length from the controls after exposure to 7,100 µg/L for the period of embryonic development and 28 days posthatch. The chronic value was 5,777 µg/L. Survival was affected at 9,200 µg/L (Table 5). The chronic tests indicate that, of the two species tested, the invertebrate was more sensitive to aluminum than the vertebrate.

The only two available acute-chronic ratios are 27.52 with Daphnia magna and 6.059 with the fathead minnow (Table 3). The Final Acute-Chronic Ratio of 12.91 was calculated as the geometric mean of these two. Division of the Final Acute Value by the Final Acute-Chronic Ratio results in a Final Chronic Value of 146.7 µg/L for fresh water at pH = 6.5 to 9.0.

Toxicity to Aquatic Plants

Single-celled plants were more sensitive to aluminum (Table 4) than the other plants tested. Growth of a diatom was inhibited at 810 µg/L, and the diatom died at 6,480 µg/L (Rao and Subramanian 1982). The green alga, Selenastrum capricornutum, was about as sensitive to aluminum as the diatom. Effects were found (Table 4) at concentrations ranging from 460 µg/L (Call 1984) to 990 µg/L (Peterson et al. 1974).

Among multicellular plants, root weight of Eurasian watermilfoil was significantly decreased at 2,500 µg/L, but duckweed was not affected at 45,700 µg/L (Table 4).

Bioaccumulation

No bioaccumulation data are available because none of the reported tissue concentrations had measured water concentrations for comparison. Also, no U.S. FDA action level or other maximum acceptable concentration in tissue is available for aluminum.

Other Data

Bringmann and Kuhn (1959a,b) found that Scenedesmus quadricauda was more tolerant of aluminum than Chlorella pyrenoidosa in river water (Table 5). They also did not find any toxic effects on Daphnia magna during a 48-h exposure to 1,000,000 µg/L. Toxicity might have been reduced by naturally occurring ligands in the river water.

Birge et al. (1980,1981) killed or deformed 10% of the embryos and fry of rainbow trout during a 28-day exposure to 369 µg/L, but Hunter et al. (1980) found no effect after a 10-day exposure of juveniles to 200,000 µg/L. Freeman (1973) studied the growth of rainbow trout after exposure to aluminum for 8 to 11 days.

Embryos and larva of the narrow-mouthed toad were very sensitive to aluminum exhibiting 50% death and deformity during a 7-day exposure to 50 µg/L (Birge 1978; Birge et al. 1979). Marbled salamander embryos and larva showed the same effect after an 8-day exposure to 2,280 µg/L (Birge et al. 1978).

Unused Data

Many data on the effects of aluminum on aquatic organisms were not used because the pH of the dilution water used in the tests was less than 6.5 (Anderson 1948; Baker and Schofield 1982; Brown 1981,1983; Brown et al. 1983; Dickson 1983; Driscoll et al. 1980; Eddy and Talbot 1983; Gunn and Keller 1984; Havas and Hutchinson 1982,1983; Jones 1940; Ogilvie and Stechey 1983; Staurnes et al. 1984; Schindler and Turner 1982; Schofield and Trojnar 1980; Tease and Coler 1984; van Dam et al. 1981; Witters et al. 1984). Data were also not used if the studies were conducted with species that are not resident in North America.

Burrows (1977), Chapman et al. (1968), Howells et al. (1983), Kaiser (1980), McKee and Wolf (1963), Phillips and Russo (1978), and Thompson et al. (1972) only present data that have been published elsewhere. Data were not used if aluminum was a component of a mixture (Hamilton-Taylor and Willis 1984; Havas and Hutchinson 1982; Markarian et al. 1980). Becker and Kellor (1983), Marquis (1982), and Stearns et al. (1978) were not used because the results were not adequately presented or could not be interpreted. Also, data were not used if only enzymes were exposed (e.g., Christensen 1971/72; Christensen and Tucker 1976).

Reports of the concentrations of aluminum in wild aquatic organisms (e.g., Ecological Analysts, Inc. 1984; Elwood et al. 1976; Wren et al. 1983) were not used if the number of measurements of the concentration in water was too small.

Field studies were not used because they either lacked aluminum concentrations in the water or reported no specific adverse effects (Buerger and Soltero 1983; Gibbons et al. 1984; Knapp and Soltero 1983; Sonnichsen 1978; Zarini et al. 1983).

Summary

Acute tests have been conducted on aluminum with 14 freshwater species at pH = 6.5 to 9.0. Quantitative LC50s or EC50s are available for only seven of these species; the other tests resulted in effects on less than 50% of the organisms at the highest concentrations tested. The tested species that was most sensitive to aluminum was the brook trout with a 96-h LC50 of 3,600 µg/L. Some studies found that the toxicity of aluminum increased with pH, whereas other studies found the opposite. Two studies have been conducted on the chronic toxicity of aluminum to aquatic animals. An acute-chronic ratio of 27.52 was obtained with Daphnia magna, and a ratio of 6.059 was obtained with the fathead minnow. The diatom, Cyclotella meneghiniana, and the green alga, Selenastrum capricornutum, were affected by concentrations of aluminum in the range of 400 to 900 µg/L. No bioconcentration or bioaccumulation factors are available for aluminum because in none of the studies were the concentrations in both tissue and water adequately measured.

National Criteria

The procedures described in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" indicate that, except possibly where a locally important species is very sensitive, freshwater aquatic organisms and their uses should not be affected unacceptably, when pH is between 6.5 and 9.0, if the four-day average concentration of aluminum does not exceed 150 µg/L more than once every three years on the average and if the one-hour average concentration does not exceed 950 µg/L more than once every three years on the average.

EPA believes that "acid-soluble" is probably the best measurement at present for expressing criteria for metals and the criterion for aluminum was developed on this basis. However, at this time, no EPA approved method for such a measurement is available to implement criteria for metals through the regulatory programs of the Agency and the States. The Agency is considering development and approval of a method for a measurement such as "acid-soluble." Until one is approved, however, EPA recommends applying criteria for metals using the total recoverable method. This has two impacts: (1) certain species of some metals cannot be measured because the total recoverable method cannot distinguish between individual oxidation states, and (2) in some cases these criteria might be overly protective when based on the total recoverable method.

The allowed average excursion frequency of three years is the Agency's best scientific judgment of the average amount of time it will take an unstressed aquatic ecosystem to recover from a pollution event in which exposure to aluminum exceeds the criterion. Stressed systems, for example one in which several outfalls occur in a limited area, would be expected to require more time for recovery. The resiliencies of ecosystems and their abilities to recover differ greatly, however, and site-specific criteria may be established if adequate justification is provided.

Use of criteria for developing water quality-based permit limits and for designing waste treatment facilities requires selection of an appropriate wasteload allocation model. Dynamic models are preferred for the application of these criteria. Limited data or other considerations might make their use impractical, in which case one must rely on a steady-state model. The Agency recommends the interim use of 1Q5 or 1Q10 for the Criterion Maximum Concentration (CMC) design flow and 7Q5 or 7Q10 for the

Criterion Continuous Concentration (CCC) design flow in steady-state models for unstressed and stressed systems respectively. These matters are discussed in more detail in the Technical Support Document for Water Quality-Based Toxics Control (U.S. EPA 1985b).

Table 1. Acute Toxicity of Aluminum to Aquatic Animals

<u>Species</u>	<u>Method*</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>pH</u>	<u>LC50 or EC50 (µg/L)**</u>	<u>Species Mean Acute Value (µg/L)**</u>	<u>Reference</u>
<u>FRESHWATER SPECIES</u>							
Planarian (adult), <u>Dugesia tigrina</u>	S, M	Aluminum chloride	47.4	7.48	>23,000 [†]	>23,000	Brooke et al. 1985
Snail (adult), <u>Physa</u> sp.	S, M	Aluminum chloride	47.4	7.46	55,500 ^{††}	-	Call 1984
Snail (adult), <u>Physa</u> sp.	S, M	Aluminum chloride	47.4	6.59	>23,400	-	Call 1984
Snail (adult), <u>Physa</u> sp.	S, M	Aluminum chloride	47.4	7.55	30,600	-	Call 1984
Snail (adult), <u>Physa</u> sp.	S, M	Aluminum chloride	47.4	8.17	>24,700	30,600	Call 1984
Cladoceran (<24 hr old), <u>Ceriodaphnia</u> sp.	S, M	Aluminum chloride	47.4	7.68	3,690	3,690	Call 1984
Cladoceran, <u>Daphnia magna</u>	S, U	Aluminum chloride	45.3	6.5- 7.5	3,900 ^{†††}	-	Blesinger and Christensen 1972
Cladoceran, <u>Daphnia magna</u>	S, M	Aluminum chloride	45.4	7.61	>25,300	-	Brooke et al. 1985
Cladoceran, <u>Daphnia magna</u>	S, M	Aluminum sulfate	-	7.05	38,200	38,200	Kimball, Manuscript
Amphipod (adult), <u>Gammarus pseudolimnaeus</u>	S, M	Aluminum chloride	47.4	7.53	22,000	22,000	Call 1984
Stonefly (nymph), <u>Acroneuria</u> sp.	S, M	Aluminum chloride	47.4	7.46	>22,600	>22,600	Call 1984
Midge (larva), <u>Tanytarsus dissimilis</u>	S, U	Aluminum sulfate	17.43	7.71- 6.85	>79,900	>79,900	Lamb and Bailey 1981
Chinook salmon (juvenile), <u>Oncorhynchus tshawytscha</u>	S, M	Sodium aluminate	28.0	7.0	>40,000	>40,000	Peterson et al. 1974

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Table 1. (continued)

Species	Method*	Chemical	Hardness (mg/L as CaCO ₃)	pH	LC50 or EC50 (µg/L)**	Species Mean Acute Value (µg/L)**	Reference
Rainbow trout (juvenile), <u>Salmo gairdneri</u>	S, M	Aluminum chloride	47.4	7.46	8,600 ^{††}	-	Call 1984
Rainbow trout (juvenile), <u>Salmo gairdneri</u>	S, M	Aluminum chloride	47.4	6.59	7,400	-	Call 1984
Rainbow trout (juvenile), <u>Salmo gairdneri</u>	S, M	Aluminum chloride	47.4	7.31	14,600	-	Call 1984
Rainbow trout (juvenile), <u>Salmo gairdneri</u>	S, M	Aluminum chloride	47.4	8.17	>24,700 ^{†††}	10,390	Call 1984
Brook trout (juvenile), <u>Salvelinus fontinalis</u>	F, M	Aluminum sulfate	-	6.5	3,600	3,600	Decker and Menendez 1974
Fathead minnow (adult), <u>Pimephales promelas</u>	S, U	Aluminum sulfate	-	7.6	>18,900	-	Boyd 1979
Fathead minnow (juvenile), <u>Pimephales promelas</u>	S, M	Aluminum chloride	47.4	7.61	>48,200	-	Call 1984
Fathead minnow (juvenile), <u>Pimephales promelas</u>	S, M	Aluminum chloride	47.4	8.05	>49,800	-	Call 1984
Fathead minnow (juvenile), <u>Pimephales promelas</u>	F, M	Aluminum sulfate	-	7.34	35,000	35,000	Kimball, Manuscript
Channel catfish (juvenile), <u>Ictalurus punctatus</u>	S, M	Aluminum chloride	47.4	7.54	>47,900	>47,900	Call 1984
Green sunfish (juvenile), <u>Lepomis cyanellus</u>	S, M	Aluminum chloride	47.4	7.55	>50,000	>50,000	Call 1984
Yellow perch (juvenile), <u>Perca flavescens</u>	S, M	Aluminum chloride	47.4	7.55	>49,800	>49,800	Call 1984

* S = static; F = flow-through; M = measured; U = unmeasured.

** Results are expressed as aluminum, not as the chemical.

† 48-hr test.

†† Aluminum chloride was added to Lake Superior water, the pH was adjusted, and the solution was aerated for 18 days prior to addition of test organisms; not used in calculations.

††† Not used in calculations.

Table 2. Chronic Toxicity of Aluminum to Aquatic Animals

<u>Species</u>	<u>Test*</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>pH</u>	<u>Limits (µg/L)**</u>	<u>Chronic Value (µg/L)**</u>	<u>Reference</u>
<u>FRESHWATER SPECIES</u>							
Cladoceran, <u>Daphnia magna</u>	LC	Aluminum sulfate	-	8.30	1,020- 1,890	1,388	Kimball, Manuscript
Fathead minnow (embryo, larva), <u>Pimephales promelas</u>	ELS	Aluminum sulfate	-	7.24- 8.15	4,700- 7,100	5,777	Kimball, Manuscript

* LC = life-cycle or partial life-cycle; ELS = early life-stage.

** Results are based on measured concentrations of aluminum.

Acute-Chronic Ratio

<u>Species</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>pH</u>	<u>Acute Value (µg/L)</u>	<u>Chronic Value (µg/L)</u>	<u>Ratio</u>
Cladoceran, <u>Daphnia magna</u>	-	7.05- 8.30	38,200	1,388	27.52
Fathead minnow, <u>Pimephales promelas</u>	-	7.24- 8.15	35,000	5,777	6.059

Table 3. Ranked Genus Mean Acute Values with Species Mean Acute-Chronic Ratios

Rank*	Genus Mean Acute Value ($\mu\text{g/L}$)	Species	Species Mean Acute Value ($\mu\text{g/L}$)**	Species Mean Acute-Chronic Ratio***
<u>FRESHWATER SPECIES</u>				
14	>79,900	Midge, <u>Tanytarsus dissimilis</u>	>79,900	-
13	>50,000	Green sunfish, <u>Lepomis cyanellus</u>	>50,000	-
12	>49,800	Yellow perch, <u>Perca flavescens</u>	>49,800	-
11	>47,900	Channel catfish, <u>Ictalurus punctatus</u>	>47,900	-
10	>40,000	Chinook salmon, <u>Oncorhynchus tshawytscha</u>	>40,000	-
9	38,200	Cladoceran, <u>Daphnia magna</u>	38,200	27.52
8	35,000	Fathead minnow, <u>Pimephales promelas</u>	35,000	6.059
7	30,600	Snail, <u>Physa</u> sp.	30,600	-
6	>23,000	Planarian, <u>Dugesia tigrina</u>	>23,000	-
5	>22,600	Stonefly, <u>Acrionurila</u> sp.	>22,600	-
4	22,000	Amphipod, <u>Gammarus pseudolimnaeus</u>	22,000	-
3	10,400	Rainbow trout, <u>Salmo gairdneri</u>	10,390	-
2	3,690	Cladoceran, <u>Cariodaphnia</u> sp.	3,690	-

Table 3. (Continued)

<u>Rank*</u>	<u>Genus Mean Acute Value (µg/L)</u>	<u>Species</u>	<u>Species Mean Acute Value (µg/L)**</u>	<u>Species Mean Acute-Chronic Ratio***</u>
1	3,600	Brook trout, <u>Salvelinus fontinalis</u>	3,600	-

* Ranked from most resistant to most sensitive based on Genus Mean Acute Value. Inclusion of "greater than" values in the rankings does not necessarily imply a true ranking, but does allow use of all genera for which data are available so that the Final Acute Value is not unnecessarily lowered.

** From Table 1.

***From Table 2.

Fresh water (pH = 6.5 to 9.0)

Final Acute Value = 1,894 µg/L

Criterion Maximum Concentration = (1,894 µg/L) / 2 = 947 µg/L

Final Acute-Chronic Ratio = 12.91

Final Chronic Value = (1,894 µg/L) / 12.91 = 146.7 µg/L

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Table 4. Toxicity of Aluminum to Aquatic Plants

<u>Species</u>	<u>Chemical</u>	<u>pH</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>Duration (days)</u>	<u>Effect</u>	<u>Result (µg/L)*</u>	<u>Reference</u>
<u>FRESHWATER SPECIES</u>							
Diatom, <u>Cyclotella meneghiniana</u>	Aluminum chloride	7.9	-	8	Inhibited growth algistatic algacidal	810 3,240 6,480	Rao and Subramanian 1982
Green alga, <u>Selenastrum capricornutum</u>	Sodium aluminate	7.0	15	14	Reduced cell counts and dry weight	990- 1,320	Peterson et al. 1974
Green alga, <u>Selenastrum capricornutum</u>	Aluminum chloride	7.6	14.9	4	EC50 (biomass)	570	Call 1984
Green alga, <u>Selenastrum capricornutum</u>	Aluminum chloride	8.2	14.9	4	EC50 (biomass)	460	Call 1984
Eurasian watermilfoil, <u>Myriophyllum spicatum</u>	Aluminum	-	-	32	EC50 (root weight)	2,500	Stanley 1974
Duckweed, <u>Lemna minor</u>	Aluminum chloride	7.6	14.9	4	Reduced frond production	>45,700	Call 1984
Duckweed, <u>Lemna minor</u>	Aluminum chloride	8.2	14.9	4	Reduced frond production	>45,700	Call 1984

* Results are expressed as aluminum, not as the chemical.

Table 5. Other Data on Effects of Aluminum on Aquatic Organisms

<u>Species</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>pH</u>	<u>Duration</u>	<u>Effect</u>	<u>Result (µg/L)*</u>	<u>Reference</u>
<u>FRESHWATER SPECIES</u>							
Green alga, <u>Chlorella vulgaris</u>	Aluminum chloride	-	<7.0	3-4 mo	Growth inhibition	4,000	DeJong 1965
Green alga, <u>Chlorella vulgaris</u>	Aluminum sulfate	-	-	30 days	Maximum growth reduced	<163,000	Becker and Keller 1973
Green alga, <u>Scenedesmus quadricauda</u>	Aluminum chloride	-	7.5- 7.8	96 hr	Incipient inhibition (river water)	1,500- 2,000	Bringmann and Kuhn 1959a,b
Protozoan, <u>Microregma heterostoma</u>	Aluminum chloride	-	7.5- 7.8	28 hr	Incipient inhibition (river water)	12,000	Bringmann and Kuhn 1959b
Protozoan, <u>Chilomonas paramecium</u>	Aluminum chloride	-	5.5- 7.4	3 hr	Some survival	110	Ruthven and Cairns 1973
Protozoan, <u>Paranema trichoporum</u>	Aluminum chloride	-	5.5- 6.5	3 hr	Some survival	62,600	Ruthven and Cairns 1973
Protozoan, <u>Tetrahymena pyriformis</u>	Aluminum chloride	-	5.5- 6.5	3 hr	Some survival	110	Ruthven and Cairns 1973
Protozoan, <u>Euglena gracilis</u>	Aluminum chloride	-	6.0 7.0	3 hr	Some survival	111,800	Ruthven and Cairns 1973
Cladoceran, <u>Daphnia magna</u>	Aluminum sulfate	-	-	16 hr	Incipient immobilization	21,450	Anderson 1944
Cladoceran, <u>Daphnia magna</u>	Ammonium aluminum sulfate	-	-	16 hr	Incipient immobilization	21,620	Anderson 1944
Cladoceran, <u>Daphnia magna</u>	Potassium aluminum sulfate	-	-	16 hr	Incipient immobilization	21,530	Anderson 1944
Cladoceran, <u>Daphnia magna</u>	Aluminum chloride	-	7.5	48 hr	Non-toxic (river water)	1,000,000	Bringmann and Kuhn 1959a

Table 5. (Continued)

<u>Species</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>pH</u>	<u>Duration</u>	<u>Effect</u>	<u>Result (µg/L)*</u>	<u>Reference</u>
<u>Cladoceran, Daphnia magna</u>	Aluminum chloride	45.3	6.5- 7.5	21 days	EC16 (reduced reproduction)	320	Blesinger and Christensen 1972
<u>Cladoceran, Daphnia magna</u>	Aluminum chloride	45.3	6.5- 7.5	21 days	LC50	1,400	Blesinger and Christensen 1972
<u>Cladoceran, Daphnia magna</u>	Sodium aluminate	27.0	7.0	96 hr	Mortality	>40,000	Peterson et al. 1974
<u>Aquatic beetle (adult), Tropisternus lateralis nimbus</u>	Aluminum chloride	-	7.0	14 days	Changed fat body	200	Wooldridge and Wooldridge 1969
<u>Midge (larva), Tanytarsus dissimilis</u>	Aluminum sulfate	17.43	6.63	55 days	37% mortality	832	Lamb and Bailey 1981
<u>Rainbow trout (fingerling), Salmo gairdneri</u>	Aluminum chloride	46.8	8.02	32 days	50% dead	5,230	Freeman and Everhart 1971
<u>Rainbow trout (fingerling), Salmo gairdneri</u>	Aluminum chloride	28.3	8.48	7.5 days	50% dead	5,140	Freeman and Everhart 1971
<u>Rainbow trout (fingerling), Salmo gairdneri</u>	Aluminum chloride	28.3	8.99	3 days	50% dead	5,200	Freeman and Everhart 1971
<u>Rainbow trout (fingerling), Salmo gairdneri</u>	Aluminum chloride	56.6	6.64	44 days	50% dead	513	Freeman and Everhart 1971
<u>Rainbow trout (fingerling), Salmo gairdneri</u>	Aluminum chloride	56.6	6.80	39 days	50% dead	5,140	Freeman and Everhart 1971
<u>Rainbow trout (embryo), Salmo gairdneri</u>	Aluminum chloride	-	7.0- 9.0	Fertiliza- tion to hatch	No reduced fertility	5,200	Everhart and Freeman 1973
<u>Rainbow trout (embryo and fry), Salmo gairdneri</u>	Aluminum chloride	104 (92-110)	7.4	28 days	EC50 (death and deformity)	560	Birge 1978; Birge et al. 1978, 1980
<u>Rainbow trout (embryo and fry), Salmo gairdneri</u>	Aluminum chloride	102 (92-110)	7.4	28 days	EC10 (death and deformity)	369	Birge et al. 1980, 1981

Table 5. (continued)

<u>Species</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>pH</u>	<u>Duration</u>	<u>Effect</u>	<u>Result (µg/L)*</u>	<u>Reference</u>
Rainbow trout (juvenile), <u>Salmo gairdneri</u>	Aluminum sulfate	25	7.0	10 days	No toxicity	200,000	Hunter et al. 1980
Rainbow trout (juvenile), <u>Salmo gairdneri</u>	Aluminum sulfate	25	8.0	96 hr	40% mortality	50,000	Hunter et al. 1980
Rainbow trout (juvenile), <u>Salmo gairdneri</u>	Aluminum sulfate	25	8.5	42 hr	100% mortality	50,000	Hunter et al. 1980
Rainbow trout (juvenile), <u>Salmo gairdneri</u>	Aluminum sulfate	25	9.0	42 hr	100% mortality	50,000	Hunter et al. 1980
Goldfish (60-90 mm), <u>Carassius auratus</u>	Aluminum potassium sulfate	-	6.8	4 days	Reduced survival time	5,700	Ellis 1937
Goldfish (embryo and fry), <u>Carassius auratus</u>	Aluminum chloride	195	7.4	7 days	EC50 (death and deformity)	150	Birge 1978
Common carp (juvenile), <u>Cyprinus carpio</u>	Aluminum chloride	-	6.5	48 hr	30% dead	4,000	Muramoto 1981
Common carp (juvenile), <u>Cyprinus carpio</u>	Aluminum chloride	-	6.6	48 hr	10% dead	4,000	Muramoto 1981
Fathead minnow (adult), <u>Pimephales promelas</u>	Aluminum chloride	-	-	-	50% reduction of acetylcholinesterase activity	18,000	Olson and Christensen 1980
Fathead minnow (juvenile), <u>Pimephales promelas</u>	Aluminum chloride	-	7.24-8.15	28 days	Incipient lethal	9,200	Kimball Manuscript
Mummichog (adult), <u>Fundulus heteroclitus</u>	Aluminum sulfate	-	-	36 hr	100% mortality	2,210	Thomas 1915
Mummichog (adult), <u>Fundulus heteroclitus</u>	Aluminum sulfate	-	-	120 hr	100% mortality	1,100	Thomas 1915

Table 5. (continued)

<u>Species</u>	<u>Chemical</u>	<u>Hardness</u> (mg/L as CaCO ₃)	<u>pH</u>	<u>Duration</u>	<u>Effect</u>	<u>Result</u> (µg/L)*	<u>Reference</u>
Mosquitofish (adult female), <u>Gambusia affinis</u>	Aluminum chloride	-	4.3- 7.2	4 days	LC50 (high turbidity)	26,900	Wallen et al. 1957
Mosquitofish (adult female), <u>Gambusia affinis</u>	Aluminum chloride	-	4.4- 7.7	4 days	LC50 (high turbidity)	18,500	Wallen et al. 1957
Threespine stickleback (adult), <u>Gasterosteus aculeatus</u>	Aluminum nitrate	-	>7.0	10 days	No toxicity	70	Jones 1939
Largemouth bass (embryo, larva), <u>Micropterus salmoides</u>	Aluminum chloride	93-105	7.2- 7.8	8 days	EC50 (death and deformity)	170	Birge et al. 1978
Narrow-mouthed toad (embryo, larva), <u>Gastrophryne carolinensis</u>	Aluminum chloride	195	7.4	7 days	EC50 (death and deformity)	50	Birge 1978; Birge et al. 1979
Marbled salamander (embryo, larva), <u>Ambystoma opacum</u>	Aluminum chloride	93-105	7.2- 7.8	8 days	EC50 (death and deformity)	2,280	Birge et al. 1978

* Results are expressed as aluminum, not as the chemical.

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