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Geotechnical
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Updated Freshwater Aquatic Life Criteria for Aluminum

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List of Acronyms

ACR	acute-chronic ratio
Al	aluminum
AWQC	ambient water quality criteria
CCC	criterion continuous concentration (chronic criterion)
CMC	criterion maximum concentration (acute criterion)
EC_{50}	median effect concentration –point estimate for 50% effect
FACR	final ACR
FAV	final acute value
FCV	final chronic value
GMAVs	genus mean acute values
LC_{50}	median lethal concentration –point estimate for 50% lethality
LOEC	lowest observed effect concentration
SMAVs	species mean acute values
USEPA	U.S. Environmental Protection Agency

1.0 Introduction

The current ambient water quality criteria (AWQC) for aluminum (Al) were released in 1988 (USEPA 1988). Background information on Al chemistry in freshwater systems can also be found in USEPA (1988) and in Sposito (1996). Of particular importance in deriving AWQC for Al is the pH of the water used in toxicity tests. Between a pH of 6.5 and 9.0, Al occurs largely as poorly soluble polymeric hydroxides and as complexes with humic acids, phosphate, sulfate, and other anions (USEPA 1988; Sposito 1996). Waters with a pH <6.5 are below the acceptable pH range identified by the USEPA, and such waters favor the dissolution of Al into more bioavailable monomeric and ionic forms. Consistent with the USEPA's existing criteria for Al, the updated Al criteria recommended here only consider toxicity studies conducted within the pH range of 6.5 to 9.0, and thus should only apply to surface waters with pH levels within this range.

This report reviews the scientific literature conducted since publication of the 1988 AWQC for Al, and uses these data to recommend updated criteria for protection of aquatic life derived according to USEPA guidance (USEPA 1985). Section 2 of this report summarizes the basis of the existing Al criteria and then Section 3 summarizes additional Al toxicity studies published after release of the 1988 AWQC document. Sections 4-6 then use these data to recommend updates to freshwater aquatic life criteria for Al in a format that is consistent with USEPA guidance.

2.0 Summary of Existing Criteria

The USEPA's current acute and chronic criteria for protection of aquatic life are 750 and 87 µg/L, respectively. Development of these criteria followed the *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (USEPA 1985). Specifically, the USEPA identified acute LC_{50} values for 15 aquatic species, which resulted in the calculation of 15 species mean acute values (SMAVs)[1]. These 15 SMAVs represented 14 genera, which resulted in the calculation of 14 genus mean acute values (GMAVs)[2]. The 5th percentile of these GMAVs, or final acute value (FAV), was calculated to be 1,496 µg/L. Division of the FAV by two resulted in an acute criterion (termed the criterion maximum concentration, or CMC) of 750 µg/L. Because limited chronic Al toxicity data were available, the final chronic value (FCV) was calculated using an acute-chronic ratio (ACR). The USEPA identified ACRs of 0.9958, 10.64, and 51.47. Because the two highest ACRs were based on acutely insensitive species, these were not considered in development of the final ACR (FACR). However, because the remaining ACR of 0.9958 was less than 2, the USEPA (1985) guidelines required that the FACR be set to 2, otherwise the chronic criterion would be higher than the acute criterion. This results in a FCV of 750 µg/L (equivalent to the CMC). Finally, the USEPA (1988) considered "other data" that were considered scientifically sound, but were from studies that did not strictly meet the guidelines for calculation of the FCV. From the "other data" cited in USEPA (1988), adverse effects were reported for two "important" species at Al concentrations below the FCV of 750 µg/L: (1) a 24 percent reduction in weight of young brook trout (*Salvelinus fontinalis*) was observed at an Al concentration of 169 µg/L (Cleveland et al. Manuscript) and (2) 58 percent striped bass (*Morone saxatilis*) mortality occurred at an Al concentration of 174.4 µg/L (Buckler et al. Manuscript). Aluminum concentrations of 88 and 87.2 µg/L from these same two studies resulted in negligible toxicity. Accordingly, the USEPA set the chronic criterion, or criterion continuous concentration (CCC), at 87 µg/L.

Since the release of the current AWQC for Al in 1988, several acute and chronic Al toxicity studies have been published in the scientific literature. Many of these toxicity studies meet the USEPA (1985) guidelines for AWQC development and also result in additional data for deriving an Al ACR. As discussed below, there is also evidence that the toxicity of Al to aquatic life is hardness-dependent (i.e., Al toxicity is greater in softer waters and decreases as water hardness increases).

[1] The species mean acute value, or SMAV, is the geometric mean of acute LC_{50} values for a single species.
[2] The genus mean acute value, or GMAV, is the geometric mean of SMAVs for a single genus.

3.0 Summary of New Toxicity Studies

The USEPA (1985) guidelines for AWQC development specify minimum study requirements for consideration in the development of acute and chronic criteria for protection of aquatic life. For example, acute toxicity studies must have an exposure duration of 96 hours (although 48 hours is acceptable for more short-lived species, such as cladocerans and midges), organisms must not be fed during the study, and the endpoint must be mortality, immobilization or a combination of the two. Chronic toxicity studies must be conducted using exposure durations that encompass the full life cycle or, for fish, early life stage and partial life cycle studies are acceptable. In addition, toxicant concentrations in the exposure solutions must be analytically verified in chronic studies. Finally, under the USEPA (1985) guidelines, toxicity studies that do not meet the specific study requirements may still be retained as "other data" if the study was otherwise scientifically valid. Such "other data" are not used in the calculation of the CMC and FCV, but may be used to justify lowering the acute or chronic criteria for a toxicant if the species and endpoint tested are considered to be "biologically or recreationally important," and if the CMC or FCV were determined to be inadequately protective of these species or endpoints. For Al, "other data" were used to lower the FCV in development of the chronic criterion, as discussed in Section 2.

The following summarizes the Al toxicity data published since 1988 that are considered acceptable for updating the Al criteria. Our primary source for these new data was a study conducted on behalf of the *Arid West Water Quality Research Project* (AWWQRP 2006), in which a thorough literature review was conducted, and recommendations made for updating aquatic life criteria. While the studies used in the present report are, for the most part, the same as those used in AWWQRP (2006), we recommend different final criteria equations to maximize consistency with USEPA guidance for derivation of aquatic life criteria (USEPA 1985).

3.1 Acute Toxicity

As summarized in Section 2, the acute Al toxicity database used to derive the current acute Al criterion was based on 14 GMAVs, which in turn was based on 15 SMAVs. The updated acute Al toxicity database includes seven additional species with tests considered to be of an acceptable type and duration according to USEPA (1985):

- *Asellus aquaticus*, isopod (Martin and Holdich 1986)
- *Crangonyx pseudogracilis*, amphipod (Martin and Holdich 1986)
- *Cyclops viridis*, copepod (Storey et al. 1992)
- *Gammarus pulex*, amphipod (Storey et al. 1992)
- *Tubifex tubifex*, worm (Khangarot 1991)
- *Hybognathus amarus*, Rio Grande silvery minnow (Buhl 2002)
- *Salmo salar*, Atlantic salmon (Hamilton and Haines 1995)

This results in acute Al toxicity data for a total of 22 species representing 19 genera. In addition, new acute toxicity studies were identified for several species already included in the 1988 AWQC, including the cladoceran *Ceriodaphnia dubia* (ENSR 1992a; Soucek et al. 2001), rainbow trout (*Oncorhynchus mykiss*) (Thomsen et al. 1988; Gundersen et al. 1994), and fathead minnow (*Pimephales promelas*) (Buhl 2002; ENSR 1992b). All acceptable acute LC_{50} and EC_{50} values for Al are summarized in Table 1a.

3.2 Chronic Toxicity

The 1988 AWQC for Al included chronic toxicity data for three species: (1) the cladoceran *C. dubia*; (2) the cladoceran *Daphnia magna*; and (3) the fathead minnow *P. promelas*. As part of this update, a chronic EC16 for reproductive effects in *D. magna* (Biesinger and Christensen 1972) was added to the chronic toxicity data set. The chronic toxicity value from Biesinger and Christensen (1972) was likely excluded in USEPA (1988) because Al test concentrations were not analytically verified. However, this study is included here because the chronic value is consistent with the corresponding measured value from the Kimball manuscript, thus reducing some of the uncertainty associated with the Al concentrations not being analytically verified. This study also provides additional useful information for deriving an ACR, as discussed further below. No additional chronic toxicity studies were identified that meet the USEPA's guidelines (i.e., life cycle study or an early life stage or partial life cycle study for fish). All acceptable chronic toxicity studies are summarized in Table 2a.

A total of four ACRs were derived: 0.9958 and 0.9236 for *C. dubia*, 12.19 and 51.47 for *D. magna*, and 10.64 for fathead minnows (Table 2b). It is uncertain why the *D. magna* ACR of 51.47 is considerably higher than the other ACRs, including the other *D. magna* ACR of 12.19. However, the combination of the high hardness (220 mg/L) and pH (8.30) would likely have mitigated the toxicity of Al compared to waters with a hardness of 45.3 mg/L and pH of 6.5-7.5 used in tests to derive the *D. magna* ACR of 12.19 from Biesinger and Christensen (1972). Therefore, it is more appropriate to select an ACR from tests conducted under conditions that likely maximize Al toxicity. The *D. magna* acute values from the two studies differed by a factor of 10, but the chronic values differed by just a factor of two (Table 2b). Because the *D. magna* ACR of 51.47 is driven by an insensitive acute value under high hardness and high pH conditions, this value was excluded from the final ACR. Calculating the geometric mean of the remaining ACRs results in a final ACR of 4.9923.

In USEPA (1988), it was noted that a Final Plant Value, as defined in USEPA (1985), was not obtained because there were no plant toxicity studies conducted with an important aquatic plant species in which Al was measured and in which the endpoint measured was biologically important. No new published algal or aquatic plant studies have been obtained, so this conclusion has not changed for the present update.

Table 1a: Acute toxicity of aluminum to aquatic animals.

Species Latin Name	Species Common Name	Method	Chemical	pH	Hardness (mg/L as $CaCO_3$)	LC_{50} or EC_{50} (µg Al/L)	LC_{50} or EC_{50} Adjusted to Hardness of 50 mg/L (µg Al/L)	Species Mean Acute Value at Hardness of 50 mg/L (µg Al/L)	Reference
Acroneuria sp.	Stonefly	S,M	$AlCl_3$	7.46	47.4	>22,600	**>24,315**	>24,315	Call 1984
Asellus aquaticus	Isopod	S,U	$Al_2(SO_4)_3$	6.75	50	4,370	**4,370**	4,370	Martin and Holdich 1986
Ceriodaphnia dubia	Cladoceran	S,M	$AlCl_3$	7.42	50	1,900	**1,900**	>2,164	McCauley et al. 1986
Ceriodaphnia dubia	Cladoceran	S,M	$AlCl_3$	7.86	50	1,500	**1,500**	-	McCauley et al. 1986
Ceriodaphnia dubia	Cladoceran	S,M	$AlCl_3$	8.13	50	2,560	**2,560**	-	McCauley et al. 1986
Ceriodaphnia dubia	Cladoceran	S,M	$AlCl_3$	7.5	26	720	**1,763**	-	ENSR 1992a
Ceriodaphnia dubia	Cladoceran	S,M	$AlCl_3$	7.6	46	1,880	**2,107**	-	ENSR 1992a
Ceriodaphnia dubia	Cladoceran	S,M	$AlCl_3$	7.8	96	2,450	**1,003**	-	ENSR 1992a
Ceriodaphnia dubia	Cladoceran	S,M	$AlCl_3$	8.1	194	>99,600	**>15,554**	-	ENSR 1992a
Ceriodaphnia dubia	Cladoceran	S,M	-	7.6	98.5	2,880	**1,138**	-	Soucek et al. 2001
Ceriodaphnia sp.	Cladoceran	S,M	$AlCl_3$	7.36	47.4	2,300	**2,475**	3,134	Call 1984
Ceriodaphnia sp.	Cladoceran	S,M	$AlCl_3$	7.68	47.4	3,690	**3,970**	-	Call 1984
Crangonyx pseudogracilis	Amphipod	S,U	$Al_2(SO_4)_3$	6.75	50	9,190	**9,190**	9,190	Martin and Holdich 1986
Cyclops viridis	Copepod	S,U	Al_2O_3	6.9	-	>27,000	**-**	-	Storey et al. 1992
Daphnia magna	Cladoceran	S,M	$Al_2(SO_4)_3$	7.05	220	38,200	**5,022**	4,735	Kimball manuscript
Daphnia magna	Cladoceran	S,M	$AlCl_3$	7.61	45.4	>25,300	>28,875	-	Brooke et al. 1985
Daphnia magna	Cladoceran	S,U	$AlCl_3$	7	45.3	3,900	**4,465**	-	Biesinger and Christensen 1972
Dugesia tigrina	Flatworm	S,M	$AlCl_3$	7.48	47.4	>16,600	**>17,859**	>17,859	Brooke et al. 1985
Gammarus pulex	Amphipod	S,M	Al_2O_3	6.9	-	>2,700	**-**	-	Storey et al. 1992
Gammarus pseudolimnaeus	Amphipod	S,M	$AlCl_3$	7.53	47.4	22,000	**23,669**	23,669	Call 1984
Physa sp.	Snail	S,M	$AlCl_3$	7.46	47.4	55,500	59,711	32,922	Call 1984
Physa sp.	Snail	S,M	$AlCl_3$	6.59	47.4	>23,400	>25,175	-	Call 1984
Physa sp.	Snail	S,M	$AlCl_3$	7.55	47.4	30,600	**32,922**	-	Call 1984
Physa sp.	Snail	S,M	$AlCl_3$	8.17	47.4	>24,700	>26,574	-	Call 1984
Tanytarsus dissimilis	Midge	S,U	$Al_2(SO_4)_3$	6.85-7.71	17.43	>79,900	**>338,321**	>338,321	Lamb and Bailey 1981
Tubifex tubifex	Worm	R,U	$Al(NH_4SO_4)_2$	7.6	245	50,230	**5,698**	5,698	Khangarot 1991
Hybognathus amarus	Rio Grande silvery minnow	S,M	$AlCl_3$	8.1	140	>59,100	**>14,428**	>14,428	Buhl 2002

Species Latin Name	Species Common Name	Method	Chemical	pH	Hardness (mg/L as $CaCO_3$)	LC_{50} or EC_{50} (µg Al/L)	LC_{50} or EC_{50} Adjusted to Hardness of 50 mg/L (µg Al/L)	Species Mean Acute Value at Hardness of 50 mg/L (µg Al/L)	Reference
Ictalurus punctatus	Channel catfish	S,M	$AlCl_3$	7.54	47.4	>47,900	**<u>>51,534</u>**	>51,534	Call 1984
Lepomis cyanellus	Green sunfish	S,M	$AlCl_3$	7.55	47.4	>50,000	**<u>>53,794</u>**	>53,794	Call 1984
Oncorhynchus mykiss	Rainbow trout	S,M	$AlCl_3$	6.59	47.4	7,400	**<u>7,961</u>**	>7,547	Call 1984
Oncorhynchus mykiss	Rainbow trout	S,M	$AlCl_3$	7.31	47.4	14,600	**<u>15,708</u>**	-	Call 1984
Oncorhynchus mykiss	Rainbow trout	S,M	$AlCl_3$	7.46	47.4	8,600	9,253	-	Call 1984
Oncorhynchus mykiss	Rainbow trout	S,M	$AlCl_3$	8.17	47.4	>24,700	>26,574	-	Call 1984
Oncorhynchus mykiss	Rainbow trout	F,M	$AlCl_3$	8.25	23.2	6,170	**<u>17,660</u>**	-	Gundersen et al. 1994
Oncorhynchus mykiss	Rainbow trout	F,M	$AlCl_3$	8.25	35	6,170	**<u>10,056</u>**	-	Gundersen et al. 1994
Oncorhynchus mykiss	Rainbow trout	F,M	$AlCl_3$	8.29	83.6	7,670	**<u>3,794</u>**	-	Gundersen et al. 1994
Oncorhynchus mykiss	Rainbow trout	F,M	$AlCl_3$	8.29	115.8	6,930	**<u>2,194</u>**	-	Gundersen et al. 1994
Oncorhynchus tshawytscha	Chinook salmon	S,M	$NaAlO_2$	7	28	>40,000	**<u>>88,495</u>**	>88,495	Peterson et al. 1974
Perca flavescens	Yellow perch	S,M	$AlCl_3$	7.55	47.4	>49,800	**<u>>53,578</u>**	>53,578	Call 1984
Pimephales promelas	Fathead minnow	S,M	$AlCl_3$	8.1	140	>59,100	>14,428	>5,869	Buhl 2002
Pimephales promelas	Fathead minnow	S,M	$Al_2(SO_4)_3$	7.34	220	35,000	**<u>4,601</u>**	-	Kimball manuscript
Pimephales promelas	Fathead minnow	S,M	$AlCl_3$	7.61	47.4	>48,200	>51,857	-	Call 1984
Pimephales promelas	Fathead minnow	S,M	$AlCl_3$	8.05	47.4	>49,800	>53,578	-	Call 1984
Pimephales promelas	Fathead minnow	S,U	$Al_2(SO_4)_3$	7.6	-	>18,900	**<u>-</u>**	-	Boyd 1979
Pimephales promelas	Fathead minnow	S,M	$AlCl_3$	7.8	26	1,160	**<u>2,840</u>**	-	ENSR 1992b
Pimephales promelas	Fathead minnow	S,M	$AlCl_3$	7.6	46	8,180	**<u>9,170</u>**	-	ENSR 1992b
Pimephales promelas	Fathead minnow	S,M	$AlCl_3$	8.1	96	20,300	**<u>8,308</u>**	-	ENSR 1992b
Pimephales promelas	Fathead minnow	S,M	$AlCl_3$	8.1	194	44,800	**<u>6,996</u>**	-	ENSR 1992b
Salmo salar	Atlantic salmon	S,M	$AlCl_3$	6.5	6.8	599	**<u>9,2051</u>**	9,205	Hamilton and Haines 1995
Salvelinus fontinalis	Brook trout	F,M	$Al_2(SO_4)_3$	6.5	-	3,600	**<u>-</u>**	-	Decker and Menendez 1974

* Bold, underlined values were used to calculate species mean acute values.

S = static, R = renewal, F = flow-through, U = unmeasured, M = measured

Table 1b: Results of covariance analysis of freshwater acute toxicity versus hardness.

Species	N	Slope	R^2 Value
Ceriodaphnia dubia	7	0.8699	0.73
Daphnia magna	2	1.4439	-
Fathead minnow	5	1.5298	0.90
All of the above	14	1.3695	0.87

Table 1c: List of studies used to estimate acute aluminum hardness slope.

Species	Hardness (mg/L)	LC_{50} or EC_{50} (µg Al/L)	Reference
Ceriodaphnia dubia	26	720	ENSR 1992a
	46	1,880	ENSR 1992a
	50	1,500	McCauley et al. 1986
	50	1,900	McCauley et al. 1986
	50	2,560	McCauley et al. 1986
	96	2,450	ENSR 1992a
	98.5	2,880	Soucek et al. 2001
	194	>99,600	ENSR 1992a
Daphnia magna	45.3	3,900	Biesinger and Christensen 1972
	220	38,200	Kimball Manuscript
Fathead minnow	26	1,160	ENSR 1992b
	46	8,180	ENSR 1992b
	96	20,300	ENSR 1992b
	194	44,800	ENSR 1992b
	220	35,000	Kimball Manuscript

Table 2a: Chronic toxicity of aluminum to aquatic animals.

Species Latin Name	Species Common Name	Test	Chemical	pH	Hardness (mg/L as $CaCO_3$)	Limits (µg Al/L)	Chronic Value (µg Al/L)	Reference
Ceriodaphnia dubia	Cladoceran	LC	$AlCl_3$	7.15	50	1,400-2,600	1,908	McCauley et al. 1986
Ceriodaphnia dubia	Cladoceran	LC	$AlCl_3$	7.75	50	1,100-2,400	1,624	McCauley et al. 1986
Ceriodaphnia dubia	Cladoceran	LC	$AlCl_3$	7.55	47.4	4,900-12,100	7,700	Call 1984
Daphnia magna	Cladoceran	LC	$Al_2(SO_4)_3$	8.30	220	540-1,020	742.2	Kimball manuscript
Daphnia magna	Cladoceran	LC	$AlCl_3$	6.5-7.5	45.3	-	320[a]	Biesinger and Christensen 1972
Pimephales promelas	Fathead minnow	ELS	$Al_2(SO_4)_3$	7.24-8.15	220	2,300-4,700	3,288	Kimball manuscript

[a] This value is an EC_{16} for reproductive effects. It was included in Table 6 ("Other Data") of USEPA (1988), presumably because Al concentrations were not measured. However, it was included in Table 2 of this updated criteria evaluation because it provides information on the chronic sensitivity of *D. magna* in water of a moderate hardness (45.3 mg/L) and the result seems reasonable in comparison to the chronic value of 742.2 µg/L at a hardness of 220 mg/L (Kimball manuscript).

Table 2b: Aluminum acute-chronic ratios.

Species Latin Name	Species Common Name	pH	Hardness (mg/L as CaCO3)	Acute Value (µg Al/L)	Chronic Value (µg Al/L)	Acute-Chronic Ratio	Species Mean Acute-Chronic Ratio
Ceriodaphnia dubia	Cladoceran	7.15	50	1,900	1,908	0.9958	0.9590
Ceriodaphnia dubia	Cladoceran	7.75	50	1,500	1,624	0.9236	-
Daphnia magna	Cladoceran	8.30	220	38,200	742.2	51.47	-
Daphnia magna	Cladoceran	6.5-7.5	45.3	3,900	320	12.19	12.19[a]
Pimephales promelas	Fathead minnow	7.24-8.15	220	35,000	3,288	10.64	10.64
						Final ACR:	**4.9923**

[a] The acute-chronic ratio of 51.47 for *D. magna* was excluded from the species mean acute-chronic ratio because it was approximately 50 times higher than that observed for *C. dubia* and the acute-chronic ratio of 12.19 is more consistent with that observed for *P. promelas*.

3.3 Other Data

Within the pH range 6.5 – 9.0, only two other studies have been published after the 1988 Al AWQC were released, but that were not already considered to be acceptable for use in deriving the updated FAV or FCV: (1) a rainbow trout study by Thomsen et al. (1988) and (2) an Atlantic salmon study by Hamilton and Haines (1995). These are discussed below.

Thomsen et al. (1988) exposed rainbow trout (*O. mykiss*) eggs to aqueous Al concentrations in water with calcium concentrations of either 1 or 150 mg/L and a pH level of 7. The Al exposure continued through 25 days post-hatch. The LC_{50} values (measured at day 25 post-hatch) were 3,800 and 71,000 µg Al/L in waters containing calcium concentrations of 1 and 150 mg/L, respectively. The increased mortality observed in the low calcium treatment may be explained more by the low calcium treatment than by increased toxicity of Al due to higher bioavailability. As Thomsen et al. (1988) noted, the greatest reduction in survival was observed in relation to the calcium ion concentrations in the test water (survival was reduced by 24 percent in the low calcium water compared to the high calcium water without the addition of Al). Hatching time was also increased from 1.2 days in high calcium water to 4.5 days in low calcium water. Overall, this study does not meet the requirements to be included as an acceptable acute test because the exposure duration ranged from approximately 26-30 days, or as an acceptable chronic test because the study was not sufficient long to meet the early life stage requirements for rainbow trout tests (60 days post-hatch). Further, much of the mortality observed in the low calcium treatment appears to be a result of the low calcium concentration itself.

Hamilton and Haines (1995) exposed Atlantic salmon (*S. salar*) alevins to aqueous Al concentrations of 0 or 200 µg/L for 30 days. The test water pH was 6.5 and the hardness was 6.8 mg/L. This study does not meet the USEPA's (1985) specific requirements for a chronic study because it does not meet the definitions of an early life stage or partial life cycle study, but it does provide useful data that the USEPA would typically categorize as "other data." The mean weight of alevins exposed to 200 µg Al/L was significantly reduced ($p<0.05$) relative to the control, which results in a lowest observed effect concentration (LOEC) of <200 µg/L.

3.4 Unused Data

In AWQC documents, studies are identified that were not used or considered for AWQC development because the study was scientifically flawed or limited, or otherwise inappropriate for derivation of AWQC. For example, studies are not used if control organisms did not respond adequately (e.g., unacceptably high mortality) or if the test water contained elevated levels of other contaminants. In addition, studies are not used if the test species is not resident to North America. All of the unused studies published since the current Al criteria were derived are not summarized here, except for a brook trout

(*S. fontinalis*) study that is briefly summarized below given the importance of brook trout to the derivation of the 1988 chronic Al criterion.

Cleveland et al. (1991) exposed brook trout to an aqueous Al concentration of 303.9 µg/L for 56 days at a pH of 7.2 (fish were also exposed to Al at pH levels of 5.0 and 6.0, but these tests are not discussed here because the pH levels were <6.5). This study did not include a control, although only 1 percent mortality was observed following 56 days. It is unknown whether growth was affected, which is important since Cleveland et al. (1989) observed that growth is a more sensitive endpoint than survival for brook trout exposed to Al. Given the lack of a growth endpoint and due to the absence of a control treatment, this study was not sufficiently robust to identify either an acceptable chronic value for Al (for inclusion in Table 2a) or as information to be evaluated as "other data."

4.0 Hardness-Toxicity Relationship

Under the USEPA (1985) guidelines for AWQC development, methods are provided for adjusting criteria if it can be demonstrated that toxicity varies as a function of a given water quality parameter. The most common example is the relationship between water hardness and toxicity for several divalent metals. For example, the current acute and chronic criteria for cadmium, lead, nickel, and zinc are all hardness-dependent (i.e., the criteria concentrations increase with increasing water hardness; USEPA 2006). For Al, the existing data also suggest that criteria concentrations should increase with increasing water hardness, or with other water quality parameters that covary with hardness. Therefore, expressing updated Al criteria on the basis of a hardness equation—rather than as a single fixed value—is now warranted.

The general approach for deriving hardness-dependent criteria entails use of an analysis of covariance to derive a log-linear slope that relates standard toxicity values (e.g., LC_{50}s) to water hardness (USEPA 1985). To evaluate whether there is a significant statistical relationship between hardness and toxicity, there must be definitive acute values (i.e., undefined "less than" or "greater than" toxicity values are not used) from Al toxicity studies that expose organisms over a range of water hardness values such that the highest hardness is at least three times higher than the lowest, and the highest hardness is also at least 100 mg/L higher than the lowest. There were three species that met this minimum requirement: (1) *C. dubia*; (2) *D. magna*; and (3) fathead minnow.

For *C. dubia*, acute LC_{50}s were available at hardness levels of 26, 46, 50, 96, 98.5, and 194 mg/L (as $CaCO_3$). The LC_{50} at a hardness of 194 mg/L was >99,600 µg/L, which should not be used to derive the hardness-toxicity relationship because it is not a definitive value. However, if this test is not included in the hardness-toxicity evaluation, the range in hardness for the remaining *C. dubia* toxicity studies is 26 to 98.5 mg/L, which does not meet the requirement that the range between the lowest and highest hardness must be >100 mg/L. Nevertheless, because the *C. dubia* data clearly demonstrate a relationship between hardness and toxicity over an acceptable range of hardness values, the *C. dubia* data were included in the pooled slope, but the LC_{50} of >99,600 µg/L was excluded because it was not a definitive value.

The slope relating aluminum toxicity to water hardness was significantly different from zero ($p<0.05$) for all three species. In addition, the slopes were similar for all three with overlapping 95 percent confidence intervals. Accordingly, a final pooled slope of 1.3695 was derived based on the data for these three species. The individual slopes for each species and the pooled slope for combined species, as well as the data used to derive the pooled slopes, are provided in Tables 1b and 1c. The raw data used to define the relationship between hardness and toxicity, as well as the pooled slope, are plotted in Figure 1.

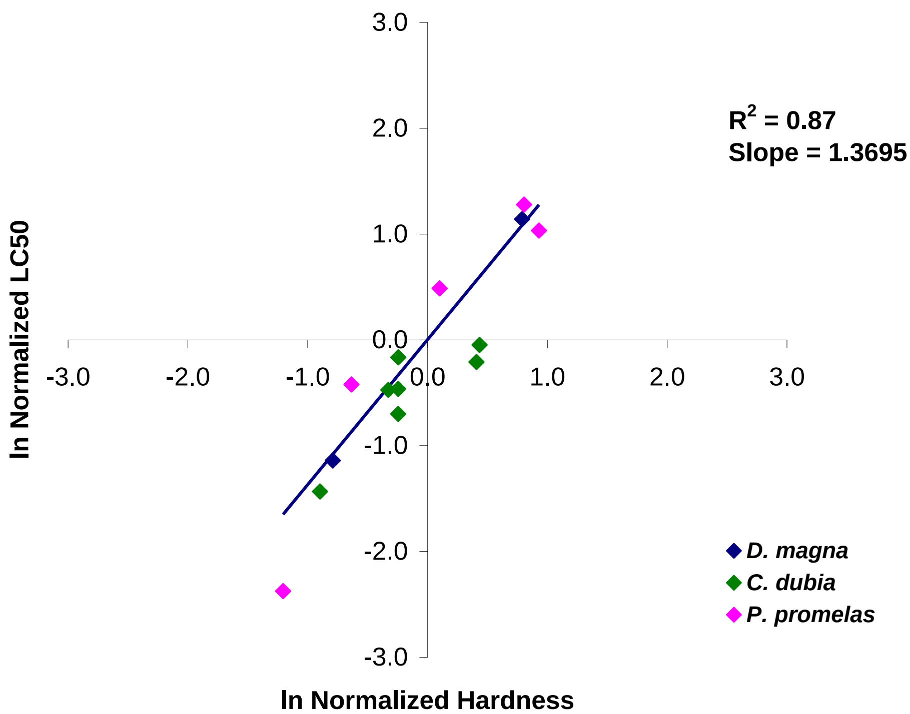

Figure 1: Relationship between hardness and acute aluminum toxicity.

5.0 Revised Aluminum Criteria

5.1 Acute Criterion

The pooled slope of 1.3695 was used to adjust the acute values in Table 1a to a hardness of 50 mg/L, except for cases where this was not possible because water hardness was not reported. Species mean acute values were calculated as the geometric mean of acceptable hardness-adjusted acute values for each species. To delineate cases in which not all toxicity values were appropriate for inclusion into a particular SMAV, the bold, underlined LC_{50} and EC_{50} values in Table 1a were ultimately used to derive the SMAVs. The SMAVs, adjusted to a hardness of 50 mg/L, ranged from >2,164 µg/L for the cladoceran *Ceriodaphnia dubia* to >338,321 µg/L for the midge *Tanytarsus dissimilis*. Genus mean acute values were calculated as the geometric mean of SMAVs and ranked from high to low (Table 3). The total number of GMAVs was 17 and the four lowest GMAVs were used to calculate the FAV following the USEPA (1985) guidelines. The FAV, at a hardness of 50 mg/L, was calculated to be 2,648 µg/L (Table 3). The FAV was then divided by two, resulting in a CMC, or acute criterion, of 1,324 µg/L at a hardness of 50 mg/L. The resulting equation for deriving the CMC over a range of hardness levels is:

$$\mathrm{CMC} = e^{(1.3695[\ln(\mathrm{hardness})]+1.8308)} \qquad \textbf{Eq. 1}$$

The hardness relationship was derived based on empirical data within a hardness range of 26 to 220 mg/L, so application of this equation to hardness levels outside of this range should be treated with caution.

5.2 Chronic Criterion

Chronic Al toxicity values did not meet the minimum data requirements for calculating the FCV as the 5th percentile of empirically derived chronic values. Accordingly, it was necessary to apply an ACR to the FAV (consistent with the calculation of the FCV for Al in USEPA [1988]). At a hardness of 50 mg/L, division of the FAV of 2,648 µg/L (see Section 5.1) by the final ACR of 4.9923 (see Section 3.2) results in a FCV of 530 µg/L (Table 3). The resulting equation for deriving the FCV over a range of hardness levels is:

$$\mathrm{FCV} = e^{(1.3695[\ln(\mathrm{hardness})]+0.9161)} \qquad \textbf{Eq. 2}$$

Similar to the acute hardness equation, because the hardness relationship was derived based on empirical data within a hardness range of 26 to 220 mg/L, application of this equation to hardness levels outside of this range should be treated with caution.

Table 3: Ranked genus mean acute values with species mean acute-chronic ratios

Rank	Genus Mean Acute Value (µg Al/L)	Species	Species Mean Acute Value (µg Al/L)	Species Mean Acute-Chronic Ratio
17	>338,321	*Tanytarsus dissimilis* (midge)	>338,321	-
16	>53,794	*Lepomis cyanellus* (green sunfish)	>53,794	-
15	>53,578	*Perca flavescens* (yellow perch)	>53,578	-
14	>51,534	*Ictalurus punctatus* (channel catfish)	>51,534	-
13	32,922	*Physa* sp. (snail)	32,922	-
12	>24,315	*Acroneuria* sp. (stonefly)	>24,315	-
11	23,669	*Gammarus pseudolimnaeus* (amphipod)	23,669	-
10	>18,189	*Dugesia tigrina* (flatworm)	>18,189	-
9	>14,428	*Hybognathus amarus* (Rio Grande silvery minnow)	>14,428	-
8	9,205	*Salmo salar* (Atlantic salmon)	9,205	-
7	9,190	*Crangonyx pseudogracilis* (amphipod)	9,190	-
6	>7,547	*Oncorhynchus mykiss* (rainbow trout)	>7,547	-
		Oncorhynchus tshawytscha (chinook salmon)	>88,495*	-
5	>5,869	*Pimephales promelas* (fathead minnow)	>5,869	10.64
4	5,698	*Tubifex tubifex* (worm)	5,698	-
3	4,735	*Daphnia magna* (cladoceran)	4,735	12.19
2	4,370	*Asellus aquaticus* (isopod)	4,370	-
1	>2,604	*Ceriodaphnia dubia* (cladoceran)	>2,164	0.9590
		Ceriodaphnia sp. (cladoceran)	3,134	-

* SMAV for chinook salmon excluded from the GMAV for *Oncorhynchus*. See text for details.

Acute Criterion:

Final Acute Value = 2,648 µg/L (calculated at a hardness of 50 mg/L from Genus Mean Acute Values)

Criterion Maximum Concentration = (2,648 µg/L) / 2 = 1,324 µg/L (at a hardness of 50 mg/L)

Pooled Slope = 1.3695 (see Table 1b)

ln (Criterion Maximum Intercept) = ln (CMC) – [slope x ln(50)] = ln (1,324) – [1.3695 x ln(50)] = 1.8308

Criterion Maximum Concentration = e(1.3695[ln(hardness)] + 1.8308)

Final Acute-Chronic Ratio = 4.9923

Chronic Criterion:

Final Chronic Value = (2,648 µg/L) / 4.9923 = 530 µg/L (at a hardness of 50 mg/L)

Pooled Slope = 1.3695 (see Table 1b)

ln (Final Chronic Intercept) = ln (FCV) – [slope x ln(50)] = ln (530) – [1.3695 x ln(50)] = 0.9161

Final Chronic Value = e(1.3695[ln(hardness)] + 0.9161)

5.3 Protectiveness of the Chronic Criterion to Brook Trout and Striped Bass

As discussed in Section 2, USEPA (1988) derived a FCV of 750 µg/L based on a FAV of 1,496 µg/L and an ACR of 2 (i.e., 1,496 µg/L / 2 = 750 µg/L). However, two chronic studies that did not meet strict acceptability criteria (USEPA 1985) for calculation of the FCV were ultimately considered to be important enough to warrant lowering of the FCV to ensure protection of the two species tested. Based on the Cleveland et al. and Buckler et al. manuscripts cited in the 1988 AWQC, the USEPA lowered the chronic criterion to 87 µg/L in order to ensure protection of brook trout (*Salvelinus fontinalis*) and striped bass (*Morone saxatilis*). The following briefly summarizes these studies, and evaluates the level of protection that the updated criteria equations 1 and 2 would provide for these species.

5.3.1 Brook Trout

USEPA (1988), citing an unpublished Cleveland et al. manuscript (and now published as Cleveland et al. 1989), reported that Al concentrations of 169 and 350 µg/L resulted in 3 percent and 48 percent larval brook trout mortality, respectively, after a 60 day exposure, and Al concentrations of 88 and 169 µg/L resulted in a 4 percent and 24 percent reduction in weight, respectively. Following the USEPA (1985) guidelines, the chronic value from this study would typically be defined as the geometric mean of the NOEC and LOEC for the most sensitive endpoint (growth), which is 88 and 169 µg/L, respectively. The chronic value for this test would, therefore, be 122 µg/L. It should be noted that this test was conducted in very soft water with a hardness of 12.3 mg/L. Based on the hardness-toxicity slope of 1.3695, this converts to an estimated chronic value of 833 µg/L at a hardness of 50 mg/L. Given that the FCV at a hardness of 50 mg/L is 530 µg/L, this suggests that brook trout would be adequately protected by the revised criterion[3].

In addition, the GMAV of 3,600 µg Al/L for brook trout reported in Table 1a is well above the FAV of 2,648 µg Al/L (Table 3), even though water hardness was not reported in this study (Decker and Menendez 1974) and so could not be included in the FAV derivation. Finally, an additional chronic brook trout study cited in Table 6 of the 1988 AWQC (Hunn et al. 1987) reports a chronic growth reduction at 283 µg Al/L, but in extremely soft waters (0.57 mg/L hardness). It would likely not be meaningful to apply a hardness slope to such a low water hardness, but given that the chronic value from Cleveland et al. (1989) conducted in harder water was lower than that of Hunn et al. (1987), a revised chronic criterion using Equation 2 would still be considered protective. Therefore, the available toxicity data suggest that the revised chronic criteria reported here would also be protective of both chronic and acute Al toxicity to brook trout, and so the calculated FCV does not need to be lowered to protect this species.

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[3] Given that the very low hardness of 12.3 mg/L is below the range of hardness levels used to develop the pooled hardness slope, there is some uncertainty associated with this evaluation.

5.3.2 Striped Bass

USEPA (1988), citing the unpublished Buckler et al. manuscript (and now published as Buckler et al. 1987), reports that Al concentrations of 87.2 and 174.4 µg/L, at a pH of 6.5, resulted in 0 percent and 58 percent mortality of 160 day-old striped bass, respectively, after a 7 day exposure. USEPA (1988) also reported that Al concentration of 174.4 and 348.8 µg/L resulted in 2 percent and 100 percent mortality in 160 day-old striped bass at a pH of 7.2 (i.e., Al was more toxic at pH 6.5 than at pH 7.2). In addition, citing the Buckler et al. manuscript, USEPA (1988) reported that an Al concentration of 390 µg/L resulted in 0 percent mortality of 159 and 195 day-old striped bass at both a pH of 6.5 and 7.2 following a 7 day exposure. These values were identical to those in the published version of the study in Buckler et al. (1987). Additional 7 day toxicity tests of younger life stages were reported in Buckler et al. (1987). However, control survival in these other studies was marginal: (1) 72-78 percent and 79 percent for 11 day old fish at a pH of 7.2 and 6.5, respectively; and (2) 80 percent and 48 percent for 13 day old fish at a pH of 7.2 and 6.5, respectively. Conversely, control mortality was 0 percent in studies with 160 day old fish at pH levels of 6.5 and 7.2. However, if it is assumed that control mortality in the range of 20-28 percent is acceptable for younger life stages, a measured Al concentration of approximately 131 µg/L was associated with 75 percent mortality in 13 day old fish at a pH of 7.2, which was significantly greater ($p<0.05$) than in the respective control that had 20 percent mortality. In another study with 11 day old fish at a pH of 7.2, survival was not significantly reduced relative to the control up to a higher Al concentration of 179 µg/L, but was significantly reduced ($p<0.05$) at an Al concentration of 358 µg/L. At a pH of 6.5, control mortality was 21 percent (compared to 26 percent in the pH 7.2 control), but survival in Al treatments ≥22 µg/L was significantly reduced ($p<0.05$) compared to the pH 7.2 control (and presumably compared to the pH 6.5 control, but this was not reported).

Overall, Al toxicity to striped bass is highly variable depending on the age of the test organism and the pH of the water (6.5 vs. 7.2). Lowest observed effect concentrations range from 22 to <393 and NOECs range from 87 to >390 (in other words, the ranges of NOECs and LOECs from the various tests substantially overlap). Even within a similar age the NOECs and LOECs are highly variable, with NOECs for 159 day old fish being >390 µg/L and LOECs for 160 day old fish being 174 to 348 µg/L. Given this variability, we suggest that the striped bass toxicity data be excluded from consideration in updating the chronic Al criterion. Nevertheless, the chronic value reported in USEPA (1988) for striped bass in soft water[4] is 123 µg/L, which, assuming a water hardness of 14 mg/L, results in a chronic value of 703 µg/L at a hardness of 50 mg/L. Therefore, the available toxicity data suggest that the revised chronic criteria reported here (530 µg/L) would also be protective of chronic Al toxicity to striped bass, and so the calculated FCV does not need to be lowered to protect this species.

[4] Buckler et al. (1987) did not report the hardness of the test water, although the authors did note that hardness was monitored. They characterized the test water as soft. The test solution was created using well water passed through a water softener, which was then treated by reverse osmosis and passed through anionic, cationic, and mixed-bed exchange resins. The alkalinity and hardness of the well water were 237 and 272 mg/L, respectively. The alkalinity of the resulting test water was 12 mg/L. If we assume that the ratio of well water-to-test water alkalinity applies to hardness, we can estimate that the hardness of the test water was approximately 14 mg/L.

6.0 Criteria Statement

The available toxicity data, when evaluated using the procedures described in the *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (USEPA 1985) indicate that, except possibly where a locally important species is unusually sensitive, freshwater aquatic life should be protected if the four-day average concentration (in µg/L) of Al does not exceed the numerical value given by $e^{(1.3695[\ln(\text{hardness})]+0.9161)}$ more than once every three years on the average, and if the 24-hour average concentration (in µg/L) does not exceed the numerical value given by $e^{(1.3695[\ln(\text{hardness})]+1.8308)}$ more than once every three years on the average. For example, at hardness levels of 50, 100, and 200 mg/L as $CaCO_3$, the four-day average Al concentrations are 530, 1,370, and 3,541 µg/L, respectively, and the 24-hour average Al concentrations are 1,324, 3,421, and 8,838 µg/L.

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