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Ambient Water Quality Criteria for

Aluminum - 1988

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 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.

Guidance 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 has been developed by EPA.

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Introduction

The chemistry of aluminum in surface water is complex because of five properties (Campbell et al. 1983; Hem 1968a,b; Hem and Roberson 1967; Hsu 1968; Roberson and Hem 1969; Smith and Hem 1972). First, it is amphoteric: it is more soluble in acidic solutions and in basic solutions than in circumneutral solutions. Second, such ions as chloride, fluoride, nitrate, phosphate, and sulfate form soluble complexes with aluminum. Third, it can form strong complexes with fulvic and humic acids. Fourth, hydroxide ions can connect aluminum ions to form soluble and insoluble polymers. Fifth, under at least some conditions, solutions of aluminum in water approach chemical equilibrium rather slowly. This document addresses the toxicity of aluminum to freshwater organisms in waters in which the pH is between 6.5 and 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 the hydrogen ion. At a pH between 6.5 and 9.0 in fresh water, aluminum occurs predominantly as monomeric, dimeric, and polymeric hydroxides and as complexes with humic acids, phosphate, sulfate, and less common anions. This document does not contain information concerning the effect of aluminum on saltwater species because adequate data and resources were not available.

Several investigators have speculated about the toxic form of aluminum. Freeman and Everhart (1971) found that the toxicity of aluminum increased as pH increased from 6.8 to 8.99. They concluded that soluble aluminum was the toxic form. 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 tests conducted by Freeman and Everhart (1971), Hunter et al. (1980), and Kimball (Manuscript) were all renewal or flow-through and showed the lowest acute values, whereas the other tests were static. In addition, because the polymerization of aluminum hydroxide is a relatively slow process, the chemical form of aluminum might have differed from test to test due to the amount of time the aluminum was in stock and test solutions.

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 to fish. Hunter et al. (1980) reported that the toxicity of test solutions was directly related to the concentration of aluminum that passed through a 0.45 μm membrane filter. In a study of the toxicity of "labile" aluminum to a 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 near the pH of minimum solubility of aluminum and maximum concentration of $Al(OH)_2^+$. 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. Seip et al. (1984) stated that "the simple hydroxides ($Al(OH)^{+2}$ and $Al(OH)_2^+$) are regarded as the most dangerous forms while organically bound Al and polymeric forms are less toxic or essentially harmless."

In dilute aluminum solutions, formation of particles and the large insoluble polynuclear complexes known as floc is primarily a function of the concentrations of organic acids and the hydroxide ion (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 and tends to settle. Mats have been reported blanketing a stream bed (Hunter et al. 1980). Laboratory studies conducted at alkaline pHs have reported floc in the exposure chambers (Brooke 1985; Call 1984; Lamb and Bailey 1981; Zarini et al. 1983). The floc did not appear to affect most aquatic species. However, the swimming ability of Daphnia magna was impeded by "fibers" of flocculated aluminum trailing from the carapaces, and the movements and perhaps feeding of midges was affected, ultimately resulting in death (Lamb and Bailey 1981). Bottom-dwelling organisms might be impacted more by aluminum floc in the field than in the laboratory.

Aluminum floc might coprecipitate nutrients, suspended material, and microorganisms. Removal of phosphorus from water has been observed in laboratory studies (Matheson 1975; Minzoni 1984; Peterson et al. 1974) and in a lake (Knapp and Soltero 1983). Turbidity due to clay has been removed from pond waters using aluminum sulfate (Boyd 1979). Unz and Davis (1975) speculated that aluminum floc might coalesce bacteria and concentrate organic matter in effluents, thus assisting the biological sorption of nutrients. Aluminum sulfate has been used to flocculate algae from water (McGarry 1970; Minzoni 1984; Zarini et al. 1983).

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, and the response to public comment (U.S. EPA 1985a) is necessary in order to understand the following text, tables, and calculations. Results of such intermediate calculations as Species Mean Acute Values are given to four significant figures to prevent roundoff error in subsequent calculations, not to reflect the precision of the value. Unless otherwise noted, all concentrations of aluminum in water reported herein from toxicity and bioconcentration tests are expected to be essentially equivalent to acid-soluble aluminum concentrations. All concentrations are expressed as aluminum, not as the chemical tested. The latest comprehensive literature search for information for this document was conducted in July, 1986; some more recent information was included.

Acute Toxicity to Aquatic Animals

The earliest study of the toxicity of aluminum to aquatic life was performed by Thomas (1915) using mummichogs acclimated to fresh water. His report lacks detail and it is unclear whether the aluminum sulfate was anhydrous or hydrated. Assuming that the anhydrous form was used, the calculated concentrations of aluminum where all of the fish died in 1.5 and 5 days were 2,200 and 1,100 µg/l, respectively. More recent tests with fish showing similar sensitivities to aluminum (Tables 1 and 6) were conducted with brook trout with a 96-hr LC50 of 3,600 µg/L (Decker and Menendez 1974), rainbow trout with a 72-hr LC50 of 5,200 µg/L (Freeman and Everhart 1971), and common carp with a 48-hr LC50 of 4,000 µg/L (Muramoto 1981). Other fish species tested were more resistant to aluminum.

The range of concentrations of aluminum that was acutely toxic to freshwater invertebrate species was about the same as the range of concentrations that was toxic to fish. The lowest acute values for invertebrates are 1,900 µg/L (McCauley et al. 1986) and 3,690 µg/L (Call 1984) for ceriodaphnids, whereas the highest acute value is 55,500 µg/L in a test with a snail (Call 1984). No data are available concerning the effect of pH on toxicity of aluminum to invertebrates.

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 Species Mean Acute Values. 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. The freshwater Final Acute Value for aluminum at a pH between 6.5 and 9.0 was calculated to be 1,496 µg/L using the procedure described in the Guidelines and the Genus Mean Acute Values in Table 3. Because acute values are available for only fourteen genera, the FAV is about one-half the acute value for the most sensitive genus

Chronic Toxicity to Aquatic Animals

Chronic toxicity values for aluminum have been determined with three freshwater species (Table 2). McCauley et al. (1986) found that 2,600 µg/L reduced survival and reproduction of *Ceriodaphnia dubia* by 23% and 92%, respectively. An aluminum concentration of 1,400 µg/L reduced survival by 11%, but increased reproduction. Although survival increased at concentrations above 2,600 µg/L, no reproduction occurred. In a life-cycle test with *Daphnia magna*, survival was the same at 540 µg/L as in the control treatment, but was reduced about 29% at 1,020 µg/L (Kimball, Manuscript). Reproduction was about the same at 1,020 µg/L as in the control treatment. Biesinger and Christensen (1972) obtained a 21-day LC50 of 1,400 µg/L with *D. magna* (Table 6). They estimated that 320 µg/L would reduce reproduction by 16%, but the concentrations of aluminum were not measured in the test solutions.

Kimball (Manuscript) reported the results of an early life-stage test with fathead minnows. An aluminum concentration of 4,700 µg/L reduced weight by 11.4%, whereas 2,300 µg/L reduced weight by 7.1%. Survival at both concentrations was as good or better than in the control treatment. These chronic tests indicate that, of the three species tested, the invertebrates are more sensitive to aluminum than the vertebrate.

The three available acute-chronic ratios for aluminum are 0.9958 with *Ceriodaphnia dubia*, 51.27 with *Daphnia magna*, and 10.64 with the fathead minnow (Table 2). These values follow the common pattern that acutely sensitive species have lower acute-chronic ratios (Table 3). The Final Acute-Chronic Ratio is meant to apply to acutely sensitive species, and, therefore, should be close to 0.9958. However, according to the Guidelines, the Final Acute-Chronic Ratio cannot be less than 2, because a ratio lower than 2 would result in the Final Chronic Value exceeding the Criterion Maximum Concentration. Thus the Final Chronic Value for aluminum is equal to the Criterion Maximum Concentration of 748.0 μg/L for fresh water at a pH between 6.5 and 9.0 (Table 3).

Data in Table 6 concerning the toxicity of aluminum to brook trout and striped bass show that the Final Chronic Value should be lowered to 87 μg/L to protect these two important species. Cleveland et al. (Manuscript) found that 169 μg/L caused a 24% reduction in the weight of young brook trout in a 60-day test, whereas 88 μg/L caused a 4% reduction in weight. In a 7-day test, 174.4 μg/L killed 58% of the exposed striped bass, whereas 87.2 μg/L did not kill any of the exposed organisms (Buckler et al., Manuscript). Both of these tests were conducted at a pH of 6.5 to 6.6.

Toxicity to Aquatic Plants

Single-celled plants were more sensitive to aluminum than the other* plants tested (Table 4). Growth of the diatom, *Cyclotella meneghiniana*, was inhibited at 810 μg/L, and the species 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 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). A Final Plant Value, as defined in the Guidelines, cannot be obtained because no test in which the concentrations of aluminum were measured and the endpoint was biologically important has been conducted with an important aquatic plant species.

Bioaccumulation

Cleveland et al. (1986) found that young brook trout contained more aluminum after exposure for 15 days than after exposure for 30 days, and the bioconcentration factors ranged from 50 to 231. No U.S. FDA action level or other maximum acceptable concentration in tissue, as defined in the Guidelines, is available for aluminum, and, therefore, no Final Residue Value can be calculated.

Other Data

Additional data on the lethal and sublethal effects of aluminum on freshwater species are presented in Table 6. Bringmann and Kuhn (1959a,b) found that Scenedesmus quadricauda was more resistant to aluminum in river water than Chlorella pyrenoidosa. They 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 and coworkers reported that 50% of the embryos and fry of the narrow-mouthed toad, goldfish, largemouth bass, and rainbow trout were killed or deformed by exposure to aluminum concentrations of 50, 150, 170, and 560 μg/L, respectively (Table 6). Freeman and Everhart (1971) obtained an LC50 of 513 μg/L with rainbow trout fingerlings, but these and other investigators also obtained much higher LC50s with embryos, fry, and fingerlings of rainbow trout. Freeman (1973) studied the growth of rainbow trout after exposure to aluminum for 4.7 to 45 days. Growth was reduced by 5,200 μg/L when pH was 7.0, 8.0, or 9.0. Normal growth resumed within two weeks in control water.

Unused Data

Many data on the effects of aluminum on freshwater 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; Buckler et al., Manuscript; Clark and LaZerte 1985; Cleveland et al. 1986; Cook and Haney 1985; Dickson 1983; Driscoll et al. 1980; Eddy and Talbot 1983; Gunn and Keller 1984; Gunn and Noakes 1986; Havas and Hutchinson 1982,1983; Hunn et al. 1987; Jones 1940; Ogilvie and Stechey 1983; Orr et al. 1986; Schindler and Turner 1982; Schofield and Trojnar 1980; Staurnes et al. 1984; 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), Doudoroff and Katz (1953), Howells et al. (1983), Kaiser (1980), McKee and Wolf (1963), Odonnell et al. (1984), Phillips and Russo (1978), and Thompson et al. (1972) compiled data from other sources. Test results (e.g., Helliwell et al. 1983) were not used when it was likely that they would have been substantially different if they had been reported in terms of acid-soluble aluminum. Data were not used when aluminum was a component of an effluent or a mixture (Buckler et al., Manuscript; Guthrie et al. 1977; Hall et al. 1985; Hamilton-Taylor et al. 1984; Havas and Hutchinson 1982; Jay and Muncy 1979; Markarian et al. 1980).

Becker and Keller (1983), Marquis (1982), and Stearns et al. (1978) were not used because the results were not adequately presented or could not be interpreted. Data were not used when only enzymes were exposed (e.g., Christensen 1971/72; Christensen and Tucker 1976). Tests conducted by McCauley et al. (1986) at higher pHs were not used because the organisms were not acclimated to the dilution water before the beginning of the test. Control mortality was too high in many tests reported by Buckler et al. (Manuscript).

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 when the number of measurements of the concentration of aluminum in water was too small. Reports of other field studies were not used when they either lacked adequate measurements of aluminum concentrations in the water or reported no specific adverse effects (Berg and Burns 1985; Brumbaugh and Kane 1985; Buergel and Soltero 1983; Gibbons et al. 1984; Knapp and Soltero 1983; Sonnichsen 1978; van Coillie and Rousseau 1974; Zarini et al. 1983).

<u>Summary</u>

Acute tests have been conducted on aluminum at pH between 6.5 and 9.0 with freshwater species in fourteen genera. In many tests, less than 50% of the organisms were affected at the highest concentration tested. Both ceriodaphnids and brook trout were affected at concentrations below 4,000 µg/L, whereas some other fish and invertebrate species were not affected by 45,000 µg/L. Some researchers found that the acute toxicity of aluminum increased with pH, whereas others found the opposite to be true. Three studies have been conducted on the chronic toxicity of aluminum to aquatic animals. The chronic values for Daphnia magna, Ceriodaphnia dubia, and the fathead minnow were 742.2, 1,908, and 3,288 μg/L, respectively. 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. Bioconcentration factors from 50 to 231 were obtained in tests with young brook trout. At a pH of 6.5 to 6.6, 169 μg/L caused a 24% reduction in the growth of young brook trout, and 174 μg/L killed 58% of the exposed striped bass.

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 the pH is between 6.5 and 9.0, if the four-day average concentration of aluminum does not exceed 87 μg/L more than once every three years on the average and if the one-hour average concentration does not exceed 750 μg/L more than once every three years on the average.

Implementation

Because of the variety of forms of aluminum in ambient water and the lack of definitive information about their relative toxicities to freshwater species, no available analytical measurement is known to be ideal for expressing aquatic life criteria for aluminum. Previous aquatic life criteria for metals and metalloids (U.S. EPA 1980) were expressed in terms of the total recoverable measurement (U.S. EPA 1983a), but newer criteria for metals and metalloids have been expressed in terms of the acid-soluble measurement (U.S. EPA 1985b). Acid-soluble aluminum (operationally defined as the aluminum that passes through a 0.45 μm membrane filter after the sample has been acidified to a pH between 1.5 and 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, and bioaccumulation of aluminum by, aquatic organisms. It is expected that the results of tests used in the derivation of the criteria would not have changed substantially if they had been reported in terms of acid-soluble aluminum.
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 is expected to 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 expected to be useful for most metals and metalloids, thus minimizing the number of samples and procedures that are necessary.
5. The acid-soluble measurement does not require filtration of the sample 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 a pH between 1.5 and 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. Ambient waters have much higher buffer intensities at a pH between 1.5 and 2.0 than they do at a pH between 4 and 9 (Stumm and Morgan 1981).
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. The U.S. EPA is considering development and approval of a method for a measurement such as acid-soluble.

The 0.45 μm membrane filter is the usual basis for an operational definition of "dissolved," at least in part because filters with smaller holes often clog rapidly when natural water samples are filtered. Some particulate and colloidal material, however, might pass through a 0.45 μm filter. The intent of the acid-soluble measurement is to measure the concentrations of metals and metalloids that are in true solution in a sample that has been appropriately acidified. Therefore, material that does not pass through a filter with smaller holes, such as a 0.1 μm membrane filter, should not be considered acid-soluble even if it passes through a 0.45 μm membrane filter. Optional filtration of appropriately acidified water samples through 0.1 μm membrane filters should be considered whenever the concentration of aluminum that passes through a 0.45 μm membrane filter in an acidified water sample exceeds a limit specified in terms of acid-soluble aluminum.

Metals and metalloids might be measured using the total recoverable method (U.S. EPA 1983a). This would have two major impacts because this method includes a digestion procedure. First, certain species of some metals and metalloids cannot be measured because the total recoverable method cannot distinguish between individual oxidation states. Second, in some cases these criteria would be overly protective when based on the total recoverable method because the digestion procedure will probably dissolve some aluminum that is not toxic and cannot be converted to a toxic form under natural conditions. This could be a major problem in ambient waters that contain suspended clay. 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 when total recoverable aluminum is much above an applicable limit, even though acid-soluble aluminum is below the limit.

In addition, metals and metalloids might be measured using the dissolved method, but this would also have several impacts. First, in many toxicity tests on aluminum the test organisms were exposed to both dissolved and undissolved aluminum. If only the dissolved aluminum had been measured, the acute and chronic values would be lower than if acid-soluble or total recoverable aluminum had been measured. Therefore, water quality criteria expressed as dissolved aluminum would be lower than criteria expressed as acid-soluble or total recoverable aluminum. Second, not enough data are available concerning the toxicity of dissolved aluminum to allow derivation of a criterion based on dissolved aluminum. Third, whatever analytical method is specified for measuring aluminum in ambient surface water will probably also be used to monitor effluents. If effluents are monitored by measuring only the dissolved metals and metalloids, carbonate and hydroxide precipitates of metals would not be measured. Such precipitates might dissolve, due to dilution or change in pH or both, when the effluent is mixed with receiving water. Fourth, measurement of dissolved aluminum requires filtration of the sample at the time of collection. For these reasons, it is recommended that aquatic life criteria for aluminum not be expressed as dissolved aluminum.

As discussed in the Water Quality Standards Regulation (U.S. EPA 1983b) and the Foreword to this document, a water quality criterion for aquatic life has regulatory impact only after it has been adopted in a State water quality standard. Such a standard specifies a criterion for a pollutant that is consistent with a particular designated use. With the concurrence of the U.S. EPA, States designate one or more uses for each body of water or segment thereof and adopt criteria that are consistent with the use(s) (U.S. EPA

1983c,1987). In each standard a State may adopt the national criterion, if one exists, or, if adequately justified, a site-specific criterion. (If the site is an entire State, the site-specific criterion is also a State-specific criterion.)

Site-specific criteria may include not only site-specific criterion concentrations (U.S. EPA 1983c), but also site-specific, and possibly pollutant-specific, durations of averaging periods and frequencies of allowed excursions (U.S. EPA 1985c). The averaging periods of "one hour" and "four days" were selected by the U.S. EPA on the basis of data concerning how rapidly some aquatic species react to increases in the concentrations of some pollutants, and "three years" is the Agency's best scientific judgment of the average amount of time aquatic ecosystems should be provided between excursions (Stephan et al. 1985; U.S. EPA 1985c). However, various species and ecosystems react and recover at greatly differing rates. Therefore, if adequate justification is provided, site-specific and/or pollutant-specific concentrations, durations, and frequencies may be higher or lower than those given in national water quality criteria for aquatic life.

Use of criteria, which have been adopted in State water quality standards, for developing water quality-based permit limits and for designing waste treatment facilities requires selection of an appropriate wasteload allocation model. Although dynamic models are preferred for the application of these criteria (U.S. EPA 1985c), limited data or other considerations might require the use of a steady-state model (U.S. EPA 1986). Guidance on mixing zones and the design of monitoring programs is also available (U.S. EPA 1985c,1987).

Table 1. Acute Toxicity of Aluminum to Aquatic Animals

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	pH	LC50 or EC50 (µg/L)[b]	Species Mean Acute Value (µg/L)	Reference
				FRESHWATER SPECIES			
Planarian (adult), *Dugesia tigrina*	S, M	Aluminum chloride	47.4	7.48	>23,000[c]	>23,000	Brooke et al. 1985
Snail (adult), *Physa* sp	S, M	Aluminum chloride	47.4	7.46	55,500[d]	-	Call 1984
Snail (adult), *Physa* sp	S, M	Aluminum chloride	47.4	6.59	>23,400	-	Call 1984
Snail (adult), *Physa* sp.	S, M	Aluminum chloride	47.4	7.55	30,600	-	Call 1984
Snail (adult), *Physa* sp.	S, M	Aluminum chloride	47.4	8.17	>24,700	30,600	Call 1984
Cladoceran (<16 hr), *Ceriodaphnia dubia*	S, M	Aluminum chloride	50.0	7.4	1,900	1,900	McCauley et al. 1986
Cladoceran (< 24 hr), *Ceriodaphnia* sp	S, M	Aluminum chloride	47.4	7.68	3,690	3,690	Call 1984
Cladoceran, *Daphnia magna*	S, U	Aluminum chloride	45.3	6.5-7.5	3,900[e]	-	Biesinger and Christensen 1972
Cladoceran, *Daphnia magna*	S, M	Aluminum chloride	45.4	7.61	>25,300	-	Brooke et al. 1985
Cladoceran, *Daphnia magna*	S, M	Aluminum sulfate	220[f]	7.05	38,200	38,200	Kimball, Manuscript
Amphipod (adult), *Gammarus pseudolimnaeus*	S, M	Aluminum chloride	47.4	7.53	22,000	22,000	Call 1984

Table 1. (continued)

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	pH	LC50 or EC50 (µg/L)[b]	Species Mean Acute Value (µg/L)	Reference
Stonefly (nymph), *Acroneuria* sp	S, M	Aluminum chloride	47.4	7.46	>22,600	>22,600	Call 1984
Midge (larva), *Tanytarsus dissimilis*	S, M	Aluminum sulfate	17.43	7.71-6.85	>79,900	>79,900	Lamb and Bailey 1981
Chinook salmon (juvenile), *Oncorhynchus tshawytscha*	S, M	Sodium aluminate	28.0	7.0	>40,000	>40,000	Peterson et al. 1974
Rainbow trout (juvenile), *Salmo gairdneri*	S, M	Aluminum chloride	47.4	7.46	8,600[d]	-	Call 1984
Rainbow trout (juvenile), *Salmo gairdneri*	S, M	Aluminum chloride	47.4	6.59	7,400	-	Call 1984
Rainbow trout (juvenile), *Salmo gairdneri*	S, M	Aluminum chloride	47.4	7.31	14,600	-	Call 1984
Rainbow trout (juvenile), *Salmo gairdneri*	S, M	Aluminum chloride	47.4	8.17	>24,700[e]	10,390	Call 1984
Brook trout (juvenile), *Salvelinus fontinalis*	F, M	Aluminum sulfate	-	6.5	3,600	3,600	Decker and Menendez 1974
Fathead minnow (adult), *Pimephales promelas*	S, U	Aluminum sulfate	-	7.6	>18,900	-	Boyd 1979

Table 1. (continued)

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	pH	LC50 or EC50 (µg/L)[b]	Species Mean Acute Value (µg/L)	Reference
Fathead minnow (juvenile), *Pimephales promelas*	S, M	Aluminum chloride	47.4	7.61	>48,200	-	Call 1984
Fathead minnow (juvenile), *Pimephales promelas*	S, M	Aluminum chloride	47.4	8.05	>49,800	-	Call 1984
Fathead minnow (juvenile), *Pimephales promelas*	F, M	Aluminum sulfate	220[f]	7.34	35,000	35,000	Kimball, Manuscript
Channel catfish (juvenile), *Ictalurus punctatus*	S, M	Aluminum chloride	47.4	7.54	>47,900	>47,900	Call 1984
Green sunfish (juvenile), *Lepomis cyanellus*	S, M	Aluminum chloride	47.4	7.55	>50,000	>50,000	Call 1984
Yellow perch (juvenile), *Perca flavescens*	S, M	Aluminum chloride	47.4	7.55	>49,800	>49,800	Call 1984

[a] S = static; R = renewal; F = flow-through, M = measured, U = unmeasured

[b] Concentration of aluminum, not the chemical

[c] 48-hr test

[d] 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

[e] Not used in calculations

[f] From Smith et al. (1976)

Table 2. Chronic Toxicity of Aluminum to Aquatic Animals

Species	Test[a]	Chemical	Hardness (mg/L as $CaCO_3$)	pH	Limits (µg/L)[b]	Chronic Value (µg/L)	Reference
			FRESHWATER SPECIES				
Cladoceran, *Ceriodaphnia dubia*	LC	Aluminum chloride	50	7.15	1,400-2,600	1,908	McCauley et al. 1986
Cladoceran, *Daphnia magna*	LC	Aluminum sulfate	220[c]	8.30	540-1,020	742.2	Kimball, Manuscript
Fathead minnow, *Pimephales promelas*	ELS	Aluminum sulfate	220[c]	7.24-8.15	2,300-4,700	3,288	Kimball, Manuscript

[a] LC = life-cycle or partial life-cycle; ELS = early life-stage

[b] Measured concentrations of aluminum.

[c] From Smith et al. (1976).

Table 2. (continued)

Acute-Chronic Ratio

Species	Hardness (mg/L as $CaCO_3$)	pH	Acute Value (µg/L)	Chronic Value (µg/L)	Ratio
Cladoceran, *Ceriodaphnia dubia*	50	7 15-7 4	1,900	1,908	0 9958
Cladoceran, *Daphnia magna*	220	7 05-8 30	38,200	742 2	51 47
Fathead minnow, *Pimephales promelas*	220	7 24-8 15	35,000	3,288	10 64

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

Rank[a]	Genus Mean Acute Value (µg/L)	Species	Species Mean Acute Value (µg/L)[b]	Species Mean Acute-Chronic Ratio[c]
14	>79,900	Midge, *Tanytarsus dissimilis*	>79,900	-
13	>50,000	Green sunfish, *Lepomis cyanellus*	>50,000	-
12	>49,800	Yellow perch, *Perca flavescens*	>49,800	-
11	>47,900	Channel catfish, *Ictalurus punctatus*	>47,900	
10	>40,000	Chinook salmon, *Oncorhynchus tshawytscha*	>40,000	-
9	38,200	Cladoceran, *Daphnia magna*	38,200	51 47
8	35,000	Fathead minnow, *Pimephales promelas*	35,000	10 64
7	30,600	Snail, *Physa* sp	30,600	-
6	>23,000	Planarian, *Dugesia tigrina*	>23,000	-
5	>22,600	Stonefly, *Acroneuria* sp	>22,600	-
4	22,000	Amphipod, *Gammarus pseudolimnaeus*	22,000	-
3	10,390	Rainbow trout, *Salmo gairdneri*	10,390	

Table 3. (continued)

Rank[a]	Genus Mean Acute Value (µg/L)	Species	Species Mean Acute Value (µg/L)[b]	Species Mean Acute-Chronic Ratio[c]
2	3,600	Brook trout, *Salvelinus fontinalis*	3,600	-
1	2,648	Cladoceran, *Ceriodaphnia dubia*	1,900	0 9958
		Cladoceran, *Ceriodaphnia* sp	3,690	-

[a] Ranked from most resistant to most sensitive based on Genus Mean Acute Value Inclusion of "greater than" values 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.

[b] From Table 1.

[c] From Table 2

Fresh water (pH between 6 5 and 9 0)

Final Acute Value = 1,496 µg/L

Criterion Maximum Concentration = (1,496 µg/L) / 2 = 748 0 µg/L

Final Acute-Chronic Ratio = 2 (see text)

Final Chronic Value = (1,496 µg/L) / 2 = 748 0 µg/L

Final Chronic Value = 87 µg/L (lowered to protect brook trout and striped bass, see text)

Table 4 Toxicity of Aluminum to Aquatic Plants

Species	Chemical	pH	Hardness (mg/L as $CaCO_3$)	Duration (days)	Effect	Concentration (µg/L)[a]	Reference
FRESHWATER SPECIES							
Diatom, *Cyclotella meneghiniana*	Aluminum chloride	7.9	-	8	Inhibited growth algistatic algicidal	810 3,240 6,480	Rao and Subramanian 1982
Green alga, *Selenastrum capricornutum*	Sodium aluminate	7.0	15	14	Reduced cell counts and dry weight	990-1,320	Peterson et al. 1974
Green alga, *Selenastrum capricornutum*	Aluminum chloride	7.6	14.9	4	EC50 (biomass)	570	Call 1984
Green alga, *Selenastrum capricornutum*	Aluminum chloride	8.2	14.9	4	EC50 (biomass)	460	Call 1984
Eurasian watermilfoil, *Myriophyllum spicatum*	-	-	-	32	EC50 (root weight)	2,500	Stanley 1974
Duckweed, *Lemna minor*	Aluminum chloride	7.6	14.9	4	Reduced frond production	>45,700	Call 1984
Duckweed, *Lemna minor*	Aluminum chloride	8.2	14.9	4	Reduced frond production	>45,700	Call 1984

[a] Concentration of aluminum, not the chemical

Table 5. Bioaccumulation of Aluminum by Aquatic Organisms

Species	Chemical	Concentration in Water (µg/L)[a]	Hardness (mg/L as $CaCO_3$)	pH	Tissue	Duration	BCF or BAF[b]	Reference
Brook trout (eyed embryo), *Salvelinus fontinalis*	Aluminum sulfate	242	13	7.24	Whole body	Post-hatch		Cleveland et al. 1986
						15 days	147	
						30 days	50	
Brook trout (37 days), *Salvelinus fontinalis*	Aluminum sulfate	242	14	7.35	Whole body	15 days	231	Cleveland et al. 1986
						30 days	136	

[a] Measured concentration of aluminum.

[b] Bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) are based on measured concentrations of aluminum in water and in tissue.

Table 6. Other Data on Effects of Aluminum on Aquatic Organisms

Species	Chemical	Hardness (mg/L as $CaCO_3$)	pH	Duration	Effect	Concentration (µg/L)[a]	Reference
				FRESHWATER SPECIES			
Green alga, *Chlorella vulgaris*	Aluminum chloride	-	<7.0	3-4 mo	Inhibited growth	4,000	De Jong 1965
Green alga, *Chlorella vulgaris*	Aluminum sulfate	-	-	30 days	Reduced maximum growth	<163,000	Becker and Keller 1973
Green alga, *Scenedesmus quadricauda*	Aluminum chloride	-	7.5-7.8	96 hr	Incipient inhibition (river water)	1,500-2,000	Bringmann and Kuhn 1959a,b
Planktonic communities	Aluminum sulfate	-	6.1-6.9	1 hr	Decreased phosphate uptake and photosynthesis	50	Nalewajko and Paul 1985
Protozoan, *Microregma heterostoma*	Aluminum chloride	-	7.5-7.8	28 hr	Incipient inhibition (river water)	12,000	Bringmann and Kuhn 1959b
Protozoan, *Chilomonas paramecium*	Aluminum chloride	-	5.5-7.4	3 hr	Some survival	110	Ruthven and Cairns 1973
Protozoan, *Peranema trichoporum*	Aluminum chloride	-	5.5-6.5	3 hr	Some survival	62,600	Ruthven and Cairns 1973
Protozoan, *Tetrahymena pyriformis*	Aluminum chloride	-	5.5-6.5	3 hr	Some survival	110	Ruthven and Cairns 1973
Protozoan, *Euglena gracilis*	Aluminum chloride	-	6.0-7.0	3 hr	Some survival	111,800	Ruthven and Cairns 1973
Cladoceran (mature), *Daphnia catawba*	Aluminum chloride	8.07	6.5	72 hr	Reduced survival	1,020	Havas and Likens 1985b

Table 6. (continued)

Species	Chemical	Hardness (mg/L as $CaCO_3$)	pH	Duration	Effect	Concentration (µg/L)[a]	Reference
Cladoceran, *Daphnia magna*	Aluminum sulfate	-	-	16 hr	Incipient immobilization	21,450	Anderson 1944
Cladoceran, *Daphnia magna*	Ammonium aluminum sulfate	-	-	16 hr	Incipient immobilization	21,620	Anderson 1944
Cladoceran, *Daphnia magna*	Potassium aluminum sulfate	-	-	16 hr	Incipient immobilization	21,530	Anderson 1944
Cladoceran, *Daphnia magna*	Aluminum chloride	-	7.5	48 hr	Non-toxic (river water)	1,000,000	Bringmann and Kuhn 1959a
Cladoceran, *Daphnia magna*	Aluminum chloride	45.3	6.5-7.5	21 days	EC16 (reduced reproduction)	320	Biesinger and Christensen 1972
Cladoceran, *Daphnia magna*	Aluminum chloride	45.3	6.5-7.5	21 days	LC50	1,400	Biesinger and Christensen 1972
Cladoceran, *Daphnia magna*	Sodium aluminate	27.0	7.0	96 hr	Mortality	>40,000	Peterson et al. 1974
Cladoceran, *Daphnia magna*	Aluminum chloride	8.26	6.5	48 hr	Mortality	320	Havas 1985, Havas and Likens 1985a
Cladoceran, *Daphnia magna*	Aluminum chloride	-	6.5	48 hr	Loss of sodium	1,020	Havas and Likens 1985a
Cladoceran, *Daphnia magna*	Aluminum chloride	8.26	6.5	24 hr	BCF = 18,000 BCF = 9,600 BCF = 11,000	20 320 1,020	Havas 1985
Cladoceran, *Daphnia magna*	Aluminum chloride	33.35	6.5	24 hr	BCF = 18,000 BCF = 14,700	20 1,020	Havas 1985

Table 6. (continued)

Species	Chemical	Hardness (mg/L as $CaCO_3$)	pH	Duration	Effect	Concentration (µg/L)[a]	Reference
Cladoceran, *Daphnia magna*	Aluminum sulfate	220[b]	7.05	48 hr	EC50 (fed)	38,200	Kimball, Manuscript
Crayfish, *Orconectes virilis*	Aluminum chloride	11.0	7.0	2 hr	Calcium uptake unaffected	200	Malley and Chang 1985
Aquatic beetle (adult), *Tropisternus lateralis nimbatus*	Aluminum chloride	-	7.0	14 days	Changed the fat body	200	Wooldridge and Wooldridge 1969
Midge (larva), *Tanytarsus dissimilis*	Aluminum sulfate	17.43	6.63	55 days	37% dead	832	Lamb and Bailey 1981
Rainbow trout (fingerling), *Salmo gairdneri*	Aluminum chloride	46.8	8.02	32 days	50% dead	5,230	Freeman and Everhart 1971
		28.3	8.48	7.5 days	50% dead	5,140	
		28.3	8.99	3 days	50% dead	5,200	
		56.6	6.64	44 days	50% dead	513	
		56.6	6.80	39 days	50% dead	5,140	
Rainbow trout (embryo), *Salmo gairdneri*	Aluminum chloride	-	7.0-9.0	Fertilization to hatch	No reduced fertility	5,200	Everhart and Freeman 1973
Rainbow trout (embryo, larva), *Salmo gairdneri*	Aluminum chloride	104 (92-110)	7.4	28 days	EC50 (death and deformity)	560	Birge 1978, Birge et al 1978,1980,1981
Rainbow trout (juvenile), *Salmo gairdneri*	Aluminum sulfate	25	7.0	10 days	0% dead	200,000	Hunter et al. 1980
			8.0	96 hr	40% dead	50,000	
			8.5	42 hr	100% dead	50,000	
			9.0	42 hr	100% dead	50,000	
Rainbow trout (embryo, larva), *Salmo gairdneri*	Aluminum sulfate	14.3	6.5	8 days	No effect	1,000	Holtze 1983
			7.2		No effect	1,000	

Table 6. (continued)

Species	Chemical	Hardness (mg/L as $CaCO_3$)	pH	Duration	Effect	Concentration (µg/L)[a]	Reference
Rainbow trout (eyed embryo), *Salmo gairdneri*	Aluminum sulfate	14 3	6 5 7 2	8 days	14 2% dead 21 6% dead	1,000 1,000	Holtze 1983
Rainbow trout (juvenile), *Salmo gairdneri*	Aluminum sulfate	-	6 5	11 days	Increased ventilation rate	75	Neville 1985
Brook trout (eyed embryo), *Salvelinus fontinalis*	Aluminum sulfate	13	7 2	To 30 days post-hatch	Reduced some behaviors	242	Cleveland et al 1986
Brook trout (37 days), *Salvelinus fontinalis*	Aluminum sulfate	14	7 3	30 days	Reduced some behaviors	242	Cleveland et al 1986
Brook trout (eyed embryo), *Salvelinus fontinalis*	Aluminum sulfate	<1	7 8	To hatch	Did not decrease % hatch	283	Hunn et al 1987
Brook trout (larva), *Salvelinus fontinalis*	Aluminum sulfate	<1	7 8	60 days	Reduced growth and some behaviors	283	Hunn et al 1987
Brook trout (embryo, larva), *Salvelinus fontinalis*	Aluminum sulfate	12 3	6 5-6 6	60 days	48% dead 3% dead 24% reduction in weight 4% reduction in weight	350 169 169 88	Cleveland et al Manuscript
Goldfish (60-90 mm), *Carassius auratus*	Aluminum potassium sulfate	-	6 8	4 days	Reduced survival time	5,700	Ellis 1937
Goldfish (juvenile), *Carassius auratus*	Aluminum sulfate	64-80	6 6-7 4	7 days	0% dead	50,000	Sanborn 1945

Table 6. (continued)

Species	Chemical	Hardness (mg/L as $CaCO_3$)	pH	Duration	Effect	Concentration (µg/L)[a]	Reference
Goldfish (embryo, larva), *Carassius auratus*	Aluminum chloride	195	7.4	7 days	EC50 (death and deformity)	150	Birge 1978
Common carp (juvenile), *Cyprinus carpio*	Aluminum chloride	-	6.5 6.6	48 hr	30% dead 10% dead	4,000 4,000	Muramoto 1981
Fathead minnow (adult), *Pimephales promelas*	Aluminum chloride	-	-	-	50% reduction of acetylcholinesterase activity	18,000	Olson and Christensen 1980
Fathead minnow (juvenile), *Pimephales promelas*	Aluminum sulfate	220[b]	7.3	8 days	LC50 (fed)	22,400	Kimball, Manuscript
Largemouth bass (juvenile), *Micropterus salmoides*	Aluminum sulfate	64-80	6.6-7.4	7 days	0% dead	50,000	Sanborn 1945
Mummichog (adult), *Fundulus heteroclitus*	Aluminum sulfate	-	-	36 hr 120 hr	100% dead 100% dead	2,210[c] 1,100[c]	Thomas 1915
Mosquitofish (adult female), *Gambusia affinis*	Aluminum chloride	-	4.3-7.7	4 days	LC50 (high turbidity)	26,900 18,500	Wallen et al. 1957
Threespine stickleback (adult), *Gasterosteus aculeatus*	Aluminum nitrate	-	>7.0	10 days	No toxicity	70	Jones 1939
Striped bass (159 days), *Morone saxatilis*	Aluminum sulfate	-	6.5 7.2	7 days	0% dead 0% dead	390 390	Buckler et al., Manuscript
Striped bass (195 days), *Morone saxatilis*	Aluminum sulfate	-	6.5 7.2	7 days	0% dead 0% dead	390 390	Buckler et al. Manuscript

Table 6. (continued)

Species	Chemical	Hardness (mg/L as $CaCO_3$)	pH	Duration	Effect	Concentration (µg/L)[a]	Reference
Striped bass (160 days), *Morone saxatilis*	Aluminum sulfate	-	6 5	7 days	0% dead	87 2	Buckler et al , Manuscript
			6 5		58% dead	174 4	
			7 2		2% dead	174 4	
			7 2		100% dead	348 8	
Largemouth bass (embryo, larva), *Micropterus salmoides*	Aluminum chloride	93-105	7 2-7 8	8 days	EC50 (death and deformity)	170	Birge et al 1978
Narrow-mouthed toad (embryo, larva), *Gastrophryne carolinensis*	Aluminum chloride	195	7 4	7 days	EC50 (death) and deformity)	50	Birge 1978, Birge et al 1979
Marbled salamander (embryo, larva), *Ambystoma opacum*	Aluminum chloride	93-105	7 2-7 8	8 days	EC50 (death and deformity)	2,280	Birge et al 1978

[a] Concentration of aluminum, not the chemical

[b] From Smith et al (1976)

[c] If the aluminum sulfate is assumed to be anhydrous

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