Arid West Water Quality Research Project

EVALUATION OF THE EPA
RECALCULATION PROCEDURE
IN THE ARID WEST
TECHNICAL REPORT

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directed by Pima County Wastewater Management Department

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cover photo: Santa Cruz River, near Tubac, AZ
Linwood Smith, photographer

FOREWARD

The Arid West Water Quality Research Project (AWWQRP or "Project") was established in 1995 as a result of a federal appropriation (Public Law 103-327) and the establishment of an Assistance Agreement between the U.S. Environmental Protection Agency (USEPA) and Pima County Wastewater Management (PCWMD), Tucson, Arizona. The establishment of this Agreement provided a significant opportunity for western water resource stakeholders to (1) work cooperatively to conduct scientific research to recommend appropriate water quality criteria, standards and uses for effluent-dependent and ephemeral waters in the arid and semi-arid regions of the West ("arid West"), and (2) improve the scientific basis for regulating wastewater and stormwater discharges in the arid West. Effluent-dependent waters are created by the discharge of treated effluent into ephemeral streambeds or streams that in the absence of effluent discharge would have only minimal flow.

With the establishment of the AWWQRP, a management infrastructure was created to support the development of peer-reviewed research products. From within the Environmental Planning Division of PCWMD, the AWWQRP Project Director, Program Manager and support staff administer the Project. A Regulatory Working Group (RWG), comprised of 15 stakeholders representing both public and private interests, works to ensure that Project research has a sound regulatory basis and that research activities focus on important regulatory concerns. The Scientific Advisory Group (SAG), comprised of scientists with experience in water quality research, makes certain that project research has a sound scientific basis and that studies are properly designed and technically sound.

This report represents the fifth in a series of research reports produced by the AWWQRP, and builds upon already completed work. The first report in the series, *Pre-Research Survey of Municipal NPDES Dischargers in the Arid and Semi-Arid West*, resulted from an RWG recommendation that the Project survey arid West wastewater facilities to compile information about their effluent discharges and associated water quality concerns.
The second report, the *Habitat Characterization Study*, utilized the findings of the Discharger Survey. Recognizing that an understanding of the attributes of effluent-dependent waters was critical to the development of appropriate water quality criteria and standards for these waters, the RWG recommended that the AWWQRP commission a major study to describe the physical, chemical, and biological characteristics of effluent-created habitats.

The *Habitat Characterization Study* evaluated the physical, chemical and biological characteristics of effluent-dependent habitats at ten case study sites in the arid West: Santa Cruz River below Nogales and below Tucson, Arizona; Salt River below Phoenix, Arizona; Santa Ana River below San Bernardino, California; Fountain Creek below Colorado Springs, Colorado; South Platte River below Denver, Colorado; Las Vegas Wash below Las Vegas, Nevada; Santa Fe River below Santa Fe, New Mexico; Carrizo Creek below Carrizo Springs, Texas; and Crow Creek below Cheyenne, Wyoming (Figure F-1). The primary objectives of this effort were to (1) review existing physical, chemical and biological data; (2) conduct a site reconnaissance to characterize habitats using established protocols and protocols adapted for arid West conditions; (3) identify similarities and differences among sites; (4) discuss potential approaches to protect these habitats in the context of existing regulatory programs; and (5) recommend areas for additional study. The final report may be downloaded from the AWWQRP website, www.co.pima.az.us/wwm/wqrp, or obtained from the AWWQRP Office in a CD hyperlinked format.

The AWWQRP's third report, *Extant Criteria Evaluation*, evaluated the applicability of national water quality criteria, as well as the methods to modify those criteria, to effluent-dependent and ephemeral waters in the arid West. This work built upon the findings presented in the *Habitat Characterization Study* using the expertise of national water quality criteria researchers. The AWWQRP used the findings and recommendations contained in the *Extant Criteria Evaluation* as the primary driver for the selection and execution of three subsequent research projects, including evaluations of 1) the Biotic Ligand Model of copper toxicity in arid west streams, 2) use of the EPA recalculation procedure in effluent-dependent streams, and 3) potential hardness-modifications to ammonia toxicity and their implications for use of the water-effect ratio.

Figure F-1. *Habitat Characterization Study* Case Study Sites.

The purpose of this fifth report, *Evaluation of EPA Recalculation Procedure in Arid West Effluent Dependent Waters*, ("Recalculation Procedure Study") was to evaluate use of the Recalculation Procedure on selected water quality criteria with different modes of toxicity in specific arid West waters. In addition, based on the findings from this evaluation, a *User's Guide for Development of Site-Specific Water Quality Standards in Arid West Effluent-dependent Streams Using USEPA's Recalculation Procedure* was also prepared as a practical guide for water quality standards practitioners regarding use of the Recalculation Procedure for developing site-specific water quality standards.

The SAG provided a technical review of the findings from the Recalculation Procedure Study. After the SAG comments were addressed, the report was submitted to the RWG and USEPA for additional technical and regulatory review. Comments of a technical nature were covered in a response matrix, with major comments addressed in the report, as necessary. Many comments were more directly related to policy and implementation issues, rather than to the scientific content and recommendations in the report. As such, even though the findings of this study have received both technical and regulatory reviews, it is strongly recommended that local state and regional USEPA staff should be consulted prior to using these findings to support or propose regulatory change.

The AWWQRP has made a significant effort to share Project results and their implications in a variety of technical, regulatory, industry and public interest forums, including publication in the primary scientific literature. This outreach effort is designed to create a broader understanding of water quality issues unique to the arid West and provide scientific and regulatory data in support of a regional approach to the development of water quality criteria, standards and uses. Heightened interest in arid West water quality issues has been fueled by the recognition that treated effluent can have a valuable role in the support and enhancement of riparian ecosystems, particularly in light of increasingly limited water resources. The AWWQRP looks forward to continuing its support of research that not only provides critical data to address unique western water quality issues, but also supports the development of innovative solutions.

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This study was conducted as part of the Arid West Water Quality Research Project (AWWQRP) under the direction of the Pima County Wastewater Management Department in Tucson, Arizona. Funding for the AWWQRP was provided by USEPA Region IX under Assistance Agreement #XP-99926701. The AWWQRP is administered by the following individuals:

- Michael Gritzuk, P.E., Director, Pima County Wastewater Management Department
- Paul M. Bennett, P.E., Deputy Director, Pima County Wastewater Management Department
- Edward F. Curley, Project Director, Pima County Wastewater Management Department
- Karen Ramage, Program Manager, Pima County Wastewater Management Department
- Richard D. Meyerhoff, Ph.D., Research Manager, Camp Dresser & McKee
- Robyn Stuber, EPA Project Officer, EPA Region IX, San Francisco, California

REGULATORY WORKING GROUP (RWG)

The Regulatory working Group (RWG) was established by the AWWQRP to assist in the identification of regulatory issues needing to be addressed by scientific research. The RWG includes representatives from State and regulatory agencies, municipalities, Indian Tribes, industry, environmental organizations, consulting firms, and universities. The RWG also provided critical review of draft reports and project presentations. Currently, the RWG consists of the following individuals:

- Michael Gritzuk, P.E., Pima County Wastewater Management, Tucson, Arizona
- Edward C. Anton, California State Water Resources Control Board, Sacramento, California
- Rodney W. Cruze, Riverside Regional Water Quality Control, Riverside, California
- Steve Davis, P.E., Malcolm Pirnie, Inc., Tucson, Arizona
- Paul D. Frohardt, Colorado Water Quality Control Commission, Denver, Colorado
- Robyn Stuber, USEPA, Region IX, San Francisco, California
- Andy Laurenzi, The Nature Conservancy, Marana, Arizona
- Patrick J. Maley, Mining Industry Representative, Boise, Idaho
- Lynn Wellman, U.S. Fish & Wildlife Service, Albuquerque, New Mexico
- James F. Pendergast, USEPA, Office Science and Technology, Washington, D.C.
- Sam Rector, Arizona Department of Environmental Quality, Phoenix, Arizona
- Eric Rich, EPA – Navajo Nation, Tuba City, Arizona
- Daniel Santantonio, Ph.D., City of Las Cruces, Utility/Water Division, Las Cruces, New Mexico
- Gary Ullinskey, City of Phoenix Water Services, Phoenix, Arizona

SCIENTIFIC ADVISORY GROUP (SAG)

The Scientific Advisory Group (SAG) was established to provide technical oversight and peer review of ongoing and planned research for the AWWQRP. The SAG provided critical review for all sections of this report. SAG members include:

- Paul Adamus, Ph.D., Corvallis, Oregon (Oregon State University)
- Gary Chapman, Ph.D., Paladin Water Quality Consulting, Corvallis, Oregon
- Karmen King, Colorado Mountain College, Leadville, Colorado
- Robert McFarlane, Ph.D., McFarlane & Associates Environmental Consultants, Houston, Texas
- Benjamin Parkhurst, Ph.D., HAF, Inc. Laramie, Wyoming

Alternates:

- Robert Gray, Ph.D., Richland, Washington
- Carlton Sims White, Ph.D., University of New Mexico, Albuquerque, New Mexico

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

All AWWQRP research products were also reviewed to ensure compliance with the project QAQC plan. This review was provided by:

- Frederick A. Amalfi, Ph.D., Aquatic Consulting and Testing, Tempe, Arizona

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ABBREVIATIONS AND ACRONYMS

µg/L	microgram(s) per liter
ACR	acute-to-chronic ratio
ADEQ	Arizona Department of Environmental Quality
AGFD	Arizona Game and Fish Department
Al	aluminum
$AV_{t,8}$	acute value, normalized to pH 8
AW-MDRs	arid West minimum data requirements
AWQC	ambient water quality criteria
AWWQRP	Arid West Water Quality Research Project
BLM	biotic ligand model
Ca	calcium
CCC	criterion continuous concentration
CDOW	Colorado Division of Wildlife
CEC	Chadwick Ecological Consultants, Inc.
CF	conversion factor for the dissolved metal fraction
CMC	criterion maximum concentration
Cu	copper
$CV_{t,8}$	chronic value, normalized to pH 8
DOC	dissolved organic carbon
DQOs	data quality objectives
EC_{20}	effect concentration, point estimate for specified effect in 20% of organisms
ECE	extant criteria evaluation
EDW	effluent-dependent waters
ELS	sensitive early life
EPA	U.S. Environmental Protection Agency
FACR	final acute-to-chronic ratio
FAV	final acute value
FCV	final chronic value
GMAV	genus mean acute value
GMCV	genus mean chronic value
HCS	habitat characterization study
ITIS	Integrated Taxonomic Information System
LC_{50}	lethal concentration – point estimate for 50% mortality
LOEC	lowest-observed-effect concentration
MDR	minimum data requirement
Mg	magnesium
mg/L	milligram per liter

ABBREVIATIONS AND ACRONYMS (Continued)

N	nitrogen
NCSS	Number Cruncher Statistical System
NH_3	ammonia
NH_4^+	ammonium ion
NOEC	no-observed-effect concentration
OP	organo-phosphate
PCWMD	Pima County Wastewater Management Department
PCWWM	Pima County Wastewater Management
SARDA	Santa Ana River Dischargers Association
SMACR	species mean acute-to-chronic ratio
SMAS	species mean acute slope
SMAV	species mean acute value
SMCV	species mean chronic value
TA-N	total ammonia as nitrogen
T&E	threatened or endangered
TMDL	total maximum daily load
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
WET	whole effluent toxicity
WWTP	wastewater treatment plant
Zn	zinc

EXECUTIVE SUMMARY

ES.1 SUMMARY OF PROJECT OBJECTIVES

Although AWQC are intended to protect many aquatic species nation-wide, they may not always represent the contaminant sensitivity of species resident to a particular site. At present, the EPA has provided guidance for the development of site-specific criteria using three primary methods (EPA 1994):

The recalculation method,
Water-effect ratios, and
The resident species procedure.

This study applies and further develops tools for modifying AWQC on a site-specific basis for arid West effluent-dependent waters (EDWs) through an evaluation of the EPA recalculation procedure.

Evaluation of the recalculation procedure has focused on AWQC that represent different modes of toxicity, robustness of toxicological databases, and other recalculation issues. The criteria chosen for evaluation include three initially addressed in the Extant Criteria Evaluation, or ECE (PCWWM 2003) - ammonia, copper, diazinon - as well as two common metals, zinc and aluminum. The selection of AWQC follows the conclusions of both the ECE and the Habitat Characterization Study, or HCS (PCWWM 2002) that the recalculation procedure in the arid West should be based on taxa more representative of communities found in either natural or effluent-dependent, non-perennial streams in the arid West.

In the present study, AWQC have been recalculated to better reflect the resident species observed in a number of effluent-dependent study streams in the arid West. Streams chosen for this study include four of the nine streams addressed in the HCS;

Santa Ana River, California
Salt/Gila Rivers Arizona,
Santa Cruz River, Arizona,
Fountain Creek, Colorado
South Platte River, Colorado

Waters from most of these sites were also used for water-effect ratio testing for copper and ammonia in two other AWWQRP studies (PCWWM 2005a, 2005b). Resident species lists were developed for these streams for comparison to the toxicity databases as a required step in the recalculation procedure.

Prior to recalculation, we also updated each criteria through: 1) review of the criteria documents for technical accuracy; 2) literature review to update the criteria toxicity databases; and 3) development of revised, updated national criteria. These updated AWQC (Chapters 3 through 7) were subsequently used as the basis for evaluating the recalculation procedure (EPA 1994) in each of our case study EDWs (Chapter 9).

ES.2 OVERVIEW OF STUDY STREAM SEGMENTS, DATA SOURCES, AND RESIDENT SPECIES LIST DEVELOPMENT

Fish and invertebrate taxa lists were compiled from a literature review to determine what taxa currently occur or could potentially occur at the effluent-dependent streams in this analysis. All stream segments were located downstream of wastewater treatment plants (WWTP) that discharge treated effluent into streams that would otherwise have low or no flow during most of the year (i.e., effluent-dependent stream segments).

According to the EPA (1994), the phrase "occur at the site" includes fish or invertebrates that are usually present at the site, either as year-round residents or as seasonal or intermittent residents, or if not currently present, they are expected to reside within the streams when conditions improve (EPA 1994). For our analysis, "occur at this site" is further separated on the basis of whether these organisms are resident (organisms that use the stream reproduction, feeding, and/or refuge) or transient taxa (organisms that are moving through the site, either actively or passively, and do not use the stream for the above functions).

The effluent-dependent stream sites chosen for this study produced a composite fish species list containing a total of 75 taxa (Chapter 2). The number of taxa collected at each stream segment varied from only three non-native fish taxa collected from sites on the Santa Cruz River near Tucson to 40 fish taxa collected from sites on the Salt/Gila Rivers. The native fish species found at each stream grouped by geographic location, as expected due to historic/biogeographical barriers (PCWMD 2002).

The effluent-dependent streams chosen for this study produced a composite invertebrate species list containing a total of 561 taxa (Chapter 2). The total number of taxa collected over the period of record used in this analysis for each stream varied from 41 taxa collected from the Santa Cruz River near Tucson to 282 taxa collected from the Santa Ana River. As with the fish cluster analysis using all fish taxa, the grouping of the invertebrate communities in these streams seems to be highly influenced by the number of studies, the number of years studied, and methods used in those studies. Regardless, the fish and invertebrate taxa lists developed provide a list of resident taxa for the recalculation effort described later in this document.

ES.3 ALUMINUM CRITERIA REVIEW AND UPDATE

The 1988 report entitled *Ambient Water Quality Criteria for Aluminum* (EPA 1988) underwent a technical review and update as the initial step for inclusion in the Arid West Water Quality Research Project AWQC Recalculation Project. The speciation and/or complexation of aluminum (Al) is highly dependent on ambient water quality characteristics and ultimately determines the mechanism of toxicity. Concentration of calcium in the water was shown to decrease toxic effects to fish.

A comprehensive literature review resulted in the addition of 36 acute data points from 15 studies to the updated aluminum acute database (Chapter 3). Additionally, 11 chronic data points from nine studies were added to the updated aluminum chronic database. The updated acute database revealed a statistically significant inverse Al toxicity and hardness relationship with a slope of 0.8327. This was not reported in the 1988 Aluminum AWQC.

The updated acute database contains values for 17 genera, while the updated Al chronic toxicity database presents data for six genera of freshwater organisms. Since the revised chronic database did not satisfy the "eight-family rule," the FACR was used to derive a FCV for Al from the acute database. New acute and chronic hardness-based equations were derived from the updated databases (Table ES-1). The updated and revised acute and chronic criteria based on these equations are presented across a wide range of hardness levels (Table ES-1). It is important to understand the boundaries of the reported equation. Since the equation models hardness values that ranged from 1 mg to 220 mg of $CaCO_3$/L, estimations made outside of this range should be treated with caution. Given that arid West EDWs can often exhibit hardness values much greater than 220 mg/L, this represents an uncertainty.

Table ES-1
Updated and Revised Acute and Chronic Al Criteria Values (µg Total Aluminum/L) Across Selected Hardness Values

	Mean Hardness (mg/Las $CaCO_3$)									
Updated/Revised National Standards	25	50	75	100	150	200	250	300	350	400
Acute Al Criterion: $e^{(0.8327\ [\ln\ (hardness)]+3.8971)}$	719	1,280	1,794	2,280	3,195	4,060	4,889	5,691	6,470	7,231
Chronic Al Criterion: $e^{(0.8327\ [\ln\ (hardness)]+2.9800)}$	287	512	717	911	1,277	1,623	1,954	2,275	2,586	2,890

NOTE: Current EPA Al criteria: 750 µg/L acute; 87 µg/L chronic

ES.4 AMMONIA CRITERIA REVIEW AND UPDATE

The "1999 Update of Ambient Water Quality Criteria for Ammonia" (EPA 1999) provides current national recommended ammonia criteria and was reviewed and updated in this effort. An extensive review of published and unpublished literature added 23 genera, representing 28 species, to the current national acute/chronic database (Chapter 4). The most noteworthy additions to the database were eight species of freshwater mussels in the Family Unionidae, which appear to be extremely sensitive to ammonia. The updated database also includes four endangered fish species found in the arid West. Additionally, 20 chronic ammonia studies were determined to be useable, which provided toxicity data for 14 species representing 12 genera. The updated chronic database still does not meet the "eight family rule" for the 5th percentile approach for development of national AWQC (Stephan et al. 1985).

Our analysis of the exisiting criteria led us to not include a temperature component in the acute ammonia relationship. However, uncertainties in the use of "large" rainbow trout data led us to an alternative approach of re-categorizing the updated database into two databases as either cold-water or warm-water species (Chapter 4). The four most sensitive warmwater genera were all mussels from the Unionidae family. Given the uncertainty of the unionid distribution within the arid West (Chapter 2), we also analyzed the warm-water database minus the Unionidae family. Acute equations were then derived for each database (i.e., cold-water, warm-water, warm-water minus Unionidae):

Updated Cold-water Ammonia Acute Criterion:

$$\mathrm{CMC}_{\mathrm{Cold}} = \frac{0.375}{1+10^{7.204-\mathrm{pH}}} + \frac{53.3}{1+10^{\mathrm{pH}-7.204}}$$

Updated Warm-water Ammonia Acute Criterion:

$$\mathrm{CMC}_{\mathrm{Warm}} = \frac{0.081}{1+10^{7.204-\mathrm{pH}}} + \frac{11.5}{1+10^{\mathrm{pH}-7.204}}$$

Updated Warm-water without Unionidae Ammonia Acute Criterion:

$$\mathrm{CMC}_{\mathrm{Warm\ without\ Unionidae}} = \frac{0.388}{1+10^{7.204-\mathrm{pH}}} + \frac{55.3}{1+10^{\mathrm{pH}-7.204}}$$

The EPA's development of the chronic equations based on temperature and pH was problematic because: 1) the chronic database does not meet EPA's "eight family rule"; 2) the temperature-dependent chronic equations are based on a single acute toxicity study in which the authors explicitly state no relationship between ammonia toxicity and temperature; 3) the amphipod *Hyalella azteca* was used to develop a temperature-based function to protect early life stage fish; and 4) this *H. azteca* test had significant control mortality.

These major shortcomings of the EPA chronic ammonia criteria led us to re-evaluate the use of acute-chronic ratios (ACR) to adjust the acute equations. A final ACR of 4.9 was derived and the resulting cold-water, warm-water, and warm water without Unionidae chronic equations are listed below. The modifications to the national acute and chronic ammonia water quality criteria are more appropriate for the range of aquatic habitats found in the arid West.

Updated Cold-water Ammonia Chronic Criterion:

$$CCC_{\text{Cold}} = \frac{0.153}{1+10^{7.204\text{-pH}}} + \frac{21.74}{1+10^{\text{pH-}7.204}}$$

Updated Warm-water Ammonia Chronic Criterion:

$$CCC_{\text{Warm}} = \frac{0.033}{1+10^{7.204\text{-pH}}} + \frac{4.69}{1+10^{\text{pH-}7.204}}$$

Updated Warm-water (without Unionidae) Ammonia Chronic Criterion:

$$CCC_{\text{Warm without Unionidae}} = \frac{0.156}{1+10^{7.204\text{-pH}}} + \frac{22.21}{1+10^{\text{pH-}7.204}}$$

ES.5 COPPER CRITERIA REVIEW AND UPDATE

Copper criteria are presently hardness-modified even though copper toxicity does not always exhibit a consistently strong relationship with water hardness (PCWWM 2003, 2005a). The 2003 Copper Draft (EPA 2003) is the first EPA AWQC document to use the biotic ligand model (BLM) to normalize toxicity values for criteria derivation. Unfortunately, requiring such BLM data reduces the database from 43 genera (EPA 1996) to 27 in the 2003 Copper Draft. Since the 2003 Copper Draft is not officially adopted by the EPA, we did not use the BLM to modify the toxicity data or our criteria updates.

The literature review resulted in the addition of 295 acute values (Chapter 5) from 47 different sources to the 1984/1995 acute copper toxicity database, including acute toxicity values for 43 new species, representing 25 new genera. These new data also included toxicity values for many T&E species. In addition to the new acute data, a total of 24 chronic values from ten sources were added to the revised chronic toxicity database. Updated acute and chronic hardness slopes weres developed from the revised and updated toxicity databases.

The revised and updated final acute and chronic dissolved copper equations and a summary of criteria at varying hardness levels are presented below (Table ES-2). *Precautionary Note:* One study in particular, Koivisto et al. (1992), highly influenced the updated final acute value, as it provides the only data for the three most sensitive species in the database - with all values unmeasured. It would not be appropriate to remove these unmeasured values without removing all unmeasured values. However, criteria calculated without acute values from Koivisto et al. (1992) may be more appropriate for revised national criteria.

Table ES-2
Summary of Existing (EPA 1996) and Revised Copper Criteria
(as µg dissolved Cu/L) at Varying Hardness Levels

Equations	Mean Hardness in mg/L $CaCO_3$									
	25	**50**	**75**	**100**	**150**	**200**	**250**	**300**	**350**	**400**
Current EPA Criteria										
Acute = 0.96 ($e^{0.9422 [\ln (hardness)]-1.7000}$	3.640	7.286	10.675	13.999	20.512	26.899	33.192	39.413	45.574	51.684
Chronic = 0.96 ($e^{0.8545 [\ln (hardness)]-1.7020}$	2.739	4.953	7.004	8.956	12.664	16.193	19.595	22.898	26.122	29.279
Updated Criteria (all data)										
Acute = 0.96 ($e^{0.9801 [\ln (hardness)]-2.2608}$	2.380	4.709	7.018	9.316	13.886	18.431	22.969	27.472	31.974	36.466
Chronic = 0.96 ($e^{0.5897 [\ln (hardness)]-1.1054}$	2.121	3.192	4.054	4.804	6.102	7.230	8.246	9.182	10.056	10.880
Updated Criteria (w/o Koivisto *et al*. 1992)										
Acute = 0.96 ($e^{0.9801[\ln(hardness)]-2.2835}$	4.082	8.077	12.039	15.980	23.818	31.615	39.382	47.124	54.846	62.551
Chronic = 0.96 ($e^{0.5897[(\ln(hardness)-1.1281}$	3.638	5.476	6.955	8.240	10.466	12.401	14.145	15.751	17.250	18.663

ES.6 DIAZINON CRITERIA REVIEW AND UPDATE

The EPA has not established national aquatic life criteria for diazinon, but has produced a *Draft Ambient Aquatic Life Water Quality Criteria Diazinon* (EPA 2000. Environmental conditions, such as site-specific channel characteristics and water quality parameters of arid West streams, may differentially affect diazinon degradation and, therefore, exposure to aquatic organisms.

The literature review contributed 25 new acute data points from 19 studies to the revised acute. Ten new freshwater chronic data points from eight studies were added to the revised chronic database. The revised and updated diazinon acute toxicity database contains data for 22 genera, satisfing the "eight-family rule" as specified in the 1985 Guidelines. The revised and updated diazinon chronic toxicity database presents data for nine genera of freshwater organisms.

The resulting updated acute criterion for diazinon is 0.11 µg/L. The updated chronic criterion is also 0.11 µg/L - equal to the acute criterion, since the FACR and acute criterion division factor that estimates an LC-low for full protection of the most sensitive species are both equal to 2. Due to diazinon behavior, mechanisms of toxicity, organism's excretion, and exposure patterns in aquatic environments, these results are not surprising and should be appropriate for the protection of aquatic life.

ES.7 ZINC CRITERIA REVIEW AND UPDATE

Over 120 data points from 35 sources were added to an updated acute zinc database. In addition to the new acute data, a total of 23 data points from 12 sources were added to the chronic database, resulting in addition of 12 new genera and 11 new species. An updated acute hardness slope was used to normalize acute values to a hardness of 50 mg/L and to develop a hardness-based final acute equation. The new acute database contains 61 genera and 78 species (previously 36 genera and 44 species). An updated final acute-chronic ratio (FACR) was also determined for chronic criteria derivation. Table ES-3 presents a summary of these revised and updated acute and chronic zinc criteria at varying hardness levels.

Table ES-3
Summary of Existing and Revised Zinc Criteria
(as µg dissolved Zn/L) at Varying Hardness Levels

Equations	Mean Hardness in mg/L $CaCO_3$									
	25	50	75	100	150	200	250	300	350	400
Current EPA Criteria										
Acute = 0.978 $(e^{0.8473\,[\ln(\text{hardness})]+0.8840}$	36.20	65.13	91.83	117.18	165.22	210.82	254.70	297.25	338.72	379.30
Chronic = 0.986 $(e^{0.8473\,[\ln(\text{hardness})]+0.8840}$	36.50	65.66	92.58	118.14	166.57	212.55	256.78	299.68	341.49	382.40
Updated Criteria										
Acute = 0.978 $(e^{0.8537\,[\ln(\text{hardness})]+1.1182}$	46.71	74.41	119.32	152.53	215.62	275.65	333.49	389.66	444.47	498.13
Chronic = 0.986 $(e^{0.8537\,[\ln(\text{hardness})]+0.9473}$	39.69	71.73	101.40	129.62	183.24	234.25	283.40	331.13	377.71	423.31

ES.8 AMBIENT WATER QUALITY CRITERIA RECALCULATION ARID WEST EFFLUENT-DOMINATED STREAMS

ES.8.1 Overview of the EPA Recalculation Procedure

National ambient water quality criteria (AWQC) are to be derived from the most up-to-date toxicity databases for species resident to North America. Established methods for data selection and national criteria derivation are published in Stephan et al. (1985), as well as "Appendix B: The Recalculation

Procedure" in EPA (1994). The basic steps involved with EPA's recalculation procedure include (EPA 1994):

a) Corrections to the national database (Chapters 3-7);

b) Updating the national database (Chapters 3-7);

c) Deletions of taxa that do not occur at the site (Chapter 9 and Appendix 3);

d) If new database does not meet MDRs, generating the data necessary to meet MDRs;

e) Recalculating new acute and chronic criteria based on the revised and updated databases (Chapters 9 and 10); and

f) Presenting results in a report (present study).

ES.8.2 Resident vs. Transient Species

A key component of the recalculation procedure, specifically with regard to deletion of non-resident taxa from the database, is the definition of the phrase "occur at the site." For this analysis, we have taken this *occur at site* phrase a step further by delineating the organisms that occur at the site into "resident" and "transient" species. A resident species is an organism using the habitat located at the site for reproduction, foraging, and/or refuge, which can include migratory species. A transient species, on the other hand, is a species that may *occur at the site*, but does not utilize the habitat for these functions, and is only passively moving through the site.

ES.8.3 Deletion Process

Resident species lists generated in Chapter 2 were used to screen the corrected and updated national toxicity databases for each criterion. When reviewing the EPA (1994) deletion process, we identified a possible conflict between 1) the stepwise process they describe, 2) their accompanying figure that shows an example of the deletion process using three Phyla, and 3) the stated goal of deriving a site-specific database that contains *the most closely related taxa* to taxa found at the site. To resolve these conflicts, we refined the EPA step-wise process with the goal of generating a site-specific toxicity dataset more representative of the species that occur at the site than what would be derived using the standard process (Chapter 8).

ES.8.4 Minimum Data Requirements

Direct calculation of a criterion requires a toxicity database contain data for eight diverse Families (Stephen et al. 1985), commonly referred to as the "eight-family rule", or minimum data requirements (MDRs). National AWQC derived from a database that meets the MDRs are calculated from a series of formulas using the geometric mean toxicity values of the four most sensitive genera, and the total number of genera represented in the database. The resulting criteria concentrations are expected to protect at least 95% of all aquatic organisms and aquatic habitats (lotic, lentic, cold-water, and warm-water habitats).

ES.8.5 Redefining the Recalculation Procedure for Arid West Streams

The EPA guidelines and MDRs are the foundation for the arid West effluent-dependent stream AWQC recalculations. However, we believe slight modifications of the MDRs and EPA guidelines may be warranted given the habitats present and organisms expected to occur in these habitats.

First, taking into consideration the non-resident taxa in the EPA MDRs and the relative importance of other taxa not included in the EPA MDRs, we propose a revised eight-family rule specific for arid West effluent-dependent streams. These revised arid West MDRs (AW-MDRs) are intended for the protection of warm water aquatic communities residing in arid West effluent-dependent stream habitats, not in lakes and/or ponds.

Arid West Stream Eight-Family Rule [AWS-MDRs]

1) An organism in the Family Centrachidae (*replacing Family Salmonidae*),
2) An organism in the Family Cyprinidae (*replacing Family in Class Osteichthyes*),
3) A Family in the Phylum Chordata,
4) An aquatic insect,
5) A second aquatic insect in a different Order (*replacing Planktonic Crustacean*),
6) A benthic crustacean,
7) A Family in a Phylum other than Arthropoda or Chordata, and
8) A Family in any Order of insect or any Phylum not already represented.

Second, for the analysis presented herein, we are proposing that criteria derived during the recalculation process be calculated from the geometric mean of species mean acute and chronic values (SMAVs and SMCVs) rather than genus mean acute and chronic values (GMAVs and GMCVs) since 1) the deletion process itself is conducted on a species level rather than a genus level; 2) toxicity of a contaminant to different species within the same genus is not always equivalent; and 3) the minimal overlap between arid West resident species lists and species within the various toxicity databases can artificially lower the criterion if derived at the GMAV level (Great Lakes Environmental Center 2005). Calculating criteria at the species level rather than genus can help increase the database sample size to help resolve potential sample size effects, without affecting the protectiveness of the resulting criteria through inclusion of SMAVs for sensitive species.

ES.8.6 Recalculation of Ambient Water Quality Criteria

The step-wise deletion process was conducted using the revised and updated national toxicity databases and resident species list for each river. Regional databases (Southwest and High Plains) were created by compliling the species lists for rivers in each respective region. Once the site-specific databases were created, checking of AWS-MDRs, the ranking process, and final site-specific criteria derivation was performed.

The first step after completion of the site-specific databases was to check for acceptance of the AWS-MDRs. In addition to compliance with the AWS-MDR, we identified threatened, endangered, and/or recreationally economically important species that reside at a site. If the AWS-MDRs were not met for a particular criterion at a particular site, then the regional site-specific criterion could provide an alternative AWQC recommendation.

ES.9 COMPARISONS OF SITE-SPECIFIC STANDARDS TO UPDATED NATIONAL CRITERIA

For comparisons of actual recalculated site-specific standards to national criteria, the equations or CMC and CCC values for each contaminant and each site were solved for mean hardness and pH of each site, as appropriate. Historical ambient water quality data for the study streams were derived using water quality data presented in the arid West HCS (PCWWM 2002) and from the BLM validation study (PCWWM 2005).

Results for the Santa Ana River, both segments of the Santa Cruz River, the Salt/Gila Rivers, Fountain Creek, and the South Platte River, as well as regional recalculated criteria are summarized in Tables ES-4 and ES-5.

Table ES-4
Site-Specific Acute Criterion Concentrations using Mean Hardness and pH when Necessary

	Site-Specific CMC						Regional CMC	
	Santa Ana River	Santa Cruz River Near Nogales	Santa Cruz River Near Tucson	Salt/ Gila River	Fountain Creek	South Platte River	Southwest Region	High Plains Region
Hardness (mg/L)	188	170	150	388	218	280	208	247
pH	7.2	7.5	7.2	7.4	7.4	7.4	7.3	7.4
Aluminum (µg total Al/L)	3463 (3856)	4527 (3546)	NA (3195)	7683 (7050)	3609 (4362)	4826 (5373)	3768 (1506)	4005 (4840)
Ammonia (mg TA-N/L)	28.35 (27.52)	18.53 (18.53)	28.47 (27.52)	21.16 (21.40)	22.05 (21.40)	21.62 (21.40)	24.94 (24.42)	21.77 (21.40)
Copper (µg dissolved Cu/L)	29.93 (16.96)	27.84 (15.36)	21.32 (13.59)	63.36 (34.49)	35.18 (19.57)	45.68 (25.05)	36.42 (18.69)	40.56 (22.14)
Diazinon (µg total diazinon/L)	8.56 (0.11)	9.12 (0.11)	12.50 (0.11)	12.72 (0.11)	9.32 (0.11)	9.32 (0.11)	9.32 (0.11)	9.32 (0.11)
Zinc (µg dissolved Zn/L)	470.2 (261.5)	329.9 (239.9)	301.4 (215.6)	565.0 (485.3)	364.2 (296.2)	464.0 (367.4)	308.2 (284.6)	439.4 (329.9)

NOTES:
NA = Data were not available to derive criteria for that site – see Chapter 9 for discussion.
Values in () = updated national acute criterion, given site hardness or pH, for comparison.

Table ES-5
Site-Specific Chronic Criterion Concentrations using Mean Hardness and pH when Necessary

	Site-Specific CCC						Regional CCC	
	Santa Ana River	Santa Cruz River		Salt/Gila Rivers	Fountain Creek	South Platte River	Southwest Region	High Plains Region
		Near Nogales	Near Tucson					
Hardness (mg/L)	188	170	150	388	218	280	208	247
pH	7.2	7.5	7.2	7.4	7.4	7.4	7.3	7.4
Aluminum (µg total Al/L)	1384 (1541)	1809 (1417)	NA (1277)	3071 (2818)	1443 (1744)	1929 (2148)	1506 (1677)	1601 (1935)
Ammonia (mg TA-N/L)	11.57 (11.23)	7.56 (7.56)	11.62 (11.23)	8.64 (8.74)	9.00 (8.74)	8.83 (8.74)	10.18 (9.97)	8.89 (8.74)
Copper (µg dissolved Cu/L)	12.31 (6.97)	11.90 (6.57)	9.57 (6.10)	19.63 (10.69)	13.65 (7.61)	16.08 (8.82)	14.39 (7.40)	14.99 (8.19)
Diazinon µg total diazinon/L)	8.56 (0.11)	9.12 (0.11)	12.50 (0.11)	12.72 (0.11)	9.32 (0.11)	9.32 (0.11)	9.32 (0.11)	9.32 (0.11)
Zinc (µg dissolved Zn/L)	399.6 (222.2)	280.4 (203.9)	256.1 (183.2)	480.2 (412.4)	310.1 (252.1)	394.3 (312.2)	262.3 (242.2)	373.6 (280.5)

NOTES:
NA = data was not available to derive criteria for that site – see Chapter 9 for discussion
Values in () = updated national chronic criterion, given site hardness or pH, for comparison.

To quantify the relative numeric implication of applying the arid West recalculation procedure for particular contaminant/site combinations, we compared these site-specific standards with their respective updated national criteria (Table ES-6). A net change of 10% in the site-specific standard vs. national criteria was used to indicate differences that were likely to be substantially different from the national criteria. Results suggest that the recalculation procedure for development of site-specific standards would generally derive substantially different criteria concentrations for all of the case-study streams. The one exception to this is ammonia, which shows no noteworthy change when compared to the updated national criteria following recalculation.

Table ES-6
Calculation Findings Decision Matrix

	Santa Ana River	Santa Cruz near Nogales	Santa Cruz Near Tucson	Salt/Gila Rivers	Fountain Creek	South Platte River	Southwest Region	High Plains Region
Aluminum	-	+	NA	=	-	-	-	-
Ammonia	=	=	=	=	=	=	=	=
Copper	+	+	+	+	+	+	+	+
Diazinon	+	+	+	+	+	+	+	+
Zinc	+	+	+	+	+	+	=	+

NOTES:
"+" = Recalculated criteria are less restrictive than national updated criteria.
"-" = Recalculated criteria are more restrictive than national updated criteria.
"=" = Less than 10% change in recalculated criteria from national updated criteria.
NA = Data were not available to conduct the analysis.

ES.9.1 Criteria-Specific Issues with the Recalculation Procedure

The following discussion provides a summary of the issues that arose during the recalculation evaluation for each criterion, with comments on the mechanics of updating the national criteria, creating site-specific databases, and deriving final site-specific criteria.

ES.9.1.1 Aluminum

Compared to the updated national aluminum criteria, site-specific aluminum criteria were more restrictive or equal to the national criteria, except for the Santa Cruz near Nogales site (Figure ES-1). These counter-intuitive findings resulted from two basic factors.

First, all site-specific databases contained greater variability in the four lowest SMAVs, resulting in less statistically confident FAV calculations and, hence, more restrictive criteria. Second, the site-specific databases resulted in fewer taxa than the updated national databases. Reduction in number of species (N) within the site-specific toxicity databases decreased the degrees of freedom afforded to the four lowest ranked SMAVs.

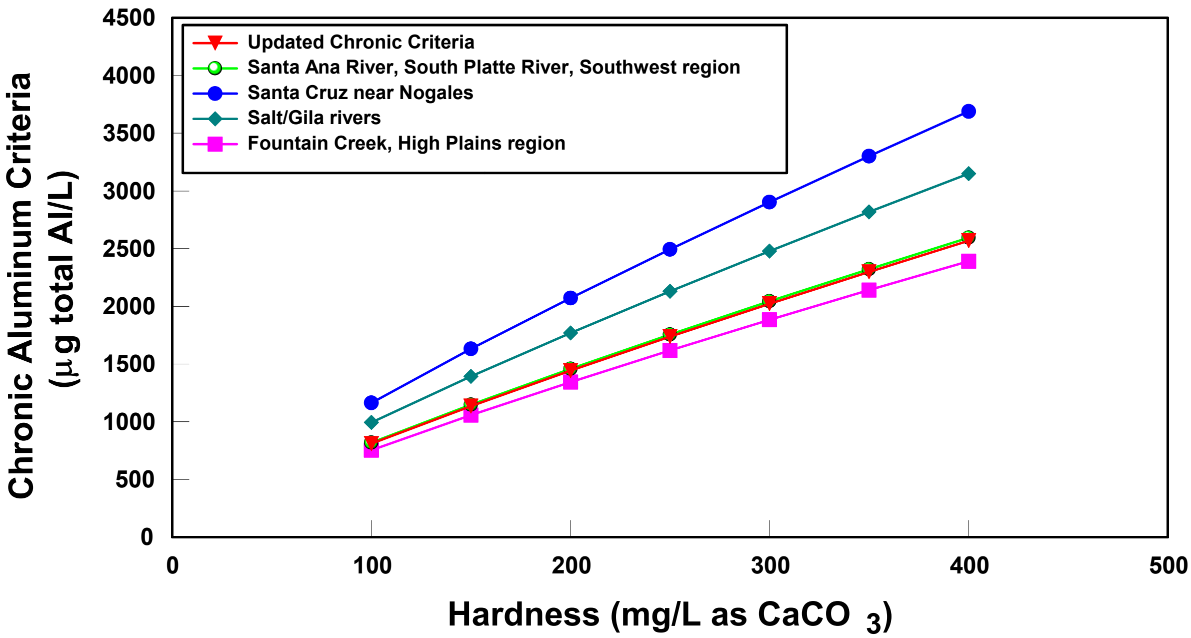

Figure ES-1
Comparison of Site-Specific Chronic Aluminum Criteria to the Updated National Criteria at Varying Hardness

In other words, the lower aluminum criteria resulting from site-specific recalculations relfect a reduction in the size of an already limited toxicity database and are not related to the species richness of the study sites. As such, we would recommend adoption of the updated aluminum AWQC presented in the national review and update (Chapter 3) and continue further investigation into site-specific recalculations when a more robust database becomes available.

ES.9.1.2 Ammonia

With regard to ammonia, there is little variability in site-specific criteria between any of the sites or regions (Figure ES-2). However, regional criteria are less restrictive than all but one site-specific criterion. This is directly associated with using the larger regional toxicity databases when compared to the site-specific databases. The similarity in results for all sites and regions with the updated national criterion suggest that site-specific recalculations for ammonia might not be necessary, as the breakdown of warm and cold water habitats proposed in our national updated ammonia criteria may already account for site-specific differences in arid-west streams, making further species-based recalculation efforts unnecessary.

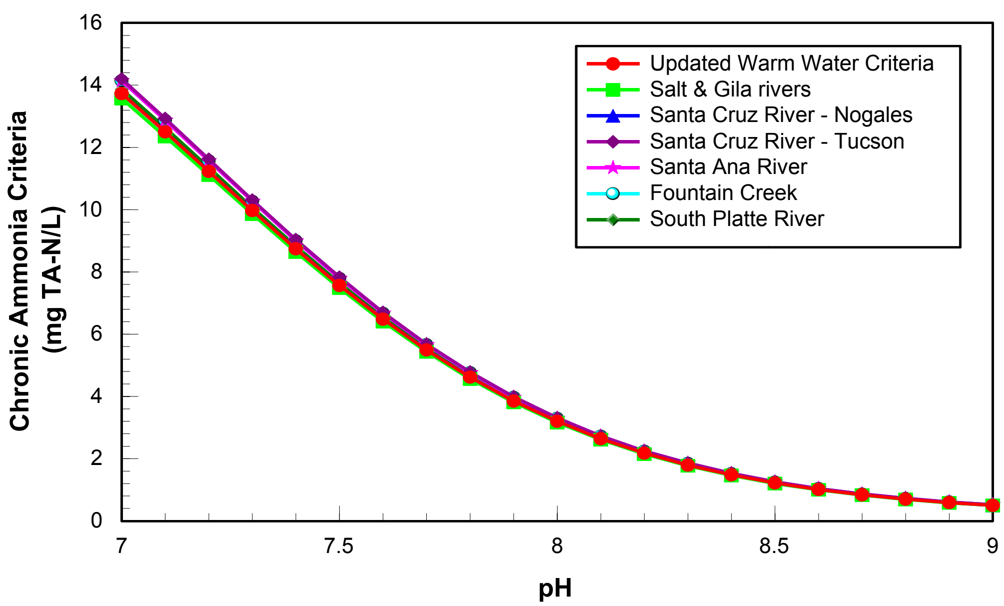

Figure ES-2
Site-Specific Chronic Ammonia Criteria as a Function of pH
(Note: Acute Criteria Distribution is Similar to Chronic)

ES.9.1.3 Copper

The recalculation procedure for copper provided substantial site-specific differences in criteria concentrations in arid West study streams compared to national criteria. Unlike ammonia, we found a substantial increase in all site-specific criteria (i.e., were less restrictive) compared to national or updated national AWQC (Figure ES-3). This was primarily a result of deletion of non-resident cladocerans.

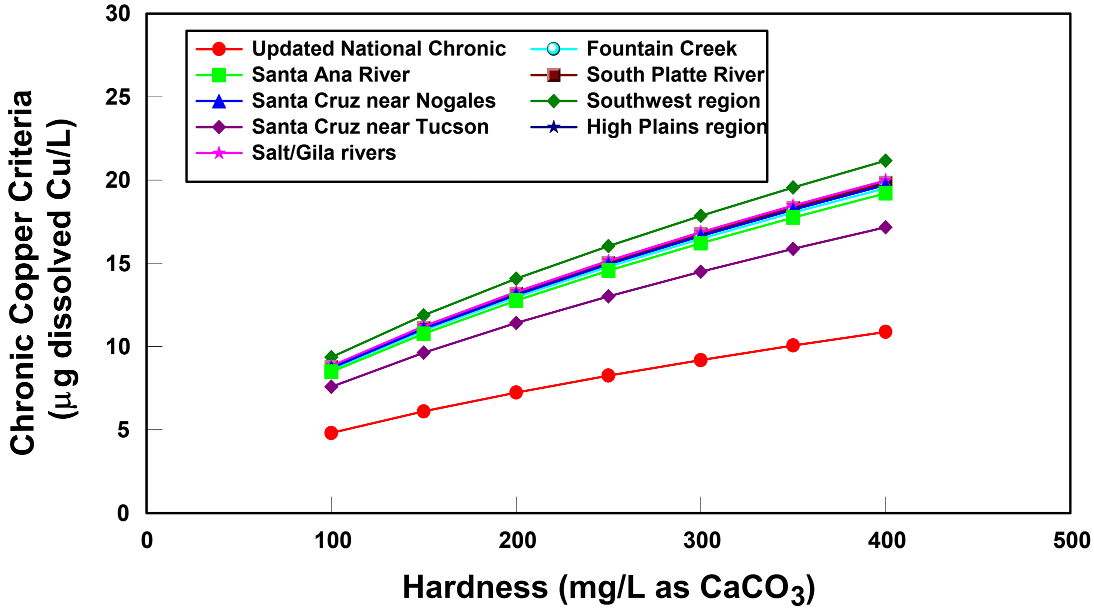

Figure ES-3
Comparison of Site-Specific Chronic Copper Criteria to the Updated National Chronic Copper Criteria at Varying Hardness Values

ES.9.1.4 Diazinon

Resulting site-specific diazinon criteria were substantially greater (i.e., less restrictive) than the updated national criteria. The site-specific databases are half as variable as the national update, which increases confidence in respective estimates and results in greater values. Furthermore, site-specific criteria for diazinon were more variable between sites than other criteria in this analysis. Although the most sensitive organisms are similar between most sites, the variability in database size between sites was substantially different. The significant increase of the recalculated criterion and the variability of criterion between sites provide some evidence that moderately sized databases are uniquely sensitive to the arid West recalculation procedure.

ES.9.1.5 Zinc

In general, the arid West recalculation procedure applied to the updated national zinc database successfully generates site-specific criteria that reflect the relative sensitivity of organisms at the site, rather than criteria that are driven by database size. The species composition of the site-specific databases and ranking were variable among sites, which greatly influenced the numeric outcome of the recalculated criteria (Figure ES-4). Initiating the deletion process with the robust updated database makes it more likely that the site-specific databases will reflect the unique species composition for each arid West site.

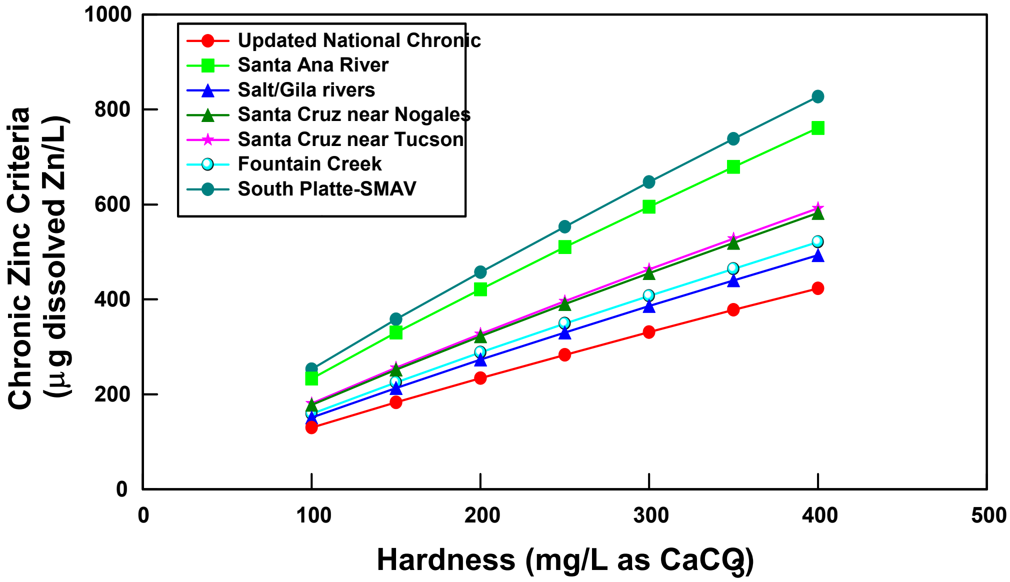

Figure ES-4
Comparison of Site-Specific Chronic Zinc Criteria to the Updated National Chronic Zinc Criteria at Various Hardness Concentrations

ES.10 FACTORS AFFECTING RECALCULATION "SUCCESS"

Based on our analysis, the recalculation procedure can be a useful tool, particularly when modified and applied to arid West streams. The results of recalculated site-specific criteria resulted in significant changes for some, but not all AWQC reviewed in this analysis.

Significant changes in site-specific critera as the result of the recalculation procedure include copper, diazinon and zinc. These toxicants produced universally less restrictive criteria than updated national criteria, while ensuring the same levels of protection for resident fauna for all study streams. It is clear that starting the deletion process for criteria with a more robust toxicity database increases the chance the taxa retained for each site will vary, which then influences the final criteria concentrations. Since ammonia criteria were already partitioned into cold and warm water equations, and many of the most sensitive species in the updated warm water database are resident to the arid West, the resulting site-specific criteria would be expected to be similar. The issues with recalculation for aluminum criteria surfaced due to the relatively limited number of species in the updated national toxicity database. Until more aluminum toxicity data are available for more aquatic organisms common to the arid West, it may be more appropriate to adopt the updated national criterion developed in this study.

Although results from the recalculation procedure could be used to derive scientifically defensible site-specific criteria, the tasks involved require considerable effort. However, the updated toxicity databases developed for this study can be used as a starting point for future updates to these five criteria. Furthermore, relevant invertebrate and fish population data are required for the development of resident species lists. Invertebrate and fish population monitoring plans should be initiated and maintained in the reach of interest. Lastly, there needs to be continued support for more toxicity testing for all AWQC, especially with species resident to arid West streams.

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1.0 INTRODUCTION

1.1 SUMMARY OF PROJECT OBJECTIVES

During the 1997 initiating symposium of the Arid West Water Quality Research Project (AWWQRP) the following question was posed as critical to Western dischargers and regulators: given the hydrologic and climatic characteristics of Arid West[1] effluent-dependent waters (EDW), are national ambient water quality criteria (AWQC) appropriate for protection of Western aquatic life and their habitats?

In response, the Habitat Characterization Study (HCS) studied nine stream systems in the arid West and determined there is a fundamental difference in the environmental conditions of effluent-dependent waters compared to perennial waters, particularly those in more mesic regions, suggesting that the first assumption might be valid (PCWWM 2002). The Extant Criteria Evaluation (ECE) (PCWWM 2003) completed the basis for the question, with an examination of the technical issues required to adapt AWQC to local ecological conditions of the arid West.

National AWQC are primarily derived from toxicity tests conducted with laboratory reared organisms that act as surrogates for all untested and untestable spieces (Stephan et al. 1985). Although the resulting criteria adequately protect many species nation-wide, these laboratory species may not always be the best representatives for species resident to the arid West. Frequently tested surrogates are most similar to those encountered in perennial streams in mesic environments (e.g., the eastern U.S., and trout species of the Pacific Northwest, and the intermountain Rocky Mountains). A much smaller body of toxicological knowledge exists for stream biota characteristic of the arid West, adapted to intermittent perennial streams. The response of species adapted to EDWs and the regulated chemical components of treated wastewater is even less complete.

These remaining open issues suggested to the AWWQRP Regulatory Working Group that development of site-specific criteria for arid West EDWs may be an appropriate solution. At present, the EPA has provided guidance for the development of site-specific criteria using three primary methods (EPA 1994):

the recalculation method,
water-effect ratios, and
the resident species procedure.

1 As has been the case in previous AWWQRP reports, "arid West" includes the arid and semiarid parts of the U.S. West of the 110th meridian in which mean annual rainfall is 20 inches (~500 mm) or less.

While the ECE examined potential modifications to each of these procedures in general terms, the current study, the EPA Recalculation Study, applies and further develops tools for modifying AWQC on a site-specific basis for arid West EDWs through an evaluation of the EPA recalculation procedure.

Evaluation of the recalculation procedure has focused on AWQC that represent different modes of toxicity, robustness of toxicological databases, and other recalculation issues. The criteria chosen for evaluation include three initially addressed in the ECE (ammonia, copper, diazinon), as well as two common metals, zinc and aluminum. The selection of example AWQC follows the conclusions of both the ECE and HCS that the recalculation procedure in the arid West should be based on taxa other than salmonids and cladocerans. The ECE demonstrated that the low sensitivity of other resident families to various naturally occurring elements in Western streams may result in over protection by the AWQC. The HCS also concluded that some of the sensitive species are simply not found in either natural or effluent-dependent, non-perennial streams in the arid West.

AWQC have been recalculated to reflect the resident species data from a number of effluent-dependent study streams in the arid West. Streams chosen for this study include five of the nine streams addressed in the HCS;

Santa Ana River, California;
Salt/Gila Rivers, Arizona;
Santa Cruz River, Arizona;
Fountain Creek, Colorado; and
South Platte River, Colorado.

Waters from most of these sites were also used for water-effect ratio testing for copper and ammonia in two other AWWQRP studies (PCWWM 2005a,b).

1.2 ARID WEST/EFFLUENT DEPENDENT STREAMS SELECTED FOR RECALCULATION ANALYSIS

The HCS investigated nine "case study" streams (two on the Santa Cruz River) across the West (PCWWM 2002). The Recalculation Study focused on five of the selected HCS study sites to illustrate the range of possible recalculation outcomes and/or alternatives derived from relevant examples of effluent-dependent waters for which adequate resident species lists are known to exist. Based on available data from both the HCS and existing monitoring programs (see Chapter 2), the following streams were chosen, according to the accompanying rationale:

Santa Ana River, California – As noted in the HCS, this effluent-dependent stream was extensively studied as part of a use-attainability analysis in the 1990s. This study included seasonal sampling of fish and invertebrates at numerous sites, which provides appropriate resident species lists for comparison to each AWQC. In addition, the Santa Ana River Dischargers Association (SARDA) and the USGS have conducted monitoring of benthic invertebrates and occasional sampling of fish populations through 2004.

Santa Cruz River, Arizona – The Santa Cruz River has been the site of extensive bioassessment, as indicated by the HCS. A site-specific water quality criteria investigation was developed in 1986 and numerous bioassessments have been conducted over the years. In 1998 the USGS began an investigation of the impact of wastewater on invertebrate communities. Currently, the U.S. Army Corps of Engineers is anticipating restoration of several reaches and baseline biological data is being collected. Two reaches of the Santa Cruz are evaluated in this study – downstream of Nogales and downstream of Tucson.

Salt/Gila Rivers, Arizona – The Gila River below its confluence with the Salt River downstream of Phoenix was also studied. The controversial listing for impairment due to pesticides in fish tissues, possibly leading to a future TMDL, has kept attention focused on the biological health of this effluent-dependent stream. In addition, the State species list for effluent-dependent waters is heavily indebted to early ecological work on the river and includes some dubious "resident" species, such as largemouth bass. Ongoing river restoration work by the Corps of Engineers and City of Phoenix provides additional sources of data.

Fountain Creek, Colorado – An HCS effluent-dominated stream, Fountain Creek has a long-term biological monitoring program in place through Colorado Springs Utilities and the USGS. This program includes benthic invertebrates at multiple sites from 1989 through 2004, and fish population data periodically through the same period.

South Platte River, Colorado – This HCS effluent-dependent stream has an abundance of aquatic biological monitoring data conducted by the Metro Wastewater Reclamation District. This monitoring program includes fish population and invertebrate communities from 1989 through the present, making it one of the most extensive aquatic biological databases available in the arid West.

1.3 AMBIENT WATER QUALITY-CRITERIA REVIEW SELECTION PROCESS AND DATABASE REVIEW

A total of five criteria were chosen for this evaluation, representing a range of robustness, modes of toxicity, and general criteria derivation issues. The criteria, along with a description of selection reasons, are:

Aluminum – Aluminum (EPA 1988) is an example of a criterion based on a very limited toxicity database, one that just barely meets the "eight-family rule" (described below). As such, it presents unique problems for the recalculation procedure. In addition, aluminum can be a metal of concern in streams throughout the arid West, given its ubiquitous presence in the clay soils common to this region. Many Western streams are listed as impaired due to aluminum, despite bioassessment evidence to the contrary.

Ammonia – This criterion (EPA 1999) was chosen for the project for a number of reasons. Firstly, it was one of the criteria evaluated in the ECE as a potential candidate for recalculation. Secondly, the mode of toxicity for ammonia is different than that for metals. Thirdly, this criterion has recently come under scrutiny by EPA as a result of newly published toxicity data, specifically on unionid clams. Lastly, EPA's final derivation of acute and chronic ammonia criteria were not directly based on standard EPA criteria calculations of final acute and final chronic values (Stephan et al. 1985). Ammonia would allow an analysis of how recalculation procedures work for irregularly derived criteria.

Copper – As with ammonia, copper (EPA 1985, 1996) was a criterion evaluated for the ECE. In addition, EPA recently produced a draft update to the copper criteria (EPA 2003), which incorporates the biotic ligand model (BLM) as a replacement to the hardness equation for derivation of site-specific copper standards. The validity of BLM predictions in very hard waters common to the arid West is also being evaluated as part of a separate AWWQRP project (PCWWM 2005a). The copper evaluation would thus facilitate analysis of the recalculation procedure for a BLM-adjusted toxicity database and build on the study currently being conducted for AWWQRP.

Diazinon - Analysis of diazinon, an organophosphate insecticide, provides an opportunity to aid in the development of AWQC that is presently in draft form (EPA 2000). Diazinon has been steadily gaining environmental significance in arid Western states due to its increasing presence in urban wastewater, where it has been suspect in numerous whole effluent toxicity (WET) testing failures. An analysis of diazinon provides an example of a contaminant with a modest sized database that presents toxicity values for many aquatic organisms with a wide range of sensitivities.

Zinc – Zinc is a common metal found throughout the West owing to the presence of mineralized soils in many locations. This metal also has a rather extensive toxicity database, so zinc represents the evaluation of the recalculation procedure for a criterion with a robust database.

Evaluating the recalculation procedure for these criteria began with a review of the criteria documents for technical accuracy and potential inclusion of new data. We reviewed five EPA AWQC documents, drafts, and updates to national toxicity database. Documents reviewed in this process include:

- Ambient Water Quality Criteria for Aluminum (EPA 1988),
- 1999 Update of Ambient Water Quality Criteria for Ammonia (EPA 1999),
- Ambient Water Quality Criteria for Copper-1984 (EPA 1985),
- 2003 Draft Update of Ambient Water Quality Criteria for Copper (EPA 2003),
- Draft Ambient Aquatic Life Water Quality Criteria Diazinon (EPA 2000),
- Ambient Water Quality Criteria for Zinc -1987 (EPA 1987), and
- 1995 Updates: Water Quality Criteria Documents for the Protection of Aquatic Life in Ambient Water (EPA 1996).

Our evaluation of these criteria was conducted in three phases – 1) review of the criteria documents for technical accuracy, 2) literature review to update the criteria toxicity databases, and 3) develop revised, updated national criteria. These three phases are outlined below and the results are summarized for each criterion under review in Chapters 3 through 7.

1.3.1 Step 1 – Technical Review of Criteria Documents

The first step of this process was a technical review of the most up-to-date EPA AWQC documents to determine if 1) suitable and correct data were included in national toxicity databases, and 2) EPA criteria development methods were followed for deriving AWQC. The EPA's *Guidelines for Deriving Numerical Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (Stephan et al. 1985); hereafter referred to as the 1985 Guidelines, provided details on the acceptable data and criteria derivation methods. Some general principles presented in the 1985 Guidelines include:

(1) Acute toxicity data must be available for species from a minimum of eight diverse and specific families. This minimum data requirement (MDR) is often referred to as the "eight-family rule," and includes

- the family Salmonidae,
- a second family in the class Osteichthyes,
- a third family in the phylum Chordata,
- a planktonic crustacean,

- a benthic crustacean,
- an insect,
- a family in a phylum other than Arthropoda or Chordata, and
- a family in any order of insect or any phylum not already represented.

(2) Precedence is given to measured toxicity values derived from flow-through tests when calculating species mean acute values (SMAVs), to the exclusion of test results with unmeasured values and/or from static tests. Geometric means of all SMAVs within a given genus are then calculated as genus mean acute values (GMAVs).

(3) If sensitivity to a contaminant is influenced by life stage, only the most sensitive life stage should be used in the SMAV or GMAV calculation.

(4) The FAV is the statistical estimation of the LC50 concentration for the theoretical 5th percentile most sensitive genus. The FAV is derived from the four GMAVs that have cumulative probabilities closest to 0.05, which is always the four most sensitive GMAVs when there are less than 59 genera in the database, and the total number of genera in the database. The FAV is divided by two to estimate an LC-low and obtain the criterion maximum concentration (CMC) (i.e., acute criterion, protective of nearly all species in the database).

(5) Chronic toxicity data must be available for at least three taxa. The chronic criterion is most often set by determining an appropriate acute-to-chronic ratio (ACR), which is the ratio of acutely toxic concentrations to the chronically toxic concentrations for the same species and then dividing the FAV by that ratio. However, if sufficient chronic data are available to meet the "eight-family rule," then the chronic value can be derived using the same statistical procedure as used for FAV derivation.

(6) When necessary, the acute and/or chronic criterion may be lowered to protect recreationally or commercially important species.

Any deviations from these general principals are clearly explained in the introduction of each individual chapter for each criterion.

1.3.2 Step 2 – Update of Toxicity Databases

The purpose of this step was to update the existing acute and chronic databases with scientific studies relevant to the derivation of AWQC for each chemical. Emphasis was placed on obtaining literature available since the most recently published database. However, literature published prior to these documents, but not cited by EPA, was reviewed as well to establish criteria based on the most complete and up-to-date database available.

1.3.3 Step 3 – Update of Criteria

Following the compilation of literature and development of the revised database, each acute and chronic AWQC was re-calculated using methods as described by the 1985 Guidelines. This process involves the calculation of SMAVs (the geometric mean of individual toxicity values) and genus mean acute values (GMAVs; the geometric mean of SMAVs when two or more species represent a genus), and ranking the GMAVs according to sensitivity. The database was reviewed for compliance with MDRs (i.e., the "eight family rule") and the criteria updated. These updated AWQC (Chapters 3-7) were subsequently used as the basis for evaluating the recalculation procedure (EPA 1994) in each of our case study EDWs (Chapter 9).

1.4 LITERATURE CITED

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2.0 DEVELOPMENT AND ANALYSES OF RESIDENT SPECIES LIST

2.1 OVERVIEW OF STUDY STREAM SEGMENTS, DATA SOURCES, AND RESIDENT SPECIES LIST DEVELOPMENT

Fish and invertebrate taxa lists were compiled from a literature review of the arid West effluent-dependent stream segments chosen for analysis in this study as outlined in Chapter 2. All stream segments included in the species list compilation were located downstream of wastewater treatment plants (WWTP) that discharge treated effluent into streams that would otherwise have low or no flow during most of the year (i.e., effluent-dependent stream segments).

Sites on the effluent-dependent portion of the Santa Ana River near San Bernardino, California, were used for the species list compilation, as well as sites on two effluent-dependent Santa Ana River tributaries, Chino Creek and San Timoteo Wash to provide additional information on effluent-dependent reaches in that river drainage. Three additional stream segments were located in southern Arizona, and included sites on the Santa Cruz River downstream of the Nogales International WWTP near Nogales, and sites on the Santa Cruz River downstream of the Roger Road WWTP near Tucson, as well as sites on the Salt River/Gila River downstream of the 91st Avenue WWTP near Phoenix. The final two stream segments used to represent effluent-dependent streams in the arid West were located in Colorado, and included the section of Fountain Creek downstream of the Las Vegas Avenue WWTP in Colorado Springs as well as the section of the South Platte River downstream of the Metro Wastewater Reclamation District discharge in Denver.

The data sources used to derive these taxa lists range in date from 1961 through 2005 - but the majority of the studies were conducted from the mid-80s through 2004. The sources of the data differ for each stream, but include studies conducted by federal and state agencies such as the USGS, EPA, U.S. Fish and Wildlife Service (USFWS), ADEQ, Arizona Game and Fish Department (AGFD), and Colorado Division of Wildlife (CDOW). The majority of the remaining sources for these taxa lists were studies conducted by private consulting companies or by personnel from the WWTP responsible for providing effluent to the streams. Brief descriptions of the sources of the biological data and timeline of collections used for each stream segment are presented in Appendix 1.

These fish and invertebrate taxa lists were compiled to determine what taxa currently occur or could potentially occur at the site for these effluent-dependent streams by incorporating both current monitoring and historical data - a necessary step in the recalculation process. If the site-specific list is sufficiently different from that in the database used to derive national WER, then water quality standards specific for the protection of the biota found in these stream segments could be developed. These taxonomic lists also provide the opportunity to detect any similarities or differences in fish and invertebrate species composition in effluent-dependent streams throughout the arid West.

According to the EPA's (1994) definition of the phrase "occur at this site," organisms considered to inhabit these streams include fish or invertebrates that are usually present at the site, either as year-round residents or as seasonal or intermittent residents. Their definition also extends to taxa not currently present in the selected stream if they were either present in the past at these sites, or are currently present in nearby bodies of water, and if they are expected to reside within the streams when conditions improve (EPA 1994).

Those taxa fitting the above description of what is considered to "occur at this site" can be further separated on the basis of whether these organisms are "resident" or "transient" species. Resident taxa would include organisms that use the stream habitat for functions such as reproduction, feeding, and/or refuge, which could include migratory species. Transient taxa, on the other hand, would include organisms that are passively moving through the site and do not use the stream habitat for above functions. A more detailed discussion on the importance of differentiating between transient and resident taxa for the purpose of determining site-specific water quality standards using the recalculation process is presented in Chapter 8. The species lists presented here generally focus on resident species rather than transient species that occur at these sites.

2.2 UPDATING TAXONOMIC NOMENCLATURE

As the fish and invertebrate taxa lists were being compiled, some nomenclature changes to the original data were necessary in order to keep the taxonomy of these groups current and to avoid inadvertent duplication of taxa within the lists. Fish genus names in parentheses in the table below indicate those for which a taxonomic change documented by the American Fisheries Society (Nelson et al. 2004) has occurred since the original data were reported in their respective AWQC documents. These scientific name changes occurred to the following fish species: the desert sucker (*Catostomus clarkii* – previously *Pantosteus clarkii*), red shiner (*Luxilus cornutus* – previously *Notropis cornutus*), loach dace (*Tiaroga cobitis* – previously *Rhinichthys cobitis*), blue tilapia (*Oreochromis aurea* – previously *Tilapia aurea*), Mossambique tilapia (*Oreochromis mossambicus* – previously *Tilapia mossambicus*), walleye (*Sander vitreus* – previously *Stizostedion vitreus*), and rainbow trout (*Oncorhynchus mykiss* – previously *Salmo gairdneri*).

As with the fish taxa list, some of the invertebrate taxa documented in the original studies required changes in nomenclature to ensure that the taxa list reflected current taxonomy. In several cases, the genus names were simply changed as new research revealed different taxonomic relationships within certain groups. The following genus names were altered from how they were recorded in the original AWQC to maintain current nomenclature (the previous names are in parenthesis): *Girardia* sp. (*Dugesia* sp., Smith 2001), *Gloiobdella elongata* (*Helobdella elongata*), *Ephemerella infrequens* (*E. dorothea*, Jacobus and McCafferty 2003), *Libellula subornata* (*Plathemis subornata*), *Stictotarsus* spp. (*Deronectes* spp.), *Laccophilus maculosus* (*L. decipiens*), *Hybomitrus minusculus* (*Tabanus minusculus*), *Caecidotea intermedius* (*Asellus intermedius*), *Ceratopysche cockerelli* (*Hydropsyche cockerelli*), *Ceratopsyche oslari* (*Hydropsyche oslari)*, and *Paralauterborniella* sp. (*Apedilum* sp.). In all cases that are not noted otherwise, these name changes were verified via ITIS (2005).

Three other changes were made to the original invertebrate data to offset differences in identification levels between the studies. For example, only one species of beetle belonging to the Hydroscaphidae family occurs in North America - *Hydroscapha natans* (ITIS 2005). Therefore, data from studies that identified these beetles at the family level were modified to reflect the species name as well. Similar changes to the original data were also made to reflect that the Asian clam *Corbicula fluminea* and the amphipod *Gammarus lacustris* are the single species within these genera that occur in these types of habitats in the arid West.

A few other minor changes were made to invertebrate nomenclature. The amphipod *Hyalella azteca* was alternately identified as *H. azteca* and *H. azteca* cx. in various studies. All *Hyalella* were designated as *H. azteca* in this effort to prevent any artificial inflation in taxa richness that would occur if a single species were listed twice. Also, two taxa were listed as a combination of genera due to the difficulty in accurately differentiating between the two: the gastropod *Physa/Physella* sp. and the dipteran *Limnophora/Lispoides* sp. These data were simplified to reflect only the first genus name. Additionally, some changes were necessary in the classification of taxa at the class, order, and family levels to maintain current taxonomic groupings.

2.3 COMPARISON OF RESIDENT FISH COMMUNITIES

A review of the literature available for the effluent-dependent stream sites chosen for this study produced a composite fish species list containing a total of 75 taxa (Table 2-1). While fish sampling has been performed on multiple occasions in San Timoteo Wash—which is a tributary to the Santa Ana River (see Appendix 1)—no fish were collected. Hence, to simplify the presentation, it is not included in Table 2-1.

Table 2-1
Fish Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River (including Chino Creek), Salt River/Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Family	Genus	Species	Common Name	Santa Ana River	Chino Creek (Santa Ana Basin)	Salt/Gila Rivers	Santa Cruz River		Fountain Creek	South Platte River
							Near Nogales	Near Tucson		
Atherinopsidae	*Menidia*	*beryllina*	Inland silverside	X						
Clupeidae	*Dorosoma*	*cepedianum*	Gizzard shad							X
		petenense	Threadfin shad			X				
Catostomidae	*Carpiodes*	*carpio*	River carpsucker							X
	Catostomus	*catostomus*	Longnose sucker						X	X
	(Pantosteus)	*clarkii*	Desert sucker			X	X			
		commersonii	White sucker						X	X
		fumeiventris	Owens sucker	X						
		insignis	Sonora sucker			X	X			
		latipinnis	Flannelmouth sucker			X				
		*santaanae**	Santa Ana sucker	X						
	Xyrauchen	*texanus**	Razorback sucker			X				
Cyprinidae	*Agosia*	*chrysogaster*	Longfin dace			X	X			
	Campostoma	*anomalum*	Stoneroller						X	X
	Carassius	*auratus*	Goldfish	X	X	X				X
	Cyprinella	*lutrensis*	Red shiner			X			X	X
	Cyprinus	*carpio*	Common carp	X	X	X			X	X
	Gila	*elegans**	Bonytail chub			X				
		intermedia	Gila chub			X				
		orcuttii	Arroya chub	X						
		robusta	Roundtail chub			X	X			
	Hybognathus	*hankinsoni*	Brassy minnow							X
		placitus	Plains minnow							X
	Luxilus (Notropis)	*cornutus*	Common shiner							X
	Meda	*fulgida*	Spike dace			X				
	Notropis	*dorsalis*	Bigmouth shiner							X
		hudsonia	Spottail shiner							X
		stramineus	Sand shiner						X	X
	Notemigonus	*crysoleucus*	Golden shiner			X				
	Phenacobius	*mirabilis*	Suckermouth minnow							X
	Phoxinus	*eos*	Northern redbelly dace							X
	Pimephales	*promelas*	Fathead minnow	X	X	X			X	X
	Plagopterus	*argentissimus*	Wound fin			X				
	Platygobio	*gracilis*	Flathead chub						X	
	Ptychocheilus	*lucius*	Colorado pikeminnow			X				
	Rhinichthys	*cataractae*	Longnose dace						X	X
	Tiaroga (Rhinichthys)	*cobitis**	Loach dace			X				
		osculus	Speckled dace			X				

Table 2-1 (Continued)
Fish Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River (including Chino Creek), Salt River/Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Family	Genus	Species	Common Name	Santa Ana River	Chino Creek (Santa Ana Basin)	Salt/Gila Rivers	Santa Cruz River		Fountain Creek	South Platte River
							Near Nogales	Near Tucson		
	Semotilus	*atromaculatus*	Creek chub						X	X
Cyprinodontidae	*Cyprinodon*	*macularius**	Desert pupfish			X				
Fundulidae	*Fundulus*	*sciadicus*	Plains topminnow							X
		zebrinus	Plains killifish						X	X
Poeciliidae	*Gambusia*	*affinis*	Mosquitofish	X	X	X	X	X		X
	Poecilia	sp.	Mollies			X				
		latipinna	Sailfin molly	X		X				
		mexicana	Shortfin molly			X				
	Poeciliopsis	*occidentalis**	Gila topminnow			X	X			
	Xiphophorus	*variatus*	Variable platyfish			X				
Gasterosteidae	*Culaea*	*inconstans*	Brook stickleback						X	X
Centrarchidae	*Lepomis*	*cyanellus*	Green sunfish	X	X	X	X	X	X	X
		gibbosus	Pumpkinseed							X
		humilis	Orangespotted sunfish							X
		macrochirus	Bluegill	X		X			X	X
		microlophus	Rehear sunfish			X				
	Micropterus	*dolomieu*	Smallmouth bass						X	X
		salmoides	Largemouth bass	X	X	X				X
	Pomoxis	*annularis*	White crappie							X
		nigromaculatus	Black crappie			X				X
Cichlidae	*Oreochromis (Tilapia)*	*aurea*	Blue tilapia			X				
		mossambicus	Mozambique tilapia	X		X				
	Tilapia	sp.	Tilapia	X		X				
		zillii	Redbelly tilapia			X				
Moronidae	*Morone*	*mississippienisi*	Yellow bass			X				
Percidae	*Etheostoma*	*cragini*	Arkansas darter						X	
		exile	Iowa darter							X
		nigrum	Johnny darter							X
	Perca	*flavescens*	Yellow perch							X
	Sander (Stizostedion)	*vitreus*	Walleye							X
Salmonidae	*Salmo*	*trutta*	Brown trout						X	
Cottidae	*Cottus*	*asper*	Prickly sculpin	X						
Ictaluridae	*Ameiurus*	*melas*	Black bullhead	X	X	X		X	X	X
		natalis	Yellow bullhead	X	X	X				
		nebulosus	Brown bullhead							X
	Ictalurus	*punctatus*	Channel catfish	X		X			X	X
	Pylodictis	*olivaris*	Flathead catfish			X				
			Number of Taxa	**18**	**8**	**40**	**7**	**3**	**19**	**38**
			Number of Native Taxa	**2**	**0**	**14**	**5**	**0**	**12**	**26**

* = Threatened or endangered species.

Over 97% of the fish taxa have been identified to the species level, with the remaining taxa identified at the genus level. The species list includes fish from a total of 15 families. The number of taxa collected at each stream segment varied from only three fish taxa (all non-native) collected from sites on the Santa Cruz River near Tucson to 40 fish taxa (14 native) historically collected from sites on the Salt/Gila Rivers. Note that of these native species, only one, the razorback sucker, has been reported from this site since 1985 (Appendix 1), presumably as a result of substantial habitat modifications over the years from Salt River Project dams and flow modifications. The tables in Appendix 1 document the fish species native to each stream.

The only fish species collected historically at all seven locations (including the Chino Creek tributary of the Santa Ana River) was the green sunfish, *Lepomis cyanellus*. This species may be native to some of the stream segments (e.g., the Colorado streams), but is non-native in most of the arid West. Two other fish species were collected at six of the seven sites: the introduced western mosquitofish, *Gambusia affinis*, which was collected at all sites, except Fountain Creek, and the black bullhead, *Ameiurus melas*, which was collected at all sites, except the Santa Cruz River below the Nogales WWTP. The common carp, *Cyprinus carpio*, and the fathead minnow, *Pimephales promelas*, were collected at five of the seven sites, but were not collected in the Santa Cruz River.

The remaining fish species included in Table 2-1 were more rare with respect to their distribution in these streams, with 46 taxa (61% of the total number of taxa) collected at only one of the six stream locations. An additional 18 taxa were collected at two locations only. Three locations had only two taxa.

Based on the differing geographic locations, native fish distributions, and pattern of fish introductions, species composition could be expected to differ somewhat between sites. Therefore, fish community composition was also compared at the genus level. The results were very similar to those seen at the species level of identification. Out of 45 total genera collected, *Lepomis* was again the only genus of fish found at all sites, with *Ameiurus* and *Gambusia* found at six of the seven locations. Five of the locations all had *Cyprinus, Micropterus, Catastomus*, and *Pimphales* collected, and four of the sites had *Ictalurus* and *Carassius* collected. As with the fish species, the majority of the genera (44%) were also unique to a single location.

2.3.1 Regional Comparisons of Fish Communities

Hierarchical cluster analysis, based on presence-absence fish data was conducted using the Number Cruncher Statistical System (NCSS) statistical software package (Hintze 2004). Cluster analysis was used to compare the species composition of the effluent-dependent streams to determine similarity in terms of the composition of their fish populations. All native and introduced fish species collected at each site were used in this analysis. Data from Chino Creek and the Santa Ana River were combined for this analysis, as Chino Creek is a tributary of the Santa Ana River, and all eight fish species collected in Chino Creek were also collected at mainstem Santa Ana River sites.

The resulting dendogram (Figure 2-1) shows the two most similar sites in terms of fish species composition to be the two Santa Cruz River sites. The Santa Ana River, followed by Fountain Creek and the South Platte River, are then linked to the cluster formed by those two sites. The fish taxa composition in the Salt/Gila Rivers was the most dissimilar from the other sites.

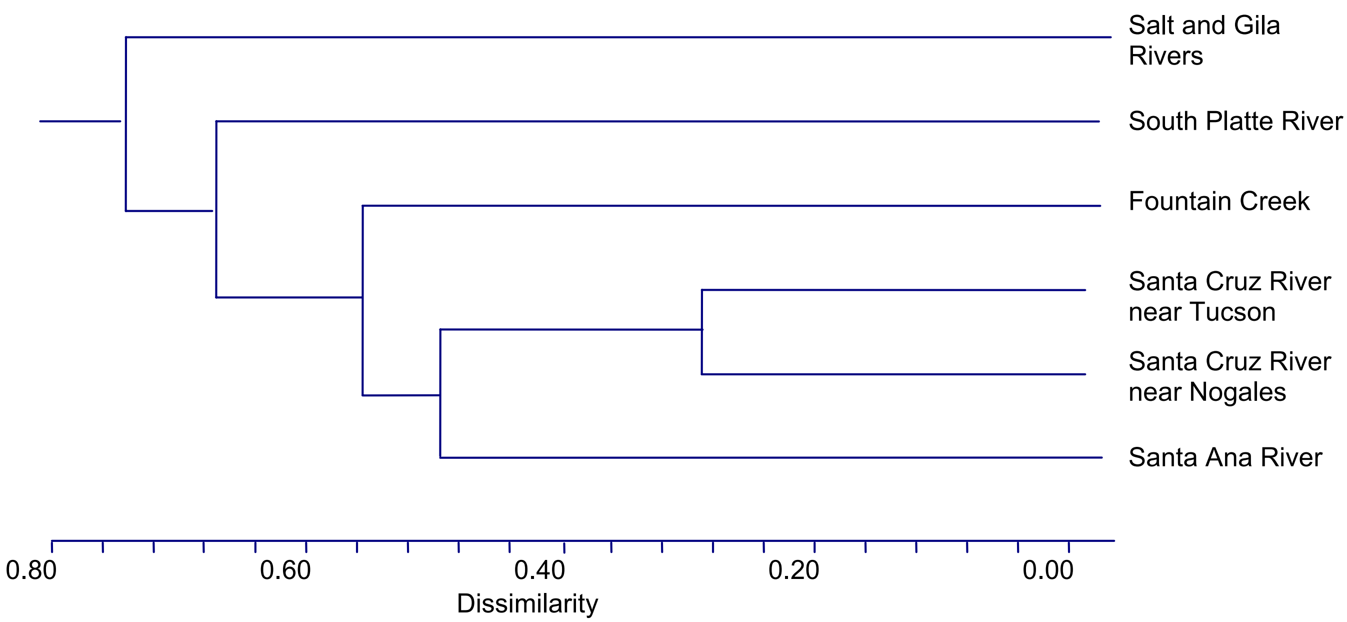

Figure 2-1
Dendogram Grouping of Arid West Effluent-Dependent Streams
Based on Fish Species Presence/Absence

The order in which the streams group together on the dendogram suggests that the number of fish taxa collected at each stream, in addition to similarities in species composition, is influencing the cluster analysis results. For example, the two most similar stream segments, in terms of their fish communities, are also the streams with the lowest number of fish taxa collected, while the streams least similar to the others, the Salt/Gila Rivers, had the highest number of fish taxa collected. Additional cluster analysis using the genus level for fish taxa resulted in similar groupings to those seen on Figure 2-1.

A second cluster analysis was performed using only the native fish species found at each stream. The resulting dendogram (Figure 2-2) presents a significantly different pattern than that based on both introduced and native fish species (Figure 2-1). Note that two stream segments—the Santa Cruz River near Tucson and Chino Creek tributary to the Santa Ana River—did not have any native fish collected and, therefore, could not be included in this second cluster analysis.

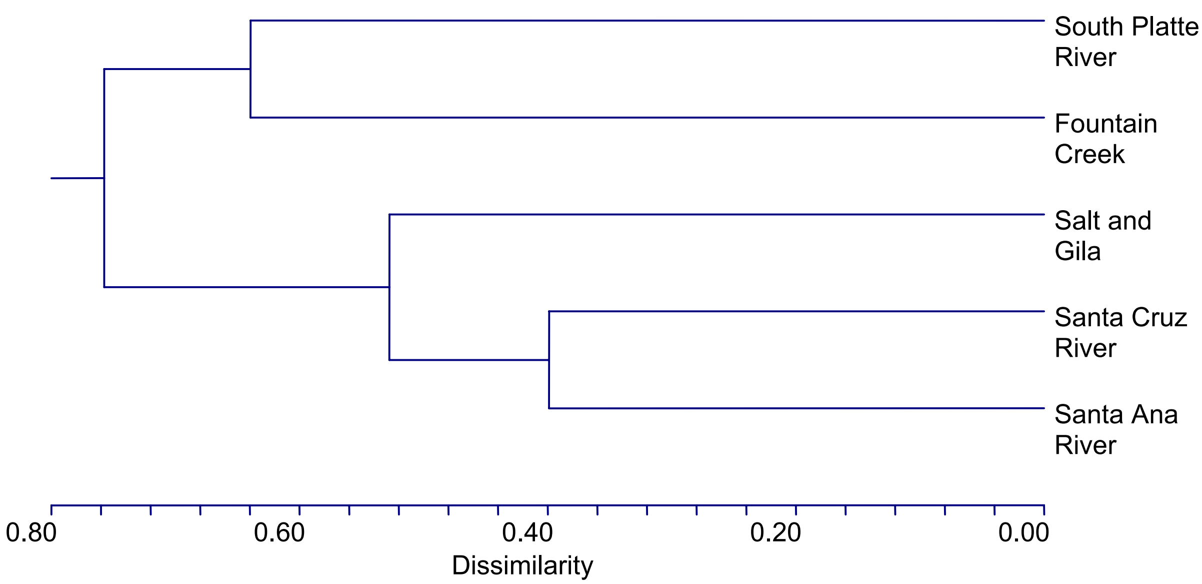

Figure 2-2
Dendogram Grouping Arid West Effluent-Dependent Streams Based On Native Fish Species Presence-Absence

For the remainder of the streams, the two that were most similar in terms of native fish species composition were the Santa Cruz River near Nogales and the Santa Ana River. The Salt/Gila Rivers then grouped with that cluster – basically representing the southwestern streams in the study. The South Platte River and Fountain Creek formed a separate cluster, indicating that the native fish communities found at those two sites were relatively dissimilar to communities at the other three sites. These groupings were less influenced by fish taxa richness and more influenced by geographic location, as expected due to historic/biogeographical barriers (PCWMD 2002), representing the southwestern U.S. sites and the sites on the high plains.

2.4 COMPARISON OF RESIDENT INVERTEBRATE COMMUNITIES

A review of the available literature for the effluent-dependent streams chosen for this study produced a composite invertebrate species list containing a total of 561 taxa (Table 2-2). Invertebrates were identified at varying taxonomic levels in these studies, somewhat complicating comparisons between studies and between sites. Of the taxa on the list, 31% were identified to the species level, 53% identified to the genus level, and the the remaining 16% identified to the family level or higher.

Taxa belonging to 119 families from 31 orders were collected at one or more of the locations. The total number of taxa collected over the period of record used in this analysis for each stream varied from 41 taxa collected from the Santa Cruz River near Tucson to 282 taxa collected from the Santa Ana River.

As Chino Creek and San Timoteo Wash are both tributaries of the Santa Ana River, the data from these creeks were included in the development of the list of resident species in the Santa Ana River. We believe this is valid since the invertebrate community composition was highly similar between the tributaries and the mainstem Santa Ana River - 80% and 88% of the taxa collected in Chino Creek and San Timoteo Wash, respectively, were also collected in the Santa Ana River. Therefore, combining the tributary data with the mainstem data led to little loss of information (in fact, potentially increased the list of potentially resident species) and simplified results of subsequent analyses.

The only invertebrate identified at the species level that was found at all sites was the midge, *Cricotopus bicinctus*. Additionally, the midge genus *Chironomus* was found at all sites, as well as several families or classes of invertebrates, including the worms, *Oligochaeta*, *Naididae*, and *Tubificidae*, and the aquatic insects, *Baetidae*, *Coenagrionidae*, *Corixidae*, *Elmidae*, *Hydrophilidae*, *Diptera*, *Chironomidae*, *Psychodidae*, and *Simuliidae*.

Other invertebrate genera found in all stream locations, except the Santa Cruz River near Tucson, include the snail *Physa* and a number of aquatic insects, *Callibaetis*, *Argia*, *Rheotanytarsus*, *Cricotopus/Orthocladius*, and *Culex*. With few exceptions, the families common to most study streams were generally collected from all locations, except the Santa Cruz River near Tucson or the Gila and Salt Rivers. The great majority of invertebrates, 312 taxa (56% of the total number of taxa), were only collected at a single site. Additional 108 and 74 taxa were found at two and three of the sites, respectively.

Table 2-2
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin				Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson		
Bryozoa			X							
Cnidaria Hydrozoa Hydroida									X	
Hydridae	*Hydra*	*americana*						X		
Nematoda						X	X		X	X
Adenophorea Dorylaimida Dorylaimidae	*Dorylaimus*	sp.					X			
Mermithida Mermithidae							X			
Nematomorpha									X	
Nemertea			X					X	X	
Enopla Hoplonemertea Tetrastemmatidae	*Prostoma*	sp.	X		X					
Platyhelminthes Turbellaria			X	X		X			X	X
Tricladida Planariidae	*Girardia (Dugesia)*	sp.	X	X					X	X
		dorotocephala	X							
		tigrina							X	X
	Polycelis	*coronata*							X	
Macrostomida Macrostomidae	*Macrostomum*	sp.								X
Annelida Clitellata (Subclass Hirudinae)						X	X		X	X
Arhynchobdellidae Erpobdellidae							X			X
	Dina	*dubia*								X
	Erpobdella	*punctata*		X			X		X	X
	Mooreobdella	*fervida*	X							
		microstoma	X	X					X	X

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

			Santa Ana Basin				Santa Cruz River			
Phylum/Class Order/Family	**Genus**	**Species**	**Santa Ana River**	**Chino Creek**	**San Timoteo Wash**	**Salt/Gila Rivers**	**Near Nogales**	**Near Tucson**	**Fountain Creek**	**South Platte River**
Rhynchobdellida Glossiphoniidae							X			X
	Gloiobdella (Helobdella)	*elongata*								X
	Glossiphonia	*complanata*		X						
	Helobdella	*fusca*		X						X
		stagnalis							X	X
Clitellata (Subclass Olighoaeta)			X		X	X	X	X	X	X
Branchiobdellida Branchiobdellidae			X							
Haplotaxida			X							
Enchytraeidae			X				X		X	X
Lumbricidae				X			X			
	Eiseniella	*tetraedra*	X						X	X
Naididae			X	X	X	X	X	X		X
	Dero	sp.					X			
	Homochaeta	*naidini*	X	X					X	
	Nais	sp.	X						X	X
		behningi							X	
		bretscheri							X	X
		communis					X		X	
		Communis/ variabilis							X	
		elinguis							X	
		pseudobtusa							X	
	Ophidonais	sp.							X	
		serpentina	X				X		X	X
	Paranais	sp.	X							
	Pristina	sp.	X				X		X	X
		longiseta	X							
	Slavina	sp.	X							
	Stephensoniana	*tandyi*	X						X	
	Uncinais	*uncinata*							X	X
Tubificidae			X	X	X	X	X	X	X	X
	Aulodrilus	*americanus*	X							
	Ilyodrilus/Tubifex	sp.							X	X
	*Isochaetides**	sp.								X
	Limnodrilus		X						X	X
		hoffmeisteri							X	X
		udekemianus							X	
	Tubifex	*tubifex*							X	

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin				Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson		
Lumbriculida Lumbriculidae			X				X		X	
	Eclipidrilus/ Rhynchelmis	sp.							X	
	Lumbriculus	*variegatus*	X	X					X	
	Rhynchelmis	sp.							X	
Polychaeta Aeolosomatida Aeolosomatidae	*Aeolosoma*	sp.	X							
Mollusca Gastropoda			X		X	X	X			X
Basommatophora Ancylidae	*Ferrissia*	sp.	X	X						X
		rivularis		X						
Lymnaeidae							X			
	Fossaria	sp.	X						X	
	Stagnicola	sp.	X							
Physidae							X		X	
	Physa	sp.	X	X	X	X	X		X	X
	Physella	sp.	X	X	X					X
Planorbidae	*Gyraulus*	sp.	X	X						X
	Menetus	sp.	X							
Bivalvia			X							
Veneroida Corbidulidae			X							
	Corbicula	*fluminea*	X							X
Pisidiidae	*Sphaerium*	sp.	X							
Arthropoda Arachnida Acari			X			X	X			X
Eylaidae	*Eylais*	sp.					X			
Hygrobatidae	*Atractides*	sp.					X			X
Lebertiidae	*Lebertia*	sp.					X			
Limnesiidae	*Limnesia*	sp.					X			
	Tyrrellia	sp.					X		X	
Sperchontidae	*Sperchon*	sp.			X		X			
	Sperchon/ Sperchonopsis	sp.	X						X	X
Unionicolidae	*Neumania*	sp.		X						
Branchiopoda Diplostraca**			X			X		X		X
Bosminidae	*Bosmina*	sp.						X		
Chydoridae	*Alona*	*costata*				X				
	Chydorus	*sphaericus*				X				
	Kurzia	*latissima*				X				

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin				Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson		
Daphnidae	*Ceriodaphnia*	sp.				X				
	Daphnia	sp.					X	X		X
Macrothricidae	*Macrothrix*	*rosea*				X				
Moinidae	*Moina*	sp.				X	X	X		
		micrurus				X				
Malacostraca Amphipoda						X			X	
Gammaridae	*Gammarus*	*lacustris*	X						X	X
Hyalellidae	*Hyalella*	*azteca*	X	X					X	X
Decapoda Astacidae	*Pacifastacus*	*leniusculus*	X	X						
Cambaridae										X
	Orconectes	sp.							X	
	Procambarus	*clarkii*	X	X						
Isopoda									X	X
Asellidae	*Asellus*	sp.							X	X
	Caecidotea	sp.	X						X	X
		communis							X	
	(Asellus)	*intermedius*								X
Insecta ollembola			X			X	X	X	X	
Entomobryidae	*Willowsia*	sp.	X							
Hypogastruridae	*Hypogastrura*	sp.	X						X	
	Odontella	sp.					X			
Isotomidae	*Isotomurus*	sp.	X							
		palustris	X						X	
		tricolor	X							
Ephemeroptera			X							X
Ameletidae	*Ameletus*	sp.							X	
Baetidae			X			X		X	X	X
	Acentrella	*insignificans*							X	X
	Apobaetis	*indeprensus*	X							
	Baetis	sp.	X				X		X	X
		sp. B								X
		bicaudatus	X	X	X				X	X
		magnus							X	
		tricaudatus	X	X	X				X	X
	Callibaetis	sp.	X			X	X		X	X
		californicus	X							
		pictus	X							

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin			Salt/Gila Rivers	Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash		Near Nogales	Near Tucson		
	Camelobaetidius	sp.	X							
		similis	X							
		warreni	X	X						
	Cloeodes	*macrolamellus*	X							
	Fallceon	*quilleri*	X	X			X		X	X
	Labiobaetis	sp.	X	X					X	
	Paracloeodes	sp.	X				X		X	
Caenidae						X				
	Caenis	sp.	X							X
		amica	X							
Ephemerellidae	*Ephemerella*	*inermis*							X	
		dorothea (infrequens)							X	
Heptageniidae			X						X	X
	Cinygmula	sp.							X	
	Epeorus	sp.								X
	Heptagenia	sp.							X	X
Leptophlebiidae			X						X	
	Paraleptophlebia	sp.	X						X	
Siphlonuridae	*Siphlonurus*	sp.							X	
Tricorythidae	*Leptohyphes*	sp.					X			
	Tricorythodes	sp.	X	X			X		X	X
		minutus					X		X	X
Odonata (Anisoptera)			X							
Aeshnidae	*Aeshna*	sp.							X	
	Anax	*junius*								X
Corduliidae	*Neurocordulia*	sp.	X							
Gomphidae			X				X		X	
	Erpetogomphus	sp.					X			
	Ophiogomphus	sp.					X		X	X
		severus							X	X
	Progomphus	sp.	X				X			
		borealis	X				X			
Libellulidae							X			
	Brechmorhoga	*mendax*	X				X		X	
	Libellula (Plathemis)	*subornata*								X
	Paltothemis	sp.			X					
		lineatipes	X				X			
	Pantala	*hymenaea*								X

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

			Santa Ana Basin				Santa Cruz River			
Phylum/Class Order/Family	Genus	Species	Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson	Fountain Creek	South Platte River
Odonata (Zygoptera)			X			X				
Calopterygidae			X			X	X			
	Calopteryx	sp.					X			
	Hetaerina	sp.	X				X			X
		americana	X						X	
Coenagrionidae			X	X	X		X		X	X
	Amphiagrion	sp.								X
	Argia	sp.	X	X	X	X	X		X	X
		alberta	X							
		sedula		X						
		vivida	X		X					
	Coenagrion	sp.					X			
		resolutum	X				X			
	Coenagrion/ Enallagma	sp.	X				X		X	X
	Enallagma	sp.	X	X		X				X
	Hesperagrion	sp.					X			
		heterodoxum					X			
	Ischnura	sp.	X			X	X	X		
	Zoniagrion	sp.	X				X			
Lestidae	*Archilestes*	sp.				X				
Plecoptera										X
Capniidae									X	
Chloroperlidae									X	
	Alloperla	sp.							X	
	Sweltsa	sp.	X					X	X	
	Triznaka	sp.							X	
Nemouridae										X
	Amphinemura	sp.							X	
	Zapada	*cinctipes*	X							
Perlodidae									X	
	Isoperla	sp.							X	
		fulva							X	
Pteronarcyidae	*Pteronarcella*	*badia*							X	
Taeniopterygidae									X	
	Taenionema	sp.	X							
Hemiptera			X				X	X		
Belostomatidae						X	X			
	Abedus		X				X			
		sp. 2					X			
		herberti					X			
	Belostoma		X	X				X		
		flumineum	X				X			

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin				Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson		
Corixidae			X			X	X	X	X	
	Callicorixa	sp.							X	
	Cenocorixa	sp.							X	
	Corisella	sp.	X	X						X
		decolor	X							
		edulis					X			
		inscripta	X	X						
	Graptocorixa	sp.					X			
		abdominalis					X			
		serrulata					X			
	Hesperocorixa	sp.	X							
	Pseudocorixa	*beameri*						X		
	Sigara		X						X	
		alternata	X							
	Tenagobia	sp.		X						
	Trichocorixa	sp.	X	X					X	
		calva	X							
Gelastocoridae	*Gelastocoris*	sp.	X	X						
Gerridae			X							
	Gerris	sp.	X					X	X	X
	Trepobates	sp.	X	X						
Hebridae	*Hebrus*	sp.	X							
	Merragata	*hebroides*	X							
Macroveliidae	*Macrovelia*	sp.	X	X					X	
Mesoveliidae	*Mesovelia*	sp.	X							
		mulsanti					X		X	
Naucoridae	*Ambrysus*	sp.	X				X		X	
Nepidae	*Ranatra*	sp.					X			
		quadridentata					X			
Notonectidae	*Notonecta*	sp.	X				X			X
Ochteridae	*Ochterus*	sp.							X	
Saldidae	*Salda*	sp.	X	X						
		buenoi		X						
	Saldula	sp.	X							
Veliidae			X	X		X				
	Microvelia	sp.	X				X		X	X
	Rhagovelia	sp.	X	X			X		X	
		distincta	X							
Megaloptera							X	X		
Corydalidae							X			
	Corydalus	sp.					X			
Hymenoptera			X							

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin: Santa Ana River	Santa Ana Basin: Chino Creek	Santa Ana Basin: San Timoteo Wash	Santa Ana Basin: Salt/Gila Rivers	Santa Cruz River: Near Nogales	Santa Cruz River: Near Tucson	Fountain Creek	South Platte River
Coleoptera								X		
Carabidae										X
Chrysomelidae	*Donacia*	sp.							X	
Curculionidae			X				X		X	
	Lixus	sp.		X						
Dryopidae			X				X			
	Helichus	sp.	X						X	
		suturalis	X				X			
	Postelichus	sp.	X				X		X	
		confluentus					X			
		immsi	X				X			
		productus	X							
Dytiscidae							X			
	Agabus	sp.					X		X	X
		semivittatus					X			
	Agabinus	sp.	X							
	Copelatus	*chevrolati*					X			
	Desmopachria	*mexicana*					X			
	Dytiscus	sp.	X						X	
	Hydaticus	sp.	X							
	Hydroporus	sp.	X							
		occidentalis	X							
	Hydrovatus	sp.	X							
	Ilybius	sp.							X	
	Laccophilus	sp.	X	X			X		X	
		fasciatus					X			
		maculosus (decipiens)	X				X		X	
		mexicanus					X			
		pictus					X			
		salvini					X			
	Liodessus	sp.	X							
		affinis cx.					X			
	Liodessus/ Neoclypeodytes	sp.	X							
	Oreodytes	sp.							X	
	Rhantus	sp.	X				X			
		gutticollis					X		X	
	Stictotarsus (Deronectes)	sp.					X			
		aequinoctialis					X			
		corpulentus					X			
		funereus	X	X						
		roffi					X			

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

			Santa Ana Basin				Santa Cruz River			
Phylum/Class Order/Family	Genus	Species	Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson	Fountain Creek	South Platte River
	Thermonectus	*nigrofasciatus*					X			
	Uvarus	sp.	X							
		amandus					X			
Elmidae						X				X
	Dubiraphia	sp.								X
	Heterelmis	*glaber*						X		
	Heterlimnius	sp.								X
		corpulentus	X						X	
	Macronychus	sp.	X							
	Microcylloepus	sp.	X				X			
		pusillus	X				X			
	Neoelmis	sp.					X			
	Optioservus	sp.							X	X
		divergens	X							
		quadrimaculatus						X		
	Phanocerus	sp.							X	
	Zaitzevia	*parvula*							X	X
Georyssidae	*Georyssus*	sp.	X							
Haliplidae							X			
	Haliplus	sp.	X							
	Peltodytes	sp.	X				X		X	
		callosus	X							
Helophoridae	*Helophorus*	sp.	X				X		X	
Hydraenidae	*Gymnochthebius*	*fossatus*					X			
	Ochthebius	sp.		X			X		X	
Hydrophilidae						X	X			
	Anacaena	sp.	X							
	Berosus	sp.							X	X
		peregrinus					X			
	Cheatarthria	sp.	X				X			
	Enochrus	sp.	X	X			X		X	
		carinatus					X			
		pectoralis	X							
		pygmaeus					X			
	Helochares		X							
		sp. 2					X			
		normatus					X			
	Hydrobius	sp.							X	
	Hydrophilus	*triangularis*								X
	Laccobius	sp.	X		X				X	
		mexicanus					X			

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

			Santa Ana Basin				Santa Cruz River			
Phylum/Class Order/Family	Genus	Species	Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson	Fountain Creek	South Platte River
	Paracymus	sp.	X						X	
	Tropisternus	sp.	X	X			X	X	X	
		sp. 3					X			
		ellipticus	X				X			
		lateralis					X		X	
Hydroscaphidae	*Hydroscapha*	*natans*	X					X		
Lampyridae										X
Noteridae	*Pronoterus*	sp.						X		
Staphylinidae										X
	Stenus	sp.	X	X						
Lepidoptera Noctuidae	*Bellura*	sp.	X							
Pyralidae			X						X	
	Crambus	sp.	X							
	Parapoynx	sp.	X							
	Petrophila	sp.	X	X						X
Trichoptera								X		
Brachycentridae									X	
	Brachycentrus	*americanus*							X	
		occidentalis								X
Glossosomatidae			X							
Helicopsychidae	*Helicopsyche*	sp.	X							X
		borealis								X
Hydropsychidae			X	X	X					
	Ceratopsyche	*bronta*								X
	(Hydropsyche)	*cockerelli*							X	
		oslari							X	
		slossonae								X
	Cheumatopsyche	sp.	X						X	X
	Hydropsyche	sp.	X	X	X				X	X
		californica	X	X						
		occidentalis	X							X
Hydroptilidae			X			X				X
	Agraylea	sp.	X	X						
	Hydroptila	sp.	X	X	X				X	X
		icona	X							
		pecos								X
	Leucotrichia	sp.							X	X
		pictipes								X
	Ochrotrichia	sp.		X						X
	Orthotrichia	sp.	X							
	Oxyethira	sp.	X							

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin				Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson		
Leptoceridae							X			
	Nectopsyche	sp.							X	
	Oecetis	sp.								X
Limnephilidae									X	
	Hesperophylax	sp.							X	
	Limnephilus/ Philarctus	sp.							X	
Philopotamidae	*Chimarra*	*utahensis*								X
	Wormaldia	sp.	X							
Rhyacophilidae	*Rhyacophila*	sp.							X	
		brunnea gr.	X							
		sibirica gr.	X							
Diptera			X	X			X		X	X
Ceratopogonidae			X	X			X	X	X	X
	Ceratopogonidae genus 1					X				
	Ceratopogonidae genus 2					X				
	Atrichopogon	sp.					X		X	
	Bezzia	sp.	X							
	Bezzia/ Palpomyia	sp.								X
	Ceratopogon	sp.							X	
	Culicoides	sp.							X	
	Dasyhelea	sp.	X				X		X	
	Forcipomyia	sp.					X		X	
	Mallochohelia	sp.	X	X			X		X	
	Palpomyia	sp.								X
	Palpomyia cx.	sp.							X	
	Sphaeromias	sp.					X			
Chaoboridae	*Chaoborus*	sp.		X			X			X
Chironomidae			X	X	X	X	X	X	X	X
Subfamily: Chironominae			X		X	X	X	X		X
	Chironomus	sp.	X	X	X	X	X	X	X	X
	Cladotanytarsus	sp.	X							
	Cryptochironomus	sp.	X	X			X		X	X
	Demicryptochironomus	sp.	X							
	Dicrotendipes	sp.	X	X			X		X	X
		fumidus								X
	Einfeldia	sp.	X		X				X	X

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin				Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson		
	Endochironomus	sp.		X			X			X
	Glyptotendipes	sp.	X	X					X	X
		amplus								X
	Goeldichironomus	sp.					X			
	Lauterborniella	sp.					X			X
	Microchironomus	sp.								X
	Micropsectra	sp.	X						X	X
	Micropsectra/ Tanytarsus	sp.	X							
	Microtendipes	sp.	X	X			X		X	X
	Nilothauma	sp.	X							
	Parachironomus	sp.	X	X			X			X
	Paracladopelma	sp.	X						X	
	Paralauterborniella (Apedilum)	sp.	X						X	
	Paratanytarsus	sp.	X	X					X	X
	Paratendipes	sp.							X	
	Phaenopsectra	sp.		X			X		X	X
	Polypedilum	sp.	X	X			X		X	X
		convictum gr.								X
		fallax gr.							X	
		illinoense gr.								X
	Pseudochironomus	sp.	X	X			X			X
	Rheotanytarsus	sp.	X	X		X	X		X	X
	Saetheria	sp.	X		X		X		X	X
	Stempellinella	sp.	X							
	Stictochironomus	sp.	X				X		X	
	Tanytarsus	sp.	X	X	X		X		X	X
	Tribelos	sp.							X	
Subfamily: Diamesinae	*Diamesa*	sp.					X		X	X
	Pagastia	sp.							X	
	Potthastia	sp.							X	
Subfamily: Orthocladinae			X	X	X		X		X	X
	Brillia	sp.			X				X	X
	Cardiocladius	sp.	X	X					X	X
	Chaetocladius	sp.		X					X	
	Corynoneura	sp.	X	X			X		X	

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin				Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson		
	Cricotopus	sp.	X	X	X		X		X	X
		bicinctus gr.	X		X	X	X	X	X	X
		cylindraceus								X
		festivellus	X							X
		fuscus								X
		nostocicola	X		X					X
		tremulus	X	X	X					X
		trifascia	X						X	X
	Cricotopus (Isocladius)	sp.	X							
		sylvestris	X	X						X
	Cricotopus/ Orthocladius	sp.	X	X	X	X	X		X	X
	Doncricotopus	sp.	X	X						
	Endotribelos	sp.	X				X			
		hesperium	X							
	Eukiefferiella	sp.	X				X	X		X
		brehmi gr.		X						
	Claripennis gr. sp. A								X	
		devonica								X
		gracei gr.		X						
		pseudomontana								X
	Euryhapsis	sp.					X			
	Heleniella	sp.			X				X	
	Heterotrissocladius	sp.	X						X	
	Hydrobaenus	sp.	X				X		X	X
	Limnophyes	sp.					X		X	X
	Mesosmittia	sp.					X			
	Nanocladius	sp.	X				X		X	X
	Orthocladius	sp.	X	X	X				X	X
	Orthocladius (Euorthocladius)	sp.	X						X	X
	Paracricotopus	sp.	X							
	Parakiefferiella	sp.							X	X
	Parametriocnemus	sp.		X			X		X	X
	Parorthocladius	sp.					X			
	Paraphaenocladius	sp.	X				X		X	X
	Pseudosmittia	sp.					X		X	
	Rheocricotopus	sp.	X	X			X		X	X
	Rheosmittia	sp.					X			
	Smittia	sp.							X	

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

			Santa Ana Basin				Santa Cruz River			
Phylum/Class Order/Family	Genus	Species	Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson	Fountain Creek	South Platte River
	Synorthocladius	sp.								X
	Thienemanniella	sp.	X		X		X		X	X
	Tvetenia	sp.	X						X	X
Subfamily: Prodiamesinae	*Odontomesa*	sp.							X	
	Prodiamesa	sp.							X	
Subfamily: Tanypodinae			X				X			X
	Ablabesmyia	sp.	X	X			X		X	
	Alotanypus	sp.							X	
	*Apsectrotanypus**	sp.							X	
	Brundiniella	sp.	X	X						
	Conchapelopia/ Thienemannmyia gr.	sp.							X	X
	Labrundinia	sp.	X				X			
	Larsia	sp.	X				X		X	X
	Natarsia	sp.	X							
	Paramerina	sp.	X				X		X	
	Pentaneura	sp.	X	X	X		X			X
	Procladius	sp.					X		X	X
	Radotanypus	sp.							X	
	Tanypus	sp.	X							
	Thienemannimyia gr.	sp.	X	X	X		X		X	X
	Zavrelimyia	sp.	X	X						
Culicidae							X			
	Aedes	sp.					X			X
	Anopheles	sp.					X			
	Culex	sp.	X	X			X	X	X	X
Dixidae	*Dixella*	sp.					X		X	
Dolichopodidae			X				X	X	X	X
	Hydrophorus	*agalma*							X	
Empididae			X							
	Chelifera	sp.							X	X
	Clinocera	sp.							X	
	Hemerodromia	sp.	X	X			X		X	X
	Neoplasta	sp.							X	
	Oreogeton	sp.	X							
	Rhamphomyia	sp.		X						
Ephydridae			X		X		X		X	X
	Ephydra	sp.	X				X			
	Hydrellia	sp.					X			
	Scatella	sp.							X	

Table 2-2 (Continued)
Invertebrate Taxa Reported from Studies of Effluent-Dependent Segments of the Santa Ana River, Chino Creek, San Timoteo Wash, Salt River, Gila River, Santa Cruz River, Fountain Creek, and the South Platte River

Phylum/Class Order/Family	Genus	Species	Santa Ana Basin				Santa Cruz River		Fountain Creek	South Platte River
			Santa Ana River	Chino Creek	San Timoteo Wash	Salt/Gila Rivers	Near Nogales	Near Tucson		
Muscidae			X			X	X		X	X
	Limnophora	sp.	X	X			X		X	X
Psychodidae			X			X	X	X	X	X
	Maruina	sp.	X							
	Pericoma	sp.	X	X	X		X	X	X	
	Pericoma/ Telmatoscopus	sp.						X		
	Psychoda	sp.					X	X	X	X
Ptychopteridae	*Bittacomorphella*	sp.								X
Sarcophagidae										X
Simuliidae			X		X	X	X	X	X	X
	Prosimulium	sp.							X	X
	Simulium	sp.	X	X	X		X		X	X
		arcticum							X	
		vittatum cx.					X		X	X
Stratiomyidae					X					X
	Allognosta	sp.							X	
	Caloparyphus	sp.	X		X		X		X	X
	Euparyphus	sp.	X	X			X		X	
	Nemotelus	sp.					X		X	
	Odontomyia	sp.	X	X			X			
	Stratiomys	sp.					X			
Syrphidae								X		
Tabanidae									X	
	Hybomitrus (Tabanus)	*minusculus*	X							
	Tabanus	sp.					X	X	X	
		punctifer	X							
Tanyderidae									X	
	Protanyderus	sp.							X	
		margarita							X	
Tipulidae			X				X		X	
	Antocha	sp.	X						X	
	Dicranota	sp.	X							
	Erioptera	sp.	X				X		X	
	Gonomyia	sp.	X						X	X
	Hexatoma	sp.							X	
	Limonia	sp.	X				X		X	
	Ormosia	sp.						X	X	
	Rhabdomastix	sp.								X
	Tipula	sp.	X				X		X	X
Total Number of Invertebrate Taxa			**282**	**101**	**42**	**44**	**211**	**41**	**253**	**192**

NOTES:
*Identification was uncertain in the original documentation.
***Diplostracans* (cladocerans) are generally considered to be transient organisms in lotic systems.

We should note that we did include cladocerans in this listing, since they were collected from some of the stream sites. Cladocerans are generally considered to be transient organisms in lotic systems (Hynes 2001) and were likely present in these effluent-dependent sites as a result of outflows from wastewater treatment ponds/lagoons (a phenomenon we have observed in stream systems throughout the west).

As with the fish data, hierarchical cluster analysis was used to compare the invertebrate community at the arid West effluent-dependent study sites. Figure 2-3 shows the dendogram resulting from the cluster analysis of all invertebrate taxa at these sites as identified to the family level or higher. Based on this dendogram, taxa composition of sites on the Salt/Gila Rivers and the Santa Cruz River near Tucson are the most similar in taxa composition and are clustered by themselves. The Santa Cruz River near Nogales and Fountain Creek form the base of the second cluster, with the South Platte River and the Santa Ana River also grouped with these two sites.

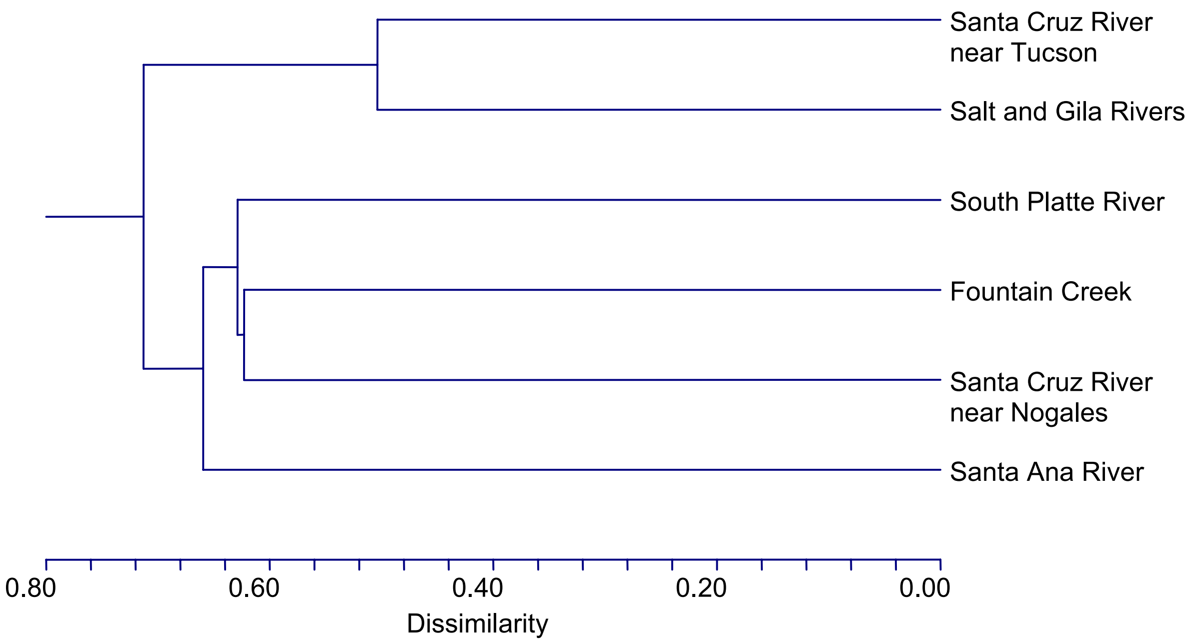

Figure 2-3
Dendogram Grouping Arid West Effluent-Dependent Streams
Based on Invertebrate Family Presence-Absence

As with the fish cluster analysis using all fish taxa, the grouping of the invertebrate communities in these streams seems to be highly influenced by the number of invertebrate families collected at each location and the similarity in the families found at the sites. The two most similar streams, the Santa Cruz River near Tucson and the Gila and Salt Rivers, both had 33 invertebrate taxa identified at the family level or higher, while the remaining streams forming the second cluster had between 67 and 98 invertebrate taxa identified at the family level or higher.

Various other cluster analyses were attempted using the invertebrate data, including analyses at the genus and species level of identification. The dendogram on Figure 2-4 resulted from a cluster analysis using invertebrate genus level data only from the most taxonomically rich class, Insecta (81% of all taxa listed in Table 2-2 are in the class Insecta). In this dendogram (Figure 2-4), the Salt/Gila Rivers and the Santa Cruz River near Tucson were again the most similar streams with respect to their invertebrate community composition, as well as being the streams with the lowest number of insect taxa collected (25 and 32 taxa, respectively, when identified at the genus level). However, the rest of the streams did not form a separate cluster as they did on Figure 2-3.

Instead, the South Platte River was then grouped with the cluster formed by the Salt/Gila Rivers and the Santa Cruz River near Tucson, followed in order by the grouping of the Santa Cruz River near Nogales, and Fountain Creek, with the Santa Ana River the last to join the cluster. As was seen previously, the number of taxa still seems to have strongly influenced the arrangement of the streams on the dendogram, with the stream most dissimilar to the others (the Santa Ana River) also having the highest number of taxa collected in the class Insecta. Notably, the regional clusters observed with native fish were not consistent with those observed with invertebrates.

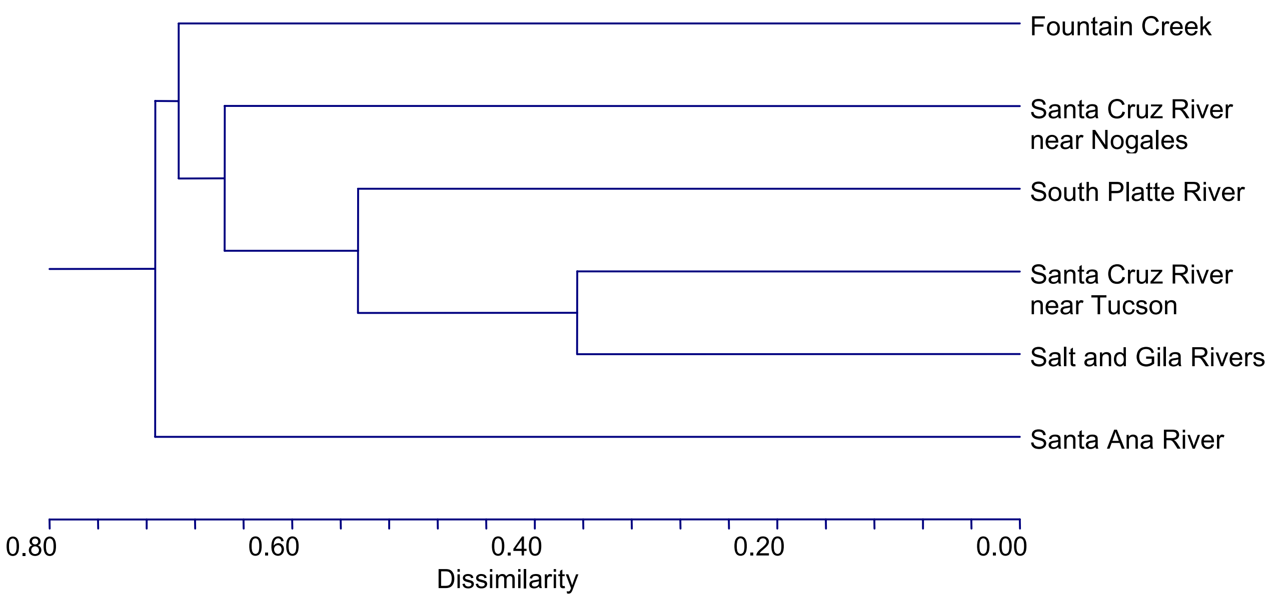

Figure 2-4
Dendogram Grouping Arid West Effluent-Dependent Streams
Based on Genera Collected at Each Site in the Class Insecta

2.5 SUMMARY OF FINDINGS

The species composition lists for the streams chosen to represent effluent-dependent streams in the arid West show that the majority of the fish and invertebrate taxa listed were only collected at a single site. Few fish or invertebrate taxa were common to all or most of these sites, which is a finding that is not necessarily unexpected given the broad geographic range of the study streams. However, those taxa that are common to these streams could potentially represent resident taxa in arid West effluent-dependent streams in any future toxicity testing conducted specifically for the purpose of adding data to the current toxicity databases.

The cluster analysis results for both fish and invertebrate communities seem to be strongly influenced by taxa richness at a site. With only presence/absence data used (and the only data available in some cases), eliminating this influence would be difficult. Additionally, differences in the number of studies, the number of years studied, and methods used in those studies is probably affecting the number of taxa collected at each site—particularly with the invertebrate data—and hence, the clustering observed. For example, when all studies were combined, the Gila and Salt Rivers had the highest number of fish species of the seven sites, yet the invertebrate list includes a disproportionately low number of taxa (Tables 2-1 and 2-2). The invertebrate data compiled for the Gila and Salt rivers came mainly from studies that sampled only over brief periods of time at one or a few sites, in comparison to other locations such as the South Platte River, Fountain Creek, and the Santa Ana River, which have data compiled from studies that sampled consistently at more than one stream site over several years (Appendix 1). Also, the protocol for many of the invertebrate studies for the Salt/Gila Rivers only required identification of invertebrates to the family level or above. Both of these factors could be responsible for limiting the number of taxa listed for the Salt/Gila Rivers.

The species lists for other locations, particularly the Santa Cruz River near Tucson, indicates that the fish and invertebrate populations at these sites are impoverished and have been so historically. The Santa Cruz River near Tucson had only 8% of the number of fish taxa and 21% of the number of invertebrate taxa collected as were found in the South Platte River. As the Santa Cruz River had been completely dry through this area for several years until the WWTP restored it to perennial flow in 1977 (Harding Lawson & Associates 1986), the biological populations would naturally not be expected to be as diverse as those found at some of the other sites with long-term perennial (even if effluent-dependent) flow.

In contrast, sites such as the South Platte River and Fountain Creek have fish and invertebrate communities that seem somewhat similar based on species composition, as might be expected due to their close geographic locations. While these similarities were not particularly highlighted in all cluster analyses, examining the species lists for both sites indicates that the two streams are relatively similar in terms of their fish and invertebrate community composition. When taxa lists for the two streams were combined, 39% of the fish taxa and 32% of the invertebrate taxa were found at both sites. This was the highest percent similarity seen between any of the study sites, with the exception of the similarity between the Santa Ana River and its tributary, Chino Creek. Water quality standards applicable to both effluent-dependent stream sections would be more likely in such scenarios.

Finally, the fish and invertebrate taxa lists provided in Tables 2-1 and 2-2, respectively, provide a list of resident taxa for the recalculation effort described later in this document.

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3.0 ALUMINUM CRITERIA REVIEW AND UPDATE

3.1 INTRODUCTION

The EPA established national aquatic life criteria for aluminum in a 1988 report entitled *Ambient Water Quality Criteria for Aluminum* (EPA 1988), hereafter referred to as the 1988 Aluminum Document. This document established a working toxicity database with recommended ambient water quality criteria (AWQC) to protect freshwater organisms. Since publication of this report information on the environmental significance of freshwater organism aluminum exposure and available toxicity studies has increased. This section summarizes the status of the technical review of the freshwater aluminum AWQC as the initial step for inclusion in the Arid West Water Quality Research Project AWQC Recalculation Project.

3.2 BACKGROUND

Aluminum (Al) is the most abundant metal and the third most abundant element in the earth's crust. Acid rain deposition has dramatically increased the amount of Al appearing in many biological systems, increasing exposure of soluble Al to aquatic species. Other anthropogenic sources include wastewater effluent (from pharmaceuticals, cooking practices, water supplies, and Al sulfate (alum) flocking of drinking water supplies or phosphorus removal in effluent), burning of coal and hydrocarbons, and suspension of fine dusts during agricultural practices.

Aluminum water solubility is a function of pH. In the neutral pH range, the thermodynamic stability of Al hydroxide, or gibbsite ($Al(OH)_3$), controls solubility with little monomeric Al^{3+} in solution. Monomeric Al^{3+} becomes more available relative to gibbsite at pH <4.7 and pH >9. At circumneutral pH range, total Al is usually much greater than monomeric species (Gensemer and Playle 1999). Al solubility is also dependent on organic compounds in solution. At circumneutral pH ranges, dissolved organic matter, and especially weak organic acids (e.g., fulvic, citric, and humic acids), increase Al solubility while decreasing aquatic organism toxicity. This is an important transport mechanism in Al cycling (Schlesinger 1997).

These complex speciation and complexation kinetics raise issues of how to measure Al in natural water and/or toxicity test media. Filtration and ion exchange resins are used to separate monomeric dissolved Al from particulate and polymeric forms (Van Benschoten and Edzwald 1990). Rapid speciation of Al in test solutions can be a potential problem when determining solid and dissolved species. Analytical and technical issues when characterizing dissolved from total Al in complex solutions are limited using kenetic modeling. Many authors use theoretical calculations such as REDEQL (Morel and Morgan 1972) and later replaced by MINEQL (Environmental Research Software, Hullowell, ME) that model speciation in relation to water quality parameters and total Al measurements (Lamb and Bailey 1981, Cleveland et al 1989, and Lacroix et al. 1993). Given these physical and methodological issues, it is recommended that these toxicity values for Al be regarded as total Al (EPA 1988).

The speciation and/or complexation of Al is highly dependent on ambient water quality characteristics and ultimately determine the mechanism of toxicity. Wilkinson and Campbell (1993) demonstrated the difficulty of determining Al speciation in complex solutions—such as natural waters with abundant DOC and silicic acid—when determining mechanisms of toxicity in fish. The primary target of Al toxicity is damage to respiratory organs, such as fish gills (Lacroix et al. 1993). The chemical conditions at the gill surface are thought to modify Al speciation and sorption. Water passing over the gills can become more basic due to nutrilization of acidic water by NH_3, This can lead to precipitation and polymerization of Al, resulting in Al deposition on the gill surface. Accumulation of Al on the gill surface epithelium and/or mucous layer has been shown to enhance rates of sloughing and hyperplasia of lamellae (Leivestad 1982). The ionoregulatory vs. respiratory effects of Al on fish are pH-dependent, with the former predominating at relatively acidic pH (Gensemer and Playle 1999). Additionally, concentration of calcium in the water was shown to decrease toxic effects to fish (Muniz and Leivestad 1980). Calcium reduces Al toxicity by competing with monomeric Al binding to negitivly charged fish gills and by keeping tight junctions between epithelial cells intact (Gensemer and Playle 1999).

The number of toxicity tests addressing Al toxicity in aquatic invertebrates is considerably less when compared to fish, but, in general, results indicate invertebrates are less sensitive than fish (Sparling 1996). Mechanisms of toxicity are confounded by H+ toxicity when testing at low pH, but published evidence supports ionoregulatory effects of Al exposure. Different H+ exchange mechanisms in different invertebrates can have different impacts on their pH-dependent Al toxicity (Gensemer and Playle 1999). Havens (1990) identified significant accumulation of particulate Al on ionoregulatory and respiratory surfaces in cladocerans. Additionally, increased membrane permeability with subsequent ion loss has been reported in acid sensitive invertebrate species (Locke 1991). In mayflies, Al accumulation on respiratory surfaces reduced oxygen consumption due to physical blockage of gill chambers (Rockwood et al. 1990).

From our understanding of Al toxicity, we can identify two distinctly different mechanisms of toxicity. The first mechanism is a physical suffocation or irritation caused by particulate Al exposure, or from precipitation in the gill microenvironment (see Gensemer and Playle 1999), leading to hypoxia-related toxic effects that often become manifest during acute exposure senerios. The second mechanism is driven by dissolved monomeric Al species that disrupt ionic regulation, an effect expected with a chronic exposure regimen (although acute effects could also be observed at acidic pH). Given Al speciation and behavior in complex solutions, the mechanism responsible for toxicity will probably be dependent on pH and calcium concentration of a given solution. Therefore, understanding Al speciation chemistry and its influence on the mechanisms of toxicity to fish and invertebrates are important to interpreting the toxicological studies which form the basis of AWQC development.

3.3 PHASE I- TECHNICAL REVIEW OF 1988 ALUMINUM DOCUMENT

Phase I of the evaluation of the 1988 Aluminum Document consisted of a thorough investigation of the data used to calculate the most recent Al criteria. This document was critically reviewed for relevance of the toxicological data and adherence to EPA methodology (Stephan et al. 1985).

3.3.1 Existing Acute Criteria for Aluminum

The 1988 Aluminum Document (EPA 1988) presents acute data for 14 genera, including seven species of invertebrates and seven species of fish. These 14 species in 11 families satisfy the "eight-family rule" as specified in the 1985 Guidelines. The 1988 Aluminum Document reports a FAV of 1,496 µg/L with a CMC = FAV/2 of 750 µg/L. When referencing reported values used in criteria development, Chadwick Ecological Consultants (CEC) identified an apparent discrepancy regarding the SMAV for *Girardia (= Dugesia) tigrina*. The authors of the toxicity test reported that the greatest Al exposure concentration of for this species was 16,000 µg/L (Brooke 1985) with the ambient acute value of >16,800 µg/L. However, the 1988 Aluminum Document reports >23,000 µg/L for the same species and reference. The implications of this discrepancy could be significant and would result in a *Girardia* GMAV rank change from 6th to 4th. Charles Stephen (pers. comm. to David Moon, December 13, 2004) has since noted that no *G. tigrina* died at 16,000 µg/L, so it was reasonable to assume that the LC_{50} was potentially two times the concentration that caused a low level of acute mortality. The geometric mean of 16,000 µg/L and 32,000 µg/L was reported for *Girardia* to account for the undefined test value. Nonetheless, the undefined value (>16,000 µg/L) is probably more appropriate, when compared to more recent evidence reported by Calevro et al. (1998) that tested Al toxicity in *G. etrusca*. The authors' results showed that this species showed lethality, abnormal mucus production, and decreased regeneration at concentrations near 16,000 µg/L. Therefore, we replaced the existing >23,000 value with the originally reported value of >16,000 µg/L.

3.3.2 Existing Chronic Criteria for Aluminum

The 1988 Aluminum Document presents chronic data for three genera of freshwater organisms, including two species of invertebrates and one fish species. These three species do not satisfy the "eight-family rule" as specified in the 1985 Guidelines. The chronic database assemblage did, however, satisfy the minimal requirements for calculation of an ACR in that one of the invertebrates is an acutely sensitive species.

After calculation of three valid ACRs for the three species, it was evident that the most acutely sensitive species had lower ACRs. Given this relationship, a final ACR (FACR) was calculated using acutely sensitive *Ceriodaphnia dubia*, which resulted in a FACR that was less than 2, which then defaults to 2 according to USEPA guidance (Stephan et al. 1985). A FACR of 2 would result in a chronic criterion equal to the acute. However, additional information on Al toxicity for *Salvelinus fontinalis* and *Morone saxatilis* (Cleveland et al. manuscript and Buckler et al. manuscript) were used by the EPA to modify the FCV to protect these two species (EPA 1988). These two studies were deemed inappropriate for the Al chronic database (i.e., they are listed in Table 5-6, "Other Data on Effects of Aluminum on Aquatic Organisms"), but were still used to reduce the FCV from ~750 to 87 µg/L. Therefore, the 1988 Aluminum Document recommended a Criteria Chronic Concentration (CCC) of 87 µg/L at which no *M. saxatilis* died after a seven-day exposure (Buckler et al. manuscript). In the same toxicity test, 174.4 µg/L killed 58% of the fish. Current practice would be to calculate the chronic value as the geometric mean of these two numbers, or 122 µg/L.

3.4 PHASE II – UPDATE TO THE NATIONAL ALUMINUM CRITERIA DATABASE

A comprehensive literature review was conducted of Al aquatic toxicity related documents used and not used in the 1988 Aluminum Document. This included a review of documents published since the 1988 Aluminum Document, as well as those published prior to 1988 that were not used in criterion derivation. Available Al documents were obtained and reviewed for relevance of toxicological data and adherence to EPA criteria development methodology (Stephen et al. 1985).

A pH range of 6.5 to 9.0 was established as a limit for data used in the update of the Al toxicity databases, because the EPA has established this as an acceptable range for pH in ambient freshwater (EPA 1976). This circumneutral pH gradient was the same range used to derive current criteria in the 1988 Aluminum Document. From the discussion on Al speciation above, we would thus expect that toxic effects of Al in test media of circumneutral pH could be attributed to exposure to non-monomeric Al species. Additionally, reported total Al measurements should be substantially greater than dissolved measurements owing to the poor solubility of Al under these pH conditions. Approximately 120 papers were reviewed, including documents cited in the 1988 Aluminum Document.

Much of the research into Al toxicity in aquatic organisms has been concerned with toxicity of Al in acidic solutions – specifically in research investigating effects of acid rain – with very few studies addressing toxic effects at circumneutral pH. Published reports that tested aquatic organism toxicity at circumneutral pH solutions often did so as part of tests over a wider range of acidic pH values. For example, a common experimental design in published Al toxicity studies was limiting the number of treatments and replicates at higher pH values to focus on lower pH values where Al is soluble and hence, more toxic. This experimental design resulted in very few data points with usable LC_{50}s or EC_{50}s (based from a narrow dose response). In addition, given that most available research was conducted to test toxicity over a pH range, rather than over an Al concentration gradient, reportable end points were often "greater than" values. Undefined values were added to the toxicity database judiciously, if they could be corroborated by additional sources of published evidence, and after careful consideration of author's qualitative effect descriptions. This aided in development of an updated Al AWQC database that did not ignore potentially important toxicity data.

3.4.1 New Aluminum Acute Toxicity Data

Following review of available studies, 36 acute data points from 15 studies (Table 3-1) were deemed suitable for addition to the revised acute database. Of the 15 studies added to the database, five were published prior to the 1988 Aluminum Document. All five of these studies published prior to the 1988 Aluminum Document were not cited in either Table 1, Acute Toxicity of Aluminum to Aquatic Animals, or Table 6, Other Data on Effects of Aluminum on Aquatic Organisms of the 1988 Aluminum Document and apparently represent data that were unknown to the EPA.

Of the 15 studies examined and accepted for database revision, three studies provided data for three species that are within the top four most sensitive genera in the revised database (*Salmo salar*, *Miropterus dolomieu*, and *Asellus aquaticus*). Hamilton and Haines (1995) tested Al toxicity in *S. salar* alevins using 96-hr static renewal exposures in reconstituted very soft water (hardness 6.8 mg/L $CaCO_2$) at a pH of 6.5. Test organisms were not fed, and total Al measurements were used to determine a 96-hr LC_{50}. Martin and Holdich (1986) performed acute toxicity tests with *A. aquaticus* to a variety of heavy metals, including Al. Static renewal test exposures were conducted in soft water (hardness 50 mg/L $CaCO_2$) at a pH of 6.75. Reported results included 96-hr LC_{50}s for both species. Kane and Rabeni (1987) provided an undefined acute value for *M. dolomieu*. At the reported toxicity value, Al-treated larva showed heavy mucous accumulations and were not active. These observations were deemed appropriate for accepting this species in the acute database.

Table 3-1
Summary of Reviewed Publications with Reported Acute Aluminum Data that were Deemed Acceptable According to 1985 Guidelines (Stephen et al. 1985) for Addition to the Updated Aluminum Acute Database

Species	Method	Hardness (mg/L $CaCO_3$)	pH	LC_{50} (µg/L)	Reference
Ictalurus punctatus	F, M	23.1	6.5	>400	Palmer et al. 1988
Ictalurus punctatus	F, M	23.1	7.5	>400	Palmer et al. 1988
Oncorhynchus mykiss	S, U	1	7	3,800	Thomsen et al. 1988
Oncorhynchus mykiss	S, U	150	7	71,000	Thomsen et al. 1988
Oncorhynchus mykiss	F, M	25	7.6	<8,000	Gundersen et al. 1994
Oncorhynchus mykiss	F, M	45	7.6	<8,000	Gundersen et al. 1994
Oncorhynchus mykiss	F, M	85	7.6	<8,000	Gundersen et al. 1994
Oncorhynchus mykiss	F, M	125	7.6	<8,000	Gundersen et al. 1994
Oncorhynchus mykiss	F, M	23.2	8.25	6,170	Gundersen et al. 1994
Oncorhynchus mykiss	F, M	35	8.25	6,170	Gundersen et al. 1994
Oncorhynchus mykiss	F, M	83.6	8.29	7,670	Gundersen et al. 1994
Oncorhynchus mykiss	F, M	115.8	8.29	6,930	Gundersen et al. 1994
Pimephales promelas	F, M	21.6	6.5	>400	Palmer et al. 1989
Pimephales promelas	F, M	21.6	7.5	>400	Palmer et al. 1989
Pimephales promelas	F, M	21.6	6.5	>400	Palmer et al. 1989
Pimephales promelas	F, M	21.6	7.5	>400	Palmer et al. 1989
Pimephales promelas	F, M	23.1	6.5	>400	Palmer et al. 1988
Pimephales promelas	F, M	23.1	7.5	>400	Palmer et al. 1988
Pimephales promelas	S, M	26	7.8	1,160	ENSR 1992b
Pimephales promelas	S, M	46	7.6	8,180	ENSR 1992b
Pimephales promelas	S, M	96	8.1	20,300	ENSR 1992b
Pimephales promelas	S, M	194	8.1	44,800	ENSR 1992b
Crangonyx pseudogracilis	S, U	50	6.75	9,190	Martin and Holdich 1986
Asellus aquaticus	S, U	50	6.75	4,370	Martin and Holdich 1986
Gammarus pulex	S, U	--	6.9	>2,698	Storey et al. 1992
Ceriodaphnia dubia	S, M	26	7.5	720	ENSR 1992a
Ceriodaphnia dubia	S, M	46	7.6	1,880	ENSR 1992a

Table 3-1 (Continued)
Summary of Reviewed Publications with Reported Acute Aluminum Data that were Deemed Acceptable According to 1985 Guidelines (Stephen et al. 1985) for Addition to the Updated Aluminum Acute Database

Species	Method	Hardness (mg/L $CaCO_3$)	pH	LC_{50} (µg/L)	Reference
Ceriodaphnia dubia	S, M	96	7.8	2,450	ENSR 1992a
Ceriodaphnia dubia	S, M	194	8.1	>99,600	ENSR 1992a
Ceriodaphnia dubia	S, M	98.5	7.6	2,880	Soucek et al. 2001
Ceriodaphnia sp.	S, M	47.4	7.36	2,300	Call 1984
Cyclops viridis	S, U	--	6.9	>2,698	Storey et al. 1992
Micropterus dolomieu	S, M	12.45	7.5	>1,000	Kane and Rabeni 1987
Salmo salar	S, M	6.8	6.5	599	Hamilton and Haines 1995
Salvelinus fontinalis	F, M	--	6.5	3,600	Decker and Menendez 1974
Hybognathus amarus	S, M	140	8.1	>59,100	Buhl 2002

NOTES:
S = static renewal test exposures
F = flow through test exposure
M = test media aluminum concentration was measured
U = test media aluminum concentration was not measured

Water quality parameters in toxicity tests were added to the updated Al database in addition to test results. Test solution pH and hardness values were needed to determine inclusion of data within the specified circumneutral pH range and to investigate a possible hardness-toxicity relationship. Most of the added studies reported hardness values of test media or reported calcium and magnesium concentrations that were used to calculate water hardness. Of the 35 new acute data points, three provided insufficient information on water quality parameters to determine test media hardness. Unfortunately, each was for a unique species (*Salvelinus fontinalis*, *Cyclops viridis*, and *Gammarus pulex*) found in the updated database that was subsequently removed during FAV derivation (see discussion below).

3.4.2 New Aluminum Chronic Toxicity Data

Following review of these studies, 11 chronic data points from nine studies (Table 3-2) were added to the revised chronic database. Of the nine studies added to the database, seven were published prior to the 1988 Aluminum Document. Three studies published prior to the 1988 Aluminum Document were not cited in either Table 1 ("Chronic Toxicity of Aluminum to Aquatic Animals") or Table 6 ("Other Data on Effects of Aluminum on Aquatic Organisms") of the 1988 Aluminum Document and apparently represent data that were unknown to the EPA at the time.

Table 3-2
Summary of Chronic Aluminum Data that were Deemed Acceptable for Criteria Derivation and Added to the Updated Aluminum Chronic Database

Species	Hardness (mg/L $CaCO_3$)	pH	NOEC- LOEC (Φg/L)	Chronic Value (µg/L)	Reference
Ceriodaphnia dubia	50	7.75	1,100-2,400	1,624	McCauley et al. 1986
Ceriodaphnia dubia	47.4	7.55	6,250-12,100	8,696.26	Call 1984
Daphnia magna	45.3	7.74	--	320[a]	Biesinger and Christenson 1972
Daphnia magna	45.3	7.74	--	1,400[b]	Biesinger and Christenson 1972
Tanytarsus dissimilis	17.43	6.8	10,000-80,000	28,284	Lamb and Bailey 1981
Salvelinus fontinalis	12.5	7.2	>303.9	>303.9	Cleveland 1991
Salvelinus fontinalis	7.5	6.5	169-350	243.21	Cleveland manuscript
Salvelinus fontinalis	12.5	6.5	57-88	70.82	Cleveland manuscript
Salvelinus fontinalis	7.5	6.5	88-169	121	Cleveland et al. 1989
Salvelinus fontinalis	0.567	7.81	0-300	<283	Hunn et al. 1987
Micropterus dolomieu	12.8	7.3	0-250	<250	Kane and Rabeni 1987

NOTES:
[a] EC_{16} for reduced reproduction
[b] 21 day LC_{50}
NOEC = no observable effect concentration
LOEC = lowest observable effect concentration.

Four publications that were found in Table 6 ("Other Data") of the 1988 Aluminum Document were reviewed and deemed appropriate for use in updating the chronic database. Biesinger and Christensen (1972) performed acute and chronic Al toxicity tests with *Daphnia magna*. Acute toxicity results were included in the acute database; yet, no explanation was given as to why chronic data from this study were not included in the chronic database. We reviewed methods used for the chronic toxicity tests, and could not find a reason to exclude these data. Therefore, two chronic values from this study were added to the database. Data from this publication were also deemed suitable for inclusion in the FACR derivation, described later.

In a 55-day Al exposure, Lamb and Bailey (1981) tested acute and chronic toxicity in *Tanytarsus dissimilis*. The authors reported high variability in mortality rates among treatments and provided little information on statistical significance of mortality among treatments. Fortunately, a figure showing the cumulative % mortality was provided and analyzed with text to derive a chronic value of 10,000 µg/L, the treatment level that produced 37% mortality.

The Cleveland manuscript, used to lower the 1988 Aluminum Document FCV, contained additional data for *Salvelinus fontinalis* that were not reported in the EPA chronic databases. CEC added these additional chronic values into the revised chronic database. *S. fontinalis* were exposed to Al in soft water with a pH of 6.5, the lowest pH in the acceptable circumneutral range. The chronic value was determined for a statistical difference in length (growth) and mortality. The growth value was more sensitive than mortality (243 µg/L) and resulted in a chronic value of 70 µg/L. Hunn et al. (1987) investigated influence of pH and Al on early life stages of developing *S. fontinalis*. Only two treatments, the control and 283 µg/L, were used in a 60-day larvae toxicity test using flow through exposure with very soft water. The authors reported a statistical decrease in growth ($p<0.001$) between treatment and control using a least squares deviation linear model with interaction terms representing treatment effects. Since a geometric mean could not be determined, a chronic value of <283 µg/L was added to the revised chronic database.

Five additional studies with appropriate toxicity tests were found that were not listed in the 1988 Aluminum Document. Three of these publications were published after the 1988 Aluminum Document. Cleveland et al. (1991) performed a 56-day Al exposure in *S. fontinalis* to examine effects on bioaccumulation, growth, and mortality. The authors reported 1% mortality in the 7.2 pH treatment at the end of the exposure period at a measured mean Al concentration of 303.88 µg/L, which resulted in an undefined chronic value of >303.88 µg/L. Although test duration was four days short of the recommended 60 days for a chronic test with this species, we decided that test methods were acceptable and suitable for use. In a chapter of a book on environmental chemistry and toxicology of Al, Cleveland (1989) reported another chronic value for *S. fontinalis*. The authors used similar methods as in prior toxicity tests with this species and Al. After a 60-day exposure at a mean pH of 6.5, statistical differences in growth were observed. The result of this partial life cycle test, that started exposures with embryos, was the lowest chronic value added to the chronic database.

The remaining three studies entered into the updated chronic database were published prior to the 1988, but were not cited in the 1988 Aluminum Document. McCauley et al. (1986) performed two acute and chronic toxicity tests using *C. dubia* with different pH exposure media. The 1988 document used only one of the chronic values from a test with a pH of 7.15, but did not report the second test that was conducted at a pH of 7.61. The chronic value that was added to the updated database was from this second test. Extensive acute data were provided by Call (1984) from the University of Wisconsin Center for Lake Superior Environmental Studies laboratory, with addition of a chronic toxicity test using *Ceriodaphnia* sp. After an eight-day Al exposure, statistical differences in survival and reproduction were observed in the 12,100 µg/L treatment (lowest-observed-effect concentration [LOEC]). The updated chronic database value was derived by taking the geometric mean of this treatment concentration and the next lowest treatment of 4,900 µg/L (no-observed-effect concentration [NOEC]). Kane and Rabeni (1987) performed a 30-day partial life cycle toxicity test using *Micropterus dolomieu*. Although the authors did not find any statistical differences in growth between control and the 250 µg/L treatment, they do note that the fish showed overt signs of Al toxicity, which included scoliosis and lordosis. Therefore, an undefined value of >250 µg/L was added to the database.

3.4.3 Potential Relationships Between Aluminum Toxicity and Water Quality Parameters

During our investigation and subsequent database update, CEC identified an inverse Al toxicity and hardness relationship that was not reported in the 1988 Aluminum Document. Acute values with relevant test media hardness measurements were regressed within and among four species: *Oncorhynchus mykiss*, *Pimephales promelas*, *C. dubia*, and *D. magna*. These species were chosen because respective hardness treatments fell within a wide range of values and each had many acute endpoints to regress (Stephen et al. 1985), except for *D. magna* that only had two values. Regression analysis for each species, excluding *D. magna*, resulted in a statistically significant positive relationship between effect measurement and test media hardness (two-sided test, to test that slope term equals zero, df = 5, 3, and 5, respectively, all p-values <0.03). A water hardness vs. Al toxicity equation was derived with this subset of data, which included values for *O. mykiss*, *P. promelas*, and *D. magna*, that minimized residual standard error ($r^2 = 76.1\%$) and resulted in a pooled slope of 0.8327 (Table 3-3). Figure 3-1 is a plot of the acute values versus the hardness values used to derive this Al hardness slope.

Table 3-3
Derivation of Acute Al Hardness Slope

Species	N	Smas	R^2
Oncorhynchus mykiss	2	0.5843	--
Daphnia magna	2	1.4439	--
Pimephales promelas	5	1.5298	0.90
	Pooled Hardness Slope =	**0.8327**	**0.76**

NOTE: SMAS = species mean acute hardness slope.

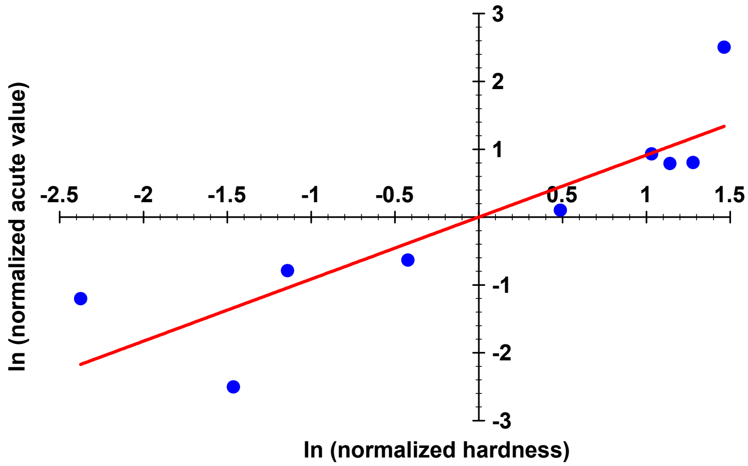

Figure 3-1
Scatter Plot of Al Toxicity and Water Hardness Values used to Derive the Al Hardness Slope

Based on this relationship, the Al toxicity data were subsequently normalized to hardness 50 mg/L using this slope, and an acute AWQC equation was developed to incorporate the protective effect of hardness, a proxy for calcium.

Additional water quality parameters such as pH also affect aquatic organism Al toxicity. The pH of a solution is a major driver of Al speciation. Over the range of EPA acceptable circumneutral pH values, we could expect that the fraction of monomeric Al in solution will change, most notably at lower (~6.5) and greater pH values (~9). Freeman and Everhart (1989) demonstrated an increase of Al toxicity in rainbow trout from a pH of 7 to 9 using the same concentration and experimental methods. They reported that test organisms showed immediate shock and heavy mortalities within the first 48 hours at a test solution pH of 9.0, effectively terminating the 45-day test after 113 hours. Although there was an apparent pH relationship within the EPA range, we could not develop a significant toxicity relationship with pH. Attempts to develop such an equation were hindered by limited studies conducted for any species at a range of pH values. In fact, the greatest pH value in the database is 8.29, at which no increased toxicity was apparent. Available data points at lower pH values ~6.5 for some taxa indicate that increased toxicity occurs at the lower end of the EPA recommended range. This trend provided qualitative evidence of a water quality toxicity relationship in some organisms. However, this relationship is not significant within, or consistent between, an acceptable sample of organisms in the updated database.

3.5 PHASE III - RECALCULATION OF AWQC FOR ALUMINUM

Data discovered and screened during phase II of this project were used to update and revise the Al acute and chronic database. The revised database was then used to derive a potentially updated acute and chronic AWQC for Al to protect freshwater aquatic organisms.

3.5.1 Updated Acute Database

Not all of the new acute data added to the database contained enough water quality information to use in derivation of the recommended updated Al AWQC. Effects data without reported hardness water quality parameters of test water were not used to generate a revised FAV since data values could not be normalized to hardness of 50 mg/L. Table 3-4 summarizes data used for calculation of the recommended updated acute Al AWQC. The updated acute database contains values for 17 genera, including 10 species of invertebrates, and nine species of fish, increased from 14 genera in the existing criteria document. These 19 species in 14 families satisfy the "eight-family rule" as specified in the 1985 Guidelines.

Addition of new species data and normalization of acute values changed three of the four most sensitive genera when compared to the 1988 Aluminum Document. The rank of the most sensitive genus (*Ceriodaphnia*) in the updated database is unchanged and its reported acute value changed very little after hardness correction. The 1988 Aluminum Document database ranked *Salvelinus* as the second ranked genus. This value was based on one study in which hardness was not measured (Decker and Menendenz 1974). Since the effect endpoint could not be normalized for hardness, this value was not included in the updated database. As a result, *Salmo* replaced *Salvelinus* as the second ranked genus in the updated database. The normalized value for *Salmo* was very similar to *Salvelinus*, so this deletion and addition process was not particularly influential in updating the FAV. The updated 3rd and 4th ranked genera, *Micropterus* and *Asellus*, replaced *Oncorhynchus* and *Gammarus* of the 1988 Aluminum Document. These updated values were lower with a range closer to the first two genera, resulting in reduced variability between the four most sensitive genera.

Table 3-4
Proposed Final Aluminum Acute Database, with Species Mean Acute Values (SMAV), Normalized to Hardness = 50 mg/L, and Ranked by Genus Mean Acute Value (GMAV)

Rank	Species	Common Name	Method	GMAV (µg/L)	SMAV (µg/L)
18	*Tanytarsus dissimilis*	Midge	S, U	192,155	192,155
17	*Lepomis cyanellus*	Green sunfish	S, M	52,274	52,274
16	*Perca flavescens*	Yellow perch	S, M	52,064	52,064
15	*Ictalurus punctatus*	Channel catfish	S, M	50,078	50,078
14	*Physa* sp.	Snail	S, M	32,907	32,907
	Oncorhynchus mykiss	Rainbow trout	F, M		10,835
13	*Oncorhynchus tschawytscha*	Chinook salmon	S, M	26,502	64,825
12	*Hybognathus amarus*	Minnow	S, M	25,075	25,075
11	*Acroneuria* sp.	Stonefly	S, M	23,628	23,628
10	*Gammarus pseudolimnaeus*	Amphipod	S, M	23,000	23,000
9	*Girardia tigrina*	Flatworm	S, M	17,355	17,355
8	*Pimephales promelas*	Fathead minnow	S, M	13,461	13,461
7	*Tubifex tubifex*	Worm	S, U	13,373	13,373
6	*Daphnia magna*	Cladoceran	S, U	10,890	10,890
5	*Crangonyx pseudogracilis*	Amphipod	S, U	9,190	9,190
4	*Asellus aquaticus*	Isopod	S, U	4,370	4,370
3	*Micropterus dolomieu*	Smallmouth bass	S, M	3,183	3,183
2	*Salmo salar*	Atlantic salmon	S, M	3,154	3,154
	Ceriodaphnia dubia	Cladoceran	S, M		2,466
1	*Ceriodaphnia* sp.	Cladoceran	S, M	2,741	3,046

NOTES:
S = static renewal test exposures.
F = flow through test exposure.
M = test media aluminum concentration was measured.
U = test media aluminum concentration was not measured.

3.5.2 Updated Chronic Database

The revised and updated Al chronic toxicity database presents data for six genera of freshwater organisms, including three species of invertebrates and three species of fish (Table 3-5). These six species found in five families do not satisfy the "eight-family rule" as specified in the 1985 Guidelines. The chronic database assemblage does, however, satisfy the minimal requirements for calculation of a FACR.

Table 3-5
Proposed Final Aluminum Chronic Values (SMCV), with Hardness Normalized (50 µg/L), and Ranked by Genus Mean Chronic Values (GMCV)

Rank	Species	Common Name	SMCV (µg/L)	GMCV (µg/L)
6	*Tanytarsus dissimilis*	Midge	68,021	68,021
5	*Ceriodaphnia dubia*	Cladoceran	4,165	4,165
4	*Pimephales promelas*	Fathead minnow	957	957
3	*Micropterus dolomieu*	Smallmouth bass	777	777
2	*Salvelinus fontinalis*	Brook trout	624*	624*
1	*Daphnia magna*	Cladoceran	274	274

*GMCV was calculated without the undefined chronic value reported by Hunn et al. (1987)

The revised FACR was derived from three SMACRs, using in the revised and updated chronic toxicity databases. Each ACR was determined from paired acute and chronic values within the same study using similar dilution water (Table 3-6). The respective SMACR used to derive the FACR were 0.98 (*C. dubia*), 10.65 (*P. promelas*), and 12.04 (*D. magna*). Including the Biesinger and Christensen (1972) data in the *D. magna* SMACR calculation (two values tested at hardness = 45.3) resulted in a substantially lower SMACR for this species than reported in the 1988 Aluminum Document (50.47). Although one chronic value measured a less sensitive endpoint that was not used in the SMCV calculation (Table 3-5), both values were retained in the FACR calculation to provide a better estimate SMACR for *D. magna.* These data resolved the previous problem noted in the 1988 Aluminum Document associated with taking a geometric mean from a wide range of results. In general, the inclusion of more chronic data resulted in a better sample of ACRs, in which values ranged roughly within a factor of 10 from one another. Because the EPA was lacking data to legitimately generate a FACR using multiple SMACRs, the FACR was set to the lowest organism then defaulted to 2.0. We feel that using a multiple SMACR approach is an improvement over the EPA's FACR estimate, which was not used to derive the final chronic criteria because it was not protective of organisms within the chronic database. The revised FCV derived from the revised FACRis expected to be protective to every organism in the chronic database, when corrected for hardness.

Table 3-6
Preliminary Updated Aluminum Final Acute-Chronic Ratio (FAVR)

Species	Hardness ($CaCO_3$ mg/L)	Chronic Value (µg/L)	Acute Value (µg/L)	ACR	SMACR
Daphnia magna	220	742.2	38,200	51.486	
Daphnia magna	45.3	1,400[a]	3,900	2.7857	
Daphnia magna	45.3	320[b]	3,900	12.1875	12.0448
Pimephales promelas	220	3,288	35,000	10.6448	10.6448
Ceriodaphnia dubia	50	1,908	1,900	0.9958	
Ceriodaphnia dubia		1,624	1,500	0.9590	0.9772
					FACR = 5.0039

NOTES:
[a]21 day LC_{50}
[b]16% decrease in reproduction
SMACR = species mean acute-chronic ratio.

3.5.3 Updated Aluminum AWQC Derivation

An updated final acute value (FAV) was derived from the four most sensitive genera in updated and revised acute toxicity database (*Ceriodaphnia, Salmo, Micropterus*, and *Asellus*), the total number of genera in the updated acute database, and newly derived acute toxicity hardness slope (Table 3-7). The resulting FAV (2,560 µg/L) is over 1,000 µg/L greater than the 1988 FAV of 1,496 µg/L, and was used to derive the hardness modified Al criteria equation.

Since the revised chronic database did not satisfy the "eight-family rule," the FACR was used to derive a FCV for Al from the acute database. Following the 1985 Guidelines, the acute hardness toxicity relationship was assumed to be similar for chronic toxicity. Therefore, a chronic Al criterion equation was also calculated using this pooled acute-hardness slope (Table 3-7). Use of the acute-hardness slope in the chronic equation should be applied cautiously given the limited chronic toxicity data do not support this assumption. However, the lack of support may be an artifact of difficulties associated with conducting chronic toxicity tests with a poorly soluble compound, rather than a true lack of relationship.

Table 3-7
Recalculation of the Final Acute Values for Aluminum using the Revised Hardness Adjusted (50 mg/L $CaCO_3$) Acute Database

Rank	Genus	GMAV (µg/L)	ln GMAV	(ln GMAV)^2	P = R/(N+1)	%P
4	*Asellus*	4,370	8.383	70.267	0.211	0.459
3	*Micropterus*	3,183	8.066	65.002	0.158	0.397
2	*Salmo*	3,154	8.057	64.909	0.118	0.343
1	*Ceriodaphnia*	2,741	7.916	62.663	0.059	0.243
		sum	32.421	262.421	0.526	1.410

NOTES:
N = 18 genera, R = sensitivity rank in database, P = rank / N+1)

Calculations:
Acute Criterion

$$S^2 = \frac{\ni (\ln GMAV)^2 - (\ni \ln GMAV)^2/4}{\Sigma P - (\Sigma\sqrt{P})^2/4} = \frac{262.421 - (32.421)^2/4}{0.526 - (1.410)^2/4} = 3.9871 \qquad S = 1.997$$

L = [∍lnGMAV - S(∍%P)]/4 = [32.421 - 1.997 (1.410)]&4 = 7.401
A = S (√0.05) + L = (1997)(0.2236) + 7.401 = 7.848
Final Acute Value = FAV = e^{A} = 2,559.98 µg/L
CMC = ½ FAV = 1,279.99 µg/L
Pooled Slope = 0.8327
ln (Criterion Maximum Intercept) = lnCMC - [pooled slope H ln (standardized hardness level)]
= ln (1,279.99) - [0.8327 H ln (50)]
= 3.8971
Acute Aluminum Criterion = $e^{(0.8327 [\ln (hardness)] + 3.8971)}$

Chronic Criterion

Chronic Slope = 0.8327
Final Acute-Chronic ratio (FACR) = 5.0039 (recalculated)

Final Chronic Value (FCV) = FAV / ACR = 2,559.98) 5.0039 = 511.60 µg/L

ln (Final Chronic Intercept) = ln FCV - [chronic slope H ln(standardized hardness level)]
= ln (511.60) - [0.8327 H ln (50)]
= 2.9800

Chronic Aluminum Criterion = $e^{(0.8327 [\ln (hardness)] + 2.9800}$

Reported updated and revised values based on these equations are presented across a wide range of hardness levels (Table 3-8). It is important to understand the boundaries of the reported equation. Since the equation models hardness values that ranged from 1 mg to 220 mg of $CaCO_3$/L, estimations made beyond outside of this range should be treated with caution.

Table 3-8
Updated and Revised Acute and Chronic Al Criterion Value Across Selected Hardness Values

	Mean Hardness (mg/Las $CaCO_3$)									
Equations	25	50	75	100	150	200	250	300	350	400
Updated/Revised National Standards										
Acute Al Criterion $e^{(0.8327\ [\ln\ (hardness)]+3.8971)}$	719	1,280	1,794	2,280	3,195	4,060	4,889	5,691	6,470	7,231
Chronic Al Criterion $e^{(0.8327\ [\ln\ (hardness)]+2.9800}$	287	512	717	911	1,277	1,623	1,954	2,275	2,586	2,890

NOTE: All values are as µg Total Aluminum/L.

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4.0 AMMONIA CRITERIA REVIEW AND UPDATE

4.1 PHASE I – TECHNICAL REVIEW OF 1999 AMMONIA DOCUMENT

Phase I of this evaluation was the technical review of the 1999 report entitled "1999 Update of Ambient Water Quality Criteria for Ammonia" (EPA 1999). This document was critically reviewed for relevance of the toxicity data and adherence to EPA methodology (Stephan et al. 1985).

4.1.1 Existing Acute Criteria for Ammonia

To explain the relationship between acute ammonia toxicity (LC_{50TA}) and pH, the EPA derived an empirical "S-shaped" model (Eq. 1), using the disassociation characteristics of total ammonia (TA).

$$LC_{50TA} = \left(\frac{LC_{50TA,8}}{\frac{R}{1+10^{pH_{TA}-8}} + \frac{1}{1+10^{8-pH_{TA}}}} \right) \times \left(\frac{R}{1+10^{pH_{TA}-pH}} + \frac{1}{1+10^{pH-pH_{TA}}} \right) \qquad \text{Eq. 1}$$

where R is the slope of the disassociation curve, pH_{TA} is the inflection point at low pH values, and $LC_{50t,8}$ is the acute toxicity value adjusted to a pH = 8. Both R and pH_{TA} are parameterized values based on the nonlinear relationship between LC_{50TA} and pH for a pooled group of organisms. The pooled dataset consisted of four studies that evaluated ammonia toxicity over a broad range of pH (6.5-9) for various freshwater species. After a thorough analysis, the EPA determined that a temperature component should not be included in the acute equations.

Substitution of the parameterized values, R (0.00704) and pH_{TA} (7.204), into Eq. 1 results in the formulation of the EPA's Acute Value model (AV_t) describing pH dependence of acute ammonia toxicity. By rearranging the equation one can convert LC_{50}'s to an equivalent value at pH = 8 ($AV_{t,8}$) – i.e., normalize all data to pH 8 (Eq. 2). Note that LC50TA and AV_{TA} are synonymous.

$$AV_{TA} = AV_{TA,8} \times \left(\frac{0.0489}{1+10^{7.204-pH}} + \frac{6.95}{1+10^{pH-7.204}} \right) \qquad \text{Eq. 2}$$

Using this normalized value ($AV_{t,8}$) for each species, the geometric mean acute values were calculated by the EPA for each species (SMAV) and Genus (GMAV) following guidelines described in Stephan et al. (1985), hereinafter referred to as the "1985 Guidelines." The GMAVs were ranked by sensitivity from 1 to n, with number 1 being the most sensitive genus. The GMAVs contained within the 5^{th} percentile were used to calculate the FAV, which is ultimately used in the development of the CMC for TA given pH. The CMC is expressed in terms of nitrogen equivalence of total ammonia (TA-N). One additional step taken by the EPA was to calculate a modified SMAV for "large" rainbow trout, *Oncorhynchus mykiss,* (11.23 mg N/L) based on a single study by Thurston and Russo (1983). Because this modified SMAV was less than the original FAV derived using the 5^{th} percentile genera, it became the basis for the "salmonids present" acute criterion (Eq. 3). To derive the "salmonids absent" criterion, all salmonid data was removed from the ranked database, and the FAV was recalculated, becoming the basis of Eq. 4.

EPA Salmonids present

$$\text{CMC} = \frac{0.275}{1+10^{7.204\text{-pH}}} + \frac{39.0}{1+10^{\text{pH-}7.204}} \qquad \text{Eq. 3}$$

EPA Salmonids absent

$$\text{CMC} = \frac{0.411}{1+10^{7.204\text{-pH}}} + \frac{58.4}{1+10^{\text{pH-}7.204}} \qquad \text{Eq. 4}$$

4.1.2 Existing Chronic Criteria for Ammonia

Because the national chronic ammonia toxicity database contains a variety of toxicological responses for fish (i.e., mortality, embryo production, embryo hatchability, biomass) and is not solely based upon survival, the EPA believed an effect due to seasonality could or should be included in model development. Ideally, using this assumption, the seasonal component would protect a range of physiological responses of various age-class organisms to chronic ammonia toxicity. Therefore, a temperature component was included in the model development as a surrogate for seasonality and life stage development.

The paucity of chronic data prohibits the direct development of chronic criteria using the 5^{th} percentile approach, since the chronic database does not meet the MDRs – specifically, the eight family rule. However, the EPA still used the 5^{th} percentile GMCVs in their chronic model development rather than using a FACR. The GMCVs were based on EC_{20} total ammonia (mg/L TA-N) results for each genera that had been normalized to pH 8 using a similar approach as in the acute database, but in addition, normalized to 25°C($CV_{t,8}$).

Note that unlike the acute analysis, EPA determined that temperature should be included in the chronic criteria. Interestingly enough, linear regression analysis of acute toxicity data presented by Arthur et al. (1987) for five fish and nine invertebrates was used to derive these temperature dependent chronic ammonia toxicity equations. It is particularly important to note that the Arthur et al. (1987) study was not specifically designed to examine temperature effects – rather it was an ammonia toxicity study conducted in outdoor streams during four seasons (winter, spring, summer, and fall), with no controls on light or temperature. Furthermore, Arthur et al. (1987) reported, "our results do not clearly demonstrate a relationship between ammonia toxicity and temperature" - a finding that supported the exclusion of temperature in the acute ammonia equations.

Nonetheless, the EPA used the Arthur et al. (1987) acute ammonia toxicity study to develop a temperature dependent chronic ammonia toxicity model. Regression analysis of the $\log_{10} LC_{50}$ and temperature values for a subset of Arthur et al. (1987) data that included *Physa, Crangonyx,* and *Musculium* resulted in an invertebrate slope of -0.044. The slope for the Arthur et al. (1987) pooled fish dataset was not significantly different from zero, thus no temperature dependent relationship was observed for fish. Because the EPA found no significant temperature response for fish, they assumed that the difference between acute and chronic slopes would be the same for fish and invertebrates. Therefore, they modified the acute invertebrate slope (-0.044) by subtracting a fish acute to chronic ratio slope (-0.016), resulting in the adjusted invertebrate slope of -0.028.

The EPA used the adjusted temperature slope (-0.028) for the three invertebrate LC_{50} response values to normalize $CV_{t,8}$ of both fish and invertebrates to 25°C for comparative baseline purposes. The reason for choosing 25°C was because the only chronic value for the most sensitive species (*Hyalella azteca*) was experimentally determined at 25°C. In addition, other "acceptable" chronic ammonia toxicity studies were performed at temperatures within 3 degrees of 25°C. The EPA chose not to include the available chronic studies of *Oncorhynchus* species because the data are extremely variable and presented as either greater than, less than, or a range of EC_{20} values.

The four most sensitive genera in the limited chronic database in order of decreasing sensitivity were *Hyalella* (1.45 mg N/L), *Musculium* (2.26 mg N/L), *Lepomis* (2.52 mg N/L), and *Pimephales* (3.03 mg N/L). Of the 28 chronic EC_{20} values presented in Table 5 of the EPA (1999) document, 21 were **not** normalized to 25°C. This slightly affects the EPA model output because their empirical model was based on the GMCV at pH8 (2.85 mg N/L) for *Lepomis* early life stages instead of the temperature adjusted (25°C) value of 2.52 mg N/L.

(Note**:** Also, the *Hyalella* and *Musculium* chronic data are suspect due to poor control organism performance in both studies and should not be used for criteria development.)

Regardless of the limited chronic data, the EPA developed their final CCC model around only two genera (*Lepomis* and *Hyalella*), which were the most sensitive early life (ELS) stage fish and invertebrate to chronic toxicity, respectively. To account for the various life stages of fish, the EPA derived two functions: one for *early life stage present* and another for *early life stage absent*. Although the "early life stage present or absent" is specific to fish, fish ammonia toxicity data did not show a temperature dependency. Therefore, the model developed by EPA follows the invertebrate response to temperature - although it cannot exceed 85.4% of the lowest fish GMCV.

When *early life stage fish are present* (Eq. 5) the CCC incorporates the following temperature based function:

$$CCC_{\text{Early life stage present}} = 0.854 \times \text{MIN}\left(2.85, 1.45 \times 10^{-0.028(25-T)}\right) \qquad \text{Eq. 5}$$

where 2.85 is the GMCV value for *Lepomis* early life stage, 1.45 is the GMCV value for *Hyalella*, -0.028 is the invertebrate slope for temperature dependency and T is temperature.

When *early life stage fish are absent* (Eq. 6) the temperature function is:

$$CCC_{\text{Early life stage absent}} = 0.854 \times 1.45 \times 10^{-0.028(25-\text{MAX}(T,7))} \qquad \text{Eq. 6}$$

which is solely based on *Hyalella*. It is important to note that neither equation is based on that organism's response to temperature. These functions were then substituted into the pH dependency equations that convert chronic effect concentrations from pH 8 to any other pH resulting in the final EPA CCC equations (Eq. 7 and Eq. 8):

EPA's Early Life Stage Fish Present Equation

$$CCC_{\text{Early life stage present}} = \left(\frac{0.0577}{1+10^{7.688-\text{pH}}} + \frac{2.487}{1+10^{\text{pH}-7.688}}\right) \times \text{MIN}\left(2.85, 1.45 \times 10^{-0.028(25-T)}\right) \qquad \text{Eq. 7}$$

EPA's Early Life Stage Fish Absent Equation

$$CCC_{\text{Early life stage absent}} = \left(\frac{0.0577}{1+10^{7.688\text{-pH}}} + \frac{2.487}{1+10^{\text{pH}-7.688}} \right) \times 1.45 \times 10^{-0.028(25-\text{MAX}(T,7))} \quad \text{Eq. 8}$$

4.1.3 Deletion of Ammonia Toxicity Data

The current national ammonia toxicity database (EPA 1999) has remained functionally unchanged since the development of criterion in 1984 (EPA 1985). The 1999 ammonia water quality update document only revised the national limits as based on the 1984 database. Upon review, it was determined that 5 studies used by the EPA in the acute database and 1 study in the chronic database failed to meet the specific data quality objectives (DQOs), as outlined in the 1985 Guidelines. All values from theses six studies (Table 4-1) were removed from the respective databases.

Table 4-1
Deletions of Inappropriate Data Presented in the EPA 1999 AWQC Ammonia Document

Species	References	Comments
Acute		
Simocephalus vetulus	Mount 1982	Insufficient data to validate results
Oncorhynchus mykiss	Calamari et al. 1977	Unable to validate citation or data-other data available by same author with this species
Oncorhynchus mykiss	Thurston et al. 1981c	Unable to validate citation or data
Oncorhynchus mykiss	Reinbold & Pescitelli 1982b	Unable to validate citation or data
Pimephales promelas	Thurston et al. 1981c	Unable to validate citation or data
Pimephales promelas	Reinbold & Pescitelli 1982b	Unable to validate citation or data
Gambusia affinis	Wallen et al. 1957	Insufficient data to validate results
Lepomis macrochirus	Reinbold & Pescitelli 1982b	Unable to validate citation or data
Sander vitreum	Reinbold & Pescitelli 1982b	Unable to validate citation or data
Chronic		
Ictalurus punctatus	Colt & Tchobanoglous 1978	Insufficient data to validate results

4.2 PHASE II - UPDATE TO THE NATIONAL AMMONIA TOXICITY DATABASES

4.2.1 New Acute Ammonia Toxicity Data

An extensive review of published and unpublished literature added 23 genera, representing 28 species, to the current national acute/chronic database (Table 4-2). Studies included in the updated database were required to meet specific DQOs as outlined in the 1985 Guidelines. We did slightly deviate from the DQOs, specifically with regard to toxicity data reported as "greater than" or "less than" - these values were excluded from the database due to the uncertainty associated with the reported value. Given the size of the updated ammonia database, however, these data became superfluous.

The most noteworthy additions to the database were eight species of freshwater mussels in the Family Unionidae, which appear to be extremely sensitive to ammonia. In fact, they are the most sensitive organisms in the acute database and could potentially decrease national criteria by approximately 80%. However, the EPA is currently reluctant to include these benthic organisms in the ambient water quality criteria until uncertainties in test procedures are resolved (*Federal Register* 2004).

The updated database also includes four endangered fish species *Acipenser brevirostrum*, *Chasmistes brevirostris*, *Deltistes luxatus*, and *Hybognathus amarus* that have very limited ranges. Of these fish, *D.luxatus* is the most influential species in criterion development, because it is the third most sensitive fish in the database. *C.brevirostris* and *H.amarus* also exhibit similar sensitivity to ammonia toxicity, and were the 5th and 6th most sensitive fish in the database. These fish may have a limited role in developing national water quality criteria; however, in an arid West regional or site-specific criteria development, these organisms provide key information. Presently, the updated CEC ammonia database represents organisms from 5 phyla, 10 classes, 22 orders, 32 families, 57 genera, and 76 species (Appendix 2).

Table 4-2
Summary of Acute Data Deemed Acceptable for use and Added to the Updated Acute Ammonia Toxicity Database

Species	Common Name	NH_3-N (mg/L)	TA-N (mg/L)	TA-N pH8 (mg/L)	Reference
Baetis rhodani	Mayfly	8.20	208.52	277.70	Khatami et al. 1998
Baetis rhodani	Mayfly	8.20	208.52	277.70	Khatami et al. 1998
Baetis rhodani	Mayfly	0.32	8.14	10.84	Khatami et al. 1998
Caecidotea racovitzai	Sowbug	5.09	148.83	103.02	Arthur et al. 1987
Callibaetis skokianus	Mayfly	3.15	263.55	153.36	Arthur et al. 1987
Ceriodaphnia dubia	Water Flea	1.54	23.55	23.54	Bailey et al. 2001
Ceriodaphnia dubia	Water Flea	1.36	20.80	20.79	Bailey et al. 2001
Ceriodaphnia dubia	Water Flea	1.22	18.66	18.65	Bailey et al. 2001
Ceriodaphnia dubia	Water Flea	1.01	15.45	15.44	Bailey et al. 2001
Ceriodaphnia dubia	Water Flea	1.54	23.55	23.54	Bailey et al. 2001
Ceriodaphnia dubia	Water Flea	1.22	18.66	18.65	Bailey et al. 2001

Table 4-2 (Continued)
Summary of Acute Data Deemed Acceptable for use and Added to the Updated Acute Ammonia Toxicity Database

Species	Common Name	NH_3-N (mg/L)	TA-N (mg/L)	TA-N pH8 (mg/L)	Reference
Ceriodaphnia dubia	Water Flea	1.36	20.80	20.79	Bailey et al. 2001
Ceriodaphnia dubia	Water Flea	1.01	15.45	15.44	Bailey et al. 2001
Ceriodaphnia dubia	Water Flea	1.56	46.21	34.98	Sarda 1994
Ceriodaphnia dubia	Water Flea	1.84	54.50	41.26	Sarda 1994
Crangonyx pseudogracillis	Amphipod	0.36	52.65	22.24	Prenter et al. 2004
Crangonyx sp.	Amphipod	2.05	163.71	92.10	Diamond et al. 1993
Daphnia magna	Water Flea	1.17	53.24	29.95	Diamond et al. 1993
Erythromma najas	Damselfly	10.42	463.98	202.02	Beketov 2002
Erythromma najas	Damselfly	37.80	140.28	534.71	Beketov 2002
Erythromma najas	Damselfly	22.14	41.44	323.90	Beketov 2002
Erythromma najas	Damselfly	12.45	679.66	259.28	Beketov 2002
Gammarus pulex	Amphipod	1.54	225.82	95.40	Prenter et al. 2004
Helisoma trivolvis	Snail	2.04	47.73	39.58	Arthur et al. 1987
Hyalella azteca	Amphipod	2.08	61.61	46.64	Sarda 1994
Hyalella azteca	Amphipod	2.52	74.64	56.51	Sarda 1994
Lestes sponsa	Dragonfly	7.30	310.69	139.48	Beketov 2002
Orconectes immunis	Calico crayfish	14.72	488.07	404.82	Arthur et al. 1987
Philarctus quaeris	Caddisfly	10.07	296.51	205.25	Arthur et al. 1987
Physa gyrina	Snail	2.49	76.29	92.27	Arthur et al. 1987
Procambarus clarkii	Red swamp crayfish	1.21	53.41	30.05	Diamond et al. 1993
Simocephalus vetulus	Water flea	1.27	21.36	25.83	Arthur et al. 1987
Sympetrum flaveolum	Dragonfly	1.72	274.34	61.73	Beketov 2002
Sympetrum flaveolum	Dragonfly	3.41	181.98	70.42	Beketov 2002
Sympetrum flaveolum	Dragonfly	6.11	58.31	88.95	Beketov 2002
Sympetrum flaveolum	Dragonfly	12.56	701.39	263.82	Beketov 2002
Actinonaias pectorosa	Pheasantshell mussel	0.25	3.76	3.76	Augspurger et al. 2003
Actinonaias pectorosa	Pheasantshell mussel	0.92	14.06	14.05	Augspurger et al. 2003
Actinonaias pectorosa	Pheasantshell mussel	0.74	17.06	14.15	Keller et al. 2000 (unpublished)
Actinonaias sp.	Mussel	0.83	17.09	15.55	Keller et al. 2000 (unpublished)

Table 4-2 (Continued)
Summary of Acute Data Deemed Acceptable for use and Added to the Updated Acute Ammonia Toxicity Database

Species	Common Name	NH_3-N (mg/L)	TA-N (mg/L)	TA-N pH8 (mg/L)	Reference
Fusconaia masoni	Atlantic pigtoe mussel	0.07	2.71	1.34	Black 2001
Lampsilis cardium	Plain pocketbook mussel	1.86	25.01	36.69	Newton et al. 2003
Lampsilis cardium	Plain pocketbook mussel	1.94	24.79	36.38	Newton et al. 2003
Lampsilis cardium	Plain pocketbook mussel	0.80	12.67	15.32	Newton et al. 2003
Lampsilis cardium	Plain pocketbook mussel	0.56	14.16	11.75	Newton et al. 2003
Lampsilis fasciola	Wavy-rayed lampmussel	0.32	17.38	12.69	Mummert et al. 2003
Lampsilis fasciola	Wavy-rayed lampmussel	0.24	13.26	9.68	Mummert et al. 2003
Lampsilis fasciola	Wavy-rayed lampmussel	0.23	12.68	9.26	Mummert et al. 2003
Lampsilis fasciola	Wavy-rayed lampmussel	0.25	13.59	9.92	Mummert et al. 2003
Lampsilis fasciola	Wavy-rayed lampmussel	0.54	12.27	11.38	Mummert et al. 2003
Lampsilis fasciola	Wavy-rayed lampmussel	0.28	6.37	5.91	Mummert et al. 2003
Lampsilis siliquoidea	Fatmucket mussel	0.09	0.78	1.39	Myers-Kinzie 1998
Lampsilis siliquoidea	Fatmucket mussel	0.28	2.39	4.26	Myers-Kinzie 1998
Lasmigona subviridis	Green floater mussel	0.13	4.28	2.49	Black 2001
Lasmigona subviridis	Green floater mussel	0.13	4.28	2.49	Black 2001
Lasmigona subviridis	Green floater mussel	0.24	3.61	3.61	Black 2001
Medionidus conradicus	Cumberland moccasinshell mussel	0.29	4.48	4.47	Augspurger et al. 2003
Pyganodon grandis	Giant floater mussel	0.20	9.19	3.88	Scheller 1997
Pyganodon grandis	Giant floater mussel	0.33	9.79	5.70	Scheller 1997
Utterbackia imbecilis	Paper pondshell mussel	0.64	7.87	9.52	Augspurger et al. 2003

Table 4-2 (Continued)
Summary of Acute Data Deemed Acceptable for use and Added to the Updated Acute Ammonia Toxicity Database

Species	Common Name	NH_3-N (mg/L)	TA-N (mg/L)	TA-N pH8 (mg/L)	Reference
Utterbackia imbecilis	Paper pondshell mussel	1.36	20.76	20.75	Augspurger et al. 2003
Utterbackia imbecilis	Paper pondshell mussel	0.72	11.00	10.99	Black 2001
Utterbackia imbecilis	Paper pondshell mussel	0.16	2.51	2.51	Black 2001
Utterbackia imbecilis	Paper pondshell mussel	0.22	3.33	3.32	Black 2001
Utterbackia imbecellis	Paper pondshell mussel	0.19	2.88	2.88	Black 2001
Utterbackia imbecilis	Paper pondshell mussel	2.02	16.28	29.01	Black 2001
Utterbackia imbecilis	Paper pondshell mussel	0.85	8.43	12.37	Black 2001
Utterbackia imbecilis	Paper pondshell mussel	0.75	7.51	11.03	Black 2001
Utterbackia imbecilis	Paper pondshell mussel	0.45	3.97	7.80	Keller et al. 2000 (unpublished)
Utterbackia imbecilis	Paper pondshell mussel	0.49	11.35	9.42	Keller et al. 2000 (unpublished)
Villosa iris	Rainbow mussel	0.36	5.46	6.60	Goudreau et al. 1993
Villosa iris	Rainbow mussel	0.17	30.31	9.71	Mummert et al. 2003
Villosa iris	Rainbow mussel	0.13	24.38	7.81	Mummert et al. 2003
Villosa iris	Rainbow mussel	0.10	18.78	6.02	Mummert et al. 2003
Villosa iris	Rainbow mussel	0.09	16.96	5.44	Mummert et al. 2003
Villosa iris	Rainbow mussel	0.35	27.51	10.20	Mummert et al. 2003
Villosa iris	Rainbow mussel	0.19	14.99	5.56	Mummert et al. 2003
Villosa iris	Rainbow mussel	0.13	10.29	3.82	Mummert et al. 2003
Villosa iris	Rainbow mussel	0.12	9.39	3.48	Mummert et al. 2003
Villosa iris	Rainbow mussel	0.10	2.56	2.12	Scheller 1997
Villosa iris	Rainbow mussel	0.96	9.58	14.06	Scheller 1997
Villosa iris	Rainbow mussel	0.87	8.65	12.70	Scheller 1997
Villosa iris	Rainbow mussel	0.48	5.95	7.20	Scheller 1997
Acipenser brevirostrum	Shortnose sturgeon	0.58	152.48	37.15	Fontenot et al. 1998
Chasmistes brevirostris	Shortnose sucker	1.06	27.74	27.73	Sakai et al. 1999
Chasmistes brevirostris	Shortnose sucker	0.53	13.87	13.86	Sakai et al. 1999

Table 4-2 (Continued)
Summary of Acute Data Deemed Acceptable for use and Added to the Updated Acute Ammonia Toxicity Database

Species	Common Name	NH_3-N (mg/L)	TA-N (mg/L)	TA-N pH8 (mg/L)	Reference
Cyprinodon sp.	Pupfish	1.42	113.40	63.79	Diamond et al. 1993
Cyprinus carpio	Common carp	1.74	48.97	29.48	Hasan and Macintosh 1986
Cyprinus carpio	Common carp	1.84	51.78	31.18	Hasan and Macintosh 1986
Deltistes luxatus	Lost River sucker	0.48	12.56	12.56	Sakai et al. 1999
Deltistes luxatus	Lost River sucker	0.78	20.42	20.40	Sakai et al. 1999
Gambusia affinis	Western mosquitofish	0.72	52.41	15.80	Sangli and Kanabur 2001
Gambusia affinis	Western mosquitofish	0.70	50.95	15.36	Sangli and Kanabur 2001
Gambusia affinis	Western mosquitofish	0.69	50.22	15.14	Sangli and Kanabur 2001
Gambusia affinis	Western mosquitofish	0.67	48.77	14.70	Sangli and Kanabur 2001
Hybognathus amarus	Rio Grande silvery minnow	1.12	16.75	20.26	Buhl 2002
Ictalurus punctatus	Channel catfish	1.82	31.87	31.85	Tomasso et al. 1980
Ictalurus punctatus	Channel catfish	1.39	233.07	54.26	Tomasso et al. 1980
Ictalurus punctatus	Channel catfish	1.49	3.71	23.57	Tomasso et al. 1980
Ictalurus punctatus	Channel catfish	1.79	300.14	69.88	Tomasso et al. 1980
Lepomis macrochirus	Bluegill	1.00	44.14	24.83	Diamond et al. 1993
Lepomis macrochirus	Bluegill	0.65	51.91	29.20	Diamond et al. 1993
Lepomis macrochirus	Bluegill	1.06	15.97	19.31	Mayes et al. 1986
Morone chrysops	White bass	0.63	155.45	36.84	Ashe et al. 1996
Morone chrysops	White bass	0.40	3.18	10.09	Harcke and Daniels 1999
Morone chrysops	White bass	0.46	81.29	18.93	Weirich et al. 1993
Oncorhynchus mykiss	Rainbow trout	1.04	12.75	22.72	Arthur et al. 1987
Oncorhynchus mykiss	Rainbow trout	0.49	60.83	22.25	Calamari et al. 1981
Oncorhynchus mykiss	Rainbow trout	0.50	31.64	24.40	Thurston et al. 1981
Oncorhynchus mykiss	Rainbow trout	0.30	27.90	17.39	Thurston et al. 1981
Oncorhynchus mykiss	Rainbow trout	0.16	20.53	10.46	Thurston et al. 1981
Oncorhynchus mykiss	Rainbow trout	0.40	111.18	31.63	Wicks and Randall 2002
Oncorhynchus mykiss	Rainbow trout	0.54	152.35	43.34	Wicks and Randall 2002
Oncorhynchus mykiss	Rainbow trout	0.42	117.76	33.50	Wicks and Randall 2002
Oncorhynchus mykiss	Rainbow trout	0.52	145.76	41.47	Wicks and Randall 2002
Oncorhynchus mykiss	Rainbow trout	0.39	108.71	30.92	Wicks and Randall 2002

Table 4-2 (Continued)
Summary of Acute Data Deemed Acceptable for use and Added to the Updated Acute Ammonia Toxicity Database

Species	Common Name	NH_3-N (mg/L)	TA-N (mg/L)	TA-N pH8 (mg/L)	Reference
Oncorhynchus mykiss	Rainbow trout	0.41	114.47	32.56	Wicks and Randall 2002
Oncorhynchus mykiss	Rainbow trout	0.41	113.65	32.33	Wicks and Randall 2002
Oncorhynchus mykiss	Rainbow trout	0.42	116.12	33.03	Wicks and Randall 2002
Oncorhynchus mykiss	Rainbow trout	0.51	143.29	40.76	Wicks and Randall 2002
Oncorhynchus mykiss	Rainbow trout	0.72	207.00	46.97	Wicks et al. 2002
Oncorhynchus mykiss	Rainbow trout	0.11	32.38	7.35	Wicks et al. 2002
Pimephales promelas	Fathead minnow	0.25	11.36	6.39	Diamond et al. 1993
Pimephales promelas	Fathead minnow	1.50	22.60	27.33	Mayes et al. 1986
Pimephales promelas	Fathead minnow	1.01	14.47	18.19	Buhl 2002
Sander vitreum	Walleye	1.04	16.21	19.61	Mayes et al. 1986
Rana pipiens	Northern leopard frog	1.44	63.56	35.76	Diamond et al. 1993
Rana pipiens	Northern leopard frog	0.42	33.54	18.87	Diamond et al. 1993

NOTE: Acute values (LC_{50}) have been adjusted to pH 8 and are reported as acute values in nitrogen equivalence of total ammonia.

4.2.2 New Chronic Ammonia Toxicity Data

Owing to the paucity of chronic ammonia studies and stringent experimental protocols (i.e., duration, dissolved oxygen, and life stage), only 15 studies (representing 9 genera) were considered acceptable by the EPA for the development of chronic ammonia criteria. Our review of the literature increased the size of the chronic database somewhat for a total of 20 studies that evaluated a variety of chronic endpoints, from egg hatching success to early life stage biomass, providing chronic ammonia toxicity data for 14 species representing 12 genera. Three new species were added to the chronic database, which include *Salvelinus namayacush, Lasmigona subviridis* and *Esox lucius* (Table 4-3).

The updated chronic database is considerably less robust than the updated acute database, and still does not meet the "eight family rule" for the development of national water quality criteria (Stephan et al. 1985). Specifically, two of the eight required families are not represented - a family in the class Insecta, and a second family from Insecta or a non-represented phylum. This shortcoming of the chronic database precluded the EPA's use of the 5^{th} percentile approach to set the CCC in the 1999 document, but EPA still developed a chronic criterion using this method.

Table 4-3
New Chronic Ammonia Toxicity Data Added to the EPA (1999) Database

Species	Common name	Temp	pH	EC_{20} TA-N @ test pH & Temp (mg/L)	EC_{20} TA-N @ pH=8 (mg/L)	EC_{20} TA-N @ pH=8 & 25°C (mg/L)	SMCV @ pH8 25°C (mg/L)	Reference
Salvelinus namayacush	Lake trout	11.60	8.02	9.13	9.40	3.96	3.96	Beamish and Tandler 1990
Lasmigona subviridis	Green floater mussel	22.00	8.00	0.56	0.56	0.46	0.46	Black 2001
Esox lucius	Northern pike	9.00	7.60	43.20	26.47	9.43	4.39	Harrahy et al. 2004
Esox lucius		9.00	7.60	20.56	12.60	4.49		Harrahy et al. 2004
Esox lucius		9.00	7.60	13.21	8.25	2.94		Harrahy et al. 2004
Esox lucius		9.00	7.60	13.44	8.40	2.99		Harrahy et al. 2004

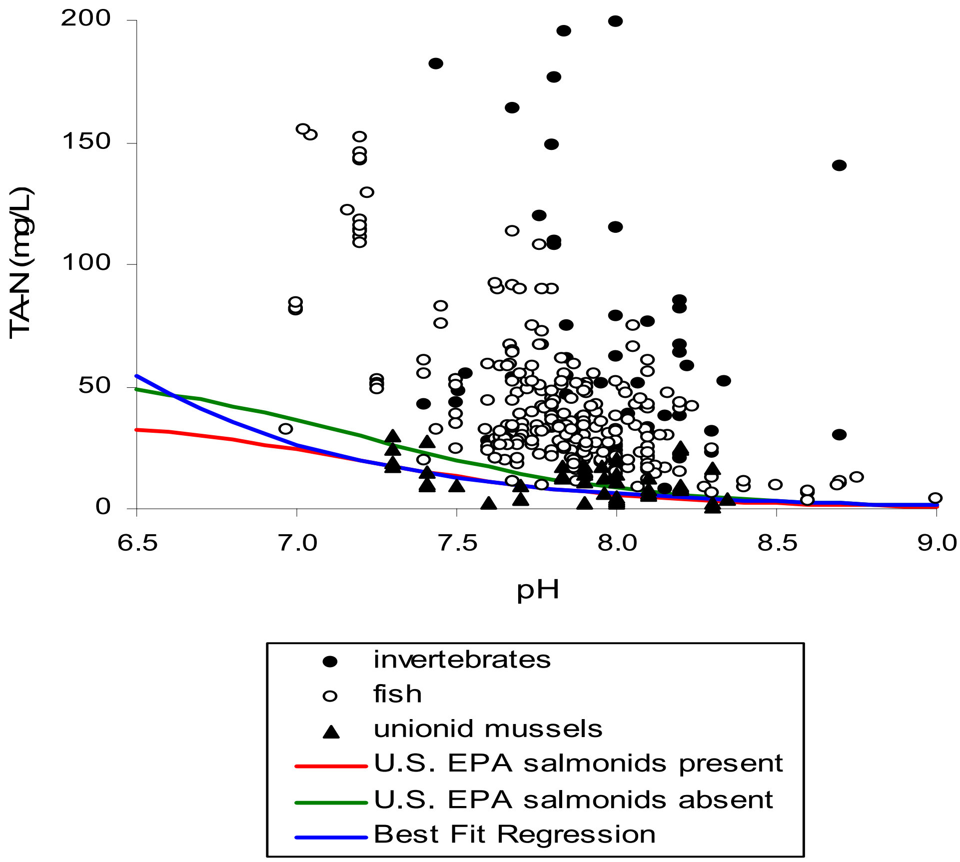
4.3 PHASE III – REVISED ACUTE AND CHRONIC AWQC FOR AMMONIA

4.3.1 Updated Acute Criteria for Ammonia

Even though the acute database doubled in terms of total species, there were only a few studies that evaluated ammonia toxicity within the range of pH (6.5 to 9) suitable to develop water quality criteria. In addition, there was a concern of developing criteria based on studies that had relatively small sample sizes. Therefore, a decision was made to again use a selected group of studies for "curve-fitting" purposes, similar to the approach used by EPA. However, the EPA never stated which four datasets they specifically used to model the inflection point of their model (i.e., 7.204) or other parameters in the equations, making the model validation and parameterization difficult. Therefore, we could only speculate on the four datasets that met the need of toxicity data obtained over a wide range of pH. For our analysis, we used data from Broderius *et al*. 1985 (n = 70), DeGraeve et al. 1987 (n = 80), Reinbold and Pescitelli 1982 (n = 32), and Thurston et al. 1986 (n = 40) to evaluate the fit of simple linear and multiple regression models to individual and pooled datasets. We believe these may be the four datasets used by EPA, but we could never exactly duplicate their inflection point.

We first re-analyzed the TA vs pH relationship and found we could not specifically fit EPA's model to the available toxicity data. Linear models were able to account for 63% of the variation observed between $\log_{10}$TA and pH in the Broderius et al. (1985) data. Similarly, 28 to 51% of the variation observed in the remaining datasets could be accounted for using linear models. It was clear that linear models showed very weak relationships between $\log_{10}$TA and temperature for the selected data, again supporting the decision to not include a temperature component in the acute ammonia relationship.

Although pH relationships were more robust than the temperature relationships, the linear model approach still has shortcomings when trying to set CMC values. For example, at lower pH's (6 to 6.5), the residual error of the linear models increased, exhibiting a poorer fit to potential ammonia toxicity (and EPA's curves) within this pH range (Figure 4-1). Theoretically, within this lower pH range, ammonia toxicity might be expected to reach an asymptotic level based on the chemical speciation of ammonia (NH_3) and ammonium ion (NH_4^+) – and this is the basis for EPA's "S-shaped" curves.



NOTES:
The red [illegible]s the EPA CMC with salmonids present; green line is EPA CMC with salmonids absent; blue line is the best fit regression model representing the 5th percentile of data.
Note the divergence between the EPA and best fit models at pH <7.

Figure 4-1
pH Dependency of Acute Ammonia Toxicity Models

Given the shortcomings of the linear model approach for developing ammonia toxicity criteria and the potential problems with developing such a different curve from the EPA versions, our review simply updated the "salmonids present" and "salmonids absent" curves using the same inflection points developed by the EPA (1999) with our updated database.

However, before adjusting the "salmonids present or absent" curves with the new data, it was necessary to address outstanding issues in the EPA acute equations. Specifically, there was a concern with EPA's use of a modified SMAV based on "large" *Oncorhynchus mykiss* in the development of their "salmonids present" equation. Thurston and Russo (1983) examined the response of various age-class rainbow trout (<1d to 4yr old) to acute toxicity and found that the tolerance to ammonia toxicity increased through larval development stages, peaking at the juvenile-yearling stage and decreasing in older fish. One caveat of their study is that age-class conclusions were based on regression results from fish that were <1d to 302 days old from the same egg lot, but then applied to fish that were 4 years old from a different egg lot.

Based on Thurston and Russo's (1983) conclusions, the EPA lowered the SMAV for *O. mykiss* from 21.95 mg N/L to 11.23 mg N/L. In our review of the Thurston and Russo (1983) data we were unable to duplicate the geometric mean of LC_{50} values of 11.23 mg N/L for "large" rainbow trout that the EPA determined and used to develop the "salmonids present" acute equation.

Because this size class relationship to acute ammonia has not been observed in other studies of rainbow trout (e.g., Calamari et al.1981, Arthur et al. 1987, Wicks and Randall 2002), and the fact that the EPA did not clearly define "large" rainbow trout (i.e., simply > 1 kg), led us to an alternative and perhaps more defensible approach to accounting for potential different sensitivities of warm and cold-water biota to ammonia. It was decided to re-categorize the updated database into two databases as either cold-water or warm-water species. This method alleviates the preferential treatment given to one age-class of a single species when setting national, or even regional, criteria. This does not mean that sensitive age-classes of a species should not be protected, rather that this aspect of the ammonia criteria should be based on a more robust scientific approach than is currently the case. This is potentially an area where further age-class studies are needed to support such hypotheses that there is a size class relationship to acute ammonia toxicity.

Due to the various data reporting methods, LC_{50} results for ammonia toxicity were converted to TA-N and normalized to pH 8, as described earlier. Toxicity values that were published as "greater than" or "less than" values were not used. No temperature adjustment was made, consistent with the EPA document. The geometric mean of the normalized pH 8 acute values (AV), were computed for each species (SMAV). Similarly, the GMAV were computed for each genera (GMAV = geometric mean of SMAV).

The database was then split into two lists of species, cold and warm water species (Table 4-4). Placement of each species was determined from their preferred habitat type. *Species commonly found in both habitat types or representative of species found in one or the other habitat type were included in both data subsets*. These species included all invertebrates, except the freshwater mussels. Once divided, each database still met the requirements for data inclusion in criteria development (i.e., the "eight family rule"), with the understandable exception that the warm-water database did not specifically include a representative from the Salmonidae family. For each habitat category, the GMAVs were ranked from the highest (n) to lowest (1) value with a cumulative probability assigned to each value (Stephan et al. 1985). The four lowest GMAVs were used to calculate the FAV for each data subset.

Table 4-4
Recalculated Species Mean Acute Values (SMAV) using the Revised and Updated Acute Toxicity Database and Ranked Genus Mean Acute Values (GMAV)

Rank	Species	Common Name	GMAV (mg TA-N/L)	SMAV (mg TA-N/L)	Habitat Type[b]
56	*Erythromma najas*	Damselfly	308.62	308.62	1, 2
55	*Philarctus quaeris*	Crayfish	282.09	282.09	1, 2
54	*Drunella grandis*	Mayfly	189.16	189.16	1, 2
53	*Orconectes immunis*	Crayfish	178.31	770.46	1, 2
	Orconectes naias	Crayfish		41.27	1, 2
52	*Caecidotea racovitzai*	Isopod	165.94	165.94	1, 2
51	*Lestes sponsa*	Dragonfly	139.48	139.48	1, 2
50	*Stenelmis sexlineata*	Beetle	113.17	113.17	1, 2
49	*Callibaetis skokianus*	Mayfly	111.62	164.08	1, 2
	Callibaetis sp.	Mayfly		75.93	1, 2
48	*Sympetrum flaveolum*	Dragonfly	100.50	100.50	1, 2
47	*Tubifex tubifex*	Tubificid worm	97.82	97.82	1, 2
46	*Gammarus pulex*	Amphipod	95.40	95.40	1, 2
45	*Baetis rhodani*	Mayfly	94.19	94.19	1, 2
44	*Crangonyx pseudogracilis*	Amphipod	87.53	83.19	1, 2
	Crangonyx sp.	Amphipod		92.10	1, 2
43	*Skwala americana*	Stonefly	77.10	77.10	1, 2
42	*Physa gyrina*	Snail	74.48	74.48	1, 2
41	*Cyprinodon* sp.	Minnow	63.79	63.79	2
40	*Helisoma trivolvis*	Snail	60.84	60.84	1, 2
39	*Cottus bairdii*	Mottled Sculpin	51.73	51.73	1
38	*Hyalella azteca*	Amphipod	51.34	51.34	1, 2
37	*Pimephales promelas*	Fathead minnow	41.89	41.89	2
36	*Simocephalus vetulus*	Cladoceran	38.13	38.13	1, 2
35	*Catostomus commersonii*	White sucker	38.12	45.82	1, 2
	Catostomus platyrynchus	Mountain sucker		31.71	1, 2

Table 4-4 (Continued)
Recalculated Species Mean Acute Values (SMAV) using the Revised and Updated Acute Toxicity Database and Ranked Genus Mean Acute Values (GMAV)

Rank	Species	Common Name	GMAV (mg TA-N/L)	SMAV (mg TA-N/L)	Habitat Type[b]
34	*Acipenser brevirostrum*	Shortnose sturgeon	37.15	37.15	1, 2
33	*Salvelinus fontinalis*	Brook trout	36.39	36.39	1
32	*Daphnia magna*	Cladoceran	36.26	35.24	1, 2
	Daphnia pulicaria	Cladoceran		37.31	1, 2
31	*Ictalurus punctatus*	Channel catfish	35.81	35.81	2
30	*Musculium transversum*	Fingernail clam	35.65	35.65	1, 2
29	*Poecilia reticulata*	Guppy	33.15	33.15	2
28	*Dendrocoelom lacteum*	Flatworm	32.82	32.82	1, 2
27	*Cyprinus carpio*	Common carp	30.32	30.32	2
26	*Procambarus clarkii*	Crayfish	30.05	30.05	1, 2
25	*Micropterus dolomieu*	Smallmouth bass	27.18	36.90	2
	Micropterus salmoides	Largemouth bass		20.03	2
24	*Campostoma anomalum*	Central stoneroller	26.97	26.97	2
23	*Rana pipiens*	Northern leopard frog	25.97	25.97	1, 2
22	*Sander vitreum*	Walleye	25.89	25.89	1, 2
21	*Cyprinella lutrensis*	Red shiner	25.60	45.65	2
	Cyprinella spilopterus	Spotfin shiner		19.51	2
	Cyprinella whipplei	Steelcolor shiner		18.83	2
20	*Morone americana*	White perch	24.33	30.89	2
	Morone chrysops	White bass		19.16	2
19	*Salmo trutta*	Brown trout	23.74	23.74	1
18	*Lepomis cyanellus*	Green sunfish	23.64	30.31	2
	Lepomis macrochirus	Bluegill		24.16	2
	Lepomis gibbosus	Pumpkinseed		18.05	2
17	*Oncorhynchus gorbuscha*	Pink salmon	22.91	42.07	1
	Oncorhynchus clarkii	Cutthroat trout		25.80	1
	Oncorhynchus aquabonita	Golden trout		22.71	1
	Oncorhynchus mykiss	Rainbow trout		19.94	1
	Oncorhynchus tshawytscha	Chinook salmon		17.34	1
	Oncorhynchus kisutch	Coho salmon		16.97	1

Table 4-4 (Continued)
Recalculated Species Mean Acute Values (SMAV) using the Revised and Updated Acute Toxicity Database and Ranked Genus Mean Acute Values (GMAV)

Rank	Species	Common Name	GMAV (mg TA-N/L)	SMAV (mg TA-N/L)	Habitat Type[b]
16	*Hybognathus amarus*	Rio grande silvery minnow	20.26	20.26	2
15	*Chasmistes brevirostris*	Shortnose sucker	19.61	19.61	2
14	*Etheostoma spectabile*	Orangethroat darter	18.14	18.14	2
13	*Ceriodaphnia dubia*	Cladoceran	17.42	22.17	1, 2
	Ceriodaphnia acanthina	Cladoceran		13.68	1, 2
12	*Deltistes luxatus*	Lost river sucker	16.01	16.01	2
11	*Gambusia affinis*	Mosquitofish	15.25	15.25	2
10	*Notemigonus chrysoleucas*	Golden shiner	14.67	14.67	2
9	*Prosopium williamsoni*	Mountain whitefish	12.11	12.11	1
8	*Actinonaias pectorosa*	Pheasantshell mussel	10.38	10.38	2[c]
7	*Utterbackia imbecilis*	Paper pondshell mussel	8.43	8.43	2[c]
6	*Lampsilis cardium*	Plain pocketbook mussel	8.01	22.14	2[c]
	Lampsilis fasciola	Wavy-rayed lampmussel		9.55	2[c]
	Lampsilis siliquoidea	Fatmucket mussel		2.43	2[c]
5	*Villosa iris*	Rainbow mussel	6.45	6.45	2[c]
4	*Pyganodon grandis*	Giant floater mussel	4.70	4.70	2[c]
3	*Medionidus conradicus*	Cumberland moccasinshell mussel	4.47	4.47	2[c]
2	*Lasmigona subviridis*	Green floater mussel	2.82	2.82	2[c]
1	*Fusconaia masoni*	Atlantic pigtoe mussel	1.34	1.34	2[c]

[a]GMAV and SMAV are reported as total ammonia nitrogen at pH = 8, mg N/L
[b]1 = cold water, 2 = warm water
[c]Unionidae

Within the cold-water species database (32 genera), the four most sensitive genera were the *Salmo* (23.7 mg TA-N/L), *Oncorhynchus* (22.9 mg TA-N/L), *Ceriodaphnia* (17.4 mg TA-N/L), and *Prosopium* (12.1 mg TA-N/L). Using these data, the FAV was 15.3 mg TA-N/L for cold-water species; a value slightly higher than the 11.23 mg TA-N/L EPA used for "salmonids present" (Table 4-5).

Table 4-5
Recalculation of the Cold-Water Criterion Maximum Concentration for Ammonia using the Updated Acute Database

Rank	Genus	GMAV	ln GMAV	(ln GMAV)^2	P = R/(N+1)	√P
4	*Salmo*	23.74	3.1672	10.0312	0.1212	0.3482
3	*Oncorhynchus*	22.91	3.1316	9.8069	0.0909	0.3015
2	*Ceriodaphnia*	17.42	2.8576	8.1659	0.0606	0.2462
1	*Prosopium*	12.11	2.494	6.22	0.0303	0.1741
		sum	**11.6504**	**34.2240**	**0.3030**	**1.0700**

$$S^2 = \frac{\sum(\ln \mathrm{GMAV})^2 - \left(\sum \ln \mathrm{GMAV}\right)^2/4}{\sum P - \left(\sum\sqrt{P}\right)^2/4} = \frac{34.2240-(11.6504)^2/4}{0.3030-(1.0700)^2/4} = 17.3186$$

$$S = 4.1616$$

$$L = \left[\sum \ln\mathrm{GMAV} - S\left(\sum\sqrt{P}\right)\right]/4 = [11.6504 - 4.1616(1.0700)]/4 = 1.7994$$

$$A = S\left(\sqrt{0.05}\right) + L = 4.1616(0.2236) + 1.7994 = 2.7299$$

$$\mathrm{FAV} = e^A = e^{2.7299} = 15.33$$

$$\mathrm{AV_t} = \mathrm{AV_{t,8}}\left[\frac{0.0489}{1+10^{7.204-\mathrm{pH}}} + \frac{6.95}{1+10^{\mathrm{pH}-7.204}}\right]$$

$$\mathrm{AV_{t,8}} = \frac{\mathrm{FAV}}{2} = \frac{15.33}{2} = 7.67 \text{ mg N/L}$$

$$\mathrm{AV_t} = 7.67\left[\frac{0.0489}{1+10^{7.204-\mathrm{pH}}} + \frac{6.95}{1+10^{\mathrm{pH}-7.204}}\right]$$

$$\mathrm{CMC_{cold}} = \frac{0.375}{1+10^{7.204-\mathrm{pH}}} + \frac{53.3}{1+10^{\mathrm{pH}-7.204}}$$

NOTES: N = 32 genera and R = sensitivity rank in database.

For the warm-water database (51 genera), the four most sensitive genera were *Pyganodon* (4.7 mg TA-N/L), *Medionidus* (4.5 mg TA-N/L), *Lasmigona* (2.8 mg TA-N/L), and *Fusconaia* (1.3 mg TA-N/L). The resulting FAV was 3.3 mg TA-N/L for the warm-water database (Table 4-6). Note that these four genera are all mussels from the Unionidae family, representing new data not available for the 1999 Update. In fact, representatives from the unionid family comprised the 8 most sensitive genera within the updated warm-water database. Inclusion of these unionid ammonia toxicity data would lead to a significant reduction in the CMC for warm-water biota, when compared to the "salmonids absent" category of the EPA document (1999).

Table 4-6
Recalculation of the Warm-Water with Unionidae CMC for Ammonia using the Updated Acute Database

Rank	Genus	GMAV	ln GMAV	(ln GMAV)^2	P = R/(N+1)	√P
4	*Pyganodon*	4.70	1.5476	2.3951	0.0769	0.2774
3	*Medionidus*	4.47	1.4974	2.2422	0.0577	0.2402
2	*Lasmigona*	2.82	1.0367	1.0747	0.0385	0.1961
1	*Fusconaia*	1.34	0.2927	0.0857	0.0192	0.1387
		sum	**4.3744**	**5.7977**	**0.1923**	**0.8524**

$$S^2 = \frac{\sum(\ln \text{GMAV})^2 - \left(\sum \ln \text{GMAV}\right)^2/4}{\sum P - \left(\sum \sqrt{P}\right)^2/4} = \frac{5.7977 - (4.3744)^2/4}{0.1923 - (0.8524)^2/4} = 95.0973$$

$$S = 9.7518$$

$$L = \left[\sum \ln \text{GMAV} - S\left(\sum \sqrt{P}\right)\right]/4 = [4.3744 - 9.7518(0.8524)]/4 = -0.9845$$

$$A = S\left(\sqrt{0.05}\right) + L = 9.7518(0.2236) - 0.9845 = 1.1961$$

$$\text{FAV} = e^{A} = e^{1.196} = 3.31$$

$$AV_t = AV_{t,8}\left[\frac{0.0489}{1+10^{7.204-\text{pH}}} + \frac{6.95}{1+10^{\text{pH}-7.204}}\right]$$

$$AV_{t,8} = \frac{\text{FAV}}{2} = \frac{3.31}{2} = 1.66 \text{ mg N/L}$$

$$AV_t = 1.66\left[\frac{0.0489}{1+10^{7.204-\text{pH}}} + \frac{6.95}{1+10^{\text{pH}-7.204}}\right]$$

$$\text{CMC}_{\text{warm}} = \frac{0.081}{1+10^{7.204-\text{pH}}} + \frac{11.5}{1+10^{\text{pH}-7.204}}$$

NOTES: N = 51 genera and R = sensitivity rank in database.

While widespread throughout the Midwest and eastern U.S., there is uncertainty for unionid distribution within the arid West (e.g., Wu and Brandauer 1978). In addition, there is apparent potential for further EPA technical review of these studies (*Federal Register* 2004). As such, we also analyzed the warm-water database minus the Unionidae family (although other freshwater clams were retained).

This modified warm-water database still contained 43 genera, with *Ceriodaphnia* (17.4 mg TA-N/L), *Deltistes* (16.0 mg TA-N/L), *Gambusia* (15.3 mg TA-N/L), and *Notemigonus* (14.7 mg TA-N/L) being the four most sensitive genera. The FAV for this warm-water database minus unionid clams was 15.9 mg TA-N/L (Table 4-7).

Table 4-7
Recalculation of the Warm-Water Without Unionidae CMC for Ammonia using the Updated Acute Database

Rank	Genus	GMAV	ln GMAV	(ln GMAV)^2	P = R/(N+1)	√P
4	*Ceriodaphnia*	17.42	2.8576	8.1659	0.0909	0.3015
3	*Deltistes*	16.01	2.7732	7.6906	0.0682	0.2611
2	*Gambusia*	15.25	2.7246	7.4234	0.0455	0.2132
1	*Notemigonus*	14.67	2.6858	7.2135	0.0227	0.1508
		sum	**11.0412**	**30.4934**	**0.2273**	**0.9266**

$$S^2 = \frac{\sum(\ln GMAV)^2 - \left(\sum \ln GMAV\right)^2/4}{\sum P - \left(\sum\sqrt{P}\right)^2/4} = \frac{30.4934-(11.0412)^2/4}{0.2273-(0.9266)^2/4} = 1.2970$$

$$S = 1.1389$$

$$L = \left[\sum \ln GMAV - S\left(\sum\sqrt{P}\right)\right]/4 = \left[11.0412 - 1.1389(0.9266)\right]/4 = 2.4965$$

$$A = S\left(\sqrt{0.05}\right) + L = 1.1389(0.2236) + 2.4965 = 2.7511$$

$$FAV = e^{A} = e^{2.7675} = 15.66$$

$$AV_t = AV_{t,8}\left[\frac{0.0489}{1+10^{7.204-pH}} + \frac{6.95}{1+10^{pH-7.204}}\right]$$

$$AV_{t,8} = \frac{FAV}{2} = \frac{15.66}{2} = 7.83 \text{ mg N/L}$$

$$AV_t = 7.83\left[\frac{0.0489}{1+10^{7.204-pH}} + \frac{6.95}{1+10^{pH-7.204}}\right]$$

$$CMC_{\text{warm without Unionidae}} = \frac{0.383}{1+10^{7.204-pH}} + \frac{54.4}{1+10^{pH-7.204}}$$

NOTES: N = 43 genera and R = sensitivity rank in database.

The FAV value for each database (i.e., cold-water, warm-water, warm-water minus Unionidae) was then used to calculate the CMC for each habitat type. Substitution of one-half the FAV into equation two for $AV_{t,8}$ provided the CMC at pH 8. Using the updated databases, and recalculated FAVs, the three resulting acute (CMC) equations for 1) cold-water [Eq. 9], 2) warm-water [Eq. 10], and 3) warm-water without the family Unionidae [Eq. 11], with respect to pH, are:

Updated Cold-water Ammonia Acute Criterion:

$$CMC_{Cold} = \frac{0.375}{1+10^{7.204-pH}} + \frac{53.3}{1+10^{pH-7.204}} \qquad \text{Eq. 9}$$

Updated Warm-water Ammonia Acute Criterion:

$$\mathrm{CMC}_{\mathrm{Warm}} = \frac{0.081}{1+10^{7.204-\mathrm{pH}}} + \frac{11.5}{1+10^{\mathrm{pH}-7.204}} \quad \text{Eq. 10}$$

Updated Warm-water without Unionidae Ammonia Acute Criterion:

$$\mathrm{CMC}_{\mathrm{Warm\ without\ Unionidae}} = \frac{0.388}{1+10^{7.204\text{-pH}}} + \frac{55.3}{1+10^{\text{pH-}7.204}} \quad \text{Eq. 11}$$

Each equation was solved for an acute criterion given a range of pH values (6.5-9), producing an ammonia concentration that protects all but the most sensitive 5% of organisms in the revised toxicity databases (see Table 4-8). These values were then compared to the existing "salmonids present" and "salmonids absent" acute ammonia equations in the EPA 1999 AWQC (Figure 4-2).

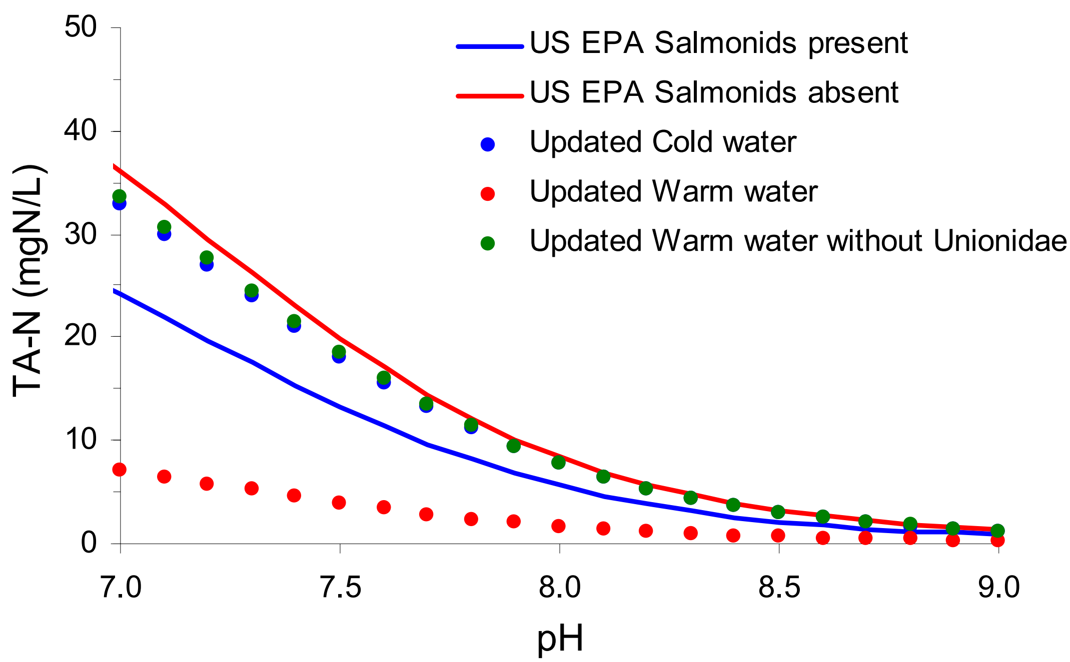


Figure 4-2
Comparison of EPA 1999 and Criterion Maximum Concentrations for TA-N given a range of pH values from 7.0 to 9.0

Table 4-8
Comparative TA-N Concentrations Given pH for
EPA (1999) Acute Criteria and Proposed Updated Acute Criteria

pH	EPA 1999 Acute Criteria			Revised and Updated Acute Criteria		
	CMC (Salmonids present)	CMC (Salmonids absent)		Cold-water Biota	Warm Water Biota with Unionids	Warm Water Biota without Unionids
	(TA-N mg/L)	(TA-N mg/L)		(TA-N mg/L)	(TA-N mg/L)	(TA-N mg/L)
6.5	32.61	48.83		44.56	9.62	45.48
6.6	31.28	46.84		42.75	9.22	43.64
6.7	29.76	44.57		40.67	8.78	41.51
6.8	28.05	42.00		38.33	8.27	39.12
6.9	26.15	39.16		35.74	7.71	36.48
7.0	24.10	36.09		32.94	7.11	33.62
7.1	21.94	32.86		29.99	6.47	30.61
7.2	19.73	29.54		26.96	5.82	27.52
7.3	17.51	26.21		23.92	5.16	24.42
7.4	15.34	22.97		20.97	4.52	21.40
7.5	13.28	19.89		18.15	3.92	18.53
7.6	11.37	17.03		15.54	3.35	15.87
7.7	9.64	14.44		13.18	2.84	13.45
7.8	8.11	12.14		11.08	2.39	11.31
7.9	6.77	10.13		9.25	2.00	9.44
8.0	5.62	8.41		7.67	1.66	7.83
8.1	4.64	6.95		6.34	1.37	6.47
8.2	3.83	5.73		5.23	1.13	5.33
8.3	3.15	4.71		4.30	0.93	4.39
8.4	2.59	3.88		3.54	0.76	3.62
8.5	2.14	3.20		2.92	0.63	2.98
8.6	1.77	2.65		2.42	0.52	2.47
8.7	1.47	2.20		2.01	0.43	2.05
8.8	1.23	1.84		1.68	0.36	1.72
8.9	1.04	1.56		1.42	0.31	1.45
9.0	0.88	1.32		1.21	0.26	1.23

The notable differences between the EPA acute equations and our revised and updated equations are the upward shift for the new "cold-water" acute values as compared to the "salmonids present" acute values in the EPA document and the 5-fold decrease in the new "warm-water with unionids" acute values as compared to the "salmonids absent" acute values from EPA. This substantial decrease is solely due to the inclusion of data for warm-water mussels in the family Unionidae. When these organisms are removed from the database, the resulting "warm-water without Unionidae" curve is comparable to the EPA "salmonids absent" curve, with only a slight downward shift in the CMC (i.e., the revised warm-water curve is more restrictive than the EPA "salmonids absent" curve).

Although verification of the EPA's acute value model (AV_{TA}) remains somewhat questionable (i.e., lack of specifics regarding empirical data), we generally accepted their formulation of acute equations with a few notable exceptions. The EPA's use of a modified *O. mykiss* SMAV combined with the decision not to include the most current data available resulted in the development of outdated and potentially biased ammonia criteria. Therefore, we believe an alternate and scientifically sound approach to developing acute ammonia criteria would be to amend the EPA database by excluding questionable data and including the most current data available, and further excluding the preferential age-class SMAV for *O. mykiss*.

The "new" database is then split based on habitat types (i.e., cold, warm, and warm-water without Unionidae), with "new" FAVs being calculated for each habitat type. These values are the basis for the updated cold, warm, and warm-water without Unionidae acute equations using the EPA's pH-dependent relationship.

4.3.2 Updated Chronic Criteria for Ammonia

The EPA's development of the chronic equations based on temperature and pH creates a variety of concerns.

1. Firstly, the existing chronic database (EPA 1999) does not meet the EPA guidelines for deriving numerical national ambient water quality criteria (Stephan et al. 1985). The database does not contain representatives from the family *Salmonidae*, class Insecta, or another phylum not already present in the database. This should have precluded development of chronic criteria directly from that database. Another approach, such as use of an ACR, should have been used.

2. The temperature-dependent chronic toxicity model developed by EPA is based on a single <u>acute toxicity</u> study in which the authors themselves explicitly state that no relationships were observed between acute ammonia toxicity and temperature.

3. The most sensitive organism in the limited chronic database, the amphipod *Hyalella azteca* (EC_{50} <1.45 mg N/L), was used to develop a temperature-based function to protect <u>early life stage fish</u>. Obviously, it is difficult to understand how an amphipod can be used as a substitution for an early life stage fish.

4. Lastly, this *H.azteca* test (Borgmann 1994) is questionable for use in criteria development since there was significant control mortality (only 66% control survival), which is much higher than should be allowed for use in development of reliable toxicity data. The EPA chronic toxicity guidelines require >80% survival in the control treatment, as partial fulfillment of MDRs before data may be included in criteria development (EPA 2002).

In addition, the use of only two genera (*Lepomis* and *Hyalella*) as the basis for the chronic equation precludes the use of the recalculation procedure to modify chronic criteria on a site-specific basis. These major shortcomings of the EPA chronic ammonia criteria led us to re-evaluate the use of acute-chronic ratios (ACR) to adjust the acute equations and simply develop chronic ammonia criteria for cold and warm-water habitats and warm-water habitats without Unionidae.

To derive ACRs, we used the SMAV and GMAV values from the updated acute database and the pH-8 corrected SMCV and GMCV values from the updated chronic database (Table 4-9) for matching species. Species mean final ACR (SM FACR, 4.7) and genus mean final ACR (GM FACR, 4.9) were calculated for all species/genera with both acute and chronic data. We did not limit our ACR calculations to studies that computed both LC_{50} and EC_{20} values for a single species given the same experimental conditions, which is a slight deviation from the 1985 Guidelines. Strict application of the 1985 Guidelines was deemed too restrictive for ammonia, given the paucity of "acceptable" chronic data - especially acceptable chronic data with concurrent acute toxicity data. Rather, we used the summary statistics for each genus or species (S/GMAVs and S/GMCVs) from the available database. Using this approach, the reported species and genus mean values may differ (e.g. *D. magna*; Table 4-9) if toxicity data are available for more than one species within a generus (Table 4.4), yet not all species have paired acute and chronic values.

The resulting GM FACR (4.9) represents a somewhat more realistic relationship between acute and chronic toxicity than the SM FACR since all ACRs included in the calculation are greater than 1 (see Table 4-9). Therefore, the GM FACR was used in the updated chronic criteria derivation.

Table 4-9
Species and Genus Mean Acute-Chronic Ratios (SMACRs and GMACRs, Respectively) for Paired Species Mean Acute Values (SMAV) and Genus Mean Acute Values (GMAV) used in the Derivation of CCC Limits

	Acute		Chronic		Acute:Chronic	
Species	**SMAV TA-N at pH8 (mg N/L)**	**GMAV TA-N at pH8 (mg N/L)**	**SMCV TA-N at pH8 (mg N/L)**	**GMCV TA-N at pH8 (mg N/L)**	**SMACR**	**GMACR**
Ceriodaphnia acanthina	13.68	16.28	19.77	16.05	0.7	1.0
Ceriodaphnia dubia	19.38		13.03		1.5	
Daphnia magna	35.24	36.26	17.14	17.14	2.1	2.1
Ictalurus punctatus	35.81	35.81	8.85	8.85	4.0	4.0
Lasmigona subviridis	2.82	2.82	0.56	0.56	5.0	5.0
Lepomis cyanellus	30.31	23.64	6.03	2.85	5.0	8.3
Lepomis macrochirus	24.16		1.35		17.9	
Micropterus dolomieu	36.90	27.18	4.56	4.56	8.1	6.0
Musculium transversum	35.65	35.65	2.62	2.62	13.6	13.6
Pimephales promelas	42.69	42.69	3.09	3.09	13.8	13.8
Salvelinus namayacush	36.39	36.39	9.40	9.40	3.9	3.9
					SM FACR =	GM FACR =
					4.7	4.9

NOTE: Final acute-chronic ratio (FACR) = the geometric mean of individual SMACRs or GMACRs.

We divided our acute FAV by the GM FACR creating CCC equations for cold-water (Eq. 12), warm-water (Eq. 13), and warm water without Unionidae (Eq. 14), resulting in the chronic equations listed below:

Updated Cold-water Ammonia Chronic Criterion:

$$CCC_{Cold} = \frac{0.153}{1+10^{7.204\text{-pH}}} + \frac{21.74}{1+10^{\text{pH-}7.204}} \qquad \text{Eq. 12}$$

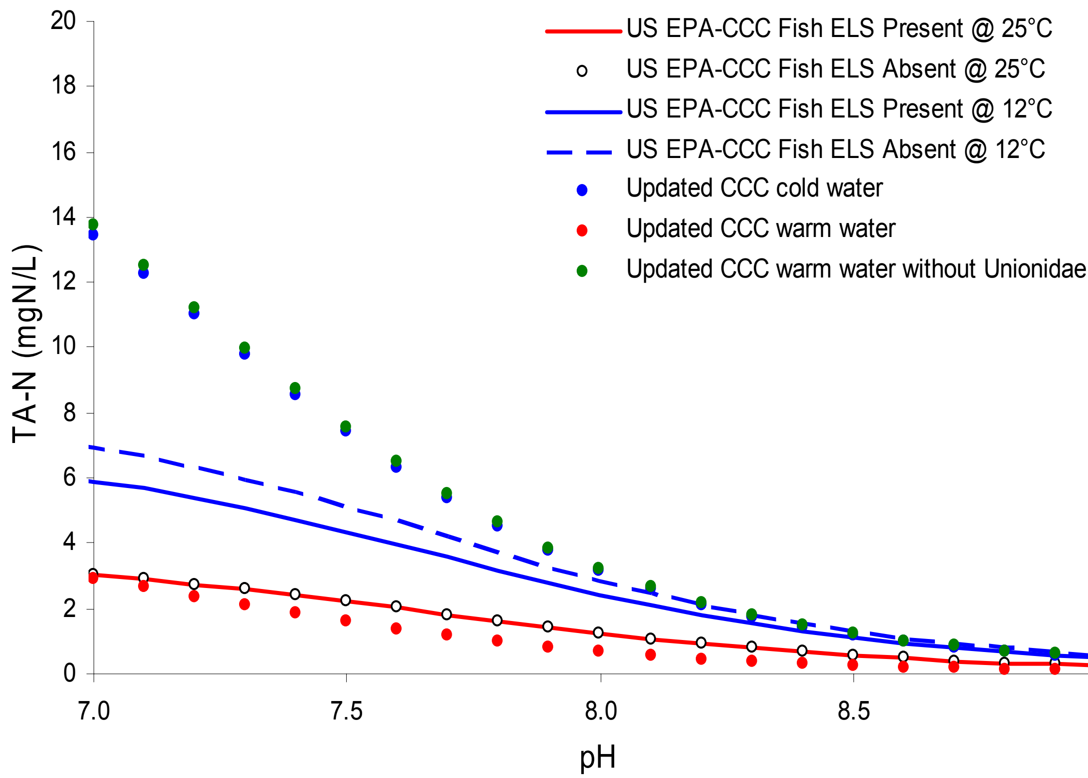
Updated Warm-water Ammonia Chronic Criterion:

$$CCC_{Warm} = \frac{0.033}{1+10^{7.204\text{-pH}}} + \frac{4.69}{1+10^{\text{pH-}7.204}} \qquad \text{Eq. 13}$$

Updated Warm-water (without Unionidae) Ammonia Chronic Criterion:

$$CCC_{Warm\ without\ Unionidae} = \frac{0.156}{1+10^{7.204\text{-pH}}} + \frac{22.21}{1+10^{\text{pH-}7.204}} \qquad \text{Eq. 14}$$

For comparative purposes, we present resulting criteria based on the original EPA chronic equations and our revised chronic equations (see Figure 4-3 and Table 4-10). For this comparison, we set the temperature values in the EPA early life stage present/absent equations to 25°C and 12°C, with the assumption that these two temperatures values would most closely match our warm water, cold-water scenario. At temperatures >14.5 °C, the EPA CCC relationship for early life stage fish present or absent are the same, because the *Hyalella* temperature-based function is controlling the CCC (Figure 4-3). At temperatures <14.5°C, these two relationships begin to diverge.



NOTE: For comparative purposes, the EPA functions were set at 25°C and 12°C to closely approximate the updated cold-water, warm water scenario.

Figure 4-3
Comparison of the EPA and updated Criterion Continuous Concentration Functions over a pH Range of 7.0-9.0

Table 4-10
Comparative TA-N Concentrations Given pH for EPA (1999) Chronic Criteria and Updated Chronic Criteria

pH	EPA Chronic Relationship					Updated Chronic Relationship		
	CCC Fish ELS Present @ 12°C	CCC Fish ELS Absent @ 12°C	CCC Fish ELS Present @ 25°C	CCC Fish ELS Absent @ 25°C		CCC Cold Water	CCC Warm Water w/ Unionids	CCC Warm Water w/o Unionids
	(TA-N mg/L)	(TA-N mg/L)	(TA-N mg/L)	(TA-N mg/L)		(TA-N mg/L)	(TA-N mg/L)	(TA-N mg/L)
6.5	6.67	7.84	3.39	3.39		18.18	3.92	18.57
6.6	6.56	7.72	3.34	3.34		17.44	3.76	17.81
6.7	6.44	7.58	3.28	3.28		16.59	3.58	16.95
6.8	6.29	7.40	3.20	3.20		15.63	3.37	15.97
6.9	6.12	7.20	3.11	3.11		14.58	3.14	14.89
7.0	5.91	6.95	3.01	3.01		13.44	2.90	13.73
7.1	5.67	6.67	2.88	2.88		12.23	2.64	12.50
7.2	5.39	6.34	2.74	2.74		11.00	2.37	11.23
7.3	5.08	5.97	2.58	2.58		9.76	2.11	9.97
7.4	4.73	5.57	2.41	2.41		8.55	1.84	8.74
7.5	4.36	5.13	2.22	2.22		7.40	1.60	7.56
7.6	3.98	4.68	2.02	2.02		6.34	1.37	6.48
7.7	3.58	4.21	1.82	1.82		5.38	1.16	5.49
7.8	3.18	3.74	1.62	1.62		4.52	0.97	4.62
7.9	2.80	3.29	1.42	1.42		3.77	0.81	3.85
8.0	2.43	2.86	1.24	1.24		3.13	0.68	3.20
8.1	2.10	2.47	1.07	1.07		2.59	0.56	2.64
8.2	1.79	2.11	0.91	0.91		2.13	0.46	2.18
8.3	1.52	1.79	0.78	0.78		1.76	0.38	1.79
8.4	1.29	1.52	0.66	0.66		1.45	0.31	1.48
8.5	1.09	1.28	0.55	0.55		1.19	0.26	1.22
8.6	0.92	1.08	0.47	0.47		0.99	0.21	1.01
8.7	0.78	0.92	0.40	0.40		0.82	0.18	0.84
8.8	0.66	0.78	0.34	0.34		0.69	0.15	0.70
8.9	0.56	0.66	0.29	0.29		0.58	0.12	0.59
9.0	0.49	0.57	0.25	0.25		0.49	0.11	0.50

This warm-water with Unionids CCC is slightly more restrictive than the EPA's CCC between a range of pH from 7.0 to 9.0. The cold-water CCC is considerably less restrictive than the EPA early life stage present at low pH, although it becomes very similar at pH levels >8.0. Similarly, the updated cold-water criteria is less restrictive at low pH values than the EPA early life stage absent function adjusted to 12 °C, and approximates the national limits at pH levels >8.0. It is important to note that if unionids are not present in warm-water habitats the updated warm water without unionids CCC is very similar to the updated cold-water criteria, and considerably less restrictive than the existing EPA early life stage CCC functions adjusted to 25°C.

Owing to the lack of chronic ammonia data (not meeting the "8 family rule"), the EPA's current derivation of chronic ammonia criteria is questionable. Additional data, as yet developed, are required to support the EPA's assumption that early life stage fish are more sensitive than juveniles or adults to chronic ammonia toxicity, and that there is a statistically significant temperature dependence chronic toxicity response for biota. As such, we strongly recommend using an FACR modified acute pH-only relationship to set chronic ammonia criteria.

4.3.3 Conclusions and Recommendations for Revised Ammonia Criteria

The modifications to the national acute and chronic ammonia water quality criteria above are more appropriate for the range of aquatic habitats found in the arid West. First, the revised acute ammonia criteria were based on the most current data available for cold-water (32 genera) and warm-water (51 genera) biota.

Initially, dividing data between the warm-water/cold-water databases appeared to circumvent concerns associated with "salmonids" present/absent criteria. However, recent toxicological studies using freshwater mussels (Unionidae) have provided insight about a highly sensitive group, one that ultimately dominated the derivation of our warm-water acute ammonia criteria. Given the lack of Unionidae in the arid West (see Chapter 2), we created a sub-category within the warm-water database excluding Unionidae. As presented, our acute equations, which are based on three distinct habitat types (cold, warm, warm water without Unionidae) should protect species along the elevation gradient from high mountain ecosystems to desert ecosystems. We believe criteria based on habitat categories are scientifically more sound and practical, because they are based on organisms typically found within each habitat type and exclude species not pertinent to any particular the ecosystem.

Unfortunately, the paucity of chronic ammonia data created many procedural inadequacies in the derivation of chronic ammonia criteria. Foremost, even the updated chronic database does not meet national criteria guidelines for deriving numerical water quality criteria via derivation of a 5^{th} percentile-based final chronic value. Therefore, we opted to derive chronic criteria equations using acute-to-chronic ratios for matched species data. We applied the FACR to our acute equations for each habitat type, creating chronic equations for cold-water, warm-water and warm-water without Unionidae.

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5.0 COPPER CRITERIA REVIEW AND UPDATE

5.1 BACKGROUND

Present EPA AWQC for copper are published in the "1995 Updates" (EPA 1996), which updated the original 1984 document (EPA 1984) with more recent acute and chronic toxicity data. The acute database meets the "eight family" rule and contains acute toxicity data for 43 genera representing 56 species. Both acute and chronic criteria are modified with a water hardness slope. The final chronic value was derived via an ACR rather than a direct calculation due to chronic toxicity database limitations.

Since the 1995 Updates, the EPA released a draft document entitled *2003 Update of Ambient Water Quality Criteria for* Copper (EPA 2003). This draft document will presumably replace existing copper water quality criteria (EPA 1995) once the peer review process is complete and the final document is accepted for publication.

Prior to the EPA 2003 copper AWQC draft document, hereafter referred to as the 2003 Copper Draft, AWQC updates have primarily constituted adding and removing toxicity data from the acute and chronic database. The updated databases may change the number of genera, toxicity-hardness relationships, and/or change the relative sensitivity of already present species. Yet, generally, the same methods of criteria derivation are followed in successive publications for a particular toxicant. Additionally, most criteria are currently modified by a single water quality parameter (e.g., water hardness, pH). Copper criteria are presently hardness-modified; yet, copper toxicity does not exhibit as consistently strong of a relationship with water hardness as other do other metals, such as zinc. Multiple studies have demonstrated other water quality characteristics, such as pH (Schubauer-Berigan et al. 11993, Long et al. 2004), humic acid (Winner 1985), alkalinity (Gensemer et al. 2002), and dissolved organic carbon (Playle and Dixon 1993; Hollis et al. 1996) have an equal or even greater effect on copper toxicity than water hardness alone. Many of these other water quality charateristic effects on copper toxicity have been incorporated into a BLM, which predicts the ameliorating effect of these parameters on copper toxicity at the gill surface (Santore et al. 2001; Di Toro et al. 2001).

The 2003 Copper Draft is a pioneer document, in that it is the first EPA AWQC document to use the BLM to normalize toxicity values for criteria derivation. The BLM uses multiple water quality characteristics (temperature, pH, DOC, % humic acid, and the concentrations of the following ions: Ca, Mg, Na, K, SO_4, Cl, HCO_3, and S) to derive predicted toxicity values, as opposed to one or two water quality characteristics generally used to modify other metal toxicity. In the 2003 Draft, acute toxicity data are first BLM-normalized and ranked on the basis of a "standard" set of water quality characteristics (i.e., a process equivalent to normalizing to a standard hardness of 50 mg/L). Then, a criterion would be calculated using the BLM based on the water quality characteristic at a given site. The resulting criteria is unique in the sense that no values are reported, and states: "freshwater aquatic organisms and their uses should not be affected unacceptably if the 4-day average concentration of dissolved copper does not exceed the BLM-derived site-water LC_{50} (i.e., FAV) divided by the FACR more than once every 3 years on the average (i.e., the CCC) and if the 24-hr average dissolved copper concentration does not exceed the BLM-derived site LC_{50} (or FAV) divided by two, more than one every 3 years on the average (i.e., the CMC)" (EPA 2003).

Although BLM normalization is ultimately a commendable goal for copper criteria derivation, this approach greatly reduces the number of studies available for criteria derivation. All test water quality parameters necessary to run the BLM need to be measured, or have the ability to be estimated, for each study with copper toxicity data. Such data are not reported in many of the available studies. As a result of requiring such BLM data, the total number of genera in the acute toxicity database was reduced from 43 (EPA 1996) to 27 in the 2003 Copper Draft. This could ultimately result in more conservative criteria values as a result of the "sample size" effect in criteria derivation. Probably of more importance is the loss of "robustness" in the toxicity database, especially when considering the updated database has 69 genera (see Section 5.4).

Since 1) the 2003 Copper Draft is not officially adopted by the EPA; 2) existing criteria are available for review and updating using conventional methods, and 3) the toxicity test BLM data requirements deviate from the 1985 Guidelines (e.g., the BLM requirements will accept values from tests conducted in water with DOC > 5.0 mg/L, which are not used in the 1985 guidelines), we mostly used this 2003 Draft Copper document as a source of potentially new data rather than the basis of our review and numeric updates to criteria calculations (i.e., we did not use the BLM to modify the toxicity data or criteria updates). Our review primarily consists of a critical evaluation of the 1984 and sequential 1995 Updates copper criteria, collectively referred to as the 1984/1995 Copper criteria. However, we do address the pros and cons of using the BLM in the criteria derivation process and compare criteria derived via the BLM to standard criteria derivation methods.

5.2 PHASE I - TECHNICAL REVIEW OF EPA COPPER CRITERIA DOCUMENTS

5.2.1 Existing Acute and Chronic Toxicity Databases

Phase 1 of the review consisted of an evaluation of studies used the 1984/1995 national acute and chronic toxicity copper databases. Two acute values were corrected and two acute values were deleted from the revised acute toxicity database. Additionally, three chronic values were corrected and three chronic values were deleted from the revised chronic toxicity database. A summary of these deletions and corrections is found in Table 5-1 and brief explanations are found below.

Table 5-1
Corrections and Deletions of Data used by the EPA in the 1984 AWQC Copper Document

Species	Existing (µg/L)	Corrected (µg/L)	Reference	Comments
Acute				
Gammarus pulex	183	104.0	Stephenson 1983	Replaced 48-hr LC_{50} with 96-hr LC_{50}
Gammarus pulex	41	249.0	Stephenson 1983	Replaced 48-hr LC_{50} with 96-hr LC_{50}
Poecilia reticulata	2,500	--	Khangarot et al. 1981	Deleted value since test duration was <96 hr
Lepomis macrochirus	1,100	--	Benoit et al. 1975	Deleted value due to insufficient description of acute test methods
Chronic				
Pimephales promelas	27.7	29.8	Pickering et al. 1977	Replaced estimated LOEC (32) with actual (measured) LOEC (37) in the chronic value calculation, NOEC = 24
Oncorhynchus tshawytscha	<7.4	2.98	Chapman 1975, 1982	7.4 = LOEC, the chronic values geometric mean of the LOEC and NOEC (1.2)
Onchorhynchus mykiss	27.77	22.27	Seim et al. 1984	Corrected value (LOEC = 16, NOEC = 31)
Lepomis macrochirus	28.98	--	Benoit et al. 1975	Deleted value due to unacceptable control survival (36-42%)
Physa integra	10.88	--	Arthur and Leonard 1970	Deleted value due to unacceptable control survival (30-60%)
Gammarus psudolimnaeus	6.066	--	Arthur and Leonard 1970	Deleted value due to unacceptable control survival (50-90%)

The acute toxicity values for the amphipod, *Gammarus pulex,* from Stephenson (1983) are the 48-hr test results. The1985 Guidelines state 96-hr tests should be used for amphipods. Because both 48-hr and 96-hr test results were presented, we replaced the 48-hr acute values with the 96-hr acute values (Table 5-1).

Benoit (1975) determined acute and chronic toxicity of copper in bluegills (*Lepomis macrochirus*). Very few details were reported concerning methods used to conduct the acute tests; in fact, so few details were given, there is no way of knowing if the 1985 Guidelines were followed. Additionally, survival of the chronic control was unacceptably low (36-42%), which suggests other factors may have contributed to fish mortality. Both acute and chronic values from this study, and consequently the acute-chronic ratio (ACR), derived from this study were removed from the revised acute and chronic databases.

It appears three chronic values for *Pimphales promelas* (Pickering et al. 1977) and *Oncorhynchus tshawytscha* (Chapman 1975; 1982) were either entered incorrectly or reported data were interpreted incorrectly. We replaced the existing chronic values with the recalculated geometric mean of the no observable effect concentration (NOEC) and lowest observable effect concentration (LOEC) reported by each study, per 1985 guidelines.

Arthur and Leonard (1970) determined acute and chronic toxicity of copper for *Campeloma decisum*, *Physa integra,* and *Gammarus pseudolimnaeus*. All chronic results were included in the national chronic database; however, only the chronic values for *C. decisum* are suitable for use due to unacceptably high control mortality in the *P. integra* and *G. pseudolimnaeus* tests. Chronic values for *P. integra* and *G. pseudolimnaeus* from this study were removed from the revised chronic database, which were the only chronic toxicity values for these species in the database.

5.2.2 Existing Toxicity Hardness-Slope Derivation for Copper

If a water quality parameter significantly affects the toxicity of a contaminant, this numeric relationship should be used for criterion derivation. The most common water quality modifier of AWQC for metals is water hardness. The toxicity hardness slope is generally derived from species-specific acute toxicity data that meet the minimum data requirements of the highest hardness tested being three times the lowest hardness tested, and 100 mg/L greater than the lowest (Stephan et al. 1985). The acute hardness slope is generally applied to both acute and chronic criteria equations when it seems reasonable that hardness influences chronic toxicity; and the chronic toxicity database is too limited to quantify this relationship.

The EPA derived an acute hardness slope from the 1984 acute toxicity database. No significant trends were observed with the chronic toxicity data and hardness; therefore, the acute hardness slope was used in the chronic criteria derivation. The direct application of the acute slope resulted in chronic values that appeared too high, so the slope was artificially lowered to produce lower chronic values at high hardness. Although decreasing the chronic slope for further protection is acceptable, a chronic hardness slope calculated from actual chronic toxicity data would be preferred and a better representation of the true relationship between chronic toxicity of copper and water hardness.

5.3 PHASE II - UPDATE TO THE NATIONAL COPPER CRITERIA DATABASES

Approximately 150 papers containing at least some copper toxicity information were located and reviewed as potential sources of data to be added to the updated copper databases. Many of the reviewed papers were cited in the 2003 Copper Draft and/or a copper update included in an ecological risk assessment for the Clark Fork River, Montana (Chapman 1999). However, not all toxicity values deemed acceptable for use in these publications were determined acceptable for use in the present review. For example, toxicity tests conducted in site water with DOC concentrations >5.0 mg/L were included in the national database in the 2003 Copper Draft. Including these toxicity values is acceptable for this analysis since the BLM was used to normalize test results, which takes into account the effect of high DOC on copper toxicity. However, they are not acceptable for a database, which is not BLM adjusted. Additionally, some of the acute values used by Chapman (1999) do not comply with test duration requirements (e.g., Jacobson et al. 1997) and/or test water restrictions (Belanger et al. 1988) and, therefore, were not included in the updated databases.

Much of the recent copper toxicity literature has evaluated the influence of site-specific water quality characteristics on copper toxicity by either using site or spring water as the test water, or using reconstituted laboratory water designed to mimic the major ion composition at a particular site. Results from such studies are not universally acceptable for use in criteria derivation due to restrictions set forth in the 1985 Guidelines. However, to avoid a loss of the valuable toxicity data generated from these studies, we carefully evaluated each study to determine the acceptability of test results. Toxicity tests conducted with filtered uncontaminated site/spring water were generally determined acceptable for use in criteria derivation, if an initial water quality analysis was documented and DOC concentrations were less than 5.0 mg/L. Most, but not all, of the tests conducted with atypical reconstituted laboratory water were determined acceptable for use. This included results from tests in which other water quality parameters varied within acceptable range (e.g., pH, alkalinity, and humic acid), while hardness was held constant. Use of such data creates a more robust database that encompasses acute copper toxicity for a variety of environmental conditions.

5.3.1 New Acute Copper Toxicity Data

The literature review resulted in the addition of 295 acute values (Table 5-2) from 47 different sources to the 1984/1995 acute copper toxicity database, including acute toxicity values for 43 new species, representing 25 new genera. These included a number of values from studies conducted prior to the 1995 Updates and apparently represent data unknown to EPA at the time. Five of the top ten most sensitive species in the updated acute database are new species added as a result of this literature search (note that much of this new data would not be available if restricted to studies with the full set of BLM parameters). Given the large volume of new toxicity data added to the database, we will only comment on papers that added information to the four most sensitive genera in the revised acute database (*Daphnia*, *Ceriodaphnia*, *Chydorus*, and *Bosmina*) and new acute copper toxicity values for threatened or endangered species.

Table 5-2
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Pimphales promelas	F,T,M	$CuSO_4$	31	75.00	Mount and Stephan 1969
Pimphales promelas	F,T,M	$CuSO_4$	202.0	460.00	Pickering et al. 1977
Pimphales promelas	F,T,M	$CuSO_4$	202.0	490.00	Pickering et al. 1977
Daphnia pulex	S,M,T	$CuSO_4$	57.5 (no HA)	23.00	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	57.5 (no HA)	28.80	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	57.5 (0.75 HA)	39.30	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	57.5 (0.75 HA)	40.30	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	57.5 (1.5 HA)	63.40	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	57.5 (1.5 HA)	71.20	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	115 (no HA)	23.30	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	115 (no HA)	32.70	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	115 (0.75 HA)	45.00	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	115 (0.75 HA)	27.20	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	115 (1.5 HA)	50.30	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	115 (1.5 HA)	52.80	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	230 (no HA)	10.00	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	230 (no HA)	17.10	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	230 (0.15 HA)	26.40	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	230 (0.15 HA)	31.40	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	230 (0.75 HA)	30.50	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	230 (0.75 HA)	45.60	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	230 (1.5 HA)	64.00	Winner 1985
Daphnia pulex	S,M,T	$CuSO_4$	230 (1.5 HA)	66.20	Winner 1985
Daphnia magna	S,M,T	$CuSO_4$	7.9	2.00	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	11.1	2.00	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	22.2	10.00	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	50.7	11.10	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	7.1	2.00	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	7.1	2.80	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	7.1	4.80	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	20.6	2.00	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	20.6	7.40	Long et al. 2004
Daphnia magna	S,M,T	$CuSO_4$	20.6	6.50	Long et al. 2004
Ceriodaphnia dubia	S,M,T	$CuNO_3$	175.0	12.00	Banks et al. 2003
Daphnia magna	S,M,T	--	170.0	31	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	38	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	35	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	58	Lazorchak and Waller 1993
			(160-180)		

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Daphnia magna	S,M,T	--	170.0	37	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	51	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	39	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	50	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	52	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	31	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	30	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	46	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	--	170.0	63	Lazorchak and Waller 1993
			(160-180)		
Daphnia magna	S,M,T	$CuSO_4$	80.0	11.3	Suedel et al. 1996
Ceriodaphnia dubia	S,M,T	$CuCl_2$	36.0	20.00	Carlson et al. 1986
Pimphales promelas	S,M,T	$CuCl_2$	36.0	180.00	Carlson et al. 1986
Ceriodaphnia dubia	S,M,T	$CuCl_2$	52.0	19	Carlson et al. 1986
Pimephales promelas	S,M,T	$CuCl_2$	52.0	55	Carlson et al. 1986
Scapholeberis spp.	S,M,T	$CuCl_2$	52.0	18	Carlson et al. 1986
Pimephales promelas	S,M,T	$Cu(NO_3)_2$	290.0	15	Schubauer-Berigan et al. 1993
			(280-300)	(pH=6-6.5)	
Pimephales promelas	S,M,T	$Cu(NO_3)_2$	290.0	44	Schubauer-Berigan et al. 1993
			(280-300)	(pH=7-7.5)	
Pimephales promelas	S,M,T	$Cu(NO_3)_2$	290.0	200	Schubauer-Berigan et al. 1993
			(280-300)	(pH=8-8.5)	
Lumbriculus variegatus	S,M,T	$Cu(NO_3)_2$	290.0	130	Schubauer-Berigan et al. 1993
			(280-300)	(pH=6-6.5)	
Lumbriculus variegatus	S,M,T	$Cu(NO_3)_2$	290.0	270	Schubauer-Berigan et al. 1993
			(280-300)	(pH=7-7.5)	
Lumbriculus variegatus	S,M,T	$Cu(NO_3)_2$	290.0	500	Schubauer-Berigan et al. 1993
			(280-300)	(pH=8-8.5)	
Hyalella azteca	S,M,T	$Cu(NO_3)_2$	290.0	17	Schubauer-Berigan et al. 1993
			(280-300)	(pH=6-6.5)	
Hyalella azteca	S,M,T	$Cu(NO_3)_2$	290.0	24	Schubauer-Berigan et al. 1993
			(280-300)	(pH=7-7.5)	

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Hyalella azteca	S,M,T	$Cu(NO_3)_2$	290.0	87	Schubauer-Berigan et al. 1993
			(280-300)	(pH=8-8.5)	
Ceriodaphnia dubia	S,M,T	$Cu(NO_3)_2$	290.0	9.5	Schubauer-Berigan et al. 1993
			(280-300)	(pH=6-6.5)	
Ceriodaphnia dubia	S,M,T	$Cu(NO_3)_2$	290.0	28	Schubauer-Berigan et al. 1993
			(280-300)	(pH=7-7.5)	
Ceriodaphnia dubia	S,M,T	$Cu(NO_3)_2$	290.0	200	Schubauer-Berigan et al. 1993
			(280-300)	(pH=8-8.5)	
Pimephales promelas	F,M,T,D	$CuSO_4$	47.0	31.75	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	243.2	117.48	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	255.7	48.26	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	47.0	73.03	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	45.0	59.06	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	45.0	78.74	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	45.5	22.23	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	49.0	6.99	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	45.0	22.23	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	43.0	107.32	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	45.0	81.28	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	45.5	241.3	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	45.0	133.35	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	44.0	93.98	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	44.0	67.95	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	22.5	4.76	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	24.0	13.97	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	23.0	29.85	Erickson et al. 1996
Pimephales promelas	F,M,T,D	$CuSO_4$	21.5	59.69	Erickson et al. 1996
Oncorhynchus mykiss	F,M,D	$CuSO_4$	362.5	102.0	Fogels and Sprague 1977
			(350-375)		
Jodanella floridae	F,M,D	$CuSO_4$	362.5	1,270.0	Fogels and Sprague 1977
			(350-375)		
Brachydanio rerio	F,M,D	$CuSO_4$	362.5	149.0	Fogels and Sprague 1977
			(350-375)		
Chydorus sphaericus	R,U	$CuSO_4$	33.8	3.3	Koivisto et al. 1992
Bosmina longirostrus	R,U	$CuSO_4$	33.8	1.4	Koivisto et al. 1992
Daphnia galeata	R,U	$CuSO_4$	33.8	4.1	Koivisto et al. 1992
Daphnia magna	R,U	$CuSO_4$	33.8	11.5	Koivisto et al. 1992
Daphnia pulex	R,U	$CuSO_4$	33.8	3.4	Koivisto et al. 1992
Daphnia magna	S,M,I	--	100.0	35.6	Borgman and Charlton 1984

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Pimephales promelas	S,M,T	$CuSO_4$	101.0	252	Bennett et al. 1995
Ceriodaphnia dubia	S,U	$CuSO_4$	90.0	11	Bright 1995
Ceriodaphnia dubia	S,U	$CuSO_4$	90.0	36.6	Bright 1995
Ceriodaphnia dubia	S,U	$CuSO_4$	90.0	19.1	Bright 1995
Ceriodaphnia dubia	S,U	$CuSO_4$	90.0	36.4	Bright 1995
Ceriodaphnia dubia	S,U	$CuSO_4$	90.0	11.7	Bright 1995
Ceriodaphnia dubia	S,U	$CuSO_4$	90.0	12.3	Bright 1995
Physella gyrina	S,U	$CuSO_4$	90.0	48.5	Bright 1995
Tropocyclops prasinus mexicanus (adults and copepodids V)	S,U,T	$CuSO_4$	10.0	29	Lalande and Pinel-Alloul 1986
Lepomis macrochirus	R,M,D	$CuCl_2$	85.0	2,200.0	Blaylock et al. 1985
Lepomis macrochirus	F,M,D	$CuCl_2$	85.0	1,300.0	Blaylock et al. 1985
Gambusia affinis (male)	S,U	--	50.0	3500	Kallanagoudar and Patil 1997
Gambusia affinis (male)	S,U	--	150.0	5,000	Kallanagoudar and Patil 1997
Gambusia affinis (male)	S,U	--	300.0	6,000	Kallanagoudar and Patil 1997
Gambusia affinis (female)	S,U	--	50.0	2,500	Kallanagoudar and Patil 1997
Gambusia affinis (female)	S,U	--	150.0	2,900	Kallanagoudar and Patil 1997
Gambusia affinis (female)	S,U	--	300.0	5,000	Kallanagoudar and Patil 1997
Gambusia affinis (fry)	S,U	--	50.0	900	Kallanagoudar and Patil 1997
Gambusia affinis (fry)	S,U	--	150.0	1,400	Kallanagoudar and Patil 1997
Gambusia affinis (fry)	S,U	--	300.0	2,000	Kallanagoudar and Patil 1997
Chironomus plumosus	S,U	$CuSO_4$	80.0	200	Fargasova 2003
Ceriodaphnia dubia	S,M,D	$CuCl_2$	182.0	15.7	Gensemer et al. 2002
Ceriodaphnia dubia	S,M,D	$CuCl_2$	390.0	22.2	Gensemer et al. 2002
Ceriodaphnia dubia	S,M,D	$CuCl_2$	584.0	21.4	Gensemer et al. 2002
Ceriodaphnia dubia	S,M,D	$CuCl_2$	786.0	25.7	Gensemer et al. 2002
Ictalurus punctatus (fingerlings)	S,U	$CuSO_4$	16.0	54	Straus and Tucker 1993
Ictalurus punctatus (fingerlings)	S,U	$CuSO_4$	16.0	55	Straus and Tucker 1993
Ictalurus punctatus (fingerlings)	S,U	$CuSO_4$	83.0	762	Straus and Tucker 1993
Ictalurus punctatus (fingerlings)	S,U	$CuSO_4$	83.0	700	Straus and Tucker 1993
Ictalurus punctatus (fingerlings)	S,U	$CuSO_4$	161.0	768	Straus and Tucker 1993
Ictalurus punctatus (fingerlings)	S,U	$CuSO_4$	161.0	1,139	Straus and Tucker 1993

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Ictalurus punctatus (fingerlings)	S,U	$CuSO_4$	287.0	1,041	Straus and Tucker 1993
Ictalurus punctatus (fingerlings)	S,U	$CuSO_4$	287.0	925	Straus and Tucker 1993
Juga plicifera	F,M,T	$CuCl_2$	21.0	15	Nebeker et al. 1986
Lithoglyphus virens	F,M,T	$CuCl_2$	21.0	8	Nebeker et al. 1986
Procambarus clarkii (larva)	F,T,M	$CuCl_2$	17.0	720	Rice and Harrison 1983
Oncorhynchus tshawytscha	F,M,D	$CuCl_2$	36.0	7.4	Welsh et al. 2000
			(Ca:Mg=0.82)		
Oncorhynchus tshawytscha	F,M,D	$CuCl_2$	35.0	12.5	Welsh et al. 2000
			(Ca:Mg=1.5)		
Oncorhynchus tshawytscha	F,M,D	$CuCl_2$	38.0	14.3	Welsh et al. 2000
			(Ca:Mg=0.75)		
Oncorhynchus tshawytscha	F,M,D	$CuCl_2$	36.0	18.3	Welsh et al. 2000
			(Ca:Mg=1.46)		
Oncorhynchus mykiss	R,M,D	$CuCl_2$	42.0	3.4	Welsh et al. 2000
			(Ca:Mg=0.17)		
Oncorhynchus mykiss	R,M,D	$CuCl_2$	39.0	8.1	Welsh et al. 2000
			(Ca:Mg=4.75)		
Oncorhynchus mykiss	R,M,D	$CuCl_2$	90.0	17.2	Welsh et al. 2000
			(Ca:Mg=0.77)		
Oncorhynchus mykiss	R,M,D	$CuCl_2$	90.0	32.0	Welsh et al. 2000
			(Ca:Mg=5.16)		
Ceriodaphnia dubia	S,M,D	---	45.0	25.0	Belanger et al. 1988
Ceriodaphnia dubia	S,M,D	---	45.0	17.0	Belanger et al. 1988
Ceriodaphnia dubia	S,M,D	---	45.0	30.0	Belanger et al. 1988
Ceriodaphnia dubia	S,M,D	---	45.0	24.0	Belanger et al. 1988
Ceriodaphnia dubia	S,M,D	---	45.0	28.0	Belanger et al. 1988
Ceriodaphnia dubia	S,M,D	---	45.0	32.0	Belanger et al. 1988
Ceriodaphnia dubia	S,M,D	---	45.0	23.0	Belanger et al. 1988
Ceriodaphnia dubia	S,M,D	---	45.0	20.0	Belanger et al. 1988
Ceriodaphnia dubia	S,M,D	---	45.0	19.0	Belanger et al. 1988
Catostomus latipinnis	S,U	$CuSO_4$	144.0	175	Hamilton and Buhl 1997b
Ephemerella subuaria	S,U	$CuSO_4$	44.0	320	Warnick and Bell 1969
Oncorhynchus gorbuscha (alevin, newly hatched)	F,M,T	$CuSO_4$	83.1	143	Servizi and Martens 1978

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Oncorhynchus gorbuscha (alevin)	F,M,T	$CuSO_4$	83.1	87	Servizi and Martens 1978
Oncorhynchus gorbuscha (fry)	F,M,T	$CuSO_4$	83.1	199	Servizi and Martens 1978
Oncorhynchus nerka (alevin, newly hatched)	F,M,T	$CuSO_4$	83.1	190	Servizi and Martens 1978
Oncorhynchus nerka (alevin)	F,M,T	$CuSO_4$	83.1	200	Servizi and Martens 1978
Oncorhynchus nerka (alevin)	F,M,T	$CuSO_4$	83.1	100	Servizi and Martens 1978
Oncorhynchus nerka (alevin)	F,M,T	$CuSO_4$	83.1	110	Servizi and Martens 1978
Oncorhynchus nerka (alevin)	F,M,T	$CuSO_4$	83.1	130	Servizi and Martens 1978
Oncorhynchus nerka (fry)	F,M,T	$CuSO_4$	83.1	150	Servizi and Martens 1978
Oncorhynchus nerka (smolt)	F,M,T	$CuSO_4$	83.1	210	Servizi and Martens 1978
Oncorhynchus nerka (smolt)	F,M,T	$CuSO_4$	83.1	170	Servizi and Martens 1978
Oncorhynchus nerka (smolt)	F,M,T	$CuSO_4$	83.1	190	Servizi and Martens 1978
Oncorhynchus nerka (smolt)	F,M,T	$CuSO_4$	83.1	240	Servizi and Martens 1978
Oncorhynchus mykiss	S,M,T	$CuSO_4$	169.0	110	Dwyer et al. 1995
Oncorhynchus mykiss	S,M,T	$CuSO_4$	169.0	50	Dwyer et al. 1995
Oncorhynchus mykiss	S,M,T	$CuSO_4$	169.0	60	Dwyer et al. 1995
Gila elegans	S,M,T	$CuSO_4$	173.0	200	Dwyer et al. 1995
Oncorhynchus apache	S,M,T	$CuSO_4$	169.0	70	Dwyer et al. 1995
Oncorhynchus clarki henshawi	S,M,T	$CuSO_4$	169.0	80	Dwyer et al. 1995
Oncorhynchus clarki henshawi	S,M,T	$CuSO_4$	169.0	60	Dwyer et al. 1995
Pimephales promelas	S,M,T	$CuSO_4$	173.0	290	Dwyer et al. 1995
Pimephales promelas	S,M,T	$CuSO_4$	173.0	630	Dwyer et al. 1995
Pimephales promelas	S,M,T	$CuSO_4$	173.0	400	Dwyer et al. 1995
Pimephales promelas	S,M,T	$CuSO_4$	173.0	390	Dwyer et al. 1995
Ptychocheilus oregonensis	S,M,T	$CuSO_4$	173.0	380	Dwyer et al. 1995
Ptychocheilus oregonensis	S,M,T	$CuSO_4$	173.0	480	Dwyer et al. 1995
Xyrauchen texanus	S,M,T	$CuSO_4$	173.0	220	Dwyer et al. 1995
Xyrauchen texanus	S,M,T	$CuSO_4$	173.0	340	Dwyer et al. 1995

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Bufo boreas	S,M,T	$CuSO_4$	167.0	120	Dwyer et al. 1999
Ethostoma lepidum	S,M,T	$CuSO_4$	167.0	260	Dwyer et al. 1999
Ethostoma rubrum	S,M,T	$CuSO_4$	167.0	60	Dwyer et al. 1999
Poeciliopsis occidentalis	S,M,T	$CuSO_4$	167.0	160	Dwyer et al. 1999
Scaphirhynchus platorynchus	S,M,T	$CuSO_4$	167.0	160	Dwyer et al. 1999
Ceriodaphnia dubia	S,M,D	--	44.0	1.6	Hyne et al. 2005
			(pH=6.5)		
Ceriodaphnia dubia	S,M,D	--	44.0	2.2	Hyne et al. 2005
			(pH=7.5)		
Ceriodaphnia dubia	S,M,D	--	44.0	9.5	Hyne et al. 2005
			(pH=6.5)		
Ceriodaphnia dubia	S,M,D	--	44.0	2.1	Hyne et al. 2005
			(pH=6.5)		
Ceriodaphnia dubia	S,M,D	--	44.0	2.8	Hyne et al. 2005
			(pH=7.5)		
Ceriodaphnia dubia	S,M,D	--	44.0	6.5	Hyne et al. 2005
			(pH=8.1)		
Ceriodaphnia dubia	S,M,D	--	44.0	16.0	Hyne et al. 2005
			(pH=8.4)		
Ceriodaphnia dubia	S,M,D	--	44.0	2.7	Hyne et al. 2005
			(pH=7.8)		
Ceriodaphnia dubia	S,M,D	--	44.0	3.6	Hyne et al. 2005
			(pH=8.1)		
Ceriodaphnia dubia	S,M,D	--	44.0	6.8	Hyne et al. 2005
Ceriodaphnia dubia	S,M,D	--	44.0	6.8	Hyne et al. 2005
			(pH=8.4)		
Oncorhynchus tshawytscha	S,U	$CuSO_4$	211.0	58	Hamilton and Buhl 1990
Oncorhynchus tshawytscha	S,U	$CuSO_4$	211.0	54	Hamilton and Buhl 1990
Ptychocheilus lucius	S,U	$CuSO_4$	144.0	293	Hamilton and Buhl 1997a
Ptychocheilus lucius	S,U	$CuSO_4$	144.0	320	Hamilton and Buhl 1997a
Ptychocheilus lucius	S,U	$CuSO_4$	199.0	363	Buhl and Hamilton 1996
Ptychocheilus lucius	S,U	$CuSO_4$	199.0	663	Buhl and Hamilton 1996
Thymallus arcticus (alevin)	S,U	$CuSO_4$	41.3	67.5	Buhl and Hamilton 1990
Thymallus arcticus (alevin)	S,U	$CuSO_4$	41.3	23.9	Buhl and Hamilton 1990
Thymallus arcticus (alevin)	S,U	$CuSO_4$	41.3	131	Buhl and Hamilton 1990
Thymallus arcticus (fry)	S,U	$CuSO_4$	41.3	9.6	Buhl and Hamilton 1990

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Thymallus arcticus (0.2g juvenile)	S,U	$CuSO_4$	41.3	2.7	Buhl and Hamilton 1990
Thymallus arcticus (0.34g juvenile)	S,U	$CuSO_4$	41.3	2.58	Buhl and Hamilton 1990
Thymallus arcticus (0.81g juvenile)	S,U	$CuSO_4$	41.3	49.3	Buhl and Hamilton 1990
Thymallus arcticus (0.85g juvenile)	S,U	$CuSO_4$	41.3	30	Buhl and Hamilton 1990
Oncorhynchus kisutch (alevin)	S,U	$CuSO_4$	41.3	21	Buhl and Hamlton 1990
Oncorhynchus kisutch (alevin)	S,U	$CuSO_4$	41.3	19.3	Buhl and Hamilton 1990
Oncorhynchus kisutch (0.41g)	S,U	$CuSO_4$	41.3	15.1	Buhl and Hamilton 1990
Oncorhynchus kisutch (0.47g)	S,U	$CuSO_4$	41.3	23.9	Buhl and Hamilton 1990
Oncorhynchus kisutch (0.87g)	S,U	$CuSO_4$	41.3	31.9	Buhl and Hamilton 1990
Oncorhynchus mykiss (alevin)	S,U	$CuSO_4$	41.3	36	Buhl and Hamilton 1990
Oncorhynchus mykiss (0.6g)	S,U	$CuSO_4$	41.3	13.8	Buhl and Hamilton 1990
Xyrauchen texanus	S,U	$CuSO_4$	199.0	404	Buhl and Hamilton 1996
Xyrauchen texanus	S,U	$CuSO_4$	199.0	331	Buhl and Hamilton 1996
Gila elegans	S,U	$CuSO_4$	199.0	364	Buhl and Hamilton 1996
Gila elegans	S,U	$CuSO_4$	199.0	231	Buhl and Hamilton 1996
Daphnia magna	R,U	$CuSO_4$	250.0	6.5	Dave 1984
Asellus aquaticus	S,U	--	50.0	9210	Martin and Holdich 1986
Actinonaias pectorosa (juvenile)	S,M,T	$CuSO_4$	96.0	24	Keller unpublished
Actinonaias pectorosa (juvenile)	S,M,T	$CuSO_4$	68.0	<29	Keller unpublished
Actinonaias pectorosa (juvenile)	S,M,T	$CuSO_4$	87.0	70	Keller unpublished
Utterbackia imbecillis	S,M,T	$CuSO_4$	39.0	86	Keller and Zam 1991
Utterbackia imbecillis	S,M,T	$CuSO_4$	90.0	199	Keller and Zam 1991
Utterbackia imbecillis	S,M,T	$Cu(NO_3)_2$	92.0	76	Keller unpublished
Utterbackia imbecillis	S,M,T	$Cu(NO_3)_2$	86.0	85	Keller unpublished
Utterbackia imbecillis	S,M,T	$Cu(NO_3)_2$	90.0	41	Keller unpublished
Utterbackia imbecillis	S,M,T	$CuSO_4$	90.0	79	Keller unpublished
Utterbackia imbecillis	S,M,T	$CuSO_4$	90.0	72	Keller unpublished
Utterbackia imbecillis	S,M,T	$CuSO_4$	86.0	38	Keller unpublished
Utterbackia imbecillis	S,M,T	$CuSO_4$	186.0	60	Keller unpublished

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Hybognathus amarus	R.M,T	$CuSO_4$	141.5	250	Buhl 2002
Pimephales promelas	R,M,T	$CuSO_4$	147.5	393	Buhl 2002
Daphnia magna	S,M,T	--	360.0	304	De Schamphelaere et al. 2002
			(pH=7.59, DOC=1.5)		
Daphnia magna	S,M,T	--	120.0	350	De Schamphelaere et al. 2002
			(pH=7.65, DOC=3.6)		
Daphnia magna	S,M,T	--	200.0	115	De Schamphelaere et al. 2002
			(pH=6.77, DOC=1.86)		
Daphnia magna	S,M,T	--	200.0	266	De Schamphelaere et al. 2002
			(pH=8.39, DOC=4.65)		
Daphnia magna	S,M,T	--	60.0	429	De Schamphelaere et al. 2002
			(pH=7.74, DOC=4.0)		
Daphnia magna	S,M,T	--	80.0	168	De Schamphelaere et al. 2002
			(pH=8.46, DOC=3.1)		
Daphnia magna	S,M,T	--	40.0	395	De Schamphelaere et al. 2002
			(pH=7.83, DOC=4.2)		
			(142-153)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	178.0	10.5	Naddy et al. 2002
			(Ca:Mg=4:0)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	178.0	17.47	Naddy et al. 2002
			(Ca:Mg=3:1)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	180.0	16.16	Naddy et al. 2002
			(Ca:Mg=1:1)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	178.0	7.92	Naddy et al. 2002
			(Ca:Mg=4:0)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	180.0	12.94	Naddy et al. 2002
			(Ca:Mg=3:1)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	180.0	14.49	Naddy et al. 2002
			(Ca:Mg=1:1)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	180.0	7.88	Naddy et al. 2002
			(Ca:Mg=4:0)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	182.0	9.14	Naddy et al. 2002
			(Ca:Mg=3:1)		
Ceriodaphnia dubia	S,M,T	$CuCl_2$	180.0	7.89	Naddy et al. 2002
			(Ca:Mg=1:1)		
Daphnia magna	S,M,T	$CuCl_2$	176.0	16.35	Naddy et al. 2002
			(Ca:Mg=4:0)		
Daphnia magna	S,M,T	$CuCl_2$	176.0	20.97	Naddy et al. 2002
			(Ca:Mg=3:1)		

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Daphnia magna	S,M,T	$CuCl_2$	180.0	57.28	Naddy et al. 2002
			(Ca:Mg=1:1)		
Daphnia magna	S,M,T	$CuCl_2$	180.0	21.55	Naddy et al. 2002
			(Ca:Mg=4:0)		
Daphnia magna	S,M,T	$CuCl_2$	182.0	31.77	Naddy et al. 2002
			(Ca:Mg=3:1)		
Daphnia magna	S,M,T	$CuCl_2$	180.0	42.68	Naddy et al. 2002
			(Ca:Mg=1:1)		
Daphnia magna	S,M,T	$CuCl_2$	90.0	12.2	Naddy et al. 2002
			(Ca:Mg=4:0)		
Daphnia magna	S,M,T	$CuCl_2$	90.0	16.93	Naddy et al. 2002
			(Ca:Mg=3:1)		
Daphnia magna	S,M,T	$CuCl_2$	92.0	11.99	Naddy et al. 2002
			(Ca:Mg=1:1)		
Gammarus sp.	R,M,T	$CuCl_2$	176.0	181	Naddy et al. 2002
			(Ca:Mg=4:0)		
Gammarus sp.	R,M,T	$CuCl_2$	176.0	103	Naddy et al. 2002
			(Ca:Mg=3:1)		
Gammarus sp.	R,M,T	$CuCl_2$	182.0	133	Naddy et al. 2002
			(Ca:Mg=1:1)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	172.0	67.9	Naddy et al. 2002
			(Ca:Mg=4:0)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	178.0	53.9	Naddy et al. 2002
			(Ca:Mg=3:1)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	176.0	35.5	Naddy et al. 2002
			(Ca:Mg=1:1)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	176.0	18.1	Naddy et al. 2002
			(Ca:Mg=1:3)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	176.0	52.5	Naddy et al. 2002
			(Ca:Mg=4:0)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	180.0	46.2	Naddy et al. 2002
			(Ca:Mg=3:1)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	178.0	30.7	Naddy et al. 2002
			(Ca:Mg=1:1)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	180.0	17.9	Naddy et al. 2002
			(Ca:Mg=1:3)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	176.0	18.1	Naddy et al. 2002
			(Ca:Mg=1:4)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	179.0	37.3	Naddy et al. 2002
			(Ca:Mg=4:0)		

Table 5-2 (Continued)
Acute Copper Toxicity Data Added to the Revised Acute Database

Species	Method[a]	Chemical	Hardness (mg/L as $CaCO_3$)	LC_{50} (µg/L)	Reference
Oncorhynchus mykiss	R,M,T	$CuCl_2$	177.0	27.7	Naddy et al. 2002
			(Ca:Mg=3:1)		
Oncorhynchus mykiss	R,M,T	$CuCl_2$	180.0	21.2	Naddy et al. 2002
			(Ca:Mg=1:1)		
Pimephales promelas	R,M,T	$CuCl_2$	176.0	837	Naddy et al. 2002
			(Ca:Mg=3:1)		
Pimephales promelas	R,M,T	$CuCl_2$	182.0	503	Naddy et al. 2002
			(Ca:Mg=1:1)		
Pimephales promelas	R,M,T	$CuCl_2$	176.0	442	Naddy et al. 2002
			(Ca:Mg=4:0)		
Pimephales promelas	R,M,T	$CuCl_2$	176.0	502	Naddy et al. 2002
			(Ca:Mg=3:1)		
Pimephales promelas	R,M,T	$CuCl_2$	182.0	434	Naddy et al. 2002
			(Ca:Mg=1:1)		
Oncorhynchus mykiss (fry)	F,M,T	--	25.4	18	Marr et al. 1998
Oncorhynchus mykiss	F,M,T	$CuCl_2$	9.2	2.8	Cusimano et al. 1986
Ceriodaphnia reticulata	S,U	--	45.0	17	Mount and Norberg 1984
Daphnia magna	S,U	--	45.0	54	Mount and Norberg 1984
Daphnia pulex	S,U	--	45.0	53	Mount and Norberg 1984
Simocephalus vetulus	S,U	--	45.0	57	Mount and Norberg 1984

NOTES:
[a] S = static; R = renewal; M = measured; U = unmeasured; and T = total measured concentration.

Acute values from 20 toxicity tests conducted by Winner (1985) were added to the revised acute toxicity database. Tests were conducted at three different water hardness levels (soft, medium, and hard) and at four levels of humic acid. The final SMAV for *D. pulex* was strictly derived from the normalized toxicity values from this study, since all other acute values for *D. pulex* in the database are derived from studies in which Cu concentrations were not measured (Appendix 2), per the 1985 Guidelines.

Lazorchak and Waller (1993) conducted a series of static 48-hour acute toxicity tests with *D. magna* to determine the effect of weight loss, or lack of weight gain, on copper toxicity. This was accomplished by comparing acute tests where organisms were fed to those that were not fed. Thirteen unfed tests were conducted and acute values were added to the updated acute database (Table 5-2).

De Schamphelaere et al. (2002) evaluated copper toxicity in *D. magna* through 48-hr acute toxicity tests conducted with 25 different reconstituted laboratory waters and 13 different natural surface waters. Only acute values generated from tests using reconstituted water with pH >6.5 and DOC (and TOC for this test)

<5.0 mg/L were added to the revised acute database. This study provided seven new acute toxicity values for *D. magna*.

A recent publication from Long *et al*. (2004) reports acute copper toxicity values for *D. magna* at various water harness and pH values. Test methods were reviewed and toxicity tests conducted at pH >6.5 were determined suitable for use in criteria development. Ten data points from this study were added to the revised acute database.

Hyne et al. (2005) conducted a series of static 48-hr acute toxicity tests with *Ceriodaphnia dubia* to evaluate the influence of pH, hardness, alkalinity, and DOC on zinc and copper toxicity. Test water consisted of soft reconstituted laboratory water, modified with the parameter of interest as well as site water. Results using reconstituted water with pH ∃6.5 and DOC <5.0 mg/L were determined acceptable for use in criteria derivation. These results added 10 acute values to *C. dubia*, a species that was not previously represented in the national acute copper toxicity database.

An additional study that contributed considerable toxicity data to the *C. dubia* SMAV is Belanger et al. (1988). Belanger et al. (1988) conducted acute and chronic toxicity tests with dechlorinated laboratory water, and two site waters (the New and Clinch rivers) that differed in hardness, and alkalinity. Only the toxicity values derived from tests using laboratory water were added to the revised acute database, since only minimal water chemistry was reported for the two river sites.

Belanger and Cherry (1990) acclimated *C. dubia* to three sites waters (New River, Clinch River, and Amy Bayou) that differed in hardness and had no detectable copper or zinc. Acute and chronic tests were conducted at pH 6, 8, and 9. No measurements of site DOC concentration were reported; yet, the 2003 Copper Draft reports all concentrations were <5.0 mg/L. Since more water chemistry, including background metal concentrations were reported in this effort and site water was acceptable for use, acute values from tests run at pH 8 and 9 were added to the revised acute database.

Naddy et al. (2002) evaluated the effect of the calcium-magnesium ratio on the toxicity of copper to *C. dubia, D. magna, Gammarus, sp., Oncorhynchyus mykiss*, and *P. promelas*, while holding hardness and alkalinity relatively constant. Appropriately assigned 48-hr and 96-hr static-renewal toxicity tests were conducted with each species in reconstituted laboratory water. All toxicity values derived from this effort were added to the revised acute database, yet were not used in the acute-hardness slope derivation (see Section 5.4.1, below), due to the increased variability associated with these data at a given hardness.

Kovisto et al. (1992) conducted acute and chronic copper toxicity tests with five cladoceran species that differed in size (*D. magna, D. pulex, D galeata, Bosmina longirostris*, and *Chydorus spaericus*). All organisms except *D. magna* were initially field collected and then cultured in the laboratory. Acute 48-hr static tests were conducted with and without feeding and chronic tests consisted of 21d renewal tests. The test water was soft spring water (hardness = 33.8 mg/L as CaCO3) and copper concentrations were not measured. Toxicity values generated from the unfed tests contribute acute copper toxicity values for three cladocerans not previously represented in the national database (*B. longirostrus, C. sphaericus,* and *D. galeata*). These species rank as the three most sensitive species in the database.

Recent efforts by Dwyer et al. (1995; 1999) have contributed a significant volume of toxicity data for a variety of toxicants in threatened or endangered (T&E) species. Authors conducted simultaneous static 96-hour acute copper toxicity tests using the T&E species and a potential surrogate species (e.g., *P. promelas* and *O. mykiss*) to determine the relative differences in copper sensitivity. T&E species tested included *Gila elegans* (Federally listed), *Oncorhynchus clarki henshawi* (Federally listed), *O. clari stomias* (Federally listed), *Ptychoceilus lucius* (Federally listed), *Xyrauchen texanus* (Federally listed), *Bufo boreas* (state listed-Colorado), *Etheostoma rubrum* (Federally listed), *E. lepidum* (state listed-Texas), and *Poeciliopsis occidentalis* (Federally listed). Acute values generated from the T&E species and potential surrogate tests were added to the revised and updated acute toxicity database.

5.3.2 New Chronic Copper Toxicity Data

In addition to the new acute data, a total of 24 chronic values from ten sources were added to the revised chronic toxicity database. The new chronic data included new chronic toxicity data for two cladocerans and one rotifer (*Brachionus calyciflorus*) not previously represented in the national chronic database (Table 5-3). Three papers (Winner 1985; Spehar and Fiandt 1986; Belanger and Cherry 1990) reported paired acute and chronic values that contribute to the (FACR) derivation.

Table 5-3
Chronic Copper Toxicity Data Added to the Revised Chronic Database

Species	Method[a]	Chemical	Hardness	NOEC	LOEC	Chronic Value (µg/L)	Reference
Brachinus calyciflorus	LC, T	$CuSO_4$	85.00	1.2	2.5	1.73	Jansen et al. 1994
Daphnia magna	LC, T	$CuCl_2$	225.00	--	--	21.5	van Leeuwin et al. 1988
Daphnia pulex	LC, T (42d)	$CuSO_4$	57.5 (HA=0mg/L)	4.0	6.0	4.90	Winner 1985
Daphnia pulex	LC, T (42d)	$CuSO_4$	57.5 (HA=0.75mg/L)	20.0	25.0	22.36	Winner 1985
Daphnia pulex	LC, T (42d)	$CuSO_4$	57.5 (HA=1.5mg/L)	30.0	40.0	34.64	Winner 1985

Table 5-3 (Continued)
Chronic Copper Toxicity Data Added to the Revised Chronic Database

Species	Method[a]	Chemical	Hardness	NOEC	LOEC	Chronic Value (µg/L)	Reference
Daphnia pulex	LC, T (42d)	$CuSO_4$	115.0 (HA=0mg/L)	5.0	10.0	7.07	Winner 1985
Daphnia pulex	LC, T (42d)	$CuSO_4$	115.0 (HA=0.75mg/L)	20.0	30.0	24.49	Winner 1985
Daphnia pulex	LC, T (42d)	$CuSO_4$	115.0 (HA=1.5mg/L)	40.0	50.0	44.72	Winner 1985
Daphnia pulex	LC, T (42d)	$CuSO_4$	230.0 (HA=0.15mg/L)	10.0	15.0	12.25	Winner 1985
Daphnia pulex	LC, T (42d)	$CuSO_4$	230.0 (HA=0.75mg/L)	10.0	20.0	14.14	Winner 1985
Daphnia pulex	LC, T (42d)	$CuSO_4$	230.0 (HA=0.75mg/L)	20.0	30.0	24.49	Winner 1985
Ceriodaphnia dubia	LC, T	$CuSO_4$	8.00	3.2	--		Suedel et al. 1996
Ceriodaphnia dubia	LC, T	--	22.00 (16-28)	4	6	4.90	Jop et al. 1995
Ceriodaphnia dubia	LC, D	$CuCl_2$	32.00	12	32	19.60	Carlson et al. 1986
Ceriodaphnia dubia	LC, T	--	97.60 (pH=8)	0	10	<10	Belanger and Cherry 1990
Ceriodaphnia dubia	LC, T	--	97.60 (pH=9)	10	20	14.14	Belanger and Cherry 1990
Ceriodaphnia dubia	LC, T	--	113.60 (pH=8)	20	40	28.28	Belanger and Cherry 1990
Ceriodaphnia dubia	LC, T	--	113.60 (pH=9)	20	40	28.28	Belanger and Cherry 1990
Ceriodaphnia dubia	LC, T	--	182.00 (pH=8)	0	20	<20	Belanger and Cherry 1990
Ceriodaphnia dubia	LC, T	--	182.00 (pH=9)	0	20	<20	Belanger and Cherry 1990
Ceriodaphnia dubia	LC, T	$CuSO_4$	27.00	--	--	24.5	Oris et al. 1991
Ceriodaphnia dubia	LC, T	$CuSO_4$	57.00	--	--	30.8	Oris et al. 1991
Oncorhynchus mykiss	ELS, T	$CuCl_2$	25	2.2	4.6	3.18	Marr et al. 1996

NOTES:
[a]ELS = early life stage and LC = life cycle or partial life cycle; T = measured total; D = measured dissolved.
[b]Value adjusted to hardness = 50 using the revised chronic slope (0.7432) found in Table 5-4.

5.4 PHASE III - RECALCULATION OF ACUTE AND CHRONIC AWQC FOR COPPER

5.4.1 Updated Acute Hardness Slope

An updated acute hardness slope was developed from the revised and updated acute toxicity database and procedures set forth in the 1985 Guidelines. All species mean acute slopes (SMAS) used in the 1984 acute hardness slope derivation were updated with new toxicity data and nine new taxa were added from our analysis (Table 5-4). SMASs ranged from 0.5149 for *O. tshawytscha* (R^2 = 0.76) to 1.5736 for *P. oregonensis* (R^2=0.99). Pooling the normalized acute and water hardness values for all 17 taxa results in a pooled acute hardness slope of 0.9801 (R^2 = 0.73) (Figure 5-1). The updated acute slope is slightly steeper than the EPA slope of 0.9422 and was derived from hardness values ranging from 7.1 to 400 mg/L as $CaCO_3$.

Table 5-4
Updated Acute Copper Hardness Slope

Species	N	SMAS	R^2	Code
Ceriodaphnia dubia	18	0.9452	0.69	3
Daphnia magna	61	0.9199	0.72	2
Daphnia pulex	6	0.9918	0.75	3
Daphnia pulicaria	11	0.6767	0.83	2
Gambusia affinis	11	1.0742	0.50	3
Ictalurus punctalus	8	1.0563	0.89	3
Lepomis macrochirus	17	1.1469	0.84	2
Morone saxatilis	5	0.5865	0.58	3
Oncorhynchus clarkii	9	0.8783	0.61	2
Oncorhynchus mykiss	64	0.9923	0.71	2
Oncorhynchus tshawytscha	12	0.5149	0.76	2
Pimephales promelas	39	1.1681	0.89	2
Poecillia reticulata	4	1.3917	0.90	2
Ptychocheilus oregonensis	4	1.5736	0.99	3
Salvelinus confluentus	5	1.5875	0.93	3
Tubifex tubifex	2	0.8669	--	3
Vilosa vibex	2	0.5697	--	3
Revised Pooled Slope =		**0.9801**	**0.73**	

NOTES:
SMAS = species mean acute slope.
2 = updated/revised SMAS
3 = new species

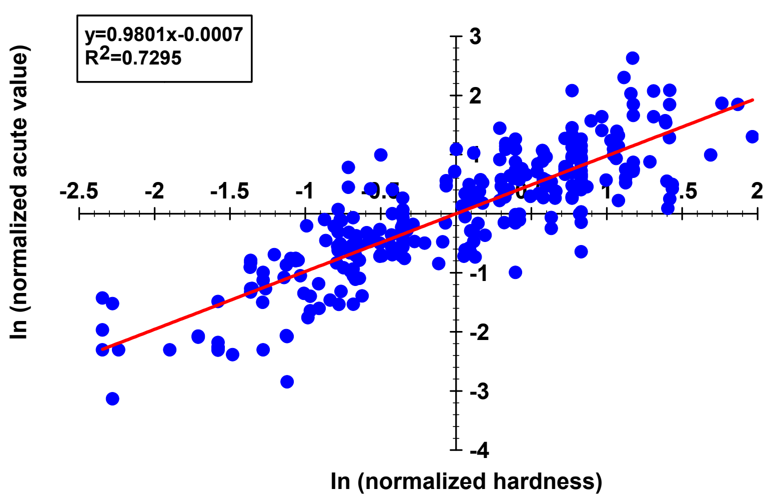

Figure 5-1
Relationship Between Acute Copper Toxicity and Water Hardness using the Revised and Updated Acute Database

The updated acute slope of 0.9801 was used to normalize all acute values to a hardness of 50 mg/L and to develop a hardness-based final acute equation. The resulting SMAV and GMAV for the species in the revised and updated database are presented in Table 5-5 and ranked from least to most sensitive.

Table 5-5
Recalculated Species Mean Acute Values (SMAVs) using Revised and Updated Acute Database and Ranked by Genus Mean Acute Values (GMAV)

Rank	Species	Common Name	GMAV (µg/L)	SMAV (µg/L)	Code
69	*Notemigonus crysoleucas*	Golden shiner	59,017.19	59,017.19	2
68	*Acroneuria lycorias*	Stonefly	9,407.86	9,407.86	1,2
67	*Corbicula manilensis*	Asiatic clam	>7,484.64	>7,484.64	1,2
66	Trichoptera spp.	Caddisfly	6,200.00	6,200.00	1,2
65	*Anguilla rostrata*	American eel	5,747.51	5,747.51	2
64	*Zygoptera* spp.	Damselfly	4,600.00	4,600.00	1,2
63	*Procambarus clarkii*	Crayfish	2,072.67	2,072.67	1,2
62	*Campeloma decisum*	Snail	1,859.40	1,859.40	1,2
61	*Oronectes rusticus*	Crayfish	1,363.30	1,363.30	1,2
60	*Crangonyx pseudogracilis*	Amphipod	1,290.00	1,290.00	1,2
59	*Lepomis gibbosus*	Pumpkinseed	929.07	619.00	2
	Lepomis macrochirus	Bluegill		1,394.46	2
58	*Amnicola* spp.	Snail	900.00	900.00	1,2
57	*Gambusia affinis*	Mosquitofish	795.54	795.54	2
56	*Fundulus diaphanus*	Banded killifish	788.32	788.32	2
55	*Cyprinus carpio*	Common carp	746.62	746.62	2
54	*Tilapia mossambica*	Mozambique tilapia	663.07	663.07	2
53	*Ephemerella subuaria*	Mayfly	362.71	362.71	1,2
52	*Notropis chrysocephalus*	Striped shiner	314.86	314.86	2
51	*Carassius auratus*	Goldfish	288.69	288.69	2
50	*Chironomus tentans*	Midge	194.13	452.70	1,2
	Chironomus spp.	Midge		30.00	1,2
	Chironomus decorus	Midge		837.64	1,2
	Chrionomus plumosus	Midge		124.86	1,2
49	*Jordanella floridae*	Flagfish	189.81	189.81	2
48	*Tropocyclops prasinus*	Copepod	140.43	140.43	1,2
47	*Acrocheilus alutaceus*	Chiselmouth	132.61	132.61	2
46	*Ictalurus nebulosus*	Brown bullhead	128.61	66.22	2
	Ictalurus punctatus	Channel catfish		249.80	1,2
45	*Pectinatella magnifica*	Bryozoan	128.27	128.27	2
44	*Salmo salar*	Atlantic salmon	114.58	114.58	1
43	*Morone americana*	White perch	95.34	5,842.52	2
	Morone saxatilis	Striped bass		95.34	2
42	*Poecilia reticulata*	Guppy	81.76	81.76	2
41	*Nais* spp.	Worm	90.00	90.00	1,2

Table 5-5 (Continued)
Recalculated Species Mean Acute Values (SMAVs) using Revised and Updated Acute Database and Ranked by Genus Mean Acute Values (GMAV)

Rank	Species	Common Name	GMAV (µg/L)	SMAV (µg/L)	Code
40	*Etheostoma caeruleum*	Rainbow darter	87.66	82.24	2
	Etheostoma spectabile	Orangethroat darter		218.44	2
	Etheostoma lepidum	Greenthroat darter		79.74	2
	Etheostoma nigrum	Johnny darter		159.55	2
	Etheostoma rubrum	Fountain darter		18.40	2
	Etheostoma flabellare	Fantail darter		107.94	2
39	*Hybognathus amarus*	Rio Grande silvery minnow	86.59	86.59	2
38	*Rhinichthys atratulus*	Blacknose dace	82.24	82.24	2
37	*Xyrauchen texanus*	Razorback sucker	81.02	81.02	2
36	*Semotilus atromaculatus*	Creek chub	79.67	79.67	2
35	*Pimephales notatus*	Bluntnose minnow	74.33	68.49	2
	Pimephales promelas	Fathead minnow		80.66	2
34	*Campostoma anomalum*	Central stoneroller	74.53	74.53	2
33	*Ptychocheilus oregonensis*	Northern pikeminnow	68.61	40.14	2
	Ptychocheilus lucius	Colorado pikeminnow		117.29	2
32	*Salvelinus fontinalis*	Brook trout	66.15	110.88	1
	Salvelinus confluentus	Bull trout		39.47	1
31	*Simocephalus vetulus*	Cladoceran	63.20	63.20	1, 2
30	*Catostomus latipinnis*	Flannelmouth sucker	62.06	62.06	2
29	*Gila elegans*	Bonytail chub	59.25	59.25	2
28	*Oncorhynchus kisutch*	Coho salmon	55.41	115.58	1
	Oncorhynchus nerka	Sockeye salmon		132.57	1
	Oncorhynchus clarki (henshawi)	Cutthroat trout		65.19	1
	Oncorhynchus tshawytscha	Chinook salmon		33.23	1
	Oncorhynchus mykiss	Rainbow trout		27.70	1
	Oncorhynchus apache	Apache trout		21.22	1
	Oncorhynchus gorbuscha	Pink salmon		82.22	1
27	*Gyraulus circumstriatus*	Snail	54.75	54.75	1, 2
26	*Limnodrilus hoffmeisteri*	Worm	51.71	51.71	1, 2
25	*Poeciliposis occidentalis*	Gila topminnow	49.07	49.07	2
24	*Scaphirhynchus platorynchus*	Shovelnose sturgeon	49.07	49.07	2
23	*Lampsilis teres*	Yellow sandshell	47.21	44.80	2
	Lampsilis s. *clairbornensis*	Freshwater mussel		49.75	2
22	*Lumbriculus variegatus*	Worm	46.40	46.40	1, 2
21	*Utterbackia imbecillis*	Paper pondshell mussel	41.83	41.83	2
20	*Physa heterostropha*	Snail	38.91	34.98	1, 2
	Physa integra	Snail		43.28	1, 2
19	*Bufo boreas*	Boreal toad	36.80	36.80	1
18	*Juga plicifera*	Snail	35.10	35.10	1, 2
17	*Lophopodella carteri*	Bryozoan	35.21	35.21	2
16	*Plumatella emarginata*	Bryozoan	35.21	35.21	2

Table 5-5 (Continued)
Recalculated Species Mean Acute Values (SMAVs) using Revised and Updated Acute Database and Ranked by Genus Mean Acute Values (GMAV)

Rank	Species	Common Name	GMAV (µg/L)	SMAV (µg/L)	Code
15	*Villosa vibex*	Rainbow mussel	33.52	45.15	2
	Villosa vilosa	Freshwater mussel		24.89	2
14	*Tubifex tubifex*	Worm	33.28	33.28	1, 2
13	*Physella gyrina*	Snail	27.26	27.26	1, 2
12	*Gammarus pseudolimnaeus*	Amphipod	23.80	22.72	1, 2
	Gammarus pulex	Amphipod		15.22	1, 2
	Gammarus sp.	Amphipod		39.00	1, 2
11	*Thymallus arcticus*	Arctic grayling	23.52	23.52	1
10	*Brachydanio rerio*	Zebrafish	22.27	22.27	2
9	*Ephoron virgo*	Mayfly	19.35	19.35	1, 2
8	*Lithoglyphus virens*	Snail	18.72	18.72	1, 2
7	*Scapholeberis* spp.	Cladoceran	17.32	17.32	1, 2
6	*Actinonaias pectorosa*	Pheasantshell mussel	16.48	16.48	2
5	*Hyalella azteca*	Amphipod	16.35	16.35	1, 2
4	*Daphnia galeata*	Cladoceran	10.42	6.02	1, 2
	Daphnia magna	Cladoceran		14.93	1, 2
	Daphnia pulex	Cadoceran		14.64	1, 2
	Daphnia pulicaria	Cladoceran		8.98	1, 2
3	*Ceriodaphnia reticulata*	Cladoceran	8.64	9.65	1, 2
	Ceriodaphnia dubia	Cladoceran		7.74	1, 2
2	*Chydorus sphaericus*	Cladoceran	4.84	4.84	1, 2
1	*Bosmina longirostrus*	Cladoceran	2.05	2.05	1, 2

NOTES:
All values are normalized to hardness = 50 mg/L as $CaCO_3$.
1 = Coldwater species.
2 = Warmwater species.

5.4.2 Chronic Hardness Slope

As previously stated, the chronic hardness slope used by the EPA in the 1984/1995 chronic criteria equation was derived from the acute hardness relationship, and then lowered for further protection at high water hardness. We evaluated the potential of deriving a chronic hardness relationship from the revised and updated chronic database. Five taxa of the 15 represented in the revised and updated chronic database were tested at the broad range of hardness values necessary for slope derivation (Stephan et al. 1985). No apparent relationship appears to exist between chronic copper toxicity and hardness for *D. magna*; yet, chronic toxicity of the four other taxa (*O. mykiss, P. promelas, D. pulex,* and *C. dubia*) all exhibit significant positive relationships with water hardness (Table 5-6). Pooling the chronic data of these four taxa results in a significant positive hardness slope of 0.5897 ($P = <0.001$, $R^2 = 0.5446$) (Figure 5-2). This slope was derived from chronic data and, therefore, better represents the relationship between chronic copper toxicity and water hardness than the existing EPA slope (0.8545).

Table 5-6
New Chronic Copper Hardness Slope Derived from the Revised and Updated Chronic Database

Species	N	SMCS	R^2
*Daphnia magna**	4	-0.0462	0.004
Oncorhynchus mykiss	4	0.8490	0.63
Pimephales promelas	5	0.4459	0.46
Daphnia pulex	3	0.6610	0.97
Ceriodaphnia dubia	11	0.5687	0.53
	Revised Pooled Slope =	**0.5897**	**0.54**

NOTES:
SMCS = Species mean chronic slope.
* = Not used in chronic pooled slope calculations.

The updated chronic slope was used to normalize all chronic toxicity data for criterion derivation and in the final chronic toxicity equation. The resulting species mean chronic values (SMCV) and genus mean chronic values (GMCV) calculated from the revised and updated chronic database are presented in Table 5-7 and ranked from least to most sensitive, per the 1985 Guidelines.

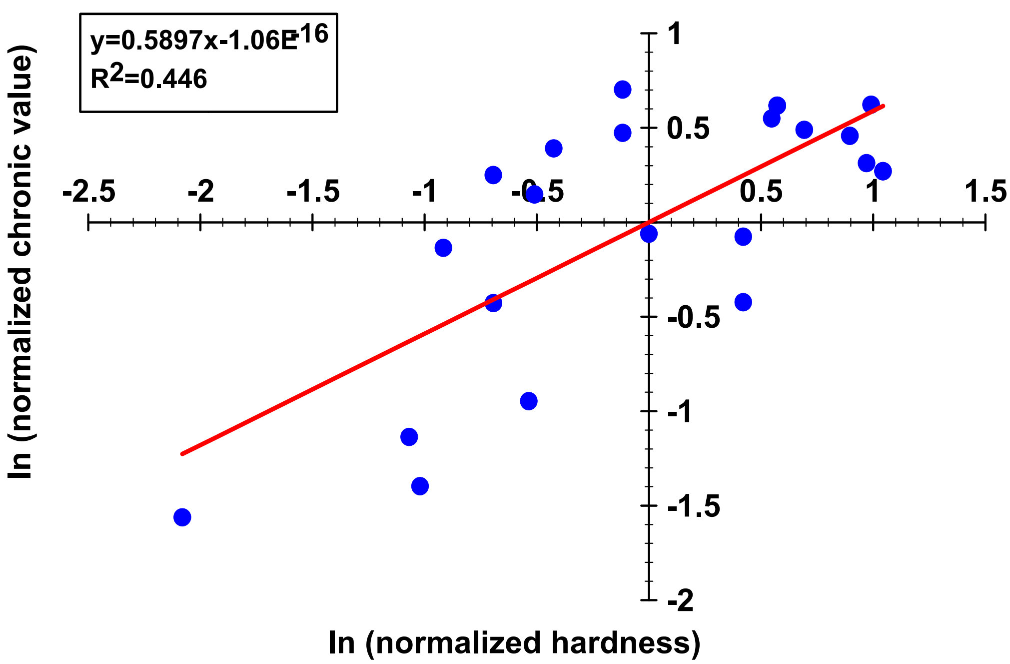

Figure 5-2
The Relationship Between Chronic Copper Toxicity and Water Hardness using the Revised and Updated Chronic Toxicity Database

Table 5-7
Recalculated Species Mean Chronic Values (SMCV) using the Revised and Updated Chronic Toxicity Database and Ranked by Genus Mean Chronic Values (GMCV)

Rank	Species	Common Name	GMCV (µg/L)	SMCV (µg/L)	Code
11	*Esox lucius*	Northern pike	63.90	63.90	1, 2
10	*Salmo trutta*	Brown trout	32.63	32.63	1
9	*Catostomus commersoni*	White sucker	22.10	22.10	1, 2
8	*Salevlinus fontinalis*	Brook trout	18.63	10.75	1
	Salvelinus namaycush	Lake trout		32.29	1
7	*Campeloma decisum*	Snail	11.58	11.58	1, 2
6	*Ceriodaphnia dubia*	Cladoceran	13.19	13.19	1, 2
5	*Daphnia magna*	Cladoceran	10.30	10.15	1, 2
	Daphnia pulex	Cladoceran		10.46	1, 2
4	*Clistornia magnifica*	Caddisfly	10.39	10.39	1, 2
3	*Oncorhynchus mykiss*	Rainbow trout	7.07	10.60	1
	Oncorhynchus tshawytscha	Chinook salmon		4.71	1
2	*Pimephales notatus*	Bluntnose minnow	7.06	3.96	2
	Pimephales promelas	Fathead minnow		12.59	2
1	*Brachionus calyciflorus*	Rotifer	1.27	1.27	1, 2

NOTES:
All values are normalized to hardness = 50 mg/L as $CaCO_3$.
1 = Coldwater species
2 = Warmwater species

5.4.3 Potential relationships with other water quality parameters

Multiple water quality factors are known to modify to toxicity of copper to aquatic life in addition to water hardness (e.g., parameters in the BLM). Recent investigations of other water quality parameters have suggested alkalinity maybe an equally important modifier of copper toxicity as water hardness (Welsh et al. 2000, Gensemer et al. 2002). We investigated this potential relationship using studies from the revised and updated acute toxicity database that published both test water hardness and alkalinity measurements. Eight species contained an appropriate range of alkalinity data of the highest concentration being three times the lowest and 100 mg/L greater than the lowest concentration tested. Theses species include two cladocerans (*D. magna,* and *C. dubia*) and six fish (*O. mykiss, O. clarki, O, tshwytscha, L. macrochirus, I. Punctatus,* and *P. promelas*). Species mean acute slopes ranged from 0.5667 to 1.5691, with a pooled slope of 1.0571 (R^2 = 0.41, P<0.001).

Although the relationship between copper toxicity and alkalinity is significant, we did not factor this relationship in the revised and updated copper criteria due to the resulting reduction in the database. Limiting the database to acute values with alkalinity data reduces the number of data points in the acute database by 59% and the number of species represented by 47% - similar to the reduction observed when limited to studies with BLM-related data. Given the goal of this study is to derive site-specific criteria via the recalculation procedure, which further refines the database via the deletion process, it is necessary to start out with as robust of a database as possible. Limiting the database to values with test water alkalinity measurements (or BLM-required data) removes important resident species of the sites under consideration for recalculation such as the amphipod, *H. azteca*, the mosquitofish, *G. affinis*, the only acute toxicity value for the insect order Odonata, and others.

5.4.4 Updated Final Acute-Chronic Ratio

An updated (FACR) was also determined using all data reported in the current criteria document and data obtained from CEC's literature review (Table 5-8). Methods followed those described by Stephan *et al*. (1985). Eight new data points were added from studies in which acute and chronic values were calculated at similar hardness values for a given species. These new data included paired toxicity values for *Daphnia pulex* and *Ceriodaphnia dubia*, which are two acutely sensitive species not previously included in the EPA FACR calculations. ACRs for *Gammarus pseudolimnaeus* and *Lepomis macrochirus* were deleted from the FACR consideration since chronic data were derived from tests with unacceptable control survival and deleted from the revised chronic database (Table 7-1). The updated FACR (2.9008) was derived from the three cladoceran species mean ACRs (SMACRs), whose SMAVs were closest to the updated FAV. The revised FACR of 2.901 is slightly greater than the EPA FACR of 2.823 (EPA 1984).

Table 5-8
Derivation of Revised Species Mean Acute-to-Chronic Ratios (ACRs) and the Final Acute-to-Chronic (FACR) for Copper

Existing ACR Data:			**New ACR Derivation Data:**	
Species	**Species Mean ACR**		**Species**	**Species Mean ACR**
Campeloma decisum	156.2		*Campeloma decisum*	153.80
Lepomis macrochirus	37.96		*Salvelinus fontinalis*	7.776
Salvelinus fontinalis	7.776		*Pimephales notatus*	26.358
Pimephales notatus	26.36		*Pimephales promelas*	12.653
Oncorhynchus tshawytscha	>4.473		*Oncorhynchus tshawytscha*	11.107
Physa integral	3.585		*Oncorhynchus mykiss*	3.592
*Gammarus pseudolimnaeus**	3.297		*Ceriodaphnia dubia**	2.097
*Daphnia magna**	2.418		*Daphnia magna**	2.418
EPA FACR =	**2.823**		*Daphnia pulex**	4.8143
			Updated FACR =	**2.901**

New ACR Data From Updated Toxicity Databases:					
Species	**Hardness**	**Acute Value**	**Chronic Value**	**ACR**	**Reference**
Ceriodaphnia dubia	97.6	31.00	14.14	2.1920	Belanger and Cherry 1990
Ceriodaphnia dubia	113.6	76.00	28.28	2.6870	Belanger and Cherry 1990
Ceriodaphnia dubia	113.6	91.00	28.28	3.2173	Belanger and Cherry 1990
Ceriodaphnia dubia	36.0	20.0	19.60	1.0204	Carolson et al. 1986
Daphnia pulex	57.5	25.74	2.83	9.0943	Winner 1985
Daphnia pulex	115.0	27.60	7.07	3.9038	Winner 1985
Daphnia pulex	230.0	28.79	9.16	3.1430	Winner 1985

*=Used in EPA FACR calculation.

The updated copper criteria are then calculated using the four most sensitive GMAVs in the updated database. (*Bosmina, Chydorus, Ceriodaphnia, and Daphnia*) (Table 5-9). A FAV of 9.6460 :g/L was calculated resulting in a revised and updated final acute equation of $0.96*e^{(0.9801\ [\ln\ (hardness)]-2.2608)}$, which includes the freshwater conversion factor of 0.960 for the dissolved fraction of copper (EPA 2002). Use of the four GMAVs that have cumulative probabilities (P) closest to 0.05 (ranks 2-5) was also evaluated since N is >59, yet the FAV only changed by 0.1 µg/L. As such, to be consistent with subsequent recalculations, the FAV from the four most sensitive GMAVs was carried forward in the analysis. Using the new FACR and chronic slope, the resulting revised and updated chronic equation would be $0.96*e^{0.5897\ [\ln\ (hardness)]-1.1054}$ (Table 5-9).

Table 5-9
Recalculation of the Final Acute and Chronic Values for Copper using the Updated Acute Database, Updated Acute and Chronic Hardness Slope, and Updated (FACR)

Rank	Genus	GMAV	ln GMAV	(ln GMAV)^2	P = R/(N+1)	%P
4	*Daphnia*	10.42	2.3440	5.4945	0.0571	0.2390
3	*Ceriodaphnia*	8.64	2.1569	4.6521	0.0429	0.2070
2	*Chydorus*	4.84	1.5777	2.4891	0.0286	0.1690
1	Bosmina	2.05	0.7202	0.5187	0.0143	0.1195
		sum	**6.7989**	**13.1545**	**0.1429**	**0.7346**

NOTE: N = 69 genera; R = sensitivity rank in database

Calculations:
Acute Criterion

$$S^2 = \frac{\ni (\ln GMAV)^2 - (\ni \ln GMAV)^2/4}{\Sigma P - (\Sigma\sqrt{P})^2/4} = \frac{13.1545 - (6.7989)^2/4}{0.1429 - (0.7346)^2/4} = 201.2907 \qquad S = 14.1877$$

L = [∋lnGMAV - S(∋%P)]/4 = [13.1545 – 14.1877 (0.7346)]&4 =- 0.9059
A = S (%0.05) + L = (14.1877)(0.2236) - 0.9059 = 2.2665

Final Acute Value = FAV = e^{A} = 9.6460 µg/L
CMC = ½ FAV = 4.8230
Pooled Slope = 0.9801 (recalculated)
ln (Criterion Maximum Intercept) = lnCMC - [pooled slope H ln (standardized hardness level)]
= ln (4.8230) - [0.9801 H ln (50)]
= -2.2608
Acute Copper Criterion (µg dissolved Cu/L) = $0.96*e^{(0.9801\ [\ln\ (hardness)]\ -\ 2.2608)}$

Chronic Criterion

Chronic Slope = 0.5897 (calculated from chronic toxicity data)
(FACR) = 2.9008 (recalculated)

Final Chronic Value (FCV) = FAV) FACR = 9.6460) 2.9008 = 3.3253 µg/L

ln (Final Chronic Intercept) = ln FCV - [chronic slope H ln(standardized hardness level)]
= ln (3.3253) - [0.5897 H ln (50)]
= -1.1054

Chronic Copper Criterion (µg dissolved Cu/L) = $0.96*e^{(0.5897\ [\ln\ (hardness)]\ -\ 1.1054)}$

Table 5-10 presents a summary of these revised and updated acute and chronic copper criteria at varying hardness levels, with inclusion of the conversion factor for dissolved criteria.

Table 5-10
Summary of Existing (EPA 1996) and Revised Copper Criteria (as µg dissolved Cu/L) at Varying Hardness Levels using the Updated Toxicity Databases, Revised Acute and Chronic Pooled-Hardness Slopes, and Updated Final Acute-Chronic Ratios

	Mean Hardness in mg/L $CaCO_3$									
Equations	**25**	**50**	**75**	**100**	**150**	**200**	**250**	**300**	**350**	**400**
Current EPA Criteria										
Acute = 0.96 ($e^{0.9422\,[\ln\,(hardness)]-1.7000}$	3.640	7.286	10.675	13.999	20.512	26.899	33.192	39.413	45.574	51.684
Chronic = 0.96 ($e^{0.8545\,[\ln\,(hardness)]-1.7020}$	2.739	4.953	7.004	8.956	12.664	16.193	19.595	22.898	26.122	29.279
CEC Update (all data)										
Acute = 0.96 ($e^{0.9801\,[\ln\,(hardness)]-2.2608}$	2.380	4.709	7.018	9.316	13.886	18.431	22.969	27.472	31.974	36.466
Chronic = 0.96 $e^{0.5897\,[\ln\,(hardness)]-1.1054}$	2.121	3.192	4.054	4.804	6.102	7.230	8.246	9.182	10.056	10.880
CEC Update (w/o Koivisto *et al*. 1992)										
Acute = 0.96 ($e^{0.9801[\ln(hardness)]-2.2835}$	4.082	8.077	12.039	15.980	23.818	31.615	39.382	47.124	54.846	62.551
Chronic = 0.96 ($e^{0.5897[(\ln(hardness)-1.1281}$	3.638	5.476	6.955	8.240	10.466	12.401	14.145	15.751	17.250	18.663

Precautionary Note:

One study in particular, Koivisto et al. 1992, highly influenced the updated final acute value. As previously mentioned, this study provides the only data for the three most sensitive species in the revised and updated acute database (*B. longirostrus*, *C. sphaericus*, and *D. galeata*). All acute values presented from this study are unmeasured. Although calculated or nominal concentrations are generally acceptable when no other toxicity data exists (as with this situation), it is a bit disconcerting and creates high uncertainty with a criterion when the three of the most sensitive SMAVs, including the two most sensitive GMAVs, are derived from unmeasured values from a single study. It would not be appropriate to remove these unmeasured values without removing all unmeasured values; therefore, these data were retained. However, criteria calculated without acute values from Koivisto et al. (1992) may be more appropriate for revised national criteria. A comparison of the calculated criteria at various hardness levels with and without the Koivisto et al. (1992) study can be found in Table 5-10.

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6.0 DIAZINON CRITERIA REVIEW AND UPDATE

The EPA has not established national aquatic life criteria for diazinon, but did produce a draft entitled *Draft Ambient Aquatic Life Water Quality Criteria Diazinon* (EPA 2000), hereinafter referred to as the 2000 Diazinon Draft. This document established a working database and draft derived AWQC to protect fresh- and saltwater organisms. Since distribution of the 2000 Diazinon Draft, additional information on the environmental significance of freshwater organism diazinon exposure and available toxicity studies has been published.

6.1 BACKGROUND

Diazinon is an organo-phosphate (OP) compound used as a broad-spectrum insecticide. Diazinon has been in use since 1948, and has effectively replaced parathion and methylparathion, which were banned due to potential high acute mammalian toxicity (rat LD_{50} <20 mg/kg). In California, diazinon is heavily used in the San Joaquin River Valley where presence in storm water runoff is a major water quality problem in agricultural areas (Werner et al. 2004). In addition to agricultural areas, diazinon may contribute to water quality problems in surface waters of developed areas where it is used in professional landscaping and maintenance, pet shampoos, and structural pest control. Hoffman et al. (2000) surveyed eight U.S. urban streams and reported diazinon detection frequency of 69.3% above 0.01 µg/L and 24.9% above 0.05 µg/L from 200 observations. In a nation-wide reconnaissance of organic wastewater contaminants in 139 streams across 30 states, Kolpin et al. (2002) identified diazinon in 25.9% of sample streams at a detection level of 0.03 µg/L, with a median and maximum value of 0.07 µg/L and 0.35 µg/L, respectively. In an agricultural setting, diazinon concentrations can be expected to spike in surface water after application and rainwater runoff events. In urban settings, surface water diazinon concentrations might be greater after rain runoff events, but wastewater effluent could contribute to chronic low-level aquatic organism exposure.

The proposed mechanism of diazinon toxicity is cholinesterase inhibition (Aldridge and Reiner 1972), briefly described below. At the intercellular neuron-axon synapses, electrical transmission of signals pass across synapses to dendrites via chemical neurotransmitters and transmitter inactivators. When a nerve impulse reaches the synapse, chemical neurotransmitters are released and then travel across the synaptic cleft to the post-synaptic dendrite. The signal strength is controlled via transmitter binding strength to the dendrite. The binding strength is controlled via acetylcholinesterase-dependent de-esterification that rapidly cleaves the neurotransmitter acetylcholine. OPs, such as diazinon, strongly bind to acetylcholinesterase and are not easily cleaved due to enzyme phosphorylation. This semi-permanent bond between acetylcholinesterase and diazinon effectively silences the nerve signal transmission inactivation, resulting in acetylcholinesterase protein and nerve terminal membrane damage (Klaassen 2001).

Invertebrates efficiently oxidize diazinon into more toxic diazoxon during P450 metabolism. This increased oxidation efficiency during metabolism and less efficient de-esterification of diazinon at the synaptic cleft might be the reason for increased toxicity in more sensitive macroinvertebrate organisms (Klaassen 2001). Since OPs, such as diazinon, are developed and used to kill pest invertebrates, it would be expected that aquatic invertebrates would be more sensitive than fish. Higher vertebrates such as fish and mammals have efficient metabolic processes that effectively reduce toxic effects of acute and chronic diazinon exposure. Unfortunately, vertebrates do not develop these metabolic processes until specific life stages are reached during development, potentially leaving early life stage organisms at risk. This lack of protective mechanisms could contribute to increased toxicity during life0-cycle toxicity testing that cover a sensitive stage of development. However, later life stages of the same organism might be relatively resistant to diazinon, which complicates comparison of acute and chronic values.

Uptake of diazinon by aquatic organisms is rapid, with body burdens reaching maximum concentrations after 3-7 days (World Health Organization 1998). When transferred to clean water, higher vertebrates, such as fish, can rapidly metabolize diazinon and efficiently excrete metabolites. Organs that show the greatest bioconcentration are associated with metabolism and excretion, i.e., the liver and kidney (Tsuda et al. 1990). This route for efficient excretion plays a protective role in fish species exposed to pulse- dominated exposure patterns and reduces risk of chronic toxicity. With such a well-understood mechanism of toxicity, a significant scientific literature base has been developed that includes effects in many aquatic organisms. Unfortunately, little is known of the environmental fate of diazinon in aquatic environments, and the toxicity of diazinon metabolites to aquatic organisms.

Inherent physical and chemical properties of diazinon predict that it is most stable in neutral media, less stable in alkaline media, and least stable in acidic media. Each diazinon molecule is subject to acid-/base-catalyzed hydrolysis, which results in the breakage at the phosphorus-oxygen bond. Faust and Gomaa (1972) reported a pH-dependent degradation of diazinon in laboratory water at 20ºC; the half-life was determined to be 0.5, 184.8, and 6.1 days at respective pH values of 3.1, 7.4, and 10.4. Medina et al. (1999) compared the half-life of diazinon in filtered river water under light and dark conditions and found a somewhat shorter half-life for sunlight-exposed samples (31 days) compared to unexposed samples (37 days). Kanazawa (1975) tested degradation in tap water and found a 27% degradation of diazinon after 30 days, but other authors (i.e., Ferrando et al. 1991) reported 49% degradation after 96 hours in toxicity test experimental water. One could expect that reported degradation rates would be greater in natural waters due to sunlight exposure and the presence of aquatic organisms that actively metabolize diazinon.

Soil and sediment microbial communities may also influence degradation of diazinon. Common soil bacteria have enzymes that can hydrolyze diazinon to harness energy from mineralized carbon molecules of the compound (Martinez-Toledo 1993). Schoen and Winterlin (1987) studied factors that affected rates of microbial degradation. The authors reported high rates in moist acidic carbon-rich microenvironments and lower rates in alkaline mineral-rich environments. From these few studies, it can be seen that environmental conditions, such as site-specific channel characteristics and water quality parameters of arid West streams, could differentially affect diazinon degradation and, therefore, exposure to aquatic organisms.

6.2 PHASE I - TECHNICAL REVIEW OF THE 2000 DIAZINON DRAFT

The 2000 Diazinon Draft was critically reviewed for relevance of the toxicological data and adherence to EPA methodology. To account for potential over or underestimation of risk, we used data from aquatic toxicity tests that reported measured, rather than nominal, values of diazinon during exposure. Given the relatively short half-life of diazinon in aqueous solutions, measurements of concentrations in acute and, especially, chronic tests are very important. Although pH-dependent degradation rates exist, not enough information is available to establish how this affects diazinon stability in natural waters.

6.2.1 Draft Acute Criterion for Diazinon

The 2000 Diazinon Draft presents acute data for 20 genera, including 12 species of invertebrates, 10 species of fish, and one amphibian species. These 23 species satisfy the "eight-family rule" in multiple combinations, as specified in the 1985 Guidelines. Additionally, calculations for the genus mean acute values (GMAVs) and corresponding final acute value (FAV) were correctly derived from the existing database. However, we determined that values for three genera used in the 2000 Diazinon Draft were unsuitable for acute criteria evaluation (Table 6-1).

Table 6-1
Summary of Acute Data from the 2000 Diazinon Draft Deemed Unsuitable for Criteria Derivation and Deleted from the Revised Acute Database

Species	Existing Value (µg/L)	Reference	Comments
Hyalella azteca	6.51	Ankley and Collyard 1995	Test organisms were fed
Chironomus tentans	10.7	Ankley and Collyard 1995	Test organisms were fed
Rana clamitans	>50	Harris et al. 1998	Possibly contaminated dilution water; DOC >5mg/L

Ankley and Collyard (1995) conducted 96-hr diazinon exposures for three invertebrates, *Hyalella azteca*, *Chironomus tentans*, and *Lumbriculus variegatus*, to determine the influence of piperonyl butoxide on toxicity. The authors stated that they fed *H. azteca* and *C. tentans* at the beginning of the exposures. Since results of these tests were the only reported data values for these species and the test solution was not measured, there was insufficient evidence to indicate that the food did not affect the toxicity or exposure of the test material. If a similar toxicity test of these species, duration, and water quality parameters in which test organisms were not fed was available, results could be compared. Unfortunately, no such data were available for comparison, providing insufficient evidence to indicate influence of feeding on diazinon toxicity. The decision to not use this study was also supported by the fact that test solution concentrations were not measured, further complicating issues with diazinon degradation and/or sorption to organics, as noted above. Toxicity data derived for *L. variegatus* from this study were used because organisms were not fed during the test, although diazinon concentrations were calculated and not measured.

Harris et al. (1998) provided data on green frog, *Rana clamitans*, diazinon toxicity as part of a larger field study using caged animals. Laboratory toxicity testing was performed with an unknown percentage of active ingredient technical diazinon pesticide formulation and reference site water. No chemical analyses were performed on the reference site water to determine whether any confounding residual contaminants were present that one might expect from an agricultural area surface water source. Additionally, reported water quality parameters of site water that were used for dilution exceeded the total organic carbon limit (5 mg/L) as stated in Stephan et al. (1985) without providing sufficient evidence of effect on toxicity.

6.2.2 Draft Chronic Criterion for Diazinon

The 2000 Diazinon Draft chronic database presents chronic data for five genera of freshwater organisms, including one species of invertebrate and four species of fish. These five species from four families do not satisfy the "eight-family rule" as specified in the 1985 Guidelines. The chronic database assemblage does, however, satisfy the minimal requirements for calculation of an acute-to-chronic ratio (ACR), if the saltwater shrimp species *Americamysis bahia* is considered. After calculations of three valid ACRs for three species, it was evident that species that were acutely sensitive had lower ACRs, and species that were acutely insensitive had higher ACRs. Given this relationship, a final ACR (FACR) value was calculated by EPA using only this most acutely sensitive *Ceriodaphnia dubia* and *A. bahia*, which resulted in a FACR that was less than 2. The 1985 Guidelines (Stephan et al. 1985) state if the most appropriate FACR is less then 2, then acclimation had probably occurred and the FACR should be assumed to be 2. Dividing the FAV by 2 resulted in a final chronic value of 0.0963 μg/L, which is equivalent to the CMC (CMC = FAV/2). Compared to the modest acute database, the chronic database on diazinon is lacking diversity and robustness.

6.3 PHASE II – UPDATE TO THE NATIONAL DIAZINON TOXICITY DATABASES

A comprehensive literature review of diazinon documents used and not used in the 2000 Diazinon Draft was conducted. This included a review of documents published since the 2000 Diazinon Draft, as well as those published prior to 1999 that were not used in the criterion derivation. Approximately 100 papers were obtained and reviewed for appropriate data.

6.3.1 New Acute Diazinon Toxicity Data

The literature review contributed 25 new acute data points from 19 studies to the revised acute database (Table 6-2). Of the 19 studies added to the database, 16 were published prior to the 2000 Diazinon Draft. Five of these studies were not cited in either Table 1 ("Acute Toxicity of Diazinon to Aquatic Animals") or Table 6 ("Other Data on Effects of Diazinon on Aquatic Organisms") of the 2000 Diazinon Draft and, apparently, represent data unknown to the EPA at the time.

Toxicity testing data points that had more than one listed reference were specifically investigated - since this may be a result of different authors citing the same test data (e.g., Cope 1965 a, b; Sanders and Cope 1966; Johnson and Finley 1980; Mayer and Ellersieck 1986). It was determined from this investigation that additional data for eight tests used in the 2000 Diazinon Draft were available, but not included. The additional data included two acceptable 48-hr LC_{50} tests for *Daphnia pulex*, two usable 48-hr LC_{50}s for *Simocephalus serrulatus*, and one usable 96-hr LC_{50} for *Lepomis macrochirus* (Table 6-2). Forty-eight-hour LC_{50} test data were also available for *Pteronarcys (=Pteronarcella) californicus*, *Oncorhynchus mykiss*, and *L. macrochirus,* but were not considered acceptable, for use in criteria calculations, due to short test duration.

Table 6-2
Summary of Acute Data that were Deemed Acceptable for use and Added to the Updated Diazinon Acute Database

Species	Method	LC_{50} (µg/L)		Reference
Girardia tigrina	S, M	630		Villar et al. 1994
Lepomis macrochirus	S, U	22		Cope 1965b
Daphnia pulex	S, U	0.9		Sanders and Cope 1966
Daphnia pulex	S, U	0.8		Johnson and Finley 1980
Simocephalus serrulatus	S, U	1.4		Johnson and Finley 1980
Simocephalus serrulatus	S, U	2		Cope 1965a
Oncorhynchus mykiss	S, U	90		Cope 1965b
Oncorhynchus mykiss	R, U	>1,000		Beauvais et al. 2000
Chironomus tentans	S, M	30		Belden 2000
Brachydanio rerio	S, M	7,304		Keizer 1993
Poecilia reticulate	S, M	669.57		Keizer 1993

Table 6-2
Summary of Acute Data that were Deemed Acceptable for use and Added to the Updated Diazinon Acute Database

Species	Method	LC_{50} (µg/L)		Reference
Lepomis macrochirus	S, U	168		Johnson and Finley 1980, Mayer and Ellersieck 1986
Ameiurus melas	S, U	8,000		Bathe et al. 1975
Carassius carassius	S, U	5,000		Bathe et al. 1975
Pimephales promelas	F, M	7,460		Geiger et al. 1988
Pimephales promelas	F, M	6,600		Allison and Hermanutz 1977
Pimephales promelas	F, M	6,800		Allison and Hermanutz 1977
Oreochromis mossambicus	S, U	161.3		Mustafa et al. 1982
Lestes congener	S, U	50		Federle and Collins 1975
Ceriodaphnia dubia	R, M	0.47		CDFG 1992a
Ceriodaphnia dubia	R, M	0.507		CDFG 1992b
Ceriodaphnia dubia	S, M	0.45		Banks et al. 2003
Gammarus lacustris	S, U	200		Sanders 1969
Clarius batrachus	R, U	11,690		Tripathi et al. 1992
Daphnia magna	R, U	0.86		Fernandez et al. 1995

NOTES:
S = static renewal test exposure
F = flow through test exposure
M = test media aluminum concentration was measured
U = test media aluminum concentration was not measured

We located acute toxicity data for five new species of aquatic organisms in published reports that were not represented in the 2000 Diazinon Draft acute database. Tripathi et al. (1992) conducted acute and chronic static renewal diazinon exposure toxicity tests with adult *Clarias batrachus*. This report was presumably unknown to the EPA and was not found in any tables or text. The endpoint was lethality after 96 hrs in which a LC_{50} was determined (11,640 µg/L). Toxicity tests on *Carassius carassius* and *Ameiurus melas* were performed by Bathe et al. (1972) using a flow-through exposure system in which concentration of diazinon was measured. Mustafa et al. (1982) reported results that were used to determine an acceptable acute value for *Oreochromus mossambicus*. An LC_{50} value was derived from a regression equation that was provided in the text. In a report on toxicity of pesticides, Sanders (1969) tested the acute toxicity of over 50 toxicants, including diazinon, in *Gammarus lacustris*. No identifiable standard testing procedures were reported, but enough information was provided to determine acceptance according to 1985 Guidelines and the study was, therefore, added to the updated acute database.

6.3.2 New Chronic Diazinon Toxicity Data

Ten new freshwater chronic data points from eight studies were added to the revised chronic database (Table 6-3). Of these eight studies, seven were published prior to the 2000 Diazinon Draft. Four of these seven studies were not cited in either Table 2 (Chronic Toxicity of Diazinon to Aquatic Animals) or Table 6 (Other Data on Effects of Diazinon on Aquatic Organisms) of the 2000 Diazinon Draft.

Allison and Hermanutz (1977) conducted 96-hr acute and partial life-cycle chronic toxicity tests with *Salvelinus fontinalis* and *Pimephales promelas* using technical grade diazinon. The EPA only presented the results from the *S. fontinalis* test, whereas a suitable chronic value for *P. promelas* was also available. The authors reported an incidence of scoliosis with *P. promelas* after 91 days of exposure and 50% mortality after 107 days of exposure in the 60.3 µg/L treatment (LOEC). The next lowest treatment without a response was 28.0 µg/L (NOEC), which results in a chronic value of 41.09 µg/L. The authors also reported 96-hr LC_{50}s for *P. promelas* (Table 6-2) that were added to the acute database and can be used in the final acute-chronic ratio (FACR) calculation.

Table 6-3
Summary of Chronic Data that were Deemed Acceptable for use and Added to the Updated Diazinon Chronic Database

Species	Method	End Point	Chronic Value (µg/L)	Reference
Pimephales promelas	PLC	S, R	41.09	Allison and Hermanutz 1977
Pimephales promelas	PLC	G	125	Suprenant 1988a
Lepomis macrochirus	PLC	G	14.23	Giddings et al. 1996
Lepomis macrochirus	PLC	S	34.467	Giddings et al. 1996
Brachionus calyciflorus	LC	S, R	15,748	Snell and Moffat 1992
Daphnia magna	PLC	S	<0.15	Fernandez et al. 1995
Daphnia magna	PLC	R	0.165	Fernandez et al. 1995
Daphnia magna	PLC	S, R	<0.05	Sanchez et al. 2000
Daphnia magna	PLC	I	0.23	Suprenant 1988b
Clarias batrachus	PLC	S	2,418.6	Tripathi et al. 1992

NOTES:
PLC = partial life cycle test
LC = life cycle test
S = survival
R = reproduction
I = immobilization

Springborne Life Sciences (Suprenant 1988 a, b) performed 21- and 34-day flow-through toxicity tests using *D. magna* and *P. promelas*, respectively. ASTM (1980) and EPA (1981) test standards were used to obtain LOECs and NOECs for immobilization in *D. magna* and growth in *P. promelas*. The resulting chronic values were added to the revised chronic database.

Giddings et al. (1996) performed a microcosm study in which *Lepomis macrochirus* were exposed to measured concentrations of diazinon. Authors reported NOECs and LOECs for growth and survival. Although microcosm studies could be questionable for use in the derivation of water quality standards, test methods were well described and followed appropriate guidelines. Therefore, we determined that the values were suitable for use in criteria derivation and added the two chronic values to the revised chronic database.

Snell and Moffat (1992) conducted a two-day life cycle test with the rotifer *Brachionus calyciflorus*. Although test duration was very short, a full life cycle test was valid due to the short maturation and generation times of this species. The values for survival and reproduction were similar and resulted in an undefined chronic value of >15,748 µg/L.

Finally, acute and chronic toxicity of diazinon exposure in *Claris batrachus* was investigated by Tripathi (1992). The author reported an LC_{50} for 96 hrs and 40days that are later used to derive an ACR for this species. Test organisms consisted of adults, rather than an early life stage, which might explain the insensitivity of *C. batrachus* to chronic and acute diazinon exposure. *C. batrachus* showed little sensitivity to diazinon exposure with a chronic value of 2,419 µg/L for survival.

Fernandez et al. (1995) conducted a 21-day static renewal chronic toxicity test with *D. magna*. Adequate data were generated to report a survival chronic value and an undefined reproduction chronic value. Acute toxicity data (Table 6-2) were also provided by Fernandez et al. (1995), which are later used in the FACR calculations. Sanchez et al. (2000) similarly tested 21-day survival and reproduction for *D. magna.*

6.4 PHASE III - REVISED AND UPDATED AWQC FOR DIAZINON

Utilizing data discovered and screened during phase II of this project, the diazinon acute and chronic databases were updated and revised. These databases were then used to derive updated acute and chronic freshwater WQC for diazinon.

6.4.1 Updated Acute Database

The revised and updated diazinon acute toxicity database contains data for 22 genera, including 12 species of invertebrates and 14 species of fish (Table 6-4). These 26 species in 17 families satisfy the "eight-family rule" as specified in the 1985 Guidelines.

Table 6-4
Updated Diazinon Species Mean Acute Values (SMAV) Calculated from the Revised and Updated Acute Database and Ranked by Genus Mean Acute Values (GMAV)

Rank	Species	Common Name	GMAV (µg/L)	SMAV (µg/L)
22	*Clarias batrachus*	Walking catfish	14,792	14,792
21	*Gyraulus altilis*	Snail	11,000	11,000
20	*Ameiurus melas*	Black bullhead	8,000	8,000
19	*Lumbriculus variegatus*	Worm	7,841	7,841
18	*Brachydanio rerio*	Zebrafish	7,644	7,644
17	*Carassius auratus*	Goldfish	6,708	9,000
	Carassius carassius	Crucian carp		5,000
16	*Pimephales promelas*	Fathead minnow	6,475	6,475
15	*Physa paludosa*	Snail	3,198	3,198
14	*Girardia tigrina*	Planaria	2,708	2,708
13	*Jordanella floridea*	Flagfish	1,643	1,643
12	*Poecilia reticulate*	Guppy	732	732
11	*Salvelinus fontinalis*	Brook trout	660	723
	Salvelinus namaycush	Lake trout		602
10	*Oncorhynchus clarki*	Cuttthroat trout	455	2,166*
	Oncorhynchus mykiss	Rainbow trout		455
9	*Oreochromis mossambicus*	Tilapia	161	161
8	*Lepomis macrochirus*	Bluegill	116	116
7	*Lestes congener*	Damselfly	50	50
6	*Chironomus tentans*	Midge	30	30
5	*Pteronarcys californicus*	Stonefly	25	25
4	*Simocephalus serrulatus*	Cladoceran	1.70	1.70
3	*Daphnia magna*	Cladoceran	0.93	1.05
	Daphnia pulex	Cladoceran		0.82
2	*Ceriodaphnia dubia*	Cladoceran	0.40	0.40
	Gammarus lacustris	Amphipod		200*
1	*Gammarus fasciatus*	Amphipod	0.20	0.20

NOTE: * = Not used in FAV calculation (see text).

During the literature review, we discovered a discrepancy in toxicity between the two species representing the genus *Gammarus*. The discrepancy was found when the species mean acute value (SMAVs) for *G. lacustris*, derived from a single static unmeasured toxicity test using technical grade diazinon (Sanders 1969), was compared to the SMAV for *G. fasciatus*. The Sanders (1969) value was 1,000-fold greater than the SMAV for *G. fasciatus* (0.20 µg/L, Table 6-4) from Johnson and Finley (1980). If both species are used in the updated genus mean acute value (GMAV) calculation for *Gammarus* by taking the geometric mean of the two SMAVs, the result would be a change in rank from 1 to 4, and the final acute value (FAV) would increase two-fold. It is difficult to assign more significance to one SMAV or the other. Both SMAVs were derived from tests using static, unmeasured exposures; and from the discussion of diazinon degradation earlier, one could expect some discrepancy in actual test concentrations after a 96-hr exposure. Since test treatments were similar, we investigated data from other closely related species. The closest species available for comparison was toxicity data from another amphipod, *Hyalella azteca* (Ankley and Collyard 1995). Although the data for this species were deemed inappropriate for criteria derivation, the GMAV for *Hyalella* (6.32 µg/L) is very close to the geometric mean of *G. lacustris* and *G. fasciatus* (6.51 µg/L). This similarity of GMAVs for *Hyalella* and *Gammarus* provides some evidence that the true value likely lies somewhere between the reported values for *G. lacustris* and *G. fasciatus*. Despite the discrepancy in toxicity between *Gammarus* species, EPA methodology was followed and only the most sensitive species was used to derive the updated GMAV for *Gammarus*.

Our updated acute national database contained a wide range of toxicity values for *O. mykiss* (90 to 3,200 µg/L) (Appendix 2). Further investigation into test methods used to derive these values uncovered a potential life stage-diazinon toxicity relationship. The greatest toxicity value reported by Bathe et al. (1975) was for large (25 to 50 g) fish, which were considerabley larger than reported fish weights from other studies. Because of this apparent life stage sensitivity observation we feel that it was necessary to drop the 3,200 µg/L value from the *O. mykiss* SMAV derivation. Additionally, due to the great difference between *O. mykiss* and *O. clarki* SMAVs (455 vs. 2,166 µg/L), we set the *Oncorhynchus* GMAV to the most sensitive species.

A possible relationship between two water quality parameters (hardness and pH) and acute diazinon toxicity was investigated using the updated acute database. Considering the physical and chemical properties of diazinon and degradation kinetics briefly discussed earlier, an equation-based diazinon AWQC with either hardness or pH is plausible. Water hardness is often influential in metal toxicity to aquatic organisms; however, no such relationship could be determined with the updated diazinon database, even with a moderately robust range of hardness values. Test water pH similarly resulted in little to no statistical relationship with acute diazinon toxicity. The lack of a relationship with pH may be the result of the limited number of tests reporting pH and the limited range of values tested. The range of pH values is 7.25 to 8.35 among all species in the database.

6.4.2 Updated Chronic Database

The revised and updated diazinon chronic toxicity database presents data for nine genera of freshwater organisms, including three species of invertebrates and six species of fish (Table 6-5). Although a substantial addition has been made to the chronic database, it still does not satisfy the "eight-family rule" requirement as defined by the 1985 Guidelines and is plagued by undefined values. The chronic criterion should, therefore, be derived via an ACR.

Table 6-5
Recalculated Species Mean Chronic Values (SMCV) using the Updated and Revised Chronic Database and Ranked Genus Mean Chronic Values (GMAV)

Rank	Species	Common Name	GMCV (µg/L)	SMCV (µg/L)
9	*Brachionus calyciflorus*	Rotifer	15,748	15,748
8	*Clarias batrachus*	Walking catfish	2,419	2,419
7	*Brachydanio rerio*	Zebrafish	>200	>200
6	*Pimephales promelas*	Fathead minnow	54	54
5	*Lepomis macrochirus*	Bluegill	14	14
4	*Jordanella floridae*	Flagfish	<14	<14
3	*Salvelinus fontinalis*	Brook trout	<0.80	<0.8
2	*Ceriodaphnia dubia*	Cladoceran	0.34	0.34
1	*Daphnia magna*	Cladoceran	<0.12	<0.12

Updating the final acute-chronic ratio (FACR) was evaluated using paired acute and chronic values from the revised and updated databases. Undefined (i.e., greater or less than) values are generally not used in an ACR calculation; however, we included these values in our evaluation to at least establish the potential range of ACRs for the existing database. Defined species mean acute-to-chronic ratios (SMACRs) could be calculated for three taxa, including *P. promelas*, *Clarias batrachus*, and *Ceriodaphnia dubia* (Table 6-6). SMACRs ranged from 1.1118 to 194.09, with no apparent trend between SMACRs and SMAVs. Therefore, the existing ACRs do not comply with 1985 Guidelines for an FACR calculation. Because of this, it was necessary to default to an ACR of 2, as was done in the 2000 Diazinon Draft.

Table 6-6
Updated Diazinon Species Mean Acute-to-Chronic Ratios (SMACR) and Species Mean Acute Values (SMAV)

Species	Common Name	Acute Value (µg/L)	Chronic Value (µg/L)	ACR	SMACR	SMAV (µg/L)
Pimephales promelas	Fathead minnow	7,800	41	189.8272		
Pimephales promelas	Fathead minnow	6,900	67	102.8623		
Pimephales promelas	Fathead minnow	9,350	25	374.4493	194.09	6,576
Jordanella floridae	Flagfish	1,643	<14	117.3571	>117.36	1,643
Salvelinus fontinalis	Brook trout	723	<0.8	903.7500	>903.75	723
Clarias batrachus	Walking catfish	14,792	24.19	6.1158	6.1158	14,792
Daphnia magna	Cladoceran	0.86	<0.15	5.7333	>5.7333	1.05
Ceriodaphnia dubia	Cladoceran	0.38	0.34	1.1118	1.1118	0.40

NOTE: SMACR = geometric mean of individual ACRs for a particular species.

6.4.3 Updated Criteria Derivation for Diazinon

The updated diazinon acute criteria were then calculated using the GMAVs for the four most sensitive genera (*Simocephalus*, *Daphnia*, *Ceriodaphnia*, and *Gammarus*). The resulting FAV of 0.22 µg/L is slightly greater than the existing FAV of 0.19 µg/L. This increase was due to a slight increase in GMAVs for three of the four most sensitive organisms and an increase in the degrees of freedom associated with new genera (Table 6-7). Uncertainty exists in the true value of the most sensitive species whose acute value is unsupported by toxicity testing using similar organisms in the same (*Gammarus*) or very similar genus (*Hyalella*). Although mechanistically feasible, no significant water quality toxicity relationships were discovered with diazinon toxicity using the updated diazinon databases. The resulting updated acute criterion for diazinon is 0.11 µg/L.

Table 6-7
Recalculation of the Final Acute and Chronic Values for Diazinon using the Revised Acute and Chronic Databases

Rank	Genus	GMAV	ln GMAV	(ln GMAV)^2	P = R/(N+1)	%P
4	*Simocephalus*	1.6979	0.5294	0.2803	0.1739	0.4170
3	*Daphnia*	0.9043	-0.1006	0.0101	0.1304	0.3612
2	*Ceriodaphnia*	0.4023	-0.9104	0.8289	0.0870	0.2949
1	*Gammarus*	0.2000	-60949	2.5903	0.0435	0.2085
		sum	**-2.0911**	**3.7096**	**0.4348**	**1.2816**

NOTES: N = 22 genera and R = sensitivity rank in database.

Calculations:

Acute Criterion

$$S^2 = \frac{\ni (\ln GMAV)^2 - (\ni \ln GMAV)^2/4}{\Sigma P - (\sqrt{P})^2/4} = \frac{3.7096 - -2.0911)^2 \& 4}{0.4348 - (1.2816)^2 \& 4} = 108.262 \qquad S = 10.4049$$

L = [∋lnGMAV - S(∋%P)]/4 = [-2.0911 - 10.4049 (1.2816)]&4 = -3.8564
A = S (%0.05) + L = (10.4049)(0.2236) - 3.8564 = -1.5298

Final Acute Value = FAV = e^{A} = 0.2166 µg/L
CMC = ½ FAV = 0.1083

Chronic Criterion

Defaulted Acute-Chronic ratio (FACR) = 2

Final Chronic Value (FCV) = FAV) ACR = 0.217) 2 = 0.108 µg/L

The updated chronic criterion of 0.11 µg/L is equal to the acute criterion, since the FACR and acute criterion divison factor to calculate an LC-low are both equal to 2. Generally, one would expect the chronic criterion to be less than the acute; yet due to diazinon behavior, mechanisms of toxicity, organism excretion, and exposure patterns in aquatic environments, these results are not surprising and should be appropriate for the protection of aquatic life. Diazinon is inherently unstable in the aquatic environment, resulting in a short half-life and, therefore, relatively rapid elimination. Furthermore, vertebrates efficiently metabolize diazinon to less toxic forms, which additionally reduces exposure duration. Lastly, since the exposure of diazinon to aquatic life is generally patchy and not continual, acute exposure likely poses the greatest threat to aquatic communities. Until additional chronic toxicity tests present the need for further chronic protection with a lower criterion, we support use of the acute criterion of 0.11 µg/L.

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7.0 ZINC CRITERIA REVIEW AND UPDATE

7.1 PHASE I - TECHNICAL REVIEW OF EPA AWQC DOCUMENTS FOR ZINC

The "1995 Updates" (EPA 1996) presents the most up-to-date national AWQC database for zinc. The acute database contains toxicity values for 36 genera of freshwater biota, including 21 species of invertebrates, 22 species of fish, and one frog species. These 44 species satisfy the "eight-family rule" as specified in the 1985 Guidelines (Stephen et al. 1985). Additionally, the 1987 zinc AWQC document (EPA 1987) presents chronic data for seven genera of freshwater organisms, including two invertebrates and seven species of fishes (the "1995 Updates" did not provide any new chronic data). These nine species do not satisfy the "eight-family rule;" therefore, chronic criteria were derived via a final acute-chronic ratio (FACR). Both acute and chronic criteria area modified with respect to water hardness with a slope of 0.8473. Overall, the databases used to derive current zinc criteria comply with toxicity test restrictions established in the 1985 Guidelines and criteria were derived appropriately. No corrections were made to the existing acute and chronic databases.

7.2 PHASE II - UPDATE TO THE NATIONAL ZINC TOXICITY DATABASES

7.2.1 New Acute Zinc Toxicity Data

Approximately 90 papers containing at least some zinc toxicity information were located and reviewed as potential sources of data to be added to the updated zinc databases. From this search, over 120 data points from 35 sources were added to an updated acute database (Table 7-1). This included a number of studies conducted by the Colorado Department of Wildlife (CDOW) published as gray literature (i.e., *Federal Aid to Fisheries* reports) and recent laboratory toxicity testing with Colorado native aquatic insects conducted by CEC on behalf of Climax Molybdenum Company (CEC 2005).

Many of the data points added to the database provided new toxicity data for sensitive species not previously in the database and additional data for the top four most sensitive genera. Given the number of toxicity values added to the database, we will not discuss each study added, but only comment on those which influenced the GMAVs used in criteria derivation.

Table 7-1
New Acute Zinc Data Added to the National Database

Species	Common Name	Method	Hardness ($CaCO_3$ mg/L)	LC_{50} (µg/L)	Reference
Oncorhynchus mykiss	Rainbow trout	F, M	350	4,520	Goettl et al. 1972
Oncorhynchus mykiss	Rainbow trout	F, M	350	1,190	Goettl et al. 1972
Oncorhynchus mykiss	Rainbow trout	F, M	30	560	Goettl et al. 1972
Oncorhynchus mykiss	Rainbow trout	F, M	30	240	Goettl et al. 1972
Oncorhynchus mykiss	Rainbow trout	F, M	38	105	Davies 1980
Oncorhynchus mykiss	Rainbow trout	F, M	38	186	Davies 1980
Oncorhynchus mykiss	Rainbow trout	F, D	33.2	125	Brinkman and Hansen 2004
Oncorhynchus mykiss	Rainbow trout	F, D	145.4	588	Brinkman and Hansen 2004
Oncorhynchus clarkii	Cutthroat trout	F, D	31.1	140	Brinkman and Hansen 2004
Oncorhynchus clarkii	Cutthroat trout	F, D	149.4	1,645	Brinkman and Hansen 2004
Salmo trutta (wild)	Brown trout (wild)	F, M	37.6	642	Davies and Brinkman 1994
Salmo trutta	Brown trout	F, M	42.3	476	Davies et al. 2000
Salmo trutta	Brown trout	F, M	52.6	484	Davies et al. 2000
Salmo trutta	Brown trout	F, M	52.6	603	Davies et al. 2000
Salmo trutta	Brown Trout	F, M	206.7	2,267	Davies and Brinkman 1999
			(alk = 37.5)		
Salmo trutta	Brown Trout	F, M	54.4	1,033	Davies and Brinkman 1999
			(alk = 37.4)		
Salmo trutta	Brown Trout	F, M	54.0	690	Davies and Brinkman, 1999
			(alk = 139.6)		
Salmo trutta	Brown Trout	F, M	207.2	>2,660	Davies and Brinkman 1999
			(alk = 141.4)		
Salvelinus fontinalis	Brook trout	F, M	52.6	738	Davies et al. 2000
Salvelinus fontinalis	Brook trout	F, M	52.6	1,178	Davies et al. 2000
Thymallus arcticus	Arctic grayling (0.34g)	S, U	41.3	112	Buhl and Hamilton 1990
Thymallus arcticus	Arctic grayling (0.2g)	S, U	41.3	142	Buhl and Hamilton 1990
Thymallus arcticus	Arctic grayling (0.85g)	S, U	41.3	166	Buhl and Hamilton 1990
Thymallus arcticus	Arctic grayling (0.97g)	S, U	41.3	168	Buhl and Hamilton 1990
Thymallus arcticus	Arctic grayling (1.85g)	S, U	41.3	168	Buhl and Hamilton 1990
Thymallus arcticus	Arctic grayling (fry)	S, U	41.3	315	Buhl and Hamilton 1990
Thymallus arcticus	Arctic grayling (alevin)	S, U	41.3	1,580	Buhl and Hamilton 1990
Thymallus arcticus	Arctic grayling (alevin)	S, U	41.3	2,920	Buhl and Hamilton 1990
Cottus bairdii	Mottled sculpin	F, M	48.6	156	Woodling et al. 2002
Cottus bairdii	Mottled sculpin	F, M	154	439	Brinkman and Woodling 2005
Cottus bairdii	Mottled sculpin	F, M	156	590	Brinkman and Woodling 2005
Catostomus latipinnis	Flannelmouth sucker		144	1,480	Hamilton and Buhl 1997a
Ptychocheilus lucius	Colorado pikeminnow (larvae)	S, U	199	3,340	Buhl and Hamilton 1996
Ptychocheilus lucius	Colorado pikeminnow (juvenile)	S, U	199	8,620	Buhl and Hamilton 1996
Gila elegans	Bonytail (larvae)	S, U	199	5,350	Buhl and Hamilton 1996
Gila elegans	Bonytail (larvae)	S, U	199	8,010	Buhl and Hamilton 1996
Xyrauchen texanus	Razorback sucker (larvae)	S, U	199	4,100	Buhl and Hamilton 1996
Xyrauchen texanus	Razorback sucker (juvenile)	S, U	199	2,920	Buhl and Hamilton 1996
Xyrauchen texanus	Razorback sucker (larvae)	S, U	144	9,800	Hamilton and Buhl 1997b
Gambusia affinis (fry)	Mosquitofish	S, U	50	50,000	Kallanagoudar and Patil 1997
Gambusia affinis (fry)	Mosquitofish	S, U	150	80,000	Kallanagoudar and Patil 1997
Gambusia affinis (fry)	Mosquitofish	S, U	300	100,000	Kallanagoudar and Patil 1997

Table 7-1 (Continued)
New Acute Zinc Data Added to the National Database

Species	Common Name	Method	Hardness ($CaCO_3$ mg/L)	LC_{50} (µg/L)	Reference
Gambusia affinis (male)	Mosquitofish	S, U	50	115,000	Kallanagoudar and Patil 1997
Gambusia affinis (male)	Mosquitofish	S, U	150	140,000	Kallanagoudar and Patil 1997
Gambusia affinis (male)	Mosquitofish	S, U	300	150,000	Kallanagoudar and Patil 1997
Gambusia affinis (female)	Mosquitofish	S, U	50	90,000	Kallanagoudar and Patil 1997
Gambusia affinis (female)	Mosquitofish	S, U	150	120,000	Kallanagoudar and Patil 1997
Gambusia affinis (female)	Mosquitofish	S, U	300	140,000	Kallanagoudar and Patil 1997
Lepomis macrochirus	Bluegill	F, M	NR	3,200	Thompson et al. 1980
Lepomis macrochirus	Bluegill	F, M, T	40.2	3,600	Thompson et al. 1980
Lepomis macrochirus	Bluegill	F, M, T	40.2	3,000	Thompson et al. 1980
Aeolosoma headleyi	Worm	--	45	18,100	Cairns, Jr., et al. 1978
Aeolosoma headleyi	Worm	--	45	17,600	Cairns, Jr., et al. 1978
Aeolosoma headleyi	Worm	--	45	15,600	Cairns, Jr., et al. 1978
Aeolosoma headleyi	Worm	--	45	15,000	Cairns, Jr., et al. 1978
Aeolosoma headleyi	Worm	--	45	13,500	Cairns, Jr., et al. 1978
Tubifex tubifex	Worm	--	224	130,000	Qureshi et al. 1980b
Tubifex tubifex	Worm	--	34.2	2,570	Brkovic-Popovic & Popovic 1977
Tubifex tubifex	Worm	--	261	60,200	Brkovic-Popovic & Popovic 1977
Tubifex tubifex	Worm	--	0.1	110	Brkovic-Popovic & Popovic 1977
Tubifex tubifex	Worm	--	34.2	2,980	Brkovic-Popovic & Popovic 1977
Tubifex tubifex	Worm	R, U	245	17,780	Khangarot 1991
Anodonta imbecilis	FW mussel	S, M, T	39	268	Keller and Zam 1991
Anodonta imbecilis	FW mussel	S, M, T	90	438	Keller and Zam 1991
Bryocamptus zschokkei (nauplius)	Copepod	S, M, T	100	920	Brown et al. 2005
Bryocamptus zschokkei (copepodid)	Copepod	S, M, T	100	620	Brown et al. 2005
Bryocamptus zschokkei (adult)	Copepod	S, M, T	100	2,070	Brown et al. 2005
Heliodiaptomus viduus	Copepod		37.6	500	Sharma and Selverai 1994
Mesocyclops hyalinus	Copepod		37.6	3,800	Sharma and Selverai 1994
Tropocyclops prasinus	Copepod	S, U	10	52	Lelande and Pinel-Alloul 1985
Asellus aquaticus	Isopod	S, U	50	18,200	Martin and Holdich 1986
Echinogammarus tibaldii	Amphipod		240	25,900	Pantani et al. 1997
Gammarus italicus	Amphipod		240	8,800	Pantani et al. 1997
Hyalella azteca	Amphipod		100	436	Eisenhauer et al. 1999
Ceriodaphnia dubia	Cladoceran	S, M	44	413	Hyne et al. 2005
			(pH = 6.5)		
Ceriodaphnia dubia	Cladoceran	S, M, D	44	200	Hyne et al. 2005
			(pH = 7.5)		
Ceriodaphnia dubia	Cladoceran	S, M, D	44	60	Hyne et al. 2005
			(pH = 6.5, DOC = 1.0)		
Ceriodaphnia dubia	Cladoceran	S, M, D	44	58	Hyne et al. 2005
			(pH = 6.5, DOC = 0.1)		
Ceriodaphnia dubia	Cladoceran	S, M, D	44	155	Hyne et al. 2005
			(pH = 7.5, Alk = 30)		
Ceriodaphnia dubia	Cladoceran	S, M, D	374	390	Hyne et al. 2005
			(pH = 7.5, Alk = 30)		
Ceriodaphnia dubia	Cladoceran	S, M, D	44	70	Hyne et al. 2005
			(pH = 8.4, Alk = 125)		
Ceriodaphnia dubia	Cladoceran	S, M, D	374	160	Hyne et al. 2005
			(pH = 8.4)		

Table 7-1 (Continued)
New Acute Zinc Data Added to the National Database

Species	Common Name	Method	Hardness ($CaCO_3$ mg/L)	LC_{50} (µg/L)	Reference
Ceriodaphnia dubia	Cladoceran	S, M	190	500	Magliette et al. 1995
Daphnia magna	Cladoceran	R, M	300	1,100	Berglind and Dave 1984
Daphnia magna	Cladoceran	S, M, T	170	1,831	Baird, et al. 1991
Daphnia magna	Cladoceran	S, M, T	170	756	Baird, et al. 1991
Daphnia magna	Cladoceran	S, M, T	170	745	Baird, et al. 1991
Daphnia magna	Cladoceran	S, M, T	170	862	Baird, et al. 1991
Daphnia magna	Cladoceran	S, M, T	170	986	Baird, et al. 1991
Daphnia magna	Cladoceran	S, M, T	170	798	Baird, et al. 1991
Daphnia magna	Cladoceran	S, M	46.1	259	Barata et al. 1998
Daphnia magna	Cladoceran	S, M	90.7	1,060	Barata et al. 1998
Daphnia magna	Cladoceran	S, M	179	962	Barata et al. 1998
Daphnia magna	Cladoceran	S, M	46.1	131	Barata et al. 1998
Daphnia magna	Cladoceran	S, M	90.7	457	Barata et al. 1998
Daphnia magna	Cladoceran	S, M	179	601	Barata et al. 1998
Daphnia magna	Cladoceran	S, M	490	1,220	Magliette et al. 1995
Moina irrasa	Cladoceran	--	5	77.46	Zou and Bu 1994
Moina irrasa	Cladoceran	--	5	152.51	Zou and Bu 1994
Moina irrasa	Cladoceran	--	5	205.31	Zou and Bu 1994
Moina irrasa	Cladoceran	--	5	49.99	Zou and Bu 1994
Moina irrasa	Cladoceran	--	5	92.88	Zou and Bu 1994
Moina irrasa	Cladoceran	--	5	59.24	Zou and Bu 1994
Moina macrocopa	Cladoceran	--	37.6	120	Sharma and Selverai 1994
Cypris sp.	Ostracod	--	114	3,000	Qureshi et al. 1980a
Stenocypris malcomsoni	Ostracod	--	37.6	3,500	Sharma and Selverai 1994
Girardia tigrina	Flatworm	--	50	7,400	See et al. 1974
Girardia tigrina	Flatworm	--	40	5,480	See 1976
Chironomus sp.	Midge	--	50	18,200	Rehwoldt et al. 1973
Chironomus plumosus	Midge	S, U	80	32,600	Fargašová 2003
Drunella grandis	Mayfly	S, M	50.6	>1,560	CEC 2005
Drunella grandis	Mayfly	S, M	54.2	>3,050	CEC 2005
Drunella grandis	Mayfly	S, M	172	>2,190	CEC 2005
Drunella grandis	Mayfly	S, M	175	>3,050	CEC 2005
Drunella grandis	Mayfly	S, M	260.7	>3,270	CEC 2005
Drunella grandis	Mayfly	S, M	277.7	>6,290	CEC 2005
Isoperla sp.	Stonefly	S, U	182.2	>27,000	CEC 2005
Lepidostoma sp.	Caddisfly	S, M	62.1	>19,100	CEC 2005
Lepidostoma sp.	Caddisfly	S, M	189.4	>38,800	CEC 2005
Lepidostoma sp.	Caddisfly	S, M	308.8	>81,700	CEC 2005
Ranatra elongata	Water scorpion	--	112.4	1,658	Shukla et al. 1983
Trichoptera	Caddisfly	--	50	58,100	Rehwoldt et al. 1973
Zygoptera	Damselfly	--	50	26,200	Rehwoldt et al. 1973

NOTES:
S = static test conditions; R = static renewal test conditions; F = flow through test conditions; U = unmeasured concentration; M = measured concentration; T = total metal concentration; D = dissolved metal concentration

Hyne et al. (2005) conducted a study to evaluate the influence of pH, alkalinity, DOC, and hardness on acute zinc and copper toxicity in *Ceriodaphnia dubia*. Synthetic soft water was modified to test the effect of different water quality characteristics; yet, only results from tests conducted at pH ∃ 6.5 and DOC <5.0 were added to the database. This study added eight new acute toxicity data points for *C. dubia*, one of the two species in the most sensitive generus *Ceriodaphnia*. Prior to these updates, only one toxicity value was present for *C. dubia* in the national database. However, even with the new datapoints, the SMAV remained virtually unchanged (old SMAV = 174, new SMAV = 175).

Recent studies conducted by Woodling et al. (2002) and Brinkman and Woodling (2005) identified the acute sensitivity of the mottled sculpin (*Cottus bairdii*) to zinc. Sculpin were not previously represented in the national database. Three acute values from these studies were added to the updated database, which places *Cottus* as the third most sensitive genus.

Buhl and Hamilton (1990) conducted static acute zinc toxicity tests with early life stage salmonids in standard soft reconstituted water. Test organisms included *Oncorhynchus mykiss, O. kisutch*, and *Thymallus arcticus*. Tested zinc concentrations were not measured. Given that flow-through, measured tests take precedence over static, unmeasured tests, the unmeasured values for *O. mykiss* and *O. kisutch* were not added to the updated database since toxicity values derived via flow-through tests already existed in the database. Toxicity data for *T. arcticus*, on the other hand, did not previously exist, and eight values were added to the updated database. These data place *Thymallus* as the fourth most sensitive genus in the updated database.

7.2.2 New Chronic Zinc Toxicity Data

In addition to the new acute data, a total of 23 data points from 12 sources have been added to the chronic database (Table 7-2). These new data resulted in addition of 12 new genera and 11 new species. The updated chronic database still does not meet the "eight-family rule" for direct criteria derivation, as it is missing a benthic crustacean and a family in a phylum other than Arthropoda or Chordata.

Table 7-2
Updated Chronic Zinc Database

Species	Common Name	Hardness ($CaCO_3$ mg/L)	Chronic Value (mg/L)	Reference
Daphnia magna	Cladoceran	45	<140.3	Biesinger et al. 1986
Daphnia magna	Cladoceran	52	135.8	Chapman et al. Manuscript
Daphnia magna	Cladoceran	104	47.29	Chapman et al. Manuscript
Daphnia magna	Cladoceran	211	46.73	Chapman et al. Manuscript
Bryocamptus zschokkei (copepodid)	Copepod	100	379.5	*Brown et al. 2005

Table 7-2 (Continued)
Updated Chronic Zinc Database

Species	Common Name	Hardness ($CaCO_3$ mg/L)	Chronic Value (mg/L)	Reference
Clistoronia magnifica	Caddisfly	31	>5,243	Nebeker et al. 1984
Hydropsyche betteni	Caddisfly	52	32,000	*Warnick and Bell 1969
Drunella grandis	Mayfly	30-70	>9,200	*Nehring 1976
Ephemerella subvaria	Mayfly	54	16,000	*Warnick and Bell 1969
Acroneuria lycoria	Stonefly	50	32,000	*Warnick and Bell 1969
Pteronarcys californicus	Stonefly	30-70	>13,900	*Nehring 1976
Tanytarsus spp.	Midge	46.8	36.8	*Anderson et al. 1980
Oncorhynchus nerka	Sockeye salmon	32-37	>242	Chapman 1978a
Oncorhynchus tshawytscha	Chinook salmon	25	371.1	Chapman 1975
Oncorhynchus mykiss	Rainbow trout	26	276.7	Sinley et al. 1974
Oncorhynchus mykiss	Rainbow trout	25	603	Cairns et al. 1982
Salvelinus fontinalis	Brook trout	45.9	854.7	Holcombe et al. 1979
Salvelinus fontinalis	Brook trout	52.6	327	*Davies et al. 2000
Salvelinus fontinalis	Brook trout	52.6	819	*Davies et al. 2000
Salmo trutta	Brown trout	52.6	234	*Davies et al. 2000
Salmo trutta	Brown trout	52.6	327	*Davies et al. 2000
Salmo trutta	Brown trout	22-35	640	*Nehring and Goettl 1974
Salmo trutta	Brown trout	54.1	381	*Davies and Brinkman 1999
Salmo trutta	Brown trout	26.8	162	*Davies and Brinkman 1999, 2002, 2003
Salmo trutta	Brown trout	48.1	196	*Davies and Brinkman 1999, 2002, 2003
Salmo trutta	Brown trout	153	1,306	*Davies and Brinkman 1999, 2002, 2003
Pimephales promelas	Fathead minnow	46	106.3	Benoit and Holcombe 1978
Cottus bairdii	Mottled sculpin	46.3	20.8	*Woodling et al. 2002
Cottus bairdii	Mottled sculpin	154	255	*Brinkman and Woodling 2005
Jordanella floridae	Flagfish	44	36.41	Spehar 1976a,b
Poecilia reticulata	Guppy	30	<173	Pierson 1981
Oncorhynchus mykiss	Rainbow trout	33.2	74	*Brinkman and Hansen 2004
Oncorhynchus mykiss	Rainbow trout	145.4	325	*Brinkman and Hansen 2004
Oncorhynchus clarkii	Cutthroat trout	31.1	134	*Brinkman and Hansen 2004
Oncorhynchus clarkii	Cutthroat trout	149.4	1,343	*Brinkman and Hansen 2004
Oncorhynchus clarkii	Cutthroat trout	34-47	670	*Nehring and Goettl 1974
NOTE: * = New data.				

7.3 PHASE III – RECALCULATION OF ACUTE AND CHRONIC AWQC FOR ZINC

7.3.1 Updating the Hardness Relationship

Using the updated acute toxicity database, an updated acute hardness slope (Table 7-3) was developed following the guidance for the determination of an acute slope described by the 1985 Guidelines. The process involves normalizing each value with respect to the species mean and the natural log transformation of the normalized values for each species in which acute values exist for a wide range of hardness values. Hardness slopes for each species are calculated as the slope from a least squares regression of the mean normalized and ln transformed acute values on the corresponding transformed hardness values. If covariance analysis shows that these individual slopes are similar, the pooled acute slope is subsequently determined by treating all normalized data as if they were from the same species and conducting a least squares regression of all the transformed acute values on the corresponding hardness values (Stephan et al. 1985).

Table 7-3
Updated Acute Zinc Hardness Slope

Species	**N**	**SMAS**	**R^2**	**Code**
Oncorhynchus mykiss	33	0.8490	0.63	2
Salvelinus fontinalis	8	1.0423	0.73	2
Salmo trutta	9	0.8801	0.68	3
Physa heterostropha	12	0.9296	0.56	1
Daphnia magna	13	0.8717	0.71	2
Pimephales promelas	27	0.9119	0.66	2
Poecillia reticulata	5	1.6441	0.82	1
Morone saxatilis	2	0.6500	--	1
Cottus bairdi	3	1.0216	0.96	3
Lepomis macrochirus	18	0.5764	0.48	2
Oncorhynchus clarki	2	1.5699	--	3
Ceriodaphnia dubia	2	0.7884	--	3
Tubifex tubifex	5	0.8235	0.87	3
Revised Pooled Slope		**0.8537**	**0.68**	

NOTES:
SMAS = species mean acute slope.
1 = SMAS equivalent to SMAS reported by EPA (1987)
2 = updated/revised SMAS
3 = new species

Using the latest data obtained from our literature review combined with the original data from the criteria documents, a revised updated acute hardness slope was determined (0.8537) (Table 9-3). This slope is only slightly steeper than the existing slope of 0.8473. One data point from a test conducted at very low hardness appears to be an outlier; yet it was retained to account for zinc toxicity at low hardness, since it does not highly skew the regression analysis (Figure 7-1). The hardness slope without this data point is slightly steeper (0.8997) than the updated acute slope of 0.8537.

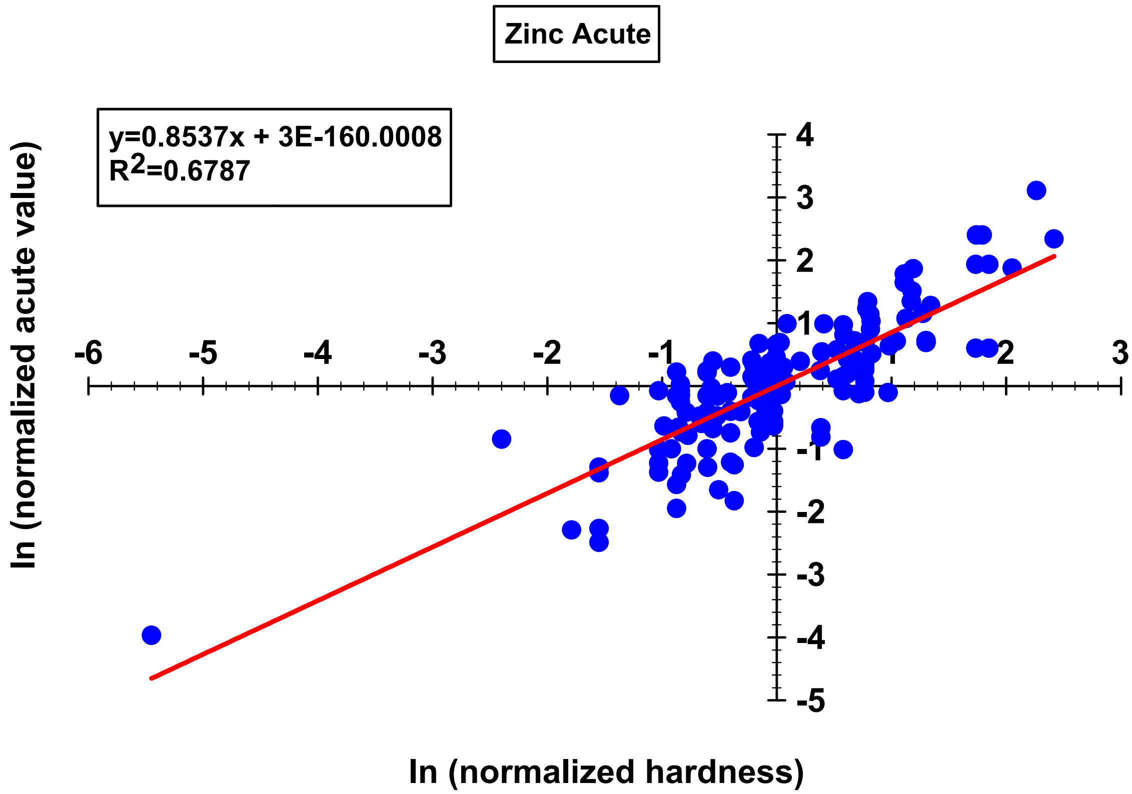

Figure 7-1
Relationship Between Acute Zinc Toxicity and Water Hardness using the Updated Acute Database

7.3.2 Updated Normalized Acute Database

The updated slope was used to normalize acute values to a hardness of 50 mg/L and to develop a hardness-based final acute equation. Table 7-4 summarizes the updated ranked acute database. All species were assigned a habitat code as either being a warm or cold-water species for future use in site-specific criteria calculations. The new acute database contains 62 genera and 78 species (previously 36 genera and 44 species; Appendix 2).

Table 7-4
Revised and Updated Acute Zinc Genus Mean Acute Values (GMAV) and Species Mean Acute Value (SMAV) Ranked from Least Sensitive to Most Sensitive Genus (all modified by revised acute hardness slope = 0.8537)

Rank	Species	Common Name	GMAV (µg/L)	SMAV (µg/L)	Habitat Code
62	*Argia* sp.	Damselfly	89,488	89,488	1, 2
61	Trichoptera	Caddisfly	58,100	58,100	1, 2
60	*Gambusia affinis*	Mosquitofish	32,370	32,370	2
59	Zygoptera	Damselfly	26,200	26,200	1, 2
58	*Chironomus* sp.	Midge	19,930	18,200	1, 2
	Chironomus plumosus	Midge		21,825	1, 2

Table 7-4 (Continued)
Revised and Updated Acute Zinc Genus Mean Acute Values (GMAV) and Species Mean Acute Value (SMAV) Ranked from Least Sensitive to Most Sensitive Genus (all modified by revised acute hardness slope = 0.8537)

Rank	Species	Common Name	GMAV (µg/L)	SMAV (µg/L)	Habitat Code
57	*Crangonyx pseudogracilis*	Amphipod	19,800	19,800	1, 2
56	*Xenopus laevis*	Frog	19,091	19,091	2
55	*Nais* sp.	Worm	18,400	18,400	1, 2
54	*Asellus aquaticus*	Isopod	18,200	18,200	1, 2
53	*Fundulus diaphanus*	Banded killifish	17,935	17,935	2
52	*Aeolosoma headleyi*	Worm	17,362	17,362	1, 2
51	*Amnicola* sp.	Snail	16,817	16,817	1, 2
50	*Lepidostoma* sp.	Caddisfly	>15,054	>15,054	1, 2
49	*Anguilla rostrata*	American eel	13,627	13,627	2
48	*Carassius auratus*	Goldfish	10,276	10,276	2
46	*Lepomis gibbosus*	Pumpkinseed	9,967	18,778	2
	Lepomis macrochirus	Bluegill		5,290	2
46	*Lumbriculus variegatus*	Worm	9,744	9,744	1, 2
45	*Tubifex tubifex*	Worm	9,612	9,612	1, 2
44	*Isoperla* sp.	Stonefly	>8,952	>8,952	1, 2
43	*Caecidotea bicrenata*	Isopod	8,120	5,677	1, 2
	Caecidotea communis	Isopod		11,614	1, 2
42	*Cyprinus carpio*	Common carp	7,245	7,245	2
41	*Girardia tigrina*	Flatworm	7,004	7,004	1, 2
40	*Echinogammarus tibaldii*	Amphipod	6,788	6,788	1, 2
39	*Notemigonus crysoleucus*	Golden shiner	6,000	6,000	2
38	*Poecilia reticulata*	Guppy	5,926	5,926	2
37	*Corbicula fluminea*	Asiatic clam	4,892	4,892	1, 2
36	*Mesocyclops hyalinus*	Copepod	4,847	4,847	1, 2
35	*Stenocypris malcomsoni*	Ostracod	4,464	4,464	1, 2
34	*Gammarus* sp.	Amphipod	4,322	8,100	1, 2
	Gammarus italicus	Amphipod		2,306	1, 2
33	*Xiphophorus maculatus*	Southern platyfish	4,308	4,308	2
32	*Pimephales promelas*	Fathead minnow	3,808	3,808	2
31	*Ptychocheilus lucius*	Colorado pikeminnow	3,790	2,211	2
	Ptychocheilus oregonensis	Northern pikeminnow		6,495	2
30	*Lirceus alabamae*	Isopod	3,242	3,242	1, 2
29	*Gila elegans*	Bonytail	2,013	2,013	2
28	*Salvelinus fontinalis*	Brook trout	1,691	1,691	1
27	*Lophopodella carteri*	Bryozoan	1,688	1,688	1, 2
26	*Jordanella floridae*	Flagfish	1,673	1,673	2
25	*Xyrauchen texanus*	Razorback sucker	1,651	1,651	2
24	*Plumatella emarginata*	Bryozoan	1,589	1,589	1, 2
23	*Helisoma campanulatum*	Snail	1,579	1,579	1, 2

Table 7-4 (Continued)
Revised and Updated Acute Zinc Genus Mean Acute Values (GMAV) and Species Mean Acute Value (SMAV) Ranked from Least Sensitive to Most Sensitive Genus (all modified by revised acute hardness slope = 0.8537)

Rank	Species	Common Name	GMAV (µg/L)	SMAV (µg/L)	Habitat Code
22	*Cypris* sp.	Ostracod	1,484	1,484	1, 2
21	*Physa gyrina*	Snail	1,354	1,686	1, 2
	Physa heterostropha	Snail		1,087	1, 2
20	*Pectinatella magnifica*	Bryozoan	1,292	1,292	1, 2
19	*Drunella grandis*	Mayfly	>1,264	>1,264	1, 2
18	*Limnodrilus hoffmeisteri*	Worm	>1,258	>1,258	1, 2
17	*Ranatra elongata*	Water scorpion	830	830	1, 2
16	*Tilapia mossambica*	Mozambique tilapia	786	786	2
15	*Oncorhynchus mykiss*	Rainbow trout	750	582	1
	Onchorhynchus kisutch	Coho salmon		1,635	1
	Oncorhynchus nerka	Sockeye salmon		1,510	1
	Oncorhynchus tshawytscha	Chinook salmon		449	1
	Oncorhynchus clarkii	Cutthroat trout		368	1
14	*Salmo salar*	Atlantic salmon	>647*	2,194	1
	Salmo trutta	Brown trout		>647	1
13	*Heliodiaptomus viduus*	Copepod	638	638	1, 2
12	*Catostomus latipinnis*	Flannelmouth sucker	600*	600	2
	Catostomus commersonii	White sucker		5,263	1,2
11	*Bryocamptus zschokkei*	Copepod	343	343	1,2
10	*Moina irrasa*	Cladoceran	320	667	1, 2
	Moina macrocopa	Cladoceran		153	1, 2
9	*Anodonta imbecilis*	Freshwater mussel	296	296	2
8	*Daphnia magna*	Cladoceran	275	299	1, 2
	Daphnia pulex	Cladoceran		253	1, 2
7	*Hyalella azteca*	Amphipod	241	241	1, 2
6	*Agrosia chrysogaster*	Longfin dace	226	226	2
5	*Tropocyclops prasinus*	Copepod	205	205	1,2
4	*Thymallus arcticus*	Arctic grayling	199	199	1
3	*Cottus bairdii*	Mottled sculpin	182	182	1
2	*Morone saxatilis*	Striped bass	119*	119	2
	Morone americana	White perch		13,439	2
1	*Ceriodaphnia dubia*	Cladoceran	94.2	175	1, 2
	Ceriodaphnia reticulata	Cladoceran		51	1, 2

NOTES:
1 - Coldwater species
2 - Warmwater species
* - Only most sensitive species used

7.3.3 Update to the Acute-to-Chronic Ratio

An updated final acute-chronic ratio (FACR) was also determined using all data reported in the current criteria document and data obtained from the literature review (Table 7-5). Methods followed those described by Stephan *et al.* (1985). Twelve new data points were added from studies in which acute and chronic values were calculated at similar hardness values for a given species. Using the existing EPA's FACR (2.000), the acute and chronic standards are the same value, since the final acute value is divided by two before the intercept for the final acute equation is determined. However, the updated FACR (2.3726) yields chronic values that are lower than acute values, which is a more realistic scenario.

Table 7-5
Updated Derivation of Revised Species Mean Acute-Chronic Ratios (ACRs) and the Final Acute-Chronic Ratio (FACR) for Zinc

Existing ACR Data:			New ACR Derivation Data:	
Species	**Species Mean ACR**		**Species**	**Species Mean ACR**
Oncorhynchus mykiss	1.554		*Daphnia magna*	7.2604
*Oncorhynchus nerka**	<6.074		*Oncorhynchus clarkii*	1.1312
Oncorhynchus tshawytscha	0.7027		*Oncorhynchus mykiss*	1.6809
Daphnia magna	7.26		*Oncorhynchus tshawytscha*	0.7027
*Pimephales promelas**	5.664		*Salvelinus fontinalis*	2.1887
*Salvelinus fontinalis**	2.335		*Salmo trutta*	1.9865
*Jordanella floridae***	41.2		*Cottus bairdii*	3.5933
			Pimephales promelas	5.664
EPA FACR =	**1.9940**		*Bryocamptus zschokkei*	2.7852
			Updated FACR =	**2.3726**
NOTES: * = Not used in EPA calculation ** = Not used because order of magnitude different				

New ACR Data From Updated Toxicity Databases:					
Species	**Hardness**	**Acute Value**	**Chronic Value**	**ACR**	**Reference**
Salvelinus fontinalis	52.6	932.4	517.5	1.8017	Davies et al. 2000
Cottus bairdii	46.3-48.6	156	20.8	7.5000	Woodling et al. 2002
Cottus bairdii	138-167	439	255	1.7216	Brinkman and Woodling 2005
Bryocamptus zschokkei	100	920	379.5	2.4244	Brown et al. 2005
Bryocamptus zschokkei	100	620	279.5	1.6338	Brown et al. 2005
Broycamptus zschokkei	100	2,070	379.5	5.4548	Brown et al. 2005
Salmo trutta	50	392	194	2.0206	Davies and Brinkman 1999
Salmo trutta	52.6	540.2	276.6	1.9530	Davies et al. 2000
Oncorhynchus mykiss	33.2	125	75	1.6892	Brinkman and Hansen 2004
Oncorhynchus mykiss	145.4	588	325	1.8092	Brinkman and Hansen 2004
Oncorhynchus clarkii	31.1	140	134	1.0448	Brinkman and Hansen 2004
Oncorhynchus clarkii	149.4	1,645	1,343	1.2249	Brinkman and Hansen 2004

7.3.4 Updated Acute and Chronic Criteria

The updated zinc criteria are then calculated using the genus mean acute values for the four most sensitive genera (*Thymallus, Cottus, Morone,* and *Ceriodaphnia;* Table 7-6). Calculations followed the EPA methods for criteria derivation (Stephan et al. 1985). A FAV of 170.6 µg/L was calculated resulting in a revised updated final acute equation of $0.978 * e^{(0.8537\ [\ln\ (\text{hardness})]+1.1182)}$, which includes the EPA (2002) acute zinc conversion factor to account for the dissolved fraction of total zinc.

Table 7-6
Recalculation of the Final Acute Values for Zinc using the Updated Acute Database

Rank	Genus	GMAV	ln GMAV	(ln GMAV)^2	P = R/(N+1)	%P
4	*Thymallus*	199.2	5.2943	28.0299	0.0635	0.2520
3	*Cottus*	181.7	5.2023	27.0643	0.0476	0.2182
2	*Morone*	119.0	4.7791	22.8400	0.0317	0.1782
1	*Ceriodaphnia*	94.2	4.5457	20.6636	0.0159	0.1260
		sum	19.8215	98.5978	0.1587	0.7744

NOTE: N = 62 genera; R = sensitivity rank in database.

Calculations:

Acute Criterion

$$S^2 = \frac{\backepsilon\ (\ln GMAV)^2 - (\backepsilon \ln GMAV)^2/4}{\Sigma P - (\Sigma\ \sqrt{P})^2/4} = \frac{98.5978 - (19.8215)^2 \& 4}{0.1587 - (0.7744)^2/4} = 42.4744 \qquad S = 6.5172$$

$$L = [\backepsilon \ln GMAV - S(\backepsilon \%P)]/4 = [19.8215 - 6.5172\ (0.7744)] \& 4 = 3.6937$$
$$A = S\ (\sqrt{0.05}) + L = (6.5172)(0.2236) + 3.6937 = 5.1510$$

Final Acute Value = FAV = e^{A} = 172.6057 µg/L
CMC = ½ FAV = 86.3029
Pooled Slope = 0.8537 (recalculated)
ln (Criterion Maximum Intercept) = lnCMC - [pooled slope H ln (standardized hardness level)]
= ln (86.3029) - [0.8537 H ln (50)]
= 1.1182
Acute Zinc Criterion (as µg dissolved Zn/L) = $0.976 * e^{(0.8537\ [\ln\ (\text{hardness})]\ +\ 1.1182)}$

Chronic Criterion

Chronic Slope = 0.8537 (recalculated)
Final Acute-Chronic ratio (FACR) = 2.3726 (recalculated)
Final Chronic Value (FCV) = FAV) FACR = 86.3029) 2.3726 = 72.7496 µg/L
ln (Final Chronic Intercept) = ln FCV - [chronic slope H ln(standardized hardness level)]
= ln (72.7496) - [0.8537 H ln (50)]
= 0.9473
Chronic Zinc Criterion (as µg dissolved Zn/L) = $0.986 * e^{(0.8537\ [\ln\ (\text{hardness})]\ +\ 0.9473)}$

Using the new FACR, the resulting revised and updated chronic equation would be $0.986{*}e^{0.8537\ [\ln(\text{hardness})]+0.9473}$, which includes the EPA (2002) chronic zinc conversion factor to account for the dissolved fraction of total zinc. Table 7-7 presents a summary of these revised and updated acute and chronic zinc criteria at varying hardness levels, with inclusion of the conversion factor for dissolved criteria.

The resulting updated criteria are less restrictive than existing criteria. This change is primarily due to the addition of substantially more acute data. These data decreased the variability in GMAVs used for criteria derivation (current and updated SD = 7.6629 and 6.5172, respectively), provided new data for the four most sensitive genera (and changed the composition of these genera), and created a more robust database (current and updated N = 36 and 62, respectively); all factors that affect the final criteria calculations. Although the updated values are less restrictive, the updated chronic criteria are lower than the acute, which is a more realistic senerio of zinc toxicity than the current USEPA values. Current USEPA chronic values are less restrictive than acute after appling the USEPA dissolved fraction conversion factor for zinc (Table 7-7). Given the greater ecotoxicological relevance, the updated zinc criteria are a considerable improvement over current criteria.

Table 7-7
Summary of Existing and Revised Zinc Criteria (as µg dissolved Zn/L) at Varying Hardness Levels using Updated Toxicity Database, Revised Pooled-Hardness Slope, and Updated Final Acute-Chronic Ratio

	Mean Hardness in mg/L $CaCO_3$									
Equations	**25**	**50**	**75**	**100**	**150**	**200**	**250**	**300**	**350**	**400**
Current EPA Criteria										
Acute = 0.978 ($e^{0.8473\ [\ln(\text{hardness})]+0.8840}$	36.20	65.13	91.83	117.18	165.22	210.82	254.70	297.25	338.72	379.30
Chronic = 0.986 ($e^{0.8473\ [\ln(\text{hardness})]+0.8840}$	36.50	65.66	92.58	118.14	166.57	212.55	256.78	299.68	341.49	382.40
Updated/Revised Criteria										
Acute = 0.978 ($e^{0.8537\ [\ln(\text{hardness})]+1.1182}$	46.71	74.41	119.32	152.53	215.62	275.65	333.49	389.66	444.47	498.13
Chronic = 0.986($e^{0.8537\ [\ln(\text{hardness})]+0.9473}$	39.69	71.73	101.40	129.62	183.24	234.25	283.40	331.13	377.71	423.31

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8.0 AMBIENT WATER QUALITY CRITERIA RECALCULATION ARID WEST EFFLUENT-DOMINATED STREAMS

This chapter provides an introduction to methods and available resources that are important in developing site-specific criteria databases and subsequent analysis of these databases using the EPA recalculation procedure. An overview of current EPA recalculation methodology provides necessary background information in understanding our interpretation of published guidance documents. The second part of this section develops recommended modifications to the recalculation procedure needed to address the problems associated with meeting minimum data requirements (MDRs) and performing site-specific recalculations in effluent-dominated, arid West streams and rivers. In the final part of this chapter, methods are provided for performing site-specific recalculations for the five case study streams described in Chapters 1 and 2, as well as two regional recalculations.

8.1 OVERVIEW OF THE EPA RECALCULATION PROCEDURE

National ambient water quality criteria (AWQC) are to be derived from the most up-to-date toxicity databases for species resident to North America. Established methods for data selection and national criteria derivation are published in *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (Stephan et al. 1985), as well as Appendix B: The Recalculation Procedure in *Interim Guidance on Determination and Use of Water-Effect Ratios for Metals* (EPA 1994).

National criteria established by the EPA provide guidance to state agencies that establish the State's AWQC, yet may need to be modified to better represent environmental conditions of the State. The EPA recognizes that some of the species within the national database may not reside in the State, or the state may have sensitive species that are not represented in the database. In these situations, the national criteria may be over or under protective for certain aquatic communities.

To resolve under- or overprotective criteria, the EPA offers a number of options to derive site-specific criteria, which take into account the local environmental conditions. General guidelines for conducting a site-specific recalculation were originally published in the criteria derivation guidance document by the EPA (1984). Since then, more specialized documents have been published (e.g., EPA 1994; 2001) to ensure that the contaminant of concern is properly accounted for. The basic steps involved with the recalculation procedure include (EPA 1994):

a) Corrections to the national database,

b) Updating the national database,

c) Deletions of taxa that do not occur at the site,

d) If new database does not meet MDRs, generating the data necessary to meet MDRs,

e) Recalculating new acute and chronic criteria based on the revised and updated databases, and

f) Presenting results in a report.

The first two steps of the recalculation procedure listed above, performing corrections and updating the national database, were presented for the selected criteria in Chapters 3-7 of this report. The next steps in generating site-specific AWQC will use these updated national databases with comparisons to resident species lists previously analyzed and presented in Chapter 2.

Before we proceed with the deletion and recalculation procedure, it is important to understand the EPA recalculation methodology, specifically the aspects related to defining resident species at a given site. We will also revisit MDRs needed to develop arid West, effluent-dependent streams, site-specific AWQC.

8.2 RESIDENT VS. TRANSIENT SPECIES

A key component of the recalculation procedure, specifically with regard to deletion of non-resident taxa from the database, is the definition of the phrase "occur at the site." This is a key factor in the potential deletion of *non-resident taxa* from the native toxicity database. The EPA (1994) defines occur at site as the species, genera, Families, Orders, Classes and Phyla that:

a) are usually present at the site,

b) are present at the site only seasonally due to migration,

c) are present intermittently because they periodically return to or extend their ranges into the site,

d) were present at the site in the past, are not currently present at the site due to degraded conditions, and are expected to return to the site when conditions improve, and

e) are present in nearby bodies of water, are not currently present at the site due to degraded conditions, and are expected to be present at the site when conditions improve.

For this analysis, we have taken this *occur at site* phrase a step further by delineating the organisms that occur at the site into "resident" and "transient" species. A resident species is defined as an organism using the habitat located at the site for reproduction, foraging, and/or refuge, which can include migratory species. A transient species, on the other hand, is defined as a species that may *occur at the site*, but does not utilize the habitat for these functions, and is only passively moving through the site.

8.3 DELETION PROCESS

After a list of resident species for a site is compiled, the formal EPA (1994) deletion process can be exercised. Resident species lists are used to screen the corrected and updated national databases for each criterion. The deletion process specifies which species must be deleted and which species must be retained. A step-wise process is applied to each species in the corrected and updated national database to determine deletion status.

The first step in the EPA process is to "circle" all species that are found at the site that are also in the toxicity database; these species must not be deleted (EPA 1994). It is important to note the significance of this first step. The EPA places greater significance on the circled species since they *occur at the site*, and assumes these species better represent a Family, Order, or Class than species that do not *occur at the site*, but would be retained by the subsequent step-wise process. Such emphasis on "circled species" is very important since the circled species can override the retention of other taxa, while the lack of a circled species can lead to the retention of multiple taxa that are only distantly related.

The remaining species in the toxicity database are then subject to further screening (EPA 1994) that is designed to ensure that:

a) Each species that occurs both in the national database and at the site also occurs in the site-specific data set,

b) Each species that occurs at the site but does not occur in the national database is represented in the site-specific database by all species in the national data set that are in the same genus,

c) Each genus that occurs at the site but does not occur in the national database is represented in the site-specific data set by all genera in the national data set that are in the same Family, and

d) Each Order, Class, and Phylum that occurs both in the national database and at the site is represented in the site-specific database by one or more species in the national database that are <u>most closely related to a species that occurs at the site</u> (emphasis added).

After reviewing the EPA (1994) deletion process, we identified a possible conflict between 1) the step-wise process they describe, 2) their accompanying figure that shows an example of the deletion process using three Phyla, and 3) the previously stated goal of deriving a site-specific database that contains *the most closely related taxa* to taxa found at the site. The discrepancy occurs during the retention of a species based on an

Order-level commonality or higher. According to the EPA step-wise procedure, a species is retained only at Order level when the national database does not contain a circled species in the same Order of the species being screened. Conversely, the explanation of the *Order* code given in the example provided by EPA states that the species being screened will be retained if the Order occurs at the site and is not represented by a lower taxon, which may or may not be a circled species. This last phrase, not represented by a lower taxon, is not consistent with the step-wise procedure when a species is retained, but not circled, at other lower levels of identification (e.g., Family). Furthermore, retaining some taxa on a high level of identification (e.g., Class and Phylum), when a representative in a lower taxon is already retained, but not circled, generally results in a *muddied* database, which is counterintuitive to the primary goal in the recalculation procedure of revising the national database to taxa that are most closely related to the species that occur at the site.

To resolve these conflicts, we refined the EPA step-wise process with the goal of generating a site-specific toxicity dataset more representative of the species that occur at the site than what would be derived using the standard process.

The first step would remain the same, which is "circling" all species that satisfy the definition of Aoccur at the site. *Note: Circled taxa may be at a higher level of identification than species if no lower level of identification is available for taxa at the site*. Some studies used to develop the resident species lists only identified invertebrates to Order, Family, or genus. When this occurred, all species in the lowest level of identification are initially circled. For example, we only have "Trichoptera" sampled at the Santa Cruz River site near Nogales. In this situation, all species in the Order Trichoptera were initially circled.

Following the initial circling process, a refined step-wise *circling process*, described below, was used to determine which of the remaining species in the toxicity database must be deleted and which must be retained.

8.3.1 Refined Step-Wise Process for Deletion of Non-Resident Taxa

1) Circle all species/taxa that satisfy the definition of "occur at the site."
    a) Then follow steps below for uncircled species.
2) Does the genus occur at the site?
    a) If no, go to step 3.
    b) If yes, are there one or more species in the genus that occur at the site but are not in the dataset?
        i) If no, go to step 3.

ii) If yes, circle all species in genus.*

3) Does the family occur at the site?

a) If no, go to step 4.

b) If yes, are there one or more genera in the family that occur at the site, but are not in the dataset?

i) If no, delete all uncircled species in family.*

ii) If yes, circle all species in the genera not already represented.*

4) Does the Order occur at the site?

a) If no, go to step 5.

b) If yes, are there one or more families in the Order that occur at the site, but are not in the dataset?

i) If no, delete all uncircled species in this family.*

ii) If yes, circle all species in families not already represented.*

5) Does the Class occur at the site?

a) If no, go to step 6.

b) If yes, does the dataset contain a circled species in the same Class?

i) If no, circle all species in this Class.*

ii) If yes, delete all uncircled species in this Class.*

6) Does the Phylum occur at the site?

a) If no, delete all species in this Phylum.

b) If yes, does the dataset contain a circled species in this Phylum?

i) If no, circle all uncircled species in this Phylum.*

ii) If yes, delete the uncircled species in this Phylum.*

7) Once all species in the national toxicity database have been considered, retain all circled species.

*Continue the deletion process by starting at step 2 for another uncircled species, unless all uncircled species in the dataset have been considered.

This revised step-wise deletion procedure was performed on the corrected and updated databases for each criterion and for each study site, as described below. The detailed results are found in Appendix 3, with a coded explanation of the deletion process used to screen each species.

The result of this site-specific deletion process is a database that best reflects the taxonomic profile of each site for each criterion. Upon completion of each site-specific database, MDRs must then be checked and each database must still satisfy the minimum requirements in order to proceed with AWQC derivation for that site. Otherwise, additional toxicity data would have to be generated to create a site-specific database that satisfies MDRs. This was not considered necessary for any of the sites we evaluated in the present study.

8.4 MINIMUM DATA REQUIREMENTS

As previously stated, a direct calculation of a criterion (not just assigning the most sensitive species in the database) requires an MDR for the toxicity database such that it contains data for eight diverse families (Stephen et al. 1985). For national criteria—and as outlined in the current recalculation procedure (EPA 1994) —these families must include:

1) the Family Salmonidae,
2) a Family in the Class Osteichthyes,
3) a Family in the Phylum Chordata,
4) a planktonic crustacean,
5) a benthic crustacean,
6) an aquatic insect,
7) a Family in a Phylum other than Arthropoda or Chordata, and
8) a Family in any Order of insect or any Phylum not already represented.

This MDR is commonly referred to as the "eight-family rule." National AWQC derived from a database that meets the eight-family rule are calculated from a series of formulas using the geometric mean toxicity values of the four most sensitive genera, and the total number of genera represented in the database. The resulting criteria concentrations are expected to protect at least 95% of all aquatic organisms and aquatic habitats (lotic, lentic, cold-water, and warm-water habitats). To ensure that the derived criteria are sufficiently protective, toxicity values for sensitive species and, sometimes, those that are limited to a particular location or habitat can also be used as the basis of the criterion to the exclusion of the other data included in the national database.

8.5 REDEFINING THE RECALCULATION PROCEDURE FOR ARID WEST STREAMS

The EPA guidelines and MDRs listed in the previous section are the foundation for the arid West effluent-dependent stream AWQC recalculations. However, we believe along with the clarification of the deletion procedure outlined above, slight modifications of the MDRs may also be warranted given the habitats present and organisms expected to occur in these habitats. For example, all sites under consideration for recalculation are classified as warm-water segments; therefore, we would not expect to find cold-water taxa such as trout or salmon at, or downstream of, these sites. This can be verified by the review of the resident species lists of the arid West study streams noted earlier (see Chapter 2). Only one of the five sites under consideration for recalculation, Fountain Creek, contains a salmonid (although those fish could arguably be classified as *transients* based on their sampling location and underlying size structure). Eliminating all non-resident trout and salmon for all other sites violates the generalized EPA MDRs, since a member of the Family Salmonidae is required for a direct criteria calculation.

Furthermore, we would not expect many arid West effluent-dependent stream sites to have resident zooplankton communities. However, the exclusion of zooplankton, including planktonic crustaceans, would be another violation of the "eight-family rule." Of course, zooplankton are not equally represented in all aquatic ecosystems with respect to abundance and ecological significance. In lentic (i.e., lake) ecosystems, these small invertebrates are an important primary consumer, with high biomass and rapid population turn over (Wetzel 2001). Zooplankton are essential to lentic ecosystem function and an integral component to many food webs. In lotic (i.e., stream) ecosystems, however, the presence of zooplankton are greatly reduced and frequently absent due to habitat limitations, since by definition, zooplankton are unable to withstand stream current. If zooplankton are sampled from high velocity streams/rivers, it is likely that these organisms were washed out of an upstream off-channel lake, pond, or reservoir and have no means of sustaining a population within the stream system without continual contributions from the source populations (Hynes 2001). Zooplankton washed into stream channels are generally thought to be transient species, since densities rapidly decline with downstream distance from the source population (Chandler 1937; Ward 1975; Novotny and Hoyt 1982; Thorp et al. 1994; Phillips 1995; Hynes 2001; Walks and Cyr 2004). In the case of effluent-dominated streams, the source population of zooplankton sampled just downstream of a WWTP discharge could likely be the WWTP tanks and/or ponds themselves (CEC, unpublished sampling data).

8.5.1 Potential Revised "Eight-Family Rule" for Arid West Streams

A possible solution is to create a revised "eight-family rule" that utilizes EPA methodology and incorporates more typical arid West stream aquatic communities. The exact method for recalculation (derivation of a 5th percentile FAV via the recalculation procedure, or defaulting the FAV to the most sensitive species) will generally be determined by the size of the database and organisms within the database. To increase the potential for a 5th percentile calculation, one option is to derive an alternate eight-family rule that better represents the aquatic communities found in these unique stream segments.

Redefining the MDRs, or providing suitable surrogate organisms for a particular habitat type would entail replacing current EPA MDRs that are expected to be non-resident in arid West effluent-dependent streams with organisms of approximately equal sensitivity that would be expected to occur in the river segments. For example, requiring a salmonid in the database serves two purposes. First, these fish are the dominant top predators in cold-water aquatic ecosystems. Second, salmonids tend to be relatively sensitive to contaminants. However, if obligate cold-water fish are not a resident species, an appropriate surrogate fish

Family for the salmonid requirement would be an organism within the Family Cyprinidae or Centrarchidae. Cyprinids represent 22-42% of fish taxa for each of the streams under consideration for recalculation, excluding one site with a limited fish population (see Chapter 2). The second most abundant Family represented is Centrarchidae, which can be the top predator in many warm water stream systems. Furthermore, Cyprinids are the most sensitive warm water fish for three (zinc, ammonia, and diazinon) of the five contaminants considered for recalculation. Thus, we suggest that the first two rules of the eight-family rule should be changed to include an organism in the Family Centrarchidae and one in Cyprinidae.

Including zooplankton as a resident species of the arid West streams will likely need to be evaluated on a site-specific basis. If zooplankton are determined to be a non-resident, once again the site will be in violation of the MDRs and a surrogate family needs to be established. A potential surrogate for a planktonic crustacean maybe an additional aquatic insect in a family not already represented in the database. The percentage of invertebrate taxa in the arid West streams that are aquatic insects ranges from 59% to 86% (Chapter 2). The toxicity database would better represent invertebrate communities of arid West streams if toxicity databases included information on at least two aquatic insect Orders. Furthermore, all databases under consideration for recalculation contain toxicity data for two aquatic insect families, making this substitution feasible without additional toxicity testing.

Considering the non-resident taxa in the EPA MDRs and the relative importance of other taxa not included in the EPA MDRs, a revised eight-family rule specific for arid West streams is proposed below. Note: This revised eight-family rule is for the protection of warm water aquatic communities residing in arid West effluent-dependent stream habitats, not in lakes and/or ponds.

<u>Arid West Stream Eight-Family Rule [AWS-MDRs]</u>

1) an organism in the Family Centrarchidae,
2) an organism in the Family Cyprinidae,
3) a Family in the Phylum Chordata,
4) an aquatic insect,
5) a second aquatic insect in a different Order,
6) a benthic crustacean,
7) a Family in a Phylum other than Arthropoda or Chordata, and
8) a Family in any Order of insect or any Phylum not already represented.

Although the AWS-MDRs better represent potential aquatic communities residing in arid West streams than national MDRs, further exceptions to MDRs may be necessary if one of the above eight families does not reside at a particular site. For example, as noted in Chapter 4, San Timoteo Wash (a tributary to the Santa

Ana River) does not contain fish due to naturally intermittent flows. Three of the eight families in the AWS-MDRs are for fish (or vertebrates), making it impossible to meet all eight of the AWS-MDRs (or EPA MDRs, as well). Additionally, the Santa Cruz River and San Timoteo Wash do not have resident benthic crustaceans. In these situations, requiring at least an eight-family database may be acceptable, or perhaps species that *could* potentially occur at the site may be retained, or the criteria could default to a generalized regional arid West stream criterion. The exact procedure used in these situations will need to be determined on site-specific basis.

Another potential problem in satisfying the MDRs would occur in site-specific databases that contain fewer then eight families. In this circumstance, the EPA states that a special version of the recalculation procedure must be used, but only if data are available for at least one species in each of the families that occur at the site. It is at this point when the lowest SMAV of a species that occurs at the site must be used as the FAV. In our situation, none of the resident species lists have fewer than eight families due to the extensive collection of aquatic invertebrate data.

We propose a slight modification of this special version of the recalculation procure. If at least eight Families are present in the site-specific toxicity database and the AWS-MDRs are still not met even after efforts to substitute taxonomically similar organisms are made, then the FAV can be set to the most sensitive species SMAV in the final site-specific database. When the final site-specific toxicity database contains less than eight Families, a FAV cannot be derived. In this situation, managers could use criteria derived from respective regional databases to provide guidance in establishing AWQC.

8.5.2 Additional Revised Recalculation Methods

AWQC are presently derived from ranked genus mean acute and chronic values (GMAV, GMCV) calculated as the geometric mean of species mean values (SMAV, SMCV). Furthermore, the number of genera represented in the database rather than the number of species determines database robustness. The decision to rank the toxicity databases at the generic level of identification over species level is not specifically addressed in the 1985 Guidelines. Many genera are represented by only one species, yet others are represented by multiple species.

For the analysis presented herein, we are proposing that criteria derived during the recalculation process be calculated from SMAVs rather than GMAVs for a number of reasons. First, the deletion process itself is conducted on a species level rather than a genus level, making it more acceptable to utilize the SMAVs for the FAV calculation (Great Lakes Environmental Center 2005). Second, while within-genus toxicity values are relatively consistent (at least more so than higher taxonomic levels), toxicity of a contaminant to different species within the same generus is not always equivalent. Even though the difference in toxicity between species may be small (< a factor of 10; e.g., *Physa* sp. for zinc), using a GMAV dilutes the sensitivity of the more sensitive species. Other genera contain species with highly divergent (> a factor of 10-100) toxicity values (e.g., *Catostomus*, *Oncorhynchus*, *Daphnia*, *Morone*, *Gammarus*). In these situations, only the SMAV for the most sensitive species is used in the GMAV calculation and valid data for other species in the genus are lost. Third, little overlap of arid West resident species lists and species within the various toxicity databases can artificially lower the criterion if derived at the GMAV level. This is because the FAV derivation procedure is designed to calculate a more conservative criterion when database size is small (Erickson and Stephan 1988).

A lower criterion due to a reduction in database sample size, rather than the presence of more sensitive species, may thus be over protective of the arid West stream community. Calculating criteria from the number of species in the database rather than genera can slightly increase the database sample size to help resolve potential sample size effects, without affecting the protectiveness of the resulting criteria through inclusion of SMAVs for sensitive species.

8.6 RECALCULATION OF AMBIENT WATER QUALITY CRITERIA

In the previous section, we provided an introduction to the methods in which site-specific databases were created, and we identified recommended alternatives to EPA deletion methods, MDRs, and use of SMAV versus GMAV, in order to derive site-specific AWQC. In this section, we provide a detailed description of the methods that were used to create the site-specific databases and subsequent analysis of the databases to derive site-specific criteria. To illustrate the potential outcome of using these revised procedures, we conducted criteria recalculations for each of the model criteria and case study streams described earlier (see Chapter 9).

8.6.1 Comparison of Resident Species Lists to Toxicity Databases

As stated above (Chapter 8.3), the first step of the deletion process is the comparison of the site resident species lists to each updated criterion database. This is accomplished by classifying (or "coding") each organism in each updated criterion database to its taxonomic classification unit from species up to Phylum (see worksheets in Appendix 3). To keep our analysis consistent between criteria and sites, we followed the steps of the revised step-wise deletion process (Section 8.3.1).

Resulting databases for each criterion and site may include cold-water salmonids and cladocerans if applicable, yet are marked with an asterisk if not used in the final calculations. Additionally, any deletion or acceptance that did not follow the exact interpretation of the revised step-wise deletion process was also marked in Appendix 3 and further explained in the respective report section.

The step-wise deletion process was conducted using the revised and updated national toxicity databases and resident species list for each river with exception of the Santa Cruz River, which was separated into two different sites. These sites were identified as the Santa Cruz River below Nogales and the Santa Cruz River below Tucson.

When the site-specific databases for the two regions (Southwest and High Plains) were created, the species lists for rivers in each respective region were compiled before the step-wise deletion process commenced. Because of the intricacies of the deletion process, one cannot simply combine all of the species in each database from each river in a region, but must treat all of the species that reside in the region as a single site, and then perform the step-wise procedure. Results of the regional deletion process were similar to those of each river and are again reported in Appendix 3. Once the site-specific databases were created, checking of AWS-MDRs, the ranking process, and final site-specific criteria derivation was performed.

8.6.2 Threatened and Endangered Species and the Use of Surrogates

According to the EPA (1994) recalculation procedure, toxicological data for "listed" species or taxonomically similar organisms must be incorporated into the site-specific database to ensure the protection of a threatened or endangered (T&E) species. Many of the robust databases (e.g. copper and zinc) already contain toxicity data for T&E species or acceptable surrogates (see Chapter 9). Criteria with limited databases (e.g., diazinon and aluminum), on the other hand, likely do not contain toxicity data for T&E species. In these situations, we need to identify a species that is most closely related to the T&E species within the toxicity database. Most databases contain a species within the same family or genus as the T&E species (the ideal situation). However, there are a few site-specific databases in which fish in a different family may be the only available toxicity data to represent a T&E fish. Despite the lack of "ideal" surrogates for T&E species, site-specific recalculations were still conducted. These criteria would undoubtedly benefit from additional toxicity testing with the contaminant and species of concern.

8.6.3 Final Recalculation of Ambient Water Quality Criteria

The first step after completion of the site-specific databases was to check for acceptance of the AWS-MDRs. In our analysis, we followed the proposed "arid West eight-family rule" discussed in the previous sections of this chapter. In addition to compliance with the AWS-MDR, it is important to identify threatened, endangered, and/or recreationally economically important species that reside at a site. Six T&E species were identified in three of the five rivers and in one of the regional resident species lists. The EPA recalculation guidance document (1994) states that these species must be accounted for by an *acceptable surrogate species* in the site-specific database for the respective site. Considerations for the best surrogate species for each listed threatened or endangered species are provided with a discussion in the text when necessary. If the AWS-MDRs were not met for a particular criterion at a particular site, then the regional site-specific criterion could provide an alternative AWQC recommendation.

Although the 1985 Guidelines and EPA (1994) AWQC guidance document specify that the GMAVs of the four most sensitive genera be used in the calculation of the FAV, we ranked species by their SMAVs instead of GMAVs for this analysis (Section 8.5.2). When the AWS-MDRs were satisfied, the four most sensitive SMAVs and the total number of species in the site-specific database were then used to calculate the FAV. Chronic criteria were derived via the final acute-chronic ratios used in each of the updated national criteria calculations. This precluded the need to create site-specific chronic databases and is the recommended procedure by the EPA.

The deletion process generated site-specific toxicity databases that were used to calculate a FAV and FCV for each site. AWQC are based on either direct calculation of the CMC (equal to half of the FAV) and CCC (equal to the FCV or FAV ÷ FACR), or these values inserted in equations that derives the CMC and CCC for a given water quality parameter, such as pH or hardness. Table 8-1 provides a summary of these generic equations.

Water quality information, slopes, intercepts, FAVs, FCVs, and conversion factors were all model parameters that were defined before solving for the final criterion. Ambient water quality parameters included hardness for aluminum, copper, and zinc and pH for ammonia. Toxicity modification slopes for each toxicant were generated in each national update Chapters (3, 5, and 7) using linear regression.

Table 8-1
Generic Equations Used to Derive Updated National and Site-Specific Criteria for Each Parameter

Criterion	Generic equation
Aluminum Acute:	$e^{(\text{pooled slope} * \ln[\text{hardness}] + \text{acute intercept})}$
Aluminum Chronic:	$e^{(\text{pooled slope} * \ln[\text{hardness}] + \text{chronic intercept})}$
Ammonia Acute:	(FAV/2)*((0.0489 / (1+10^(7.204 – pH)))+(6.95 / (1+10^(pH – 7.204)))
Ammonia Chronic:	(FAV/FACR)*(0.0489 / (1+10^(7.204 – pH)))+(6.95 / (1+10^(pH – 7.204)))
Copper Acute:	$CF * e^{(\text{acute slope} * \ln[\text{hardness}] + \text{acute intercept})\ *}$
Copper Chronic:	$CF * e^{(\text{chronic slope} * \ln[\text{hardness}] + \text{chronic intercept})\ *}$
Diazinon Acute:	FAV/2
Diazinon Chronic:	FAV/FACR
Zinc Acute:	$CF * e^{(\text{pooled slope} * \ln[\text{hardness}] + \text{acute intercept})\ *}$
Zinc Chronic:	$CF * e^{(\text{pooled slope} * \ln[\text{hardness}] + \text{acute intercept})\ *}$

*CF = Conversion factor to convert criteria to dissolved fraction (U.S. EPA 2002). The aluminum criteria are based on the total metal, thus no conversion factor.

Water quality equations for aluminum, copper, and zinc are simple natural logarithmic functions that utilize a water hardness (mg/L of $CaCO_3$) to modify the respective criteria. Ammonia criteria use $\log_{10}$ based equations to model the effect of pH. Since no significant toxicity water quality relationships were determined for diazinon, acute and chronic criteria were derived directly from the FAV and FACR. Since the AWQC for copper and zinc are based on the dissolved fraction, vs. total metal in solution, EPA (2002) conversion factors were used the in our final calculations.

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9.0 CASE STUDIES FOR EVALUATION OF THE RECALCULATION PROCEDURE IN ARID WEST EFFLUENT DEPENDENT STREAMS

This chapter presents the results from the recalculation procedure for each site and toxicant based on the calculated FAV and FCV. Comparisons between sites and to the updated national values were conducted at the FAV and FCV level since these values are normalized to a common water hardness or pH. This approach allows us to quantify the effect of the recalculation procedure on the foundational criterion, without the influence of ambient water quality conditions later used to compare the site-specific criteria (Chapter 10).

9.1 ALUMINUM

The derivation of site-specific criteria for each study stream is based on the recalculation methods outlined above (Chapter 8). Following deletion of non-resident taxa, site-specific toxicity databases were developed (Appendix 3; Tables 3.1.1 through 3.1.6) and criteria were calculated for each study stream and the two proposed regions. All values presented below are normalized to hardness = 50 mg/L as $CacO_3$.

9.1.1 Santa Ana River

Following deletion of non-resident taxa, the new site-specific aluminum toxicity database for Santa Ana River contains 14 species, found in 10 families (Table 9-1). Of these 14 species, six are fish and eight are invertebrates. The 10 families found in the Santa Ana River-specific database satisfy the AWS-MDRs.

Compared to the updated national database, the deletion process resulted in six species being removed, including the two most sensitive organisms (the zooplankter, *Ceriodaphnia* and the trout/salmon, *Salmo*), and the next two most sensitive genera have been re-ranked. The most sensitive organism in the Santa Ana River database is the smallmouth bass, *Micropterus dolomieu* (retained to represent the non-native largemouth bass, *Micropterus salmoides*, present in the Santa Ana River). The SMAV for *M. dolomieu* was derived from a single undefined value that was added to the updated national toxicity database (Table 5-2). In site-specific databases that include *M. dolomieu*, there might be some question as to the validity of accepting a "greater than" undefined value as the most sensitive organism. We decided to use this value in this site-specific database because an organism within the same genus was present at this site and non-lethal toxic effects were noted, such as lethargy and abnormal mucus production, in fish exposed to the reported concentration of aluminum at which 20% mortality occured (Kane and Rabeni 1987).

Table 9-1
Site-Specific Aluminum Acute Toxicity Database, with Ranked Species Mean Acute Values (SMAV) Specific to Each Study Stream

			Site-Specific Ranking							
				Santa Cruz River						
Species	**Organism**	**SMAV (µg/L)**	**Santa Ana River**	**Near Nogales***	**Near Tucson**	**Salt/ Gila Rivers**	**Fountain Creek**	**South Platte River**	**SW**	**HP**
Tanytarsus dissimilis	Midge	>192,155	14	9	8	13	15	14	14	15
Lepomis cyanellus	Green sunfish	>52,274	13	8	7	12	14	13	13	14
Perca flavescens	Yellow perch	>52,064	12			11	13	12	12	13
Ictalurus punctatus	Channel catfish	>50,078	11		6	10	12	11	11	12
Physa sp.	Snail	32,907	10	7		9	11	10	10	11
Hybognathus amarus	Rio Grande silvery minnow	>25,075	9	6		8	10	9	9	10
Acroneuria sp.	Stonefly	>23,628	8		5	7	9	8	8	9
Gammarus pseudolimnaeus	Amphipod	23,000	7	5	4	6	8	7	7	8
Girardia tigrina	Flatworm	>17,355	6			5	7	6	6	7
Pimephales promelas	Fathead minnow	13,461	5	4		4	6	5	5	6
Tubifex tubifex	Worm	13,373	4	3	3	3	5	4	4	5
Crangonyx pseudogracilis	Amphipod	9,190	3	2	2	2	4	3	3	4
Asellus aquaticus	Isopod	4,370	2	1	1		3	2	2	3
Micropterus dolomieu	Smallmouth bass	>3,183	1			1	2	1	1	2
Salmo salar	Atlantic salmon	3,154					1			1
	Final Acute Value (µg/L) =		**2,299**	**4,370**	**N/A**	**2,819**	**2,118**	**2,299**	**2,299**	**2,118**
	Final Chronic Value (µg/L) =		**459**	**873**	**N/A**	**563**	**423**	**459**	**459**	**423**

* = Did not satisfy the MDR "arid West eight-family rule."
NOTE: Values normalized for hardness = 50 mg/L of CaCO3. SW = southwest region, HP = High Plains region.

Recalculation of the aluminum acute and chronic criteria resulted in values that were slightly lower than the updated national criteria (Figure 9-1). The recalculated Santa Ana River FAV is 2,299 µg/L, which is almost 300 µg less than the updated national value (2,560 µg). Using our recommended ACR of 5.0039, the resultant FCV is 459 µg/L.

The Santa Ana River resident species analysis identified one species listed as threatened, *Catostomus santaanae*. According to the EPA (1994), toxicological data for listed species or taxonomically similar organisms must be incorporated into the site-specific database for the protection of a threatened or endangered species. The Santa Ana River aluminum toxicity database does not contain any toxicity information for the family Catostomidae. Therefore, following EPA guidance, the next most closely related family, Cyprinidae, would have to provide potential surrogate species for *C. santaanae*. Given the ecological similarity of these two families and the abundance of cyprinids in the Santa Ana River (Chapter 2), this seems a reasonable approach.

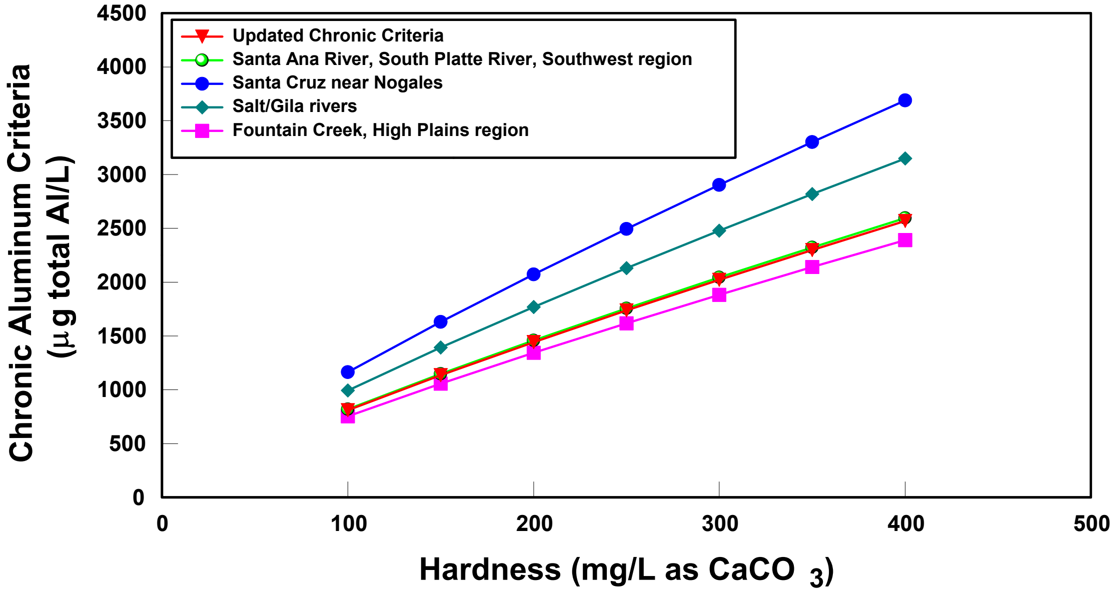

Figure 9-1
Comparison of Site-Specific Chronic Aluminum Criteria to the Updated National Criteria at Varying Hardness

9.1.2 Santa Cruz River

9.1.2.1 Santa Cruz near Nogales

The Santa Cruz River near the Nogales site-specific database contains aluminum toxicity data for nine species in seven Families (Table 9-1). Of the nine species, three are fish and six are invertebrates. Because a family not already represented in the Phylum Chordata and a second insect did not exist, the AWS-MDRs were not met, even after three benthic crustaceans were re-added after the deletion process. Only one species was common between the resident species list and the updated national database due to the low diversity at this site.

Compared to the updated national database, 11 non-resident species had been removed including three of the most sensitive genera. Since the site-specific database did not meet the AWS-MDRs and more than eight families were present at the site, we defaulted the FAV to the SMAV of the most sensitive organism in the remaining database (EPA 1994). The most sensitive organism was *Asellus aquaticus*, resulting in a FAV of 4,370 µg/L. Using our recommended ACR of 5.0039, the resultant FCV is 873 µg/L.

The Santa Cruz River near Nogales resident species analysis identified one possible threatened or endangered species, *Poeciliopsis occidentalis*, as a resident at this site. The site-specific database for aluminum in the

Santa Cruz River near Nogales does not contain any fish species in the listed species, genus, family, or order of the species; therefore, an unrelated fish in the site-specific toxicity database (e.g., *P. promelas*) would have to serve as a surrogate, based on EPA recalculation guidance. While not a preferred surrogate, this is basically the only reasonable species available.

9.1.2.2 Santa Cruz near Tucson

The Santa Cruz River near Tucson revised site-specific database included aluminum toxicity data for eight species of aquatic organisms found in seven families (Table 9-1). Since the database includes just seven families, the AWS-MDRs were not satisfied. Because of the limited Families present in the Santa Cruz River near Tucson site-specific database, setting the FAV to the most sensitive SMAV or using the recalculation procedure to generate a FAV was not possible. Therefore, it might be preferable to consider the southwest arid stream regional site-specific analysis (described below in Section 9.1.7) when developing site-specific aluminum criteria for Santa Cruz River near Tucson. The Santa Cruz River near Tucson resident species analysis did not identify any threatened or endangered species.

9.1.3 Salt/Gila Rivers

The Salt/Gila Rivers species composition analysis resulted in a site-specific database that includes aluminum toxicity data for 13 species found in 10 families (Table 9-1). The AWS-MDRs were met after the addition of *Acroneuria* sp. Other than providing a second insect family, this nonresident species would be a good surrogate for other potentially sensitive insects found at the site and not in the toxicity database.

The most sensitive organism in the Salt/Gila Rivers' database was *Micropterus dolomieu*. Reasons for retaining this organism in the database are similar to that reported for Santa Ana River, as discussed in Section 9.1. The FAV for the Salt/Gila Rivers is 2,819 μg/L. Using our recommended ACR of 5.0039, the resultant FCV is 563 μg/L, again with both values at hardness = 50 mg/L.

The Salt/Gila Rivers' resident species analysis identified five possible threatened or endangered species. The five species are *Xyauchen texanus*, *Cyprinodon macularus*, *Poeciliopsis occidentalis*, *Gila elegans*, and *Rhinichthys cobitis*. The Salt/Gila Rivers aluminum database does not contain any Catostomids; therefore, a potential surrogate species for *X. texanus* would have to an unrelated species, such as a cyprinid. The updated national database also lacks species in the Class Cyprinodontiformes that could be surrogates for *C. macularus* and *P. occidentalis*. The site-specific database does contain aluminum toxicity data on *Pimephales promelas*, a species that could represent *G. elegans* and *R. cobitis*, as these species could reside together in warm water streams and rivers, and all are Cyprinids. However, as with the Santa Ana River, *P. promelas* would also need to serve as a surrogate for the razorback sucker (*Xyrauchen*).

9.1.4 Fountain Creek

The Fountain Creek site-specific database contains aluminum toxicity data for 15 species in 11 Families. Of the 15 species, seven are fish and eight are invertebrates (Table 9-1). Because of the diversity of the 9 families present in the site-specific database, the AWS-MDRs were satisfied (plus, inclusion of a "resident" salmonid). Compared to the updated national database, only five species had been removed that included the most sensitive organism (*Ceriodaphnia*), and the other three most sensitive genera have been re-ranked. The most sensitive organism in the Fountain Creek database was *Salmo salar*, followed by *Micropterus dolomieu*– both retained to represent species found at the site without toxicity data.

Recalculation of the aluminum acute and chronic criteria resulted in values that were more restrictive than the revised national criteria (Figure 9-1). The recalculated Fountain Creek FAV and FCV are 2,118 and 423 µg/L, respectively. The FAV for Fountain Creek was one of the lowest of all sites. This was directly associated with the addition of the second most sensitive organisms in the updated national database (*S. salar*)– which was retained to represent brown trout (*Salmo trutta*) which is present at the site, but possibly more "transient" than "resident" (see discussion in Chapter 2).

9.1.5 South Platte River

The South Platte River's site-specific database has the second greatest number of taxa of the five sites in our analysis. Of the 14 species in 11 families, the database includes acute values for six fish and eight invertebrates (Table 9-1). The South Platte River site-specific database satisfies all of the MDRs, including the AWS-MDRs. The most sensitive organism in the South Platte River database was *Micropterus dolomieu*.

Recalculation of the aluminum acute and chronic criteria resulted in values that were lower than the revised national criteria. The recalculated South Platte River FAV is 2,299 µg/L. Using our recommended ACR of 5.0039 and the above FAV resulted in an FCV of 459 µg/L (again, at hardness = 50 mg/L).

9.1.6 Southwest Arid Stream Systems (CA, AZ, NV, NM)

The Southwest arid stream region species composition analysis resulted in a site-specific database containing aluminum toxicity data for 14 species found in 11 families. The Southwest region site-specific database contains six species of fish and eight invertebrate species (Table 9-1). Because of the diversity of organisms in the database, the AWS-MDRs were satisfied.

The four most sensitive species were the same as in the Santa Ana and South Platte Rivers' site-specific toxicity databases. Recalculation of the aluminum acute and chronic criteria resulted in values that were lower than the revised national criteria and were based on a toxicity database more robust than most sites that are in the Southwest region (Fig. 9-1). The recalculated Southwest regional FAV is 2,299 µg/L. Using our recommended ACR of 5.0039, the resultant FCV is 459 µg/L (at hardness = 50 mg/L).

Since the Southwest region species list was created from a pooled river species list, the regional list included endangered or threatened species found in those rivers. The regional species list contained two Catostomid, one Poeciliid, and one Cyprinodontid, *Catostomus santaanae*, *Xyauchen texanus*, *Poeciliopsis occidentalis*, and *Cyprinodont macularus*, respectively, in which no acceptable surrogates could be added to the regional database. However, available potential surrogates for the remaining listed species, *Gila elegans* and *Rhinichthys cobitis*, could be accounted for by *Pimephales promelas*, which is found in the updated national and regional database, because they are all Cyprinids and occur together at most sites in this region.

9.1.7 High Plains Arid Stream Systems (WY, CO, NM)

The High Plains arid stream regional species composition analysis resulted in a site-specific database that presents aluminum toxicity for 15 species found in 11 families. The High Plains regional site-specific database contains seven species of fish and eight invertebrate species. Because of the diversity of organisms in the database, the AWS-MDRs were satisfied. The four most sensitive ranked species were the same as in Fountain Creek, with *Salmo salar* ranked first, followed by *Micropterus dolomieu*.

Recalculation of the aluminum acute and chronic criteria resulted in values that were lower than the revised national criteria and slightly lower than the Southwest region. The recalculated High Plains regional FAV and FCV normalized to hardness = 50 mg/L are 2,118 and 423 µg/L, respectively. These derived AWQC are comparable to the criteria derived for each river in the region. These results indicate that High Plains regional AWQC can perhaps better be applied to individual rivers and streams within this region than can the Southwest regional aluminum criteria to streams in that region. The High Plains regional species list did not identify any threatened or endangered species; therefore, identifying surrogate species is not necessary.

9.2 AMMONIA

The derivation of site-specific criteria for each study stream is based on the recalculation methods outlined in Chapter 8. Following deletion of non-resident taxa, site-specific toxicity databases were developed (Appendix 3; Tables 3.2.1 through 3.2.6) and criteria calculated for each study stream and the two proposed regions. All values presented below are normalized to pH 8 for comparisons between sites.

9.2.1 Santa Ana River

As a result of the step-wise deletion process for compiling site-specific databases, 40 species representing 25 families were included in the Santa Ana River ammonia database. The robust database satisfies the AWS-MDRs, with the four most sensitive species in the Santa Ana River database being *Notemigonus crysoleucas*, *Gambusia affinis*, *Etheostoma spectable*, and *Cyprinella whipplei* (Table 9-2). Collectively, these fish are four of the six most sensitive species in the updated warm water database. The Santa Ana database also contains *Catostomus platyrynchus*, which serves as a surrogate species for the endangered Santa Ana sucker (*Catostomus santaanae*).

Table 9-2
Site-Specific Preliminary Updated Ammonia Acute Toxicity Database
Ranked Species Mean Acute Values (SMAV)

			Site-Specific Ranking							
				Santa Cruz River						
Species	**Common Name**	**SMAV (TA-N mg/L@ pH 8)**	**Santa Ana River**	**Near Nogales**	**Near Tucson***	**Salt/Gila Rivers**	**Fountain Creek**	**South Platte River**	**SW**	**HP**
Orconectes immunis	Calico crayfish	770.46		33	19		40	44		46
Erythromma najas	Damselfly	308.62	40	32	18	38	39	43	47	45
Philarctus quaeris	Caddisfly	282.09	39	31	17	37	38	42	46	44
Ephemerella grandis	Mayfly	189.16	38	30			37	41	45	43
Caecidotea racovitzai	Sowbug	165.94	37	29	16		36	40	44	42
Callibaetis skokianus	Mayfly	164.08	36	28	15	36	35	39	43	41
Lestes sponsa	Dragonfly	139.48	35	27		35	34	38	42	40
Stenelmis sexlineata	Riffle beetle	113.17	34	26	14	34	33	37	41	39
Sympetrum flaveolum	Dragonfly	100.50	33	25			32	36	40	38
Tubifex tubifex	Tube worm	97.82	32	24	13	33	31	35	39	37
Gammarus pulex	Amphipod	95.40	31	23	12	32	30	34	38	36
Baetis rhodani	Mayfly	94.19	30	22	11	31	29	33	37	35
Crangonyx sp.	Amphipod	92.10		21	10	30	28		36	34
Crangonyx seudogracillis	Amphipod	83.19		20	9	29	27		35	33
Arcynopteryx parallela	Stonefly	77.10	29		8		26	32	34	32
Callibaetis sp.	Mayfly	75.93	28	19	7	28	25	31	33	31
Physa gyrina	Snail	74.48	27	18		27	24	30	32	30
Cyprinodon sp.	Pupfish	63.79				26	23	29	31	29
Helisoma trivolvis	Snail	60.84	26	17		25	22	28	30	28
Cottus bairdi	Mottled sculpin	51.73	25						29	
Hyalella azteca	Amphipod	51.34	24	16	6	24	21	27	28	27
Catostomus commersonii	White sucker	45.82	23	15		23	20	26	27	26
Cyprinella lutrensis	Red shiner	45.65	22	14		22	19	25	26	25
Pimephales promelas	Fathead minnow	41.89	21	13		21	18	24	25	24

Table 9-2 (Continued)
Site-Specific Preliminary Updated Ammonia Acute Toxicity Database
Ranked Species Mean Acute Values (SMAV)

Species	Common Name	SMAV (TA-N mg/L@ pH 8)	Site-Specific Ranking							
			Santa Ana River	Santa Cruz River		Salt/Gila Rivers	Fountain Creek	South Platte River	SW	HP
				Near Nogales	Near Tucson*					
Orconectes naias	Crayfish	41.27		12	5		17	23		23
Micropterus dolomieui	Smallmouth bass	36.90				20	16	22	24	22
Ictalurus punctatus	Channel catfish	35.81	20		4	19	15	21	23	21
Musculium transversum	Fingernail clam	35.65	19					20	22	20
Poecilia reticulata	Guppy	33.15	18	11		18	14	19	21	
Dendrocoelom lacteum	Flat worm	32.82	17			17	13	18	20	19
Catostomus platyrynchus	Mountain sucker	31.71	16	10		16	12	17	19	18
Morone americana	White perch	30.89	15			15			18	
Cyprinus carpio	Common carp	30.32	14	9		14	11	16	17	17
Lepomis cyanellus	Green sunfish	30.31	13	8	3	13	10	15	16	16
Procambarus clarkii	Red swamp crayfish	30.05	12	7	2			14	15	15
Campostoma anomalum	Central stoneroller	26.97	11	6		12	9	13	14	14
Sander vitreus	Walleye	25.89	10					12	13	13
Lepomis machrochirus	Bluegill	24.16	9			11	8	11	12	12
Salmo trutta	Brown trout	23.74					7			11
Hybognathus amarus	Rio Grande silvery minnow	20.26	8	5		10	6	10	11	10
Micropterus salmoides	Largemouth bass	20.03	7			9		9	10	9
Chasmistes brevirostris	Shortnose sucker	19.61				8		8	9	8
Cyprinella spilopterus	Spotfin shiner	19.51	6	4		7	5	7	8	7
Morone chrysops	White bass	19.16	5			6			7	
Cyprinella whipplei	Steelcolor shiner	18.83	4	3		5	4	6	6	6
Etheostoma spectabile	Orangethroat darter	18.14	3				3	5	5	5
Lepomis gibbosus	Pumpkinseed	18.05				4		4	4	4
Deltistes luxatus	Lost river sucker	16.01				3		3	3	3
Gambusia affinis	Western mosquitofish	15.25	2	2	1	2	2	2	2	2
Notemigonus crysoleucas	Golden shiner	14.67	1	1		1	1	1	1	1
		Final Acute Value (mg/L) =	**16.1**	**15.7**	**15.3**	**15.5**	**16.1**	**15.8**	**16.0**	**15.9**
		Final Chronic Value (mg/L) =	**3.3**	**3.2**	**3.1**	**3.2**	**3.3**	**3.2**	**3.3**	**3.2**

NOTES:
*Did not satisfy the MDR Aarid West eight-family rule”, therefore the FAV was set to the most sensitive species in database
SW = Southwest Region
HP = High Plains Region

The 5th percentile derivation process results in a site-specific pH-normalized FAV of 16.1 mg/L TA-N, which is slightly greater than the updated acute warm water FAV (15.7 mg/L TA-N). This value results in site-specific acute criterion that is slightly less restrictive throughout a range of pH values from 6.5 to 9.0 than updated warm water criterion. Using the proposed FACR methodology to derive chronic criterion, the FCV is 3.29 mg/L TA-N. This value results in site-specific chronic criterion that is less restrictive throughout a range of pH values than updated warm water criterion (Figure 9-2).

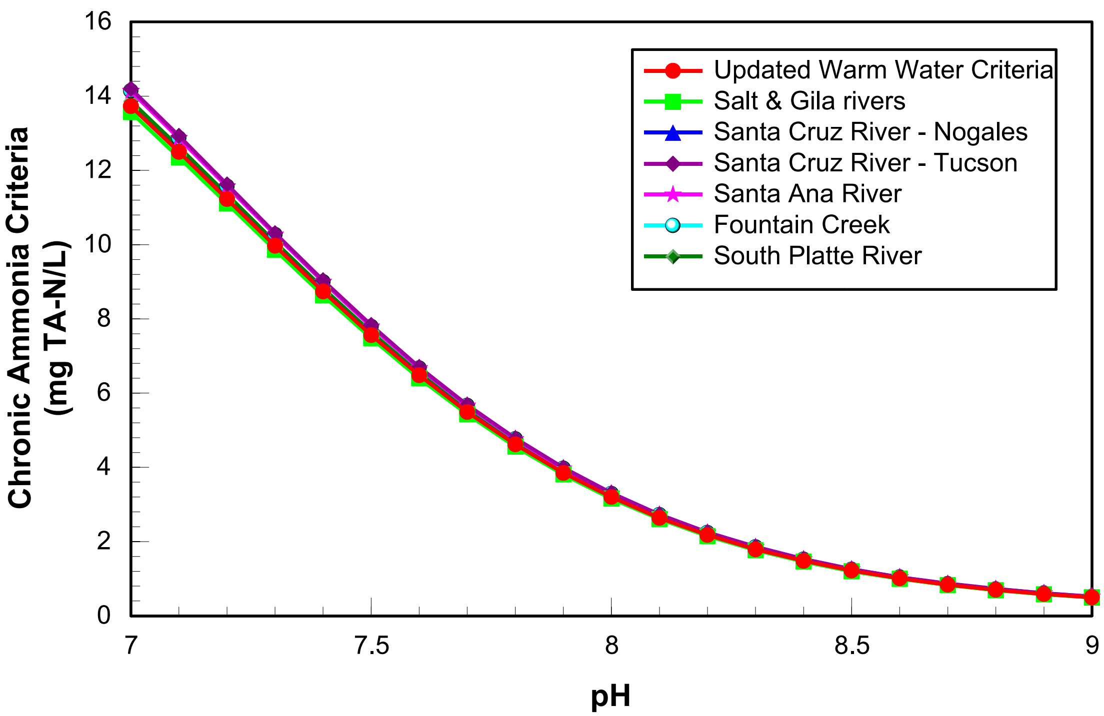

Figure 9-2
Site-Specific Chronic Ammonia Criteria as a Function of pH
(Acute Criteria Distribution is Similar to Chronic)

9.2.2 Santa Cruz River

9.2.2.1 Santa Cruz Near Nogales

The site-specific database contains 33 species representing 18 families; however, it initially failed to meet the AWS-MDRs because benthic crustaceans have not been observed at this study site. For reasons discussed earlier, all eight species in the Class Malacostroca were added to the site-specific database to meet the MDRs and allow derivation of site-specific criteria. The four most sensitive species in the modified site-specific database include *N. crysoleucas*, *G. affinis*, *C. whipplei*, and *N. spiloperus* (Table 9-2). The modified FAV is 15.7 mg/L TA-N, which would result in acute criterion the same as the updated warm water criteria concentration. The FACR approach for developing site-specific chronic criteria results in a FCV of 3.20

mg/L TA-N, which would also result in criterion that is the same as the updated warm water value (Figure 9-2).

9.2.2.2 Santa Cruz near Tucson

The site-specific database contains 19 species, representing 13 Families of aquatic organisms. This site did not meet the AWS-MDRs even after addition of the eight benthic crustaceans because cyprinids have not been observed at this study site. Therefore, by default, the site-specific criteria shall be based upon the lowest SMAV in the site-specific database. In this circumstance, the western mosquito fish (*Gambusia affinis*) is the most sensitive species in the database; thus, the FAV is 15.3 mg/L TA-N and the FCV is 3.12 mg/L TA-N. Arguably, deriving site-specific criteria using a non-native, nuisance species is problematic. However, the *G. affinis* (SMAV)-driven criteria is functionally the same as the proposed updated warm water criterion (FAV 15.7 mg/L TA-N). Thus, the mosquito fish remained as the driving force in the Santa Cruz River near Tucson database.

9.2.3 Salt/Gila Rivers

The site-specific ammonia database for the Salt/Gila Rivers contains 38 species representing 19 families of aquatic organisms, and satisfies the AWS-MDRs. The four most sensitive genera include *Notemigonus crysoleucas*, *Gambusia affinis*, *Deltiste luxatus*, and *Lepomis gibbosus* (Table 9-2), which are also the four most sensitive fish species in the warm water database. The site-specific FAV (15.5 mg/L TA-N, again at pH 8) results in an acute criterion, which is similar to the updated warm water criterion. The FACR approach to deriving site-specific chronic criteria also results in criterion similar to the updated warm water limits (Figure 9-2), with an FCV of 3.2 mg/L.

The Salt/Gila Rivers also contain five threatened and endangered fish species, which include *Xyrauchen texanus*, *Gila elegans*, *Rhinichthys cobitis*, *Cyprinodon macularius*, and *Poeciliopsis occidentalis*. Fish species that serve as surrogates for these endangered species include: *Deltistes luxatus* (for *X. texanus*), which is also a threatened and endangered species, *N. crysoleucas* (for *G. elegans* and *R. cobitis*), which is the most sensitive fish in the updated acute database, *Cyprinodon* sp. (for *C. macularius*), and *G. affinis* (for *P. occidentalis*).

9.2.4 Fountain Creek

The site-specific database contains 40 species representing 25 families, and satisfies the AWS-MDRs. The database is unique among the arid West sites because it contains *Salmo trutta*, a coldwater species. This fish was retained for recalculation purposes, even though it may potentially be considered a transient (see discussion in Chapter 4). However, this species had a minimal affect on the FAV because it was the seventh most sensitive species in the database. The four most sensitive species in this database are *N. crysoleucas*, *G. affinis*, *E. spectabile*, and *C. whipplei* (Table 9-2). As a result, the FAV was 16.1 mg/L TA-N, which led to site-specific acute criterion less restrictive than the updated warm water limits. Similar to the other arid West recalculations, the FACR approach resulted in chronic criterion less restrictive over a range of pH when compared to the updated warm water limits (Figure 9-2), with an FCV of 3.3 mg/L.

9.2.5 South Platte River

The site-specific South Platte River ammonia database contained the largest number of species of the selected arid West study sites. A total of 44 species representing 24 Families were included in the database, which satisfies the AWS-MDRs. The four most sensitive genera include *N. crysoleucas*, *G. affinis*, *D. luxatus,* and *L. gibbosus,* which are also the four most sensitive fish in the updated warm water database. As a result, the site-specific FAV is 15.8 mg/L TA-N, which leads to site-specific acute criterion that is similar to the updated warm water limits. Again, the FACR derived chronic criterion is similar to updated warm water limits (Figure 9-2), with a normalized FCV of 3.2 mg/L.

9.2.6 Southwest Arid Stream Systems (CA, AZ, NV, NM)

Site-specific ammonia toxicity databases for the Santa Ana River, Santa Cruz River (near Nogales and near Tucson), Salt/Gila Rivers were combined to form a Southwest region database. The Southwest region database contains 47 species representing 27 families of aquatic organisms, which satisfies the AWS-MDRs. The resulting FAV of 16.0 mg/L TA-N derives an acute criterion very similar to the updated warm water acute criterion. Again, the derivation of chronic criteria using the FACR results in criterion very similar to the updated warm water limits (Figure 9-3), with a normalized FCV of 3.3 mg/L. Since the Southwest region species list was crated from a pooled river resident species list, the regional list included all six threatened or endangered species found in those rivers. The site-specific database also contains all of the species that were identified as surrogates in each of the pooled rivers; therefore, surrogate species for the Southwest region are similar, and were identified in previous sections.

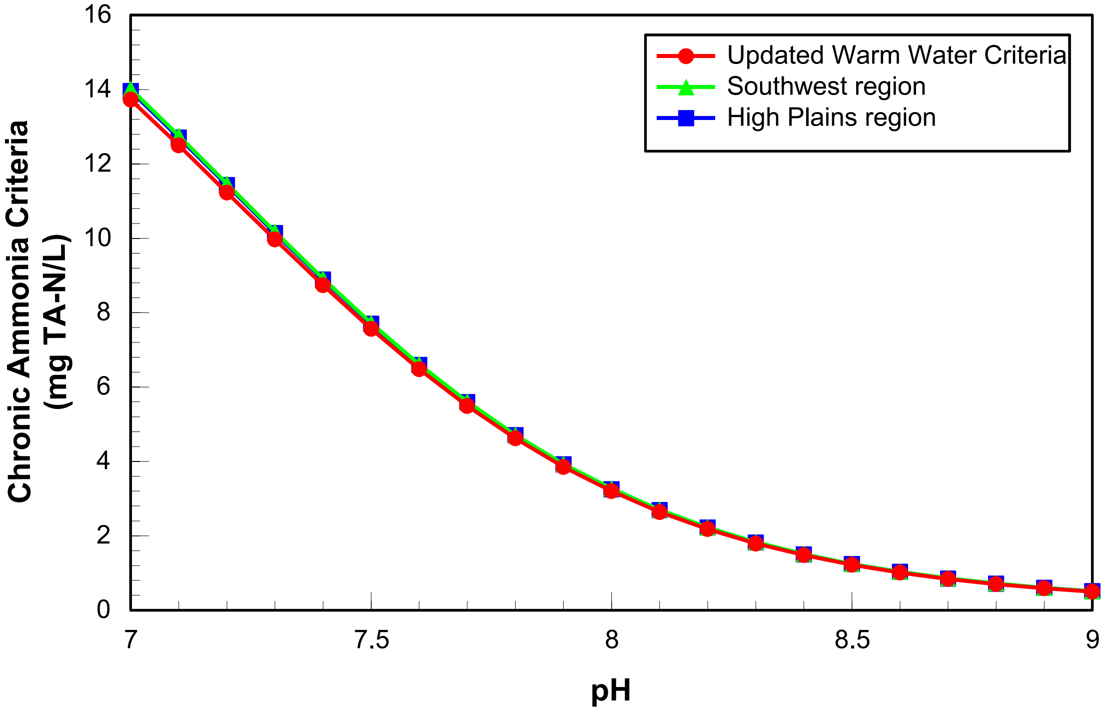

Figure 9-3
Regional Chronic Ammonia Criteria as a Function of pH
Compared to the Updated Warm Water Criteria
(Acute Criteria Distribution is Similar to Chronic.)

9.2.7 High Plains Arid Stream Systems (WY, CO, NM)

Site-specific databases for Fountain Creek and South Platte River were combined to create the High Plains region database. Given the similarities of the regional toxicity databases, the High Plains database results in criteria very similar to the Southwest region. The High Plains database contains 46 species representing 26 families of aquatic organisms, which satisfies the AWS-MDRs. The four most sensitive species are the same as the Southwest region, and results in a FAV of 15.9 mg/L TA-N. Again, both the regional acute and chronic criteria are very similar to the updated warm water criterion (Figure 9-3), with a normalized FCV of 3.2 mg/L.

9.3 COPPER

The derivation of site-specific copper criteria for each study stream is based on the recalculation methods outlined above (Chapter 8). Following deletion of non-resident taxa, site-specific toxicity databases were developed (Appendix 3; Tables 3.3.1 through 3.3.6) and criteria calculated for each study stream and the two proposed regions. All values presented below are normalized to hardness = 50 mg/L as $CacO_3$, not to site hardness, which is presented in Chapter 10.

A general deletion common to all sites includes the removal of zooplankton (including cladocerans) due to their transient nature in these streams (see Section 10.2). Cladocerans accounted for the four most sensitive genera and eight most sensitive species in the updated national toxicity database for copper. The lack of zooplankton in the site-specific and regional databases shifts the national criterion, which is highly influenced by cladocerans, to site-specific criteria that better reflect the sensitivity of taxa that are more representative of the resident species of arid West effluent-dependent/dominated streams. Discussions of the resulting site-specific values are found below.

9.3.1 Santa Ana River

The site-specific acute copper toxicity database for the Santa Ana River contains 37 species. Given the level of identification (some invertebrate taxa are only identified to Order), these species represent at least 22 families and meet the AWS-MDRs (Table 9-3). The four most sensitive species in the site-specific database include *Gammarus pulex*, *Hyalella azteca*, *Ephoron virgo*, and *G. pseudolimnaeus*. All of these species are macroinvertebrates, which confirms the sensitivity of invertebrates to copper. The resulting FAV and FCV are 17.03 µg/L and 5.87 µg/L (at hardness = 50 mg/L), respectively, which are approximately 76% greater than the updated copper values presented in Chapter 7 of this report (Figures 9-4 and 9-5).

The resident species analysis identified one threatened species, *Catostomus santaanae*, at this site. Although this species is not in the updated national acute toxicity database, the database contains *C. latipinnis* (Table 9-3), which is a potential surrogate species for *C. santaana*e.

Table 9-3
Site-Specific Acute Toxicity Databases for Copper, Ranked Species Mean Acute Values (SMAV)

Species	Organism	SMAV (µg/L)	Site-Specific Ranking							
			Santa Ana River	Santa Cruz River		Salt/ Gila Rivers	Fountain Creek	South Platte River	SW	HP
				Near Nogales	Near Tucson *					
Notemigonus crysoleucas	Golden shiner	59,017		41		43	47	51	52	52
Acroneuria lycorias	Stonefly	9,408	37		23		46	50	51	51
Corbicula manilensis	Asiatic clam	7,485	36					49	50	50
Trichoptera spp.	Caddisfly	6,200	35	40	22	42	45	48	49	49
Morone americana	White bass	5,843				41			48	
Zygoptera spp.	Damselfly	4,600	34	39	21	40	44	47	47	48
Procambarus clarkii	Crayfish	2,073	33	38	20			46	46	

Table 9-3 (Continued)
Site-Specific Acute Toxicity Databases for Copper, Ranked Species Mean Acute Values (SMAV)

Species	Organism	SMAV (µg/L)	Site-Specific Ranking							
			Santa Ana River	Santa Cruz River		Salt/ Gila Rivers	Fountain Creek	South Platte River	SW	HP
				Near Nogales	Near Tucson *					
Lepomis macrochirus	Bluegill	1,394	32	37	19	39	43	45	45	47
Orconectes rusticus	Crayfish	1,363		36	18		42	44		46
Crangonyx pseudogracilis	Amphipod	1,290				38				
Chironomus decorus	Midge	838	31	35	17	37	41	43	44	45
Gambusia affinis	Mosquitofish	796	30	34	16	36		42	43	44
Fundulus diaphanus	Banded killifish	788					40	41		43
Cyprinus carpio	Common carp	727	29	33		35	39	40	42	42
Oreochromis mossambicus	Tilapia	663	28			34			41	
Lepomis gibbosus	Pumpkinseed	619	27	32	15	33	38	39	40	41
Chironomus tentans	Midge	453	26	31	14	32	37	38	39	40
Ephemerella subvaria	Mayfly	363	25	30	13	31	36	37	38	39
Notropis chrysocephalus	Striped shiner	315		29		30	35	36	37	38
Carassius auratus	Goldfish	289	24	28		29	34	35	36	37
Ictalurus punctatus	Channel catfish	250	23		12	28	33	34	35	36
Etheostoma spectabile	Orangethroat darter	218					32	33		35
Jordanella floridae	Flagfish	190				27			34	
Etheostoma nigrum	Johnny darter	160					31	32		34
Acrocheilus alutaceus	Chisselmouth	133		27		26	30	31	33	33
Pectinatella magnifica	Bryozoan	128	22						32	
Chrionomus plumosus	Midge	125	21	26	11	25	29	30	31	32
Ptychocheilus lucius	Colorado pikeminnow	117		25		24	28	29	30	31
Salmo salar	Atlantic salmon	115					27			30
Etheostoma flabellare	Fantail darter	108					26	28		29
Morone saxatilis	Striped bass	95.3				23			29	
Nais spp.	Worm	90.0	20	24	10	22	25	27	28	28
Hybognathus amarus	Rio Grande silvery minnow	86.6		23		21	24	26	27	27
Rhinichthys atratulus	Blacknose dace	82.2		22		20	23	25	26	26
Etheostoma caeruleum	Rainbow darter	82.2					22	24		25
Poecilia reticulata	Guppy	81.8	19	21		19			25	
Xyrauchen texanus§	Razerback sucker	81.0				18		23	24	24
Pimephales promelas	Fathead minnow	80.7	18	20		17	21	22	23	23
Semotilus atromaculatus	Creek chub	79.7					20	21		22
Etheostoma lepidum	Greenthroat darter	79.7		19		16	19	20	22	21
Campostoma anomalum	Central stoneroller	74.5		18		15	18	19	21	20
Ictalurus nebulosus	Brown bullhead	66.2			9			18		19
Catostomus latipinnis	Flannelmouth sucker	62.1	17	17		14	17	17	20	18
Gila elegans§	Bonytail chub	59.3	16	16		13	16	16	19	17
Gyraulus circumstriatus	Snail	54.8	15	15			15	15	19	16
Limnodrilus hoffmeisteri	Worm	51.7	14	14	8	12	14	14	17	15

Table 9-3 (Continued)
Site-Specific Acute Toxicity Databases for Copper, Ranked Species Mean Acute Values (SMAV)

Species	Organism	SMAV (µg/L)	Site-Specific Ranking							
			Santa Ana River	Santa Cruz River		Salt/ Gila Rivers	Fountain Creek	South Platte River	SW	HP
				Near Nogales	Near Tucson *					
Poeciliopsis occidentalis§	Gila topminnow	49.1		13		11			16	
Lumbriculus variegatus	Worm	46.4	13	12			13		15	14
Physa integral	Snail	43.3	12	11		10	12	13	14	13
Ptychocheilus oregonensis	Northern pikeminnow	40.1		10			11	12	13	12
Gammarus sp.	Amphipod	39.0	11	9	7	9	10	11	12	11
Plumatella emarginata	Bryozoan	35.2	10						11	
Lophopodella carteri	Bryozoan	36.2	9						10	
Physa heterostropha	Snail	35.0	8	8		8	9	10	9	10
Tubifex tubifex	Worm	33.3	7	7	6	7	8	9	8	9
Chironomus spp.	Midge	30.0	6	6	5	6	7	8	7	8
Physella gyrina	Snail	27.3	5					7	6	7
Gammarus pseudolimnaeus	Amphipod	22.7	4	5	4	5	6	6	5	6
Brachydanio rerio	Zebrafish	22.3		4		4	5	5	4	5
Ephoron virgo	Mayfly	19.4	3	3	3	3	4	4	3	4
Etheostoma rubrum	Fountain darter	18.4					3	3		3
Hyalella azteca	Amphipod	16.4	2	2	2	2	2	2	2	2
Gammarus pulex	Amphipod	15.2	1	1	1	1	1	1	1	1
	Final Acute Value (µg/L =		**17.0**	**17.5**	**15.2**	**17.7**	**17.3**	**17.6**	**18.8**	**17.7**
	Final Chronic Value (µg/L) =		**5.9**	**6.0**	**5.2**	**6.1**	**6.0**	**6.1**	**6.5**	**6.1**

NOTES:
§ = Threatened or endangered species
* = Did not meet the MDRs; therefore FAV was set to the most sensitive species in database
All SMAVs are normalized to hardness = 50 mg/L as $CaCO_3$. SW = Southwest region; HP = High Plains region.

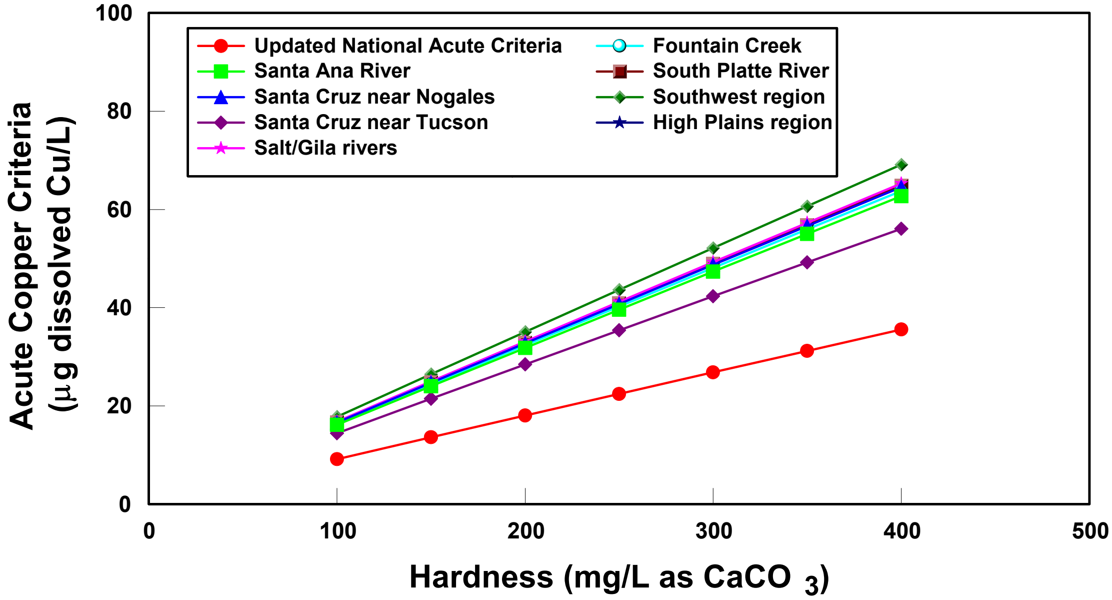

Figure 9-4
Comparison of Site-Specific Acute Copper Criteria to the Updated National Acute Copper Criteria at Varying Hardness Values

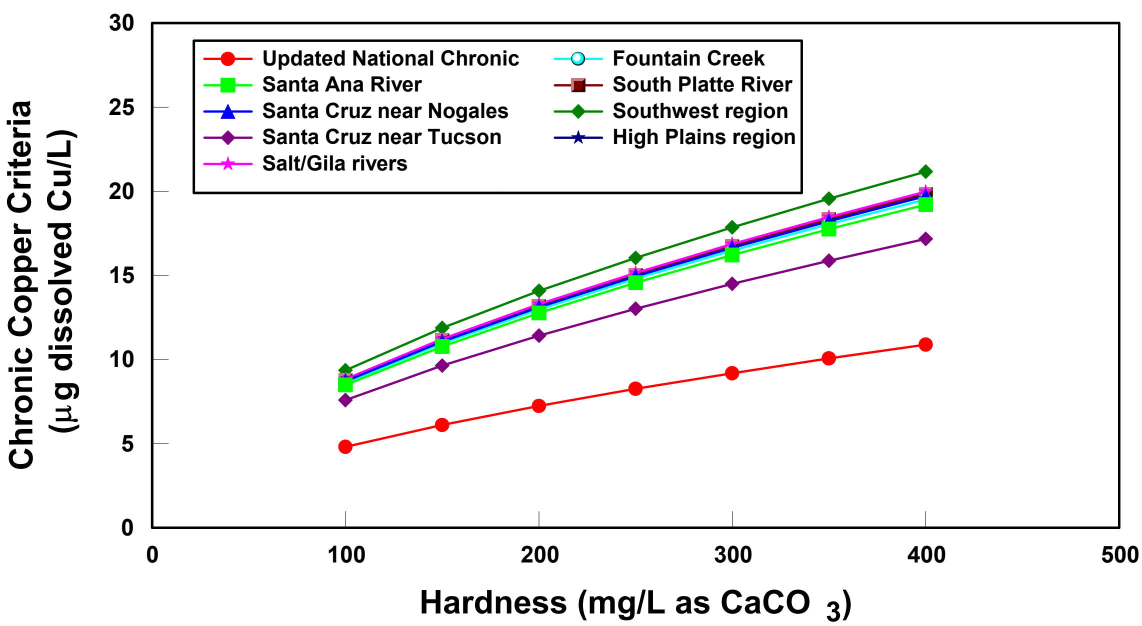

Figure 9-5
Comparison of Site-Specific Chronic Copper Criteria to the Updated National Chronic Copper Criteria at Varying Hardness Values

9.3.2 Santa Cruz River

Both river segments (near Nogales and near Tucson) initially did not meet the AWS-MDRs since benthic crustaceans are not included in the resident species list. Given that both sites contain other benthic macroinvertebrates as resident taxa, which suggests that the appropriate habitat exists, we determined benthic crustaceans could occur at these sites. Therefore, two crayfish (*Orconectes rusticus*, and *Procambarus clarkii*) and four amphipods (*Hyalella azteca*, *Gammarus* sp., *G. pulex*, and *G. pseudolimnaeus*)—retained at genus level or lower at the other arid West sites—were retained in the Santa Cruz calculations. An additional code not previously used by the U.S. EPA of "R" ("retained") was assigned to these species in Appendix 3 of this report.

9.3.2.1 Santa Cruz near Nogales

The resulting site-specific acute copper toxicity database for the Santa Cruz River near Nogales contains 41 species that represent at least 15 Families and meet the AWS-MDRs. The four most sensitive species in the database include *G. pulex*, *H. azteca*, *E. virgo*, and *Brachydanio rerio* (Table 9-3). Although the genus *Brachydanio* does not reside at this site, this species—in addition to all genera in the Family Cyprinidae—were retained to represent *Agosia chrysogaster*, which is a resident species without copper toxicity data. The resulting FAV and FCV are 17.48 and 6.03 µg/L, respectively, which are approximately 81% greater than the updated copper values presented in Chapter 7 of this report (Figures 9-4 and 9-5).

One endangered species, *Poeciliopsis occidentalis*, was identified as a resident in the Santa Cruz River near Nogales site. Acute copper toxicity data are available for this species, which ranks as the 13th most sensitive of the 41 species at this site (Table 9-3).

9.3.2.2 Santa Cruz near Tucson

The resulting site-specific acute copper toxicity database for the Santa Cruz River near Tucson contains 23 species, representing 12 Families (Table 9-3), which is the most limited database of all sites under consideration for recalculation. The resulting Families do not meet the AWS-MDRs, since an organism within the Family Cyprinidae does not reside at the site. The four most sensitive species in this database (*G. pulex*, *H. azteca*, *Ephron virgo,* and *G. pseudolimnaeus*) are identical to the Santa Ana site-specific database (Table 9-3). Since the site-specific database does not meet the AWS-MDRs and at least eight Families are represented, the FAV defaults to the SMAV of the most sensitive species in the site-specific database. The resulting FAV and FCV are 15.2 and 5.2 µ/L, respectively. These values are the most restrictive of all of the site-specific copper recalculations, yet are still approximately 57% greater than the updated copper values presented in Chapter 7 of this report.

9.3.3 Salt/Gila Rivers

The only documentation of benthic crustaceans for the Salt/Gila Rivers is the presence of the Order Amphipoda. Therefore, all species within this Order were retained in the site-specific copper toxicity database. The resulting site-specific acute copper toxicity database for the Salt/Gila Rivers contains 39 species, representing at least 18 Families, and meets the AWS-MDRs (Table 9-3). The four most sensitive species in the database include *Gammarus pulex, Hyalella azteca*, *Ephoron virgo,* and *Brachydanio rerio*. Once again, *B. rerio* is not a resident species at the site, yet was retained—in addition to all genera in the Family Cyprinidae that were not already in the site-specific database—to represent the five genera of Cyprinids that are found at the site without copper toxicity data. The resulting FAV and FCV are 17.72 and 6.11 µg/L, respectively, which are approximately 85% greater than the updated copper values presented in Chapter 7 of this report (Figures 9-4 and 9-5).

The Salt/Gila Rivers resident species analysis identified five threatened or endangered species including *Xyrauchen texanus*, *Gila elegans*, *Rhinichthys cobitis*, *Cyprinodon macularius*, and *Poeciliopsis occidentalis*. Three of these species, *X. texanus*, *G. elegans*, and *P. occidentalis*, contain acute copper toxicity data are already represented in the site-specific database (i.e., no surrogates are needed). All Cyprinids in the updated national database were retained, except *Ptychocheilus oregonenis* because the genus was already represented. Any of these Cyprinids are a potential surrogate for *R. colitis*. Lastly, the only species in the Family Cyprinodontidae was retained at the Family level to represent *C. macularius* (Appendix 3; Table 3.3.3).

9.3.4 Fountain Creek

The site-specific acute copper toxicity database for the Fountain Creek contains 47 species, representing at least 19 Families, and meets the AWS-MDRs (Table 9-3). The four most sensitive species in the database include *G. pulex*, *H. azteca*, *Etheostoma rubrum*, and *E. virgo*. The resulting FAV and FCV are 17.30 µg/L and 5.97 µg/L (hardness = 50 mg/L), respectively, which are approximately 80% greater than the updated copper values presented in Chapter 7 of this report (Figures 9-4 and 9-5).

9.3.5 South Platte River

The site-specific acute copper toxicity database for the South Platte River contains 51 species, representing at least 19 families, and meets the AWS-MDRs. This is the largest site-specific database of all sites under consideration for recalculation. The four most sensitive species in the database include *G. pulex*, *H. azteca*, *E. rubrum*, and *E. virgo* (Table 9-3), which are identical to the four most sensitive species for Fountain Creek. The resulting site-specific FAV and FCV are 17.59 µg/L and 6.06µg/L, respectively, which are approximately 82% greater than the updated copper values presented in Chapter 7 of this report (Figures 9-4 and 9-5).

9.3.6 Southwest Arid Stream Systems (CA, AZ, NV, NM)

Combining the resident species lists for the Santa Ana River, Salt/Gila Rivers, and both sites for the Santa Cruz River resulted in a Southwest regional acute copper toxicity database containing 52 species, representing at least 24 families (Table 9-3). This regional database is in compliance with the AWS-MDRs. The top four most sensitive species include *G. pulex*, *H. azteca*, *E. virgo*, and *B. rerio*. Three of these species are the same as the top four most sensitive species in the site-specific databases already discussed in Sections 9.3.1 through 9.3.5. The higher degrees of freedom associated with the regional toxicity database resulted in slightly greater final acute and chronic values (18.76 µg/L and 6.47 µg/L, respectively, at hardness = 50 mg/L) than any of the site-specific recalculations. The resulting Southwest regional values are approximately 95% greater than the updated copper values presented in Chapter 7 of this report (Figures 9-4 and 9-5).

9.3.7 High Plains Arid Stream Systems (WY, CO, NM)

Combining the resident species lists for the Fountain Creek and the South Platte River for the High Plains region resulted in a regional acute copper toxicity database containing 52 species, representing at least 21 families (Table 9-3). This regional database is in compliance with the AWS-MDRs. Since the database size is only slightly greater than the site-specific databases and four more the sensitive species are identical for both sites, the resulting FAV and FCV of 17.67 µg/L and 6.09 µg/L, respectively, are only moderately greater than the site-specific recalculations. The resulting High Plains regional values are approximately 83% greater than the updated copper values presented in Chapter 7 of this report (Figures 9-4 and 9-5).

9.4 DIAZINON

The derivation of site-specific criteria for each study stream is based on the recalculation methods outlined in Chapter 8. Following deletion of non-resident taxa, site-specific toxicity databases were developed (Appendix 3; Tables 3.4.1 through 3.4.6) and criteria calculated for each study stream and the two proposed regions. Here we compare only the site-specific final chronic values (FCVs) to the national FCV, since acute and chronic criteria calculate are the same when the final acute-chronic ratio is equal to 2 (see Chapter 8).

Although zooplankton are influential organisms in deriving the diazinon AWQC in the national database, they were deemed transient organisms in the arid West sites and not used in our site-specific analyses. This removal has been discussed in Chapter 8.2, but it is important to note their significance in the diazinon national update (Chapter 6). Toxicity data indicated that zooplankton, such as Cladocerans, are extremely sensitive to diazinon exposure (>tenfold difference from other invertebrates in the database). Removal of Cladocerans from site-specific databases could greatly affect site-specific diazinon criteria.

9.4.1 Santa Ana River

The site-specific database for Santa Ana River contains 15 species, representing 13 families (Table 9-4). Of these 15 species, seven are fish and eight are invertebrates. The 13 Families found in the Santa Ana database satisfy the AWS-MDRs. The four most sensitive genera in the national database that were deleted include three Cladocerans (*Ceriodaphnia*, *Daphnia*, and *Simocephalus*) and one species within the genus *Gammarus*. *G. fasciatus* was removed from the site-specific database, since the other *Gammarus* species in the toxicity database was reported to occur at this site and found in the updated database. Resident species, *G. lacustris*, was less acutely toxic to diazinon than the deleted species, and represents the sixth most sensitive species in the Santa Ana site-specific database.

The recalculated Santa Ana River FCV is 8.56 µg/L, which is considerably greater than the revised national value. The significant increase in the site-specific values are directly associated with the deletion of the cladocerans and the most sensitive *Gammarus* species. Although these invertebrates were removed, the four most sensitive organisms in the site-specific toxicity database include three invertebrate species, supporting the observation that invertebrates are the most sensitive organisms to diazinon exposure.

Table 9-4
Site-Specific Diazinon Acute Toxicity Databases,
with Ranked Species Mean Acute Values (SMAV) for Each Site

			Site-Specific Ranking							
				Santa Cruz River						
Species	**Organism**	**SMAV (µg/L)**	**Santa Ana River**	**Near Nogales**	**Near Tucson ***	**Salt/ Gila Rivers**	**Fountain Creek**	**South Platte River**	**SW**	**HP**
Clarias batrachus	Walking catfish	14,792	16			17	18	18	18	18
Gillia altilis	Pebble snail	11,000	15	12		16	17	17	17	17
Carassius auratus	Goldfish	9,000	14	11		15	16	16	16	16
Ameiurus melas	Black bullhead	8,000	13		8	14	15	15	15	15
Lumbriculus variegatus	Worm	7,841	12	10	7	13	14	14	14	14
Brachydanio rerio	Zebrafish	7,044	11	9		12	13	13	13	13
Pimephales promelas	Fathead minnow	6,416	10	8		11	12	12	12	12
Carassius carassius	Crucian carp	5,000		7		10	11	11	11	11
Pomacea paludosa	Fla. apple snail	3,198	9	6		9	10	10	10	10
Girardiaia tigrina	Planaria	2,708	9			8	9	9	9	9
Jordanella floridea	Flagfish	1,643	8			7	8	8	8	8
Poecilia reticulata	Guppy	732	7	5	6	6	7	7	7	7
Gammarus lacustris	Amphipod	200	6	4	5	5	6	6	6	6
Oreochromis mossambicus	Tilapia	161	5			4	5	5	5	5

Table 9-4 (Continued)
Site-Specific Diazinon Acute Toxicity Databases,
with Ranked Species Mean Acute Values (SMAV) for Each Site

			Site-Specific Ranking							
				Santa Cruz River						
Species	Organism	SMAV (µg/L)	Santa Ana River	Near Nogales	Near Tucson*	Salt/ Gila Rivers	Fountain Creek	South Platte River	SW	HP
Lepomis macrochirus	Bluegill	116	4	3	4	3	4	4	4	4
Lestes congener	Damselfly	50	3	2	3	2	3	3	3	3
Chironomus tentans	Midge	30	2	1	2	1	2	2	2	2
Pteronarcella californica	Stonefly	25	1		1		1	1	1	1
Final Acute Value (µg/L) =			**17.13**	**18.24**	**25.00**	**25.44**	**18.63**	**18.63**	**18.63**	**18.63**
Final Chronic Value (µg/L) =			**8.56**	**9.12**	**12.50**	**12.72**	**9.32**	**9.32**	**9.32**	**9.32**

NOTES:
* = Did not meet the MDRs; therefore FAV was set to the most sensitive species in database
SW = Southwest Region
HP = High Plains Region

The Santa Ana River analysis identified one possible threatened species, *Catostomus santaanae*, as a resident. According to U.S. EPA (1994), toxicological data for listed species or taxonomically similar organisms must be incorporated into the site-specific database. The Santa Ana River site-specific toxicity database for diazinon does not contain any Catostomids; therefore, we were unable to identify a potential surrogate species for *C. santaanae* other than the remaining fish in the database.

9.4.2 Santa Cruz River

9.4.2.1 Santa Cruz Near Nogales

The Santa Cruz River near Nogales site-specific database contains diazinon toxicity data for 12 species in nine Families. Of the 12 species, six are fish and six are invertebrates, including a benthic crustacean in the site-specific database. Although no benthic crustaceans were reported to reside in the Santa Cruz River, *Gammarus* species were retained in order to satisfy the AWS-MDRs. Our decision was supported by the fact that at least one *Gammarus* species was retained in all other rivers in our site-specific analysis, and the presence of other macroinvertebrates at this site suggests that appropriate habitat could exist. This decision sets up the next decision to either use the most sensitive *Gammarus* species or use data from the most appropriate species when deriving the AWQC. A literature review on each of the two *Gammarus* species reveled that *G. fasciatus* is primarily a Great Lakes species and has not been reported in arid West states (e.g., Cole 1988). Although no specific identification resources for the state of Arizona were found, we favored the use of *G. lacustris* in the site-specific database due to its common occurrence in the arid Western states when compared to *G. fasciatus*.

The nine families found in the Santa Cruz River near Nogales database satisfy the AWS-MDRs. The most sensitive organism in the Santa Cruz River near Nogales species ranked database was the midge *Chironomus tentans* (Table 9-4). The recalculated Santa Cruz River near Nogales FCV is 9.12 µg/L.

The Santa Cruz River near Nogales resident species analysis identified one possible endangered species, *Poeciliopsis occidentalis*, as a resident at this site. The diazinon Santa Cruz River site-specific database contains *Poecilia reticulata*, which is a potential surrogate for *P. occidentalis*, since both taxa are within the Family Poecilidae.

9.4.2.2 Santa Cruz Near Tucson

The Santa Cruz River near Tucson had the fewest number of taxa among all sites. The revised site-specific database included diazinon toxicity data for eight species of aquatic organisms found in eight Families, after addition of *G. lacustris* (Table 9-4). Although the database includes eight Families, the AWS-MDRs were not satisfied, since the resident species list lacked a Cyprinid species. Because the MDRs were not met, and at least eight Families were present in the toxicity database, we defaulted the FAV to the most sensitive SMAV in the site-specific database. The most sensitive organism in the Santa Cruz River near Tucson site-specific database was the stonefly *Pteronarcys californica* with a SMAV of 25 µg/L; therefore, the FCV is 12.5 µg/L.

9.4.3 Salt/Gila Rivers

The Salt/Gila Rivers species composition analysis resulted in a site-specific database that contains diazinon toxicity data for 17 species found in 13 Families (Table 9-4). The Salt/Gila Rivers site-specific database contains 10 species of fish and seven invertebrate species. Because of the diversity of organisms in the database, the AWS-MDRs were satisfied. Both *Gammarus* species were in the site-specific database, but only *G. lacustris* was retained in the working database for site-specific criteria calculations for reasons explained above.

The four most sensitive organisms are slightly different than all other site-specific databases, in that *Oreochromis mossambicus* ranked fourth most sensitive. Recalculation of the acute and chronic diazinon criteria resulted in values that were greater than the revised national criteria and all other diazinon site-specific AWQC. The recalculated Salt/Gila Rivers FCV is 12.72 µg/L, which is the greatest site-specific FCV of all the sites evaluated.

The Salt/Gila Rivers resident species analysis identified five possible threatened or endangered species, including *Xyauchen texanus*, *Gila elegans*, *Rhinichthys cobitis*, *Cyprinodon macularus*, and *Poeciliopsis occidentalis*. The Salt/Gila rivers database does not contain any Catostomids; therefore, a potential surrogate species for *X. texanus* might have to be an unrelated fish species. The site-specific database does contain diazinon toxicity data on *Pimephales promelas*, a species that potentially best represents *G. elegans* and *R. cobitis*, as these species are all within the Family Cyprinidae. A potential surrogate for *C. macularus* is *Jordanella floridea*, because these two species are in the same Family, Cyprinodontiformes. The diazinon Salt/Gila Rivers site-specific database also contains *Poecilia reticulata* that could possibly represent *P. occidentalis*, since both are Poecilids.

9.4.4 Fountain Creek

Fountain Creek species composition analysis resulted in a site-specific database that contains diazinon toxicity data for 18 species found in 14 families (Table 9-4). Of the 18 species, 10 are fish and eight are invertebrates. Because of the diversity of the Families present in the site-specific database, the AWS-MDRs were satisfied. The most sensitive organism in the Fountain Creek database was *Pteronarcys californica*. The four most sensitive genera in the Fountain Creek database are the same organisms from the same order as in the Santa Ana River and Santa Cruz River near Tucson site-specific diazinon databases.

Recalculation of the diazinon acute and chronic criteria resulted in values that were greater than the revised national criteria. The recalculated Fountain Creek FCV is 9.32 µg/L. The FCV for Fountain Creek was very similar to that of Santa Ana River. The slight difference in the FCV was due to the different degrees of freedom associated with two more species found in the Fountain Creek database.

9.4.5 South Platte River

South Platte River species composition analysis resulted in a site-specific database that presents diazinon toxicity data for 18 species found in 14 Families (Table 9-4). Of the 14 Families present, the database includes acute toxicity data for 10 fish and eight invertebrate species, and satisfies all of the AWS-MDRs. The four most sensitive genera for this site are the same organisms as in the site-specific diazinon databases for Santa Ana River, Santa Cruz River near Tucson, and Fountain Creek. The amphipod *G. lacustris* was found at this site (Table 4-2); therefore, *G. fasciatus* was deleted from the site-specific database according to EPA guidelines (1994). The recalculated South Platte River FCV is 9.32 µg/L.

9.4.6 Southwest Arid Stream Systems (CA, AZ, NV, NM)

The Southwest arid stream region species composition analysis resulted in a site-specific database that presents diazinon toxicity data for 18 species found in 14 Families (Table 9-4). The Southwest region site-specific database contains 10 species of fish and eight invertebrate species, and satisfies the AWS-MDRs. The four most sensitive ranked species were the same as most of the other sites; therefore, the number of species in the database was influential in the derivation of the diazinon AWQC. The recalculated Southwest region FCV is 9.32 µg/L.

Because the Southwest region species list was created from a pooled river resident species list, the regional list included threatened or endangered species found in those rivers. The regional species list contained two Catostomids, *Catostomus santaanae* and *Xyauchen texanus*, in which no acceptable surrogates existed in the updated national toxicity database, although other fish are in the site-specific database. However, the remaining listed species, *Gila elegans*, *Rhinichthys cobitis*, *Cyprinodon macularus*, and *Poeciliopsis occidentalis*, were accounted for with species found in the updated national database because they shared common Families with listed species.

9.4.7 High Plains Arid Stream Systems (WY, CO, NM)

The High Plains arid stream region species composition analysis resulted in a site-specific database that presents diazinon toxicity data for 18 species found in 14 Families (Table 9-4). The High Plains region site-specific database contains 10 species of fish and eight invertebrate species, and the AWS-MDRs were met. The four most sensitive species were similar to those found at the sites in the High Plains region. The recalculated High Plains region FCV is 9.32 µg/L. The similarity of these results to individual High Plains sites provided some evidence that a regional AWQC can be applied to individual rivers and streams within the region. The High Plains region resident species list did not identify any threatened or endangered species; therefore, no surrogate species needed to be identified.

9.5 ZINC

The derivation of site-specific criteria for each study stream is based on the recalculation methods outlined above (Chapter 8). Following deletion of non-resident taxa, site-specific toxicity databases were developed (Appendix 3; Tables 3.5.1 through 3.5.6) and criteria calculated for each study stream and the two proposed regions. As with copper and aluminum, all values presented below are normalized to hardness = 50 mg/L as $CacO_3$, rather than to site-specific hardness, which is included in Chapter 10.

9.5.1 Santa Ana River

The site-specific acute zinc toxicity database for the Santa Ana River contains 39 species. Given the lowest level of identification (some invertebrates are only identified to Order), these species represent at least 26 Families and meet the AWS-MDRs. The four most sensitive species in the database include *Cottus bairdi*, *Hyalella azteca*, *Catostomus latipinnis*, and *Oreochromis mossambicus* (Table 9-5). The resulting FAV and FCV are 310 and 131 µg/L, respectively (at hardness = 50 mg/L), which are approximately 80% greater than the updated zinc values presented in Chapter 9 of this report (Figure 9-6). The resident species analysis identified one threatened species in the Santa Ana River, *Catostomus santaanae*. The Santa Ana database contains two Catostomid species, *C. commersonii* and *C. latipinnis*, that serve as potential surrogates for *C. santaanae*.

9.5.2 Santa Cruz River

Both river segments (near Nogales and near Tucson) initially did not meet the AWS-MDRs following deletion of non-resident taxa, since benthic crustaceans are not included in the resident species list (Table 2-2). Given that both sites could contain appropriate habitat because other benthic macroinvertebrates are resident taxa, we determined that benthic crustaceans could potentially occur at these sites. Therefore, the three isopods (*Asellus aquaticus*, *Caecidotea communis*, and *Caecidotea bicrenata*) and three amphipods (*Hyalella azteca*, *Gammarus italicus*, and *Gammarus* sp.) retained at genus level or lower at the other arid West sites were retained in the calculation. An additional code not previously used by the EPA of "R" ("retained") was assigned to these species in Appendix 3 of this report.

Table 9-5
Site-Specific Acute Zinc Toxicity Databases Ranked by Species Mean Acute Values (SMAV)

Species	Common Name	SMAV (µg/L)	Site-Specific Ranking							
			Santa Ana River	Santa Cruz River		Salt/Gila Rivers	Fountain Creek	South Platte River	SW	HP
				Near Nogales	Near Tucson *					
Argia Sp.	Damselfly	89,488	39	27	21	38	40	41	47	43
Trichoptera	Caddisfly	58,100	38	26	20	37	39	40	46	42
Gambusia affinis	Mosquitofish	32,370	37	25	19	36		39	45	42
Zygoptera	Damselfly	26,200	36	24	18	35	38	38	44	40
Chironomus plumosus	Midge	21,825	35	23	17	34	37	37	43	39
Crangonyx pseudogracilis	Amphipod	19,800				33				
Lepomis gibbosus	Pumpkinseed	18,778	34	22	16	32	36	36	42	38
Nais Sp.	Worm	18,400	33	21	15	31	35	35	41	37
Chironomus Sp.	Midge	18,200	32	20	14		34	34	40	36
Asellus aquaticus	Isopod	18,200		19	13		33	33		35

Table 9-5 (Continued)
Site-Specific Acute Zinc Toxicity Databases Ranked by Species Mean Acute Values (SMAV)

Species	Common Name	SMAV (µg/L)	Site-Specific Ranking: Santa Ana River	Santa Cruz River: Near Nogales	Santa Cruz River: Near Tucson *	Salt/Gila Rivers	Fountain Creek	South Platte River	SW	HP
Fundulus diaphanus	Banded killifish	17,935					32	32		34
Aeolosoma headleyi	Worm	17,362	31						39	
Lepidostoma sp.	Caddisfly	15,054	30	18	12	29	31	31	38	33
Morone americana	White perch	13,439				28	30	30	37	32
Caecidotea communis	Isopod	11,614	29	17	11		29	29	36	31
Carassius auratus	Goldfish	10,276	28			27	28	28	35	30
Lumbriculus variegatus	Worm	9,744	27	16			27		34	29
Tubifex tubifex	Worm	9,612	26	15	10	26	26	27	33	28
Isoperla sp.	Stonefly	8,952	25		9		25	26	32	27
Gammarus sp.	Amphipod	8,100	24	14	8	25	24	25	31	26
Cyprinus carpio	Common carp	7,245	23			24	23	24	30	25
Girardia tigrina	Flatworm	7,004	22			23	22	23	29	24
Echinogammarus tibaldii	Amphipod	6,788				22				
Ptychocheilus oregonensis	Northern pikeminnow	6,495				21	21	22	28	23
Notemigonus crysoleucus	Golden shiner	6,000				20	20	21	27	22
Poecilia reticulata	Guppy	5,926	21			19			26	
Caecidotea bicrenata	Isopod	5,677	20	13	7		19	20	25	21
Lepomis macrochirus	Bluegill	5,290	19	12	6	18	18	19	24	20
Catostomus commersonii	White sucker	5,263	18	11		17	17	18	23	19
Corbicula fluminea	Asiatic clam	4,892	17					17	22	18
Xiphophorus maculatus	Southern platyfish	4,308				16			21	
Pimephales promelas	Fathead minnow	3,808	16			15	16	16	20	17
Gammarus italicus	Amphipod	2,306	15	10	5	14	15	15	19	16
Ptychocheilus lusius	Colorado pikeminnow	2,186					14	14		15
Gila elegans	Bonytail	2,013	14	9		13	13	13	18	14
Lophopodella carteri	Bryozoan	1,688	13						17	
Physa gyrina	Snail	1,686	12	8		12	12	12	16	13
Jordanella floridae	Flagfish	1,673				11			15	
Xyrauchen texanus	Razorback sucker	1,632				10		11	14	12
Plumatella emarginata	Bryozoan	1,589	11						13	
Helisoma campanulatum	Snail	1,579	10				11	10	12	11
Pectinatella magnifica	Bryozoan	1,292	9						11	
Drunella grandis	Mayfly	1,264	8	7	4	9	10	9	10	10
Limnodrilus hoffmeisteri	Worm	1,258	7	6	3	8	9	8	9	9
Physa heterostropha	Snail	1,087	6	5		7	8	7	8	8
Ranatra elongata	Water scorpion	830	5	4	**2	6	7	6	7	7
Oreochromis mossambicus	Mozambique tilapia	786	4			5	6	5	6	6
Salmo trutta	Brown trout	647					5			5
Catostomus latipinnis	Flannelmouth sucker	600	3	3		4	4	4	5	4
Hyalella azteca	Amphipod	241	2	2	1	3	3	3	4	3
Agosia chrysogaster	Longfin dace	226		1		2	2	2	3	2
Cottus bairdi	Mottled sculpin	182	1						2	
Morone saxatilis	Striped bass	119				1	1	1	1	1
	Final Acute Value (µg/L) =	**310**	**237**	**241**	**200**	**212**	**218**	**187**	**230**	
	Final Chro[illegible] Value (µg/L) =	**131**	**100**	**102**	**85**	**90**	**92**	**79**	**97**	

NOTES: SW = Southwest Region HP = High Plains Region
* = Did not meet the MDRs; therefore FAV was lowered to the most sensitive species in database
SMAV and resulting FAV/FCV based on hardness = 50 mg/L

9.5.2.1 Santa Cruz near Nogales

The resulting site-specific acute zinc toxicity database for the Santa Cruz River near Nogales contains 27 species (Table 9-5). Once again, given the lowest level of identification, these species represent at least 16 families and meet the AWS-MDRs. The four most sensitive species in the database include *Morone saxatilis*, *Agosia chrysogaster*, *Hyalella azteca*, and *Catostomus latipinnis* (Table 9-5). The resulting FAV and FCV are 237 and 100 µg/L, respectively, which are approximately 38% greater than the updated zinc values presented in Chapter 7 of this report (Figure 9-6). Only one endangered species, *Poeciliopsis occidentalis*, was identified as a resident in the Santa Cruz River near Nogales site. Possible surrogates could be *Xiphophorus maculates*, *Gambusia affinis*, or *Poecilia reticulata*, since all are Poecilids.

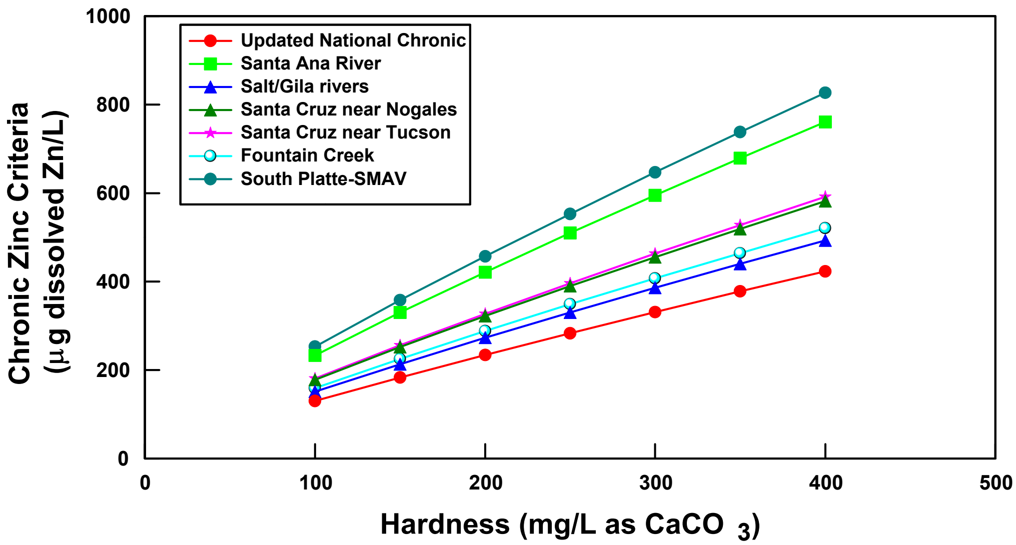

Figure 9-6
Comparison of Site-Specific Chronic Zinc Criteria to the
Updated National Chronic Zinc Criteria at Various Hardness Concentrations

9.5.2.2 Santa Cruz near Tucson

The resulting site-specific acute zinc toxicity database for the Santa Cruz River near Tucson contains 21 species representing 13 families, which is the most limited database of all sites under consideration for recalculation for zinc. The resulting numbers of families do not meet the AWS-MDRs, since an organism within the Family Cyprinidae does not reside at the site. The four most sensitive species in this database (*H. azteca*, *Ranatra elongate*, *Limodrilus hoffmeisteri*, and *Drunella grandis*) result in the widest range of SMAVs of all sites (Table 15-1). However, the FAV must default to the SMAV of the most sensitive species in the site-specific database because more eight Families are present, but the specific AWS-MDRs are not met. The resulting FAV and FCV are 241 and 102 µg/L, respectively, which are approximately 40% greater than the updated zinc values presented in Chapter 7 of this report (Figure 9-6). This defaulted FAV is only slightly lower than what would result from a 5th percentile FAV calculation.

9.5.3 Salt/Gila Rivers

The only documentation of benthic crustaceans for the Salt/Gila Rivers is the presence of the Order Amphipoda. Therefore, all species within this Order were retained in the site-specific database. The resulting site-specific acute zinc toxicity database for the Salt/Gila Rivers contains 39 species representing at least 18 Families, and meets the AWS-MDRs. The four most sensitive species in the database include *M. saxatilis*, *A. chrysogaster*, *H. azteca*, and *Catostomus latipinnis* (Table 9-5). The resulting FAV and FCV are 201 and 85 µg/L, respectively, which are approximately 15% greater than the updated zinc values presented in Chapter 7 of this report (Figure 9-6).

The Salt/Gila Rivers resident species analysis identified five threatened or endangered species, including *Xyrauchen texanus*, *Gila elegans*, *Rhinichthys cobitis*, *Cyprinodon macularius*, and *Poeciliopsis occidentalis*. Two of these species, *X. texanus* and *G. elegans*, are in the database therefore no surrogates are required. *R. cobitis*, is not in the site-specific database. However, all Cyprinids in the updated national zinc database were retained, except *Ptychocheilus oregonensis* because the genus was already represented. Any of these Cyprinids could be a surrogate for *R. cobitis*. *C. macularius* is within the Family Cypridonotidae. The updated national database contains only one species within this Family, *Jordanella floridae*. *J. floridae* was retained at the Family level (Appendix 3), and is a potential surrogate for *C. macularius*. Possible surrogates for *P. occidentalis* are *X. maculates*, *G. affinis*, or *P. reticulata*, since all are Poecilids.

9.5.4 Fountain Creek

The site-specific acute zinc toxicity database for the Fountain Creek contains 40 species, representing at least 22 families and meets the AWS-MDRs. The four most sensitive species in the database include *M. saxatilis*, *A. chrysogaster*, *H. azteca*, and *C. latipinnis* (Table 9-5). The resulting FAV and FCV are 212 and 90 µg/L, respectively (at hardness = 50 mg/L), which are approximately 25% greater than the updated zinc values presented in Chapter 7 of this report (Figure 9-6).

9.5.5 South Platte River

The site-specific acute zinc toxicity database for the South Platte River contains 41 species, representing at least 22 Families and meets the AWS-MDRs. The South Platte River analysis resulted in the largest database of all sites under consideration for recalculation. The four most sensitive species in the database include *M. saxatilis*, *A. chrysogaster*, *H. azteca*, and *C. latipinnis* (Table 9-5), which are identical to the four most sensitive species for Fountain Creek. The resulting FAV and FCV are 218 and 92 µg/L, respectively, which are approximately 27% greater than the updated zinc values presented in Chapter 7 of this report (Figure 9-6).

9.5.6 Southwest Arid Stream Systems (CA, AZ, NV, NM)

Combining the resident species lists for the Santa Ana River, Salt/Gila Rivers, and both sites for the Santa Cruz River resulted in a Southwest regional acute zinc toxicity database containing 48 species, representing at least 28 families (Table 9-5). This regional database is in compliance with the AWS-MDRs. Although the Southwest database is more robust than any individual site-specific database, the distribution of the SMAVs for the four most sensitive species (*M. saxatilis*, *Cottus bairdi*, *A. chrysogaster*, and *H. azteca)* results in a more restrictive criterion than any of the site-specific recalculations. The resulting FAV and FAC are 187 and 79 µg/L, respectively, which are only 9% greater than the updated zinc values presented in Chapter 7 of this report (Figure 9-7). Because the Southwest region species list was created from a pooled river resident species list, the regional list included all six threatened or endangered species found in those rivers. The site-specific database also contains all of the species that were identified as surrogates in each of the pooled rivers therefore surrogate species for the Southwest region are similar and were identified in previous sections.

9.5.7 High Plains Arid Stream Systems (WY, CO, NM)

Combining the resident species lists for the Fountain Creek and the South Platte River results in a High Plains regional acute zinc toxicity database containing 43 species, representing at least 24 families (Table 9-5). This regional database is in compliance with the AWS-MDRs. Since the database size is only slightly greater than the site-specific databases for the two study streams and the four most sensitive species are identical for both sites, the resulting FAV and FCV are only moderately greater than the site-specific values. The resulting criteria (Figure 9-7) are approximately 34% greater than the updated zinc values presented in Chapter 7 of this report.

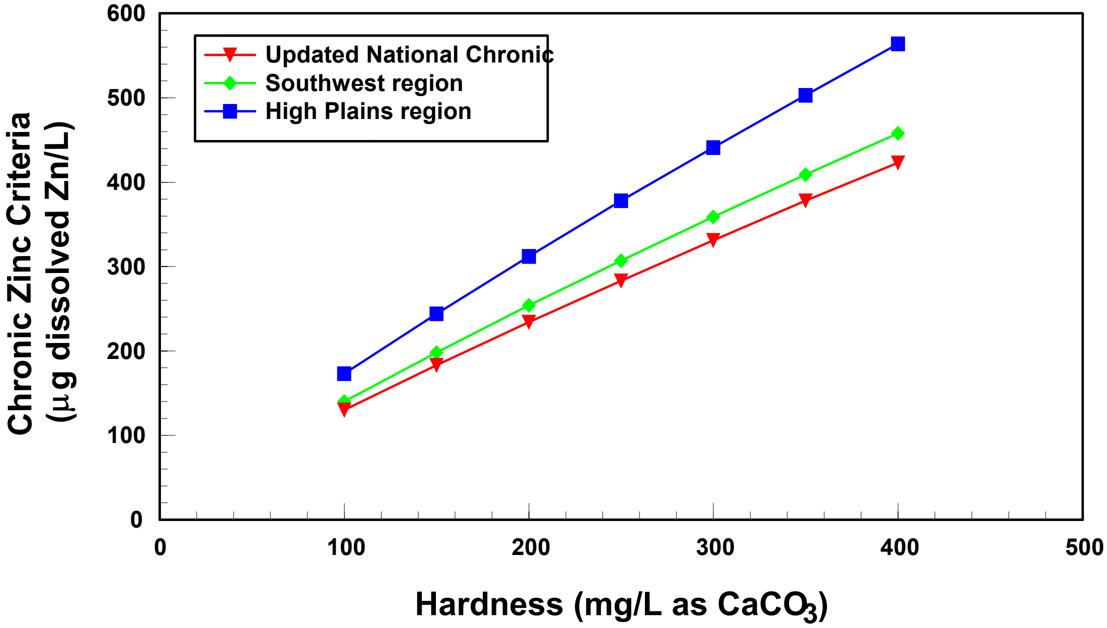

Figure 9-7
Comparison of the Region (Southwest and High Plains) Specific Chronic Zinc Criteria to the Updated National Chronic Zinc Criteria at Various Hardness Concentrations

9.6 LITERATURE CITED

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10.0 SUMMARY OF RECALCULATION ANALYSES

10.1 COMPARISONS OF SITE-SPECIFIC STANDARDS TO UPDATED NATIONAL CRITERIA

For ease of analysis, Chapter 9 used "absolute" toxicity values (FAV or FCV) for comparison of the results of recalculated vs. national criteria. In this way, values normalized to like hardness or pH could be compared directly.

To present comparisons of actual recalculated site-specific standards to national criteria, the equations or CMC and CCC values for each contaminant and each site are solved for mean hardness and pH of each site, as appropriate. Historical ambient water quality data for the study streams were derived using water quality data presented in the arid West HCS (PCWWM 2002) and from the BLM validation study (PCWWM 2005).

10.1.1 Santa Ana River

An average total hardness of 188 mg/L as $CaCO_3$ and average pH of 7.2 were used in the site-specific criteria derivation process below, based on water quality data from the HCS and BLM validation study. Site-specific criteria are less restrictive than the updated copper, daizinon and zinc criteria, near equivalent to the updated ammonia criteria, and more restrictive than the updated aluminum criteria (Tables 10-1 and 10-2).

10.1.2 Santa Cruz River

Average ambient water quality data for the Santa Cruz River near Nogales and Tucson sites were estimated from the arid West HCS (PCWWM 2002) water quality figures. An average hardness of 170 mg/L as $CaCO_3$ and pH of 7.5 for the Santa Cruz near Nogales site, and hardness of 150 mg/L as $CaCO_3$ and pH of 7.2 for the near Tucson sites, were used in the site-specific criteria derivations below. Site-specific criteria for the near Nogales site were less restrictive than the updated aluminum, copper, daizinon and zinc criteria, and near equivalent to the updated ammonia criteria (Tables 10-1 and 10-2). Similar relationships with the updated criteria resulted for the near Tucson site, except no criterion was derived for aluminum.

Table 10-1
Site-Specific Acute Criterion Concentrations for Each Chemical Using Mean Hardness and pH When Necessary

	Site-Specific CMC						Regional CMC	
	Santa Ana River	Santa Cruz Near Nogales	Santa Cruz Near Tucson	Salt/ Gila River	Fountain Creek	South Platte River	Southwest Region	High Plains Region
Hardness (mg/L)	188	170	150	388	218	280	208	247
pH	7.2	7.5	7.2	7.4	7.4	7.4	7.3	7.4
Aluminum (µg total Al/L)	3464 (3856)	6054 (3546)	NA (3195)	7763 (7050)	3609 (4362)	4826 (5373)	3768 (4195)	4005 (4840)
Ammonia (mg TA-N/L)	28.38 (27.52)	18.53 (18.53)	26.81 (27.52)	21.16 (21.40)	22.07 (21.40)	21.63 (21.40)	24.96 (24.42)	21.79 (21.40)
Copper (µg dissolved Cu/L)	29.93 (16.96)	27.84 (15.36)	21.32 (13.59)	63.36 (34.49)	35.18 (19.57)	45.68 (25.05)	36.42 (18.69)	40.56 (22.14)
Diazinon (µg total diazinon/L)	8.56 (0.11)	9.12 (0.11)	12.50 (0.11)	12.72 (0.11)	9.32 (0.11)	9.32 (0.11)	9.32 (0.11)	9.32 (0.11)
Zinc (µg dissolved Zn/L)	470.2 (261.5)	329.9 (239.9)	301.4 (215.6)	565.0 (485.3)	364.2 (296.2)	464.0 (367.4)	308.2 (284.6)	439.4 (329.9)

NOTES:
NA = Data were not available to derive criteria for that site (see Chapter 9 for discussion).
Values in () = updated national acute criterion, given site hardness or pH, for comparison.

Table 10-2
Site-Specific Chronic Criterion Concentrations for Each Chemical Using Mean Hardness and pH when Necessary

	Site-Specific CCC						Regional CCC	
	Santa Ana River	Santa Cruz Near Nogales	Santa Cruz Near Tucson	Salt/ Gila River	Fountain Creek	South Platte River	Southwest Region	High Plains Region
Hardness (mg/L)	188	170	150	388	218	280	208	247
pH	7.2	7.5	7.2	7.4	7.4	7.4	7.3	7.4
Aluminum (µg total Al/L)	1384 (1541)	2420 (1417)	NA (1277)	3103 (2818)	1443 (1744)	1929 (2148)	1506 (1677)	1601 (1935)
Ammonia (mg TA-N/L)	11.58 (11.23)	7.56 (7.56)	10.94 (11.23)	8.64 (8.73)	9.00 (8.73)	8.83 (8.73)	10.19 (9.97)	8.89 (8.73)
Copper (µg dissolved Cu/L)	12.31 (6.97)	11.90 (6.57)	9.57 (6.10)	19.63 (10.69)	13.65 (7.61)	16.08 (8.82)	14.39 (7.40)	14.99 (8.19)
Diazinon (µg total diazinon/L)	8.56 (0.11)	9.12 (0.11)	12.50 (0.11)	12.72 (0.11)	9.32 (0.11)	9.32 (0.11)	9.32 (0.11)	9.32 (0.11)
Zinc (µg dissolved Zn/L)	399.6 (222.2)	280.4 (203.9)	256.1 (183.2)	480.2 (412.4)	310.1 (252.1)	394.3 (312.2)	262.3 (242.2)	373.6 (280.5)

NOTES:
NA = Data were not available to derive criteria for that site – see Chapter 9 for discussion
Values in () = updated national chronic criterion, given site hardness or pH, for comparison.

10.1.3 Salt/Gila Rivers

Salt/Gila Rivers chemical data were based on water quality data from the HSC and BLM validation study. The Salt/Gila Rivers have an average hardness of 388 mg/L with a pH of 7.4, which were used in the site-specific criteria calculations below. Aluminum and ammonia site- specific criteria for the Salt/Gila Rivers are nearly equivalent to the updated national criteria, where as results for site-specific copper, diazinon, and zinc criteria are less restrictive than the updated national criteria (Tables 10-1 and 10-2).

10.1.4 Fountain Creek

Fountain Creek historical ambient water quality data were obtained from the arid West HCS (PCWWM 2002). Average water hardness of 218 mg/L as $CaCO_3$ and pH of 7.4 were used for the site-specific criteria derivations below. Like the Santa Ana River, site-specific criteria are more restrictive than the updated national criteria for aluminum, near equivalent to the updated ammonia criteria, and less restrictive than the updated national copper diazinon, and zinc criteria (Tables 10-1 and 10-2).

10.1.5 South Platte River

South Platte River historical chemical data were based on water quality data from the HSC and BLM validation study. The South Platte has an average hardness of 280 mg/L as $CaCO_3$ and pH of 7.4, which were used in the site-specific criteria calculations. Comparisons of these site-specific standards to national criteria are summarized in Tables 10-1 and 10-2.

10.1.6 Southwest Region

Ambient water quality data should be used in the application of a regional criterion to a particular site. To provide an example of potential criteria that would be derived using the southwest databases, we estimated an average water hardness and pH for the southwest region by taking the geometric mean of respective values. The resulting average water hardness of 208 mg/L as $CaCO_3$ and pH of 7.3 were used in the regional criteria calculations. Southwest region criteria are generally similar to the site-specific values, except for zinc, which is nearly equivalent to the updated national criteria (Tables 10-1 and 10-2).

10.1.7 High Plains Region

Once again, ambient water quality should be used in the application of regional criteria to a particular site. To provide an example of criteria using the high plains databases we calculated an average water hardness and pH from the water quality data of two high plains sites used in this analysis. The resulting average hardness of 247 mg/L as $CaCO_3$ and pH of 7.4 were used in the example high plains regions calculations below. The

High Plains database derived moderate criteria that are between the site-specific values for the two sites taken into consideration (Tables 10-1 and 10-2), except for daizinon, in which all criteria are equivalent.

10.1.8 Conclusions on Usefulness of Recalculation Procedure for Arid West Effluent Dominated Streams

To quantify the relative numeric implication of applying the arid West recalculation procedure for particular contaminant/site combinations, we compared these site-specific standards with their respective updated national criteria (Table 10-3). A net change of 10% in the site-specific standard vs. national criteria was used to quantify whether calculating site-specific criteria via the recalculation procedure would have a significant impact relative to national criteria for a particular contaminant at a particular site. Note that the "significance" of the recalculation procedure in this context is not based on the results being less or more restrictive than national criteria, but rather on whether a recalculated criterion was more than 10% different.

Table 10-3
Recalculation Findings Decision Matrix

	Santa Ana River	Santa Cruz near Nogales	Santa Cruz near Tucson	Salt/Gila Rivers	Fountain Creek	South Platte River	Southwest Region	High Plains Region
Aluminum	-	+	NA	=	-	-	-	-
Ammonia	=	=	=	=	=	=	=	=
Copper	+	+	+	+	+	+	+	+
Diazinon	+	+	+	+	+	+	+	+
Zinc	+	+	+	+	+	+	=	+

NOTES:
+ = recalculated criteria are less restrictive than national updated criteria.
- = recalculated criteria are more restrictive than national updated criteria.
= = less than 10% change in recalculated criteria from national updated criteria.
NA = Data were not available to conduct the analysis.

Results suggest that the recalculation procedure for development of site-specific standards would generally derive substantially different criteria concentrations for all of the case-study streams. The one exception to this is ammonia, which shows no noteworthy change when compared to the updated national criteria following recalculation.

10.2 CRITERIA-SPECIFIC ISSUES WITH THE RECALCULATION PROCEDURE

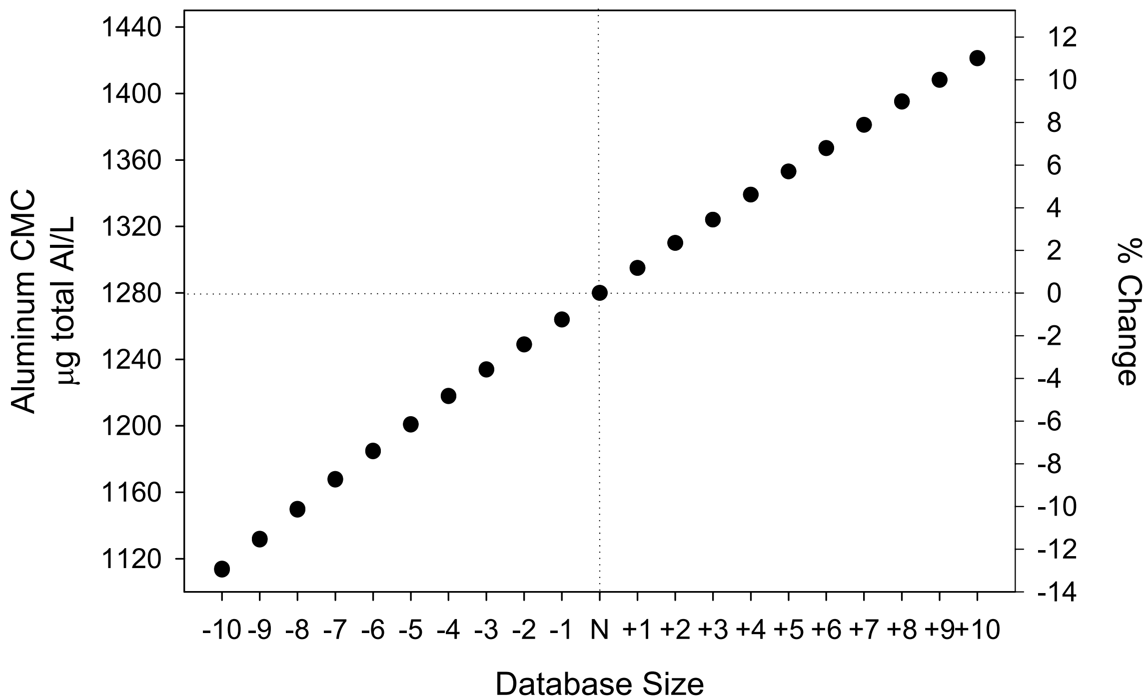
The following discussion provides a summary of the issues that arose during the recalculation evaluation for each criterion, with comments on the mechanics of updating the national criteria, creating site-specific databases, and deriving final site-specific criteria.

10.2.1 Aluminum

Since publication of EPA's (1988) aluminum AWQC document, many refinements on the AWQC derivation process and published aquatic organism toxicity data have become available. The relatively outdated aluminum criteria document was a good candidate for an update (Chapter 3), which would also include hardness-based equations for criteria derivation (Table 3-8). This is particularly important in arid Western streams that average moderate to high hardness (PCWWM 2002). These new criteria reflect our findings that aluminum becomes less toxic to aquatic organisms as hardness increases, probably through complex speciation dynamics that determine the solubility and, ultimately, exposure of organisms to aluminum.

Compared to the updated national aluminum criteria, site-specific aluminum criteria were more restrictive or equal to the national criteria, except for the Santa Cruz near Nogales site (Table 10-4; Chapter 9.1). This would appear to be counterintuitive at first, considering that the most sensitive species, *Salmo salar*, was deleted from all but one site-specific database, Fountain Creek (Section 9.1.4).

These counter intuitive findings resulted from two general commonalities among all databases that influence the FAV calculation. First, all site-specific databases contained greater variability in the four lowest SMAVs, resulting in less confident FAV calculations and, hence, more restrictive criteria. Variance of these site-specific recalculations was on average 10 fold greater than the national update variance. Second, the site-specific databases resulted in fewer taxa than the updated national databases. This reduction in number of species (N) within the site-specific toxicity databases decreases the degrees of freedom afforded to the four lowest ranked SMAVs. As with sample variability, the degrees of freedom (i.e., database size or sample size) is very influential in final criteria calculations (Figure 10-1). A larger database lowers the weight of the four lowest SMAVs, as the probability of 95% protection is diluted among more organisms.



NOTE: Each addition or deletion of a taxon creates in approximate ±1.2% change from the original CMC. This change is constant regardless of initial size of the database (N).

Figure 10-1
Range of Aluminum Criterion Maximum Concentrations (CMC) Resulting from a Change in Database Size, While Holding the Four Most Sensitive Species Constant (N = Number of Genera in the Updated National Acute Toxicity Database for Aluminum [N=18])

This scenario is exemplified when comparing criteria calculated from two databases with four identically ranked SMAVs and a dissimilar number of ranked species. For example, the four most sensitive species in the Santa Ana River and high plains region databases were identical (Table 9-1), yet the Santa Ana River site-specific aluminum standard was more restrictive than the high plains regions due to its smaller site-specific toxicity database. Although not as influential as variability among the four most sensitive SMAVs, the total numbers of ranked species (i.e., sample size or degrees of freedom) determines the probability of 95% protection in FAV calculations, and so should be considered when comparing criteria or evaluating the utility of the recalculation procedure for criteria with small toxicity databases.

In other words, the lower aluminum criteria that resulted after our site-specific recalculation procedure were not necessarily due to the presence of more sensitive species, but the result when using a criterion with a toxicity database that contains few species. Increased variability between the four lowest SMAVs, coupled with smaller site-specific databases, was more influential in the final recalculation procedure outcomes than using the more representative assemblage of arid West organisms. In fact, the assemblages of organisms in the site-specific aluminum databases were less sensitive to aluminum than the national updated database, although five of the eight recalculated criteria were more restrictive than updated national criteria (Table 10-3).

We would recommend adoption of the updated aluminum AWQC presented in the national review and update (Chapter 3) and continue further investigation into site-specific recalculations when a more robust database becomes available. The updated national recalculations provide new criteria derived by a water quality equation that could potentially supersede the outdated U.S. EPA criteria recommendations (EPA 1988). The updated aluminum criteria with hardness- based criteria equations thus may prove to be a more useful tool than the recalculation procedure for adjusting criteria for arid West streams.

10.2.2 Ammonia

The EPA national ammonia (EPA 1999) criteria utilize two acute equations as a function of pH to derive ammonia criteria, one equation for sites with salmonids and one for sites without salmonids. In our review of the national criteria (Chapter 4), we critically addressed issues of including or excluding "large" *Oncorhynchus mykiss* age-class toxicity values that were influential in establishing the separate equations, as well as recently published unionid clam toxicity data.

We also reviewed and updated the chronic criterion and deriving chronic criteria via a FACR calculation, rather than the approach used by EPA. This approach was suggested because of the limited chronic toxicity database that did not meet important MDRs. Generally, when the chronic toxicity database does not meet the MDRs, the chronic criterion is derived via a FACR (Stephan et al. 1985). Furthermore, the EPA 1999 document assumed a possible age-dependent ammonia chronic toxicity relationship. To account for this, final chronic criteria included a temperature component as a surrogate to protect early life stage fish in the form of two separate chronic equations. Unfortunately, evidence of a temperature-dependent chronic ammonia toxicity relationship was based on only one study (Arthur et al. 1987), which reported a non-statistically significant relationship in their acute testing. Coupled with conflicting fish and invertebrate temperature data, this led to development of national chronic criteria primarily driven only by *Lepomis* and *Hyalella*. It is questionable that a criterion derived from two organisms provides the diversity of data needed to protect aquatic organisms from chronic ammonia exposure.

The irregularly and questionably derived acute and chronic ammonia criteria provided us with an opportunity to improve the national criteria development as part of the arid West recalculation procedure evaluation.

Considerable changes in the updated criteria were recommended in how the acute criteria are developed, while still using basic methodologies set forth in the original document (EPA 1999). Instead of separate equations for "salmonids present or absent," we proposed updated criteria that included warm water biota and cold water biota equations. Additionally, given the sensitivity and distribution of Unionids, the warm water criterion was separated into two equations for sites with and without Unionids. These habitat-based criteria account for potential differences in sensitivity of cold and warm water species. Both the updated acute and chronic criteria equations are solely a function of pH, with no temperature component beyond habitat characterization, consistent with the current EPA acute equations.

Another major improvement over existing criteria derivation was the development of a FACR for use in the derivation of chronic criteria rather than the approach used by the EPA. Although we slightly deviated from the 1985 Guidelines when deriving the FACR by using acute and chronic toxicity values derived among different studies, we believe this approach is more scientifically defensible than methods used by the authors of the current national criteria (EPA 1999). In summary, our critical review and update to the national AWQC was very important in clarifying technical issues with the existing criteria and created a user-friendly, habitat-oriented database which is more useable in deriving arid West site-specific ammonia criteria with the recalculation procedure than the existing equations.

Selection of ammonia to exemplify steps in arid West site-specific criteria development provided an opportunity to practice recalculation procedures on a robust updated national database while utilizing unique criteria derivation equations. From our analysis, a few technical generalizations can be made. First, there is little variability in site-specific standards between any of the sites or regions (Table 10-2). This was still the case in the Santa Cruz near Tucson site in which the FAV defaulted to the most sensitive species, and among sites with dissimilar ranked or total number of ranked SMAVs. Second, regional criteria are less restrictive than all but one site-specific criterion. This is directly associated with using the larger regional toxicity databases when compared to the site-specific databases. As previously mentioned in the aluminum analysis, a larger database numerically lowers the influence of the four most sensitive SMAVs, as the probability of 95% protection is diluted among more organisms. Finally, recalculated site-specific criteria do not deviate far from the updated national warm water without Unionid ammonia criterion. The similarity in results for all sites and regions with the updated national criterion suggest that site-specific recalculations for ammonia might not be necessary, as our breakdown of warm and cold water habitats proposed in our national updated ammonia criteria accounts for site-specific differences in arid-west streams, making further species-based recalculation efforts unnecessary.

10.2.3 Copper

Copper was selected due to its prevalence in effluent-dependent streams, and to provide an example of the recalculation procedure using a toxicant with a large toxicity database that could be modified by multiple ambient water quality characteristics. The original copper AWQC were developed in 1984 (EPA 1985) and later updated in 1995 (EPA 1996). The most recent draft update (EPA 2003) is still in review and uses a BLM to normalize toxicity values according to a myriad of water quality parameters such as temperature, pH, DOC, % humic acid, and major ions.

Although promising, very few toxicity tests found in the national database report all of the model variables needed to run the BLM. The resulting database will be severely limited if the BLM criteria are fully accepted, and application of the recalculation procedure to a BLM-based criteria is not necessarily straightforward. This is because the proposed BLM-based criterion depends numerically on the 50% lethal metal accumulation (LA_{50}) value of a single hypothetical species of 5th percentile sensitivity. Therefore, we decided to abandon the BLM approach in favor of a more robust updated national copper toxicity database (N = 69 genera vs N = 27 genera for the BLM-adjusted database) for our analysis. However, it should be noted that BLM-based criteria tend to be much less restrictive than more traditional hardness-based criteria for many of the same effluent-dependent waters evaluated in the present study (PCWWM 2005).

Many improvements were made to the current copper national criteria during our review (Chapter 5). First, the acute and chronic hardness toxicity water quality relationships were updated and corrected. After our additions to the chronic database, enough chronic toxicity data were available to adequately model a separate chronic toxicity-hardness relationship (Figure 5-2) that did not previously exist. Interestingly, the chronic hardness-relationship is not as "steep" as found in acute data, providing evidence of a less dramatic change in toxicity as a function of hardness. Second, the FACR was revised using the data from similar toxicity tests reported in updated acute and chronic databases. Lastly, we provided updated criteria equations. Our updated criteria are substantially more restrictive than current EPA criteria (Table 5-10) due to the addition of new acute copper toxicity data for sensitive Cladocerans that were not previously represented. However, we suggest cautious acceptance of these updated criteria with all Cladocerans included, since values are highly influenced by the three most sensitive species with SMAVs derived from single, LC_{50}s derived from unmeasured concentrations and reported from one study (Koivisto et al. 1992).

Site-specific copper toxicity databases were created using the arid-west stepwise deletion process and resident species list created for each site. Although zooplankton species were identified at a few of the sites, it was determined that these species were transient organisms and they were removed from the site-specific databases when not formally removed during the deletion process (Appendix 3). Removal of these species effectively muted concern regarding inclusion of the three most sensitive species with single, unmeasured acute values.

The next most sensitive organisms, after zooplankton, were amphipods. In fact, *Hyalella azteca* and *Gammarus pulex* were the most sensitive species found in each site-specific database. In contrast, remaining lists of the less acutely sensitive species were quite variable between sites. Since these amphipods demonstrated roughly seven-fold greater tolerance to copper exposure than the deleted Cladocerans, site-specific copper FAVs were almost double that derived in the updated national database. Although species lists were variable between sites, the site-specific standards were similar among most sites (Tables 10-1 and 10-2). The greatest recalculated copper criteria were derived from the southwest regional database that was one of the two most robust databases. The lowest copper FAV was derived from the Santa Cruz near Tucson database, where the FAV was set to the lowest SMAV. Although the FAVs and FCVs were not diverse among sites, modifying the criteria with site-specific average hardness resulted in substantial differences between sites (Tables 10-1 and 10-2).

In summary, the recalculation procedure for copper provided substantial site-specific differences in criteria concentrations in arid West study streams compared to national criteria. Unlike ammonia, we found a substantial increase in all site-specific criteria compared to national or updated national AWQC (Table 10-2).

10.2.4 Diazinon

Diazinon criteria provided an opportunity to evaluate the recalculation procedure using a nonmetal contaminant for which no final EPA national criteria have yet been established. The environmental significance of diazinon exposure is gaining concern in arid West states such as California, where diazinon runoff from the San Joaquin Valley is resulting in frequent exposure to aquatic life (Werner et al. 2004). Furthermore, diazinon as been suspect in WET testing failures of urban wastewater dominated streams. Our updated criteria were slightly greater than the criteria presented in the (2000) Diazinon Draft (0.22 vs. 0.19 µg/L), which was the result of the increased number of genera that were added to the acute database in our critical review and update of the national criteria (Chapter 6).

Diazinon toxicity databases that reflect the taxonomic profiles for each site were used to calculate criteria that are uniquely protective of resident organisms or their close surrogates. Only one site failed to meet the AWS-MDRs (Santa Cruz River near Tucson), but alternative methods for FAV derivation were successful in generating site-specific criteria. Generally, the two regional criteria were similar to their respective site-specific criteria, and might be helpful in investigating sites beyond those evaluated in the present study.

Resulting site-specific diazinon criteria were substantially greater (i.e., less restrictive) than the updated national criteria. As explained in our aluminum summary above, the relative sensitivity and variability of the four most sensitive taxa are the most influential factors in calculating the FAV. The national database contains sensitive organisms with a high variability in the GMAVs, which resulted in very restrictive national criteria. The hundredfold increase in the site-specific diazinon criteria was therefore due to removal of the most sensitive amphipod (*Gammarus fasciatus*) and the three Cladoceran species that essentially drove the updated national criterion. Additionally, the site-specific databases, with the cladocerans and amphipod removed, are half as variable as the national update, which increases confidence in respective estimates and results in greater values. This added confidence in the FAV calculations, in addition to the loss of more sensitive organisms, led to the considerably less restrictive site-specific diazinon criteria.

Furthermore, the site-specific criterion for diazinon was more variable between sites (8.56 – 12.72 µg/L) than other criteria in this analysis. This variability was partly due to the manipulation of diazinon's moderately sized toxicity database with respect to the resident species lists. Although the most sensitive organisms are similar between most sites, the variability in database size between sites was substantially different. The numbers of species in the site-specific databases range from 8 to 18, resulting in dissimilar degrees of freedom assigned to the 5th percentile organisms. It is also important to note that the greatest site-specific criterion, derived for the Salt/Gila Rivers site was the result of having a high N in conjunction with a unique assemblage of less sensitive species that were specific to the site. The significant increase of the recalculated criterion and the variability of criterion between sites provide some evidence that moderately sized databases are uniquely sensitive to the arid West recalculation procedure. This sensitivity supports our opinion that the arid West recalculation procedure can be useful when establishing diazinon AWQC for effluent dominated streams.

10.2.5 Zinc

Substantial additions to the acute and chronic toxicity databases were made during our update of the current national zinc criteria (EPA 1996). The number of genera in the acute database was increased from 36 to 61 and the chronic database increased from 7 to 10 genera. Two sensitive species were added that previously did not exist in the national database that directly influenced the derivation of the updated national acute criteria, and four toxicity values for *Cottus bairdii* were added from two separate published sources (Woodling et al. 2002; Brinkman and Woodling 2005). These data resulted in ranking *Cottus* as the third most sensitive genus when normalized for hardness. Additionally, new data on acute zinc toxicity to *Thymallus articus* (Buhl and Hamilton 1990) ranked *Thymallus* as the fourth most sensitive genus. Although more sensitive organisms are represented, the larger acute database resulted in updated national acute criteria that were slightly less restrictive than the 1996 zinc criteria.

Although significant additions were made to the national chronic database, the "eight family rule" was still not satisfied. Generally, chronic data are lacking the diversity and robustness seen in the acute database. We were able to refine the FACR from 1.9940 to 2.3726 after addition of newly paired acute and chronic data. This slight adjustment resulted in updated chronic criteria, which are more restrictive than the updated acute criteria. Furthermore, unlike current EPA criteria, chronic values are less restrictive than acute values after application of the conversion factors for dissolved criteria (Table 7-7). Setting a chronic criterion to be higher than the acute criterion is not biologically plausible; therefore the revised FACR is a noteworthy improvement.

Application of the arid West deletion process and subsequent removal of zooplankton resulted in exclusion of half of the species found in the updated national database. These reductions in database size alone could have resulted in more restrictive criteria (e.g., Figure 10-1). However the retained species were generally less sensitive to zinc than the national database. The four most sensitive species in most of the site-specific databases contained three fish and one invertebrate species. This was the same pattern of organisms found in the updated national database, supporting our observation that fish are as acutely sensitive to zinc exposure as invertebrates, even after the most sensitive *Ceriodaphnia* genus was removed.

With the most sensitive zooplankton species in the updated national database removed, the recalculation procedure resulted in less restrictive site-specific criteria than updated national criteria. The difference between site-specific criteria and updated national criteria (Tables 10-1 and 10-2) could have been greater, but the generally high variability among the four most sensitive species and the reduced size of the site-specific databases restrained the final acute value derivations. Low numbers of organisms found in the Santa Cruz sites lowered these site-specific criteria by reducing the degrees of freedom, which also led to MDR failure at the Santa Cruz near Tucson site.

In general, the arid West recalculation procedure applied to the updated national zinc database successfully generates site-specific criteria that reflect the relative sensitivity of organisms at the site, rather than criteria that strictly reflect a change in database size. The species composition of the site-specific databases and ranking were variable among sites, which greatly influenced the variability in the recalculated criteria.

Initiating the deletion process with the robust updated database makes it more likely the site-specific databases will reflect the unique species composition for each arid West site. The significant improvements made when updating the national criteria, coupled with the diversity of resident taxa found in site-specific databases, produces scientifically defendable site-specific zinc criteria.

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11.0 RECOMMENDATIONS

11.1 CONCLUSIONS

11.1.1 Factors Affecting Recalculation "Success"

Based on our analysis, the recalculation procedure can be a useful tool, particularly when modified and applied to arid West streams as recommended in this report. The results of recalculated site-specific criteria were successful for some, but not all AWQC reviewed in this analysis. Success was measured by a change in values of at least 10% from the updated national criteria (any change less than this may or may not be worth the effort) and the biological relevance of the site-specific values.

Successful recalculations conducted in this effort include copper, diazinon and zinc. These toxicants produced universally less restrictive criteria than updated national criteria, while ensuring the same levels of protection for resident fauna for all study streams. Site-specific criteria for diazinon were in general similar among all sites, whereas copper and zinc site-specific criteria were variable among sites. This variability reflected the differences in sensitivity of resident species and community composition between sites, as well as the size of the toxicity database when initiating the deletion process and overlap of resident species with the national toxicity database. It is clear that starting the deletion process for criteria with a more robust toxicity database increases the chance the taxa retained for each site will vary, which then influences the final values.

Criteria that were generally unsuccessful at deriving biologically relevant and/or significant changes compared to national AWQC include ammonia and aluminum, but for two different reasons. For ammonia, the primary reasons are: 1) ammonia criteria are already partitioned into cold and warm water equations. This initial separation at the national level essentially removes many non-resident arid West taxa from the national database, which generates a refined toxicity database for initiating the step-wise deletion process; and 2) the most sensitive species in the updated warm water database are all resident to the arid West. If resident species lists are similar to the toxicity database, the resulting site-specific criteria will be similar.

The issues with recalculation for aluminum criteria were the result of the relatively limited number of species in the updated national toxicity database. Once non-resident taxa were removed during the deletion process, the "sample size effect" overwhelmed the resulting site-specific criteria. Until more aluminum toxicity data are available for more aquatic organisms common to the arid West, it may be more appropriate to adopt the updated national criterion developed in this study, which now incorporates a hardness modification, rather than initiating site-specific standards via the recalculation procedure.

11.1.2 Data Needs and Effort Involved in Recalculation

Although results from the recalculation procedure could successfully be used to derive scientifically defensible site-specific criteria, the tasks involved require considerable effort. The EPA prefers the toxicity database for each criterion to be updated prior to the recalculation, since many of the criteria are based on documents produced up to 20 years ago. This initial step can take considerable effort, especially for the older criteria that have many years of studies to track down and review. Chapters 3 through 7 of this report present the results of this initial step for aluminum, ammonia, copper, diazinon, and zinc AWQC. These updated databases (Appendix 2) can be used as a starting point for future updates to these criteria.

Furthermore, relevant invertebrate and fish population data are required for the development of resident species lists. If no monitoring data exists for a particular stream segment, data from similar rivers in the region could be used. However, there is a chance these data are not very representative of species found at your site. Rather than taking this chance, invertebrate and fish population monitoring plans should be initiated and maintained in the reach of interest.

11.1.3 Is it Worth the Effort?

Regardless of the outcome of the recalculation values, we believe our analysis shows that the investment will be worth the effort. Specifically, the findings assure that any resulting criteria are more relevant for a particular stream than a generalized, often out-dated national value. In fact, simply updating the national criteria, without proceeding with the recalculation procedure, can be worth the effort by establishing more confidence in the calculated values. Alternatively, regional-specific recalculated criteria, such as those presented here for the Southwest and High Plains, would be a cost-effective and protective solution for smaller dischargers in these regions.

11.2 RECOMMENDATIONS

Completion of this analysis of the recalculation procedure in arid West streams has generated the following recommendations:

1) Adopt the arid West modifications to the recalculation procedure outlined in Chapter 8. These modifications include:
   - Use of a revised arid West eight family rule (AW-MDRs), which was specifically designed to better represent aquatic communities expected to occur in arid West stream segments relative to the default eight family rule.

- Use of the refined step-wise deltion process for deriving site-specific toxicity databases.
- Conducting the recalculation procedure on the species level (with SMAVs), rather than at the genus level (with GMAVS) that is presently used in AWQC derivation. Use of SMAVs maximizes the size of the toxicity database, which is particularly important in effluent-dependent waters that may posses limited numbers of resident species.

2) Develop a resident species list for each river segment of interest for development of a site-specific water quality standard.
   - Based the species list on existing monitoring program, if this effort has already been established.
   - Establish a monitoring program if none exists.
     - Data collected should include both fish and invertebrate communities.
     - Efforts can be shared with other dischargers in the basin and potentially coordinated with State and Federal agencies.
3) Support continued updates of existing EPA AWQC.
   - Recommend that the EPA update their older criteria.
     - Permits would then be based on AWQC using most up-to-date toxicity data and information.
   - Alternatively, updates can be completed by other entities.
     - AWWQRP special project
     - WESTCAS
     - Other consortium?
   - However, any update must be approved by the EPA, as well as State and local authorities. This should be done as an open, multi-stakeholder process to ensure any approach would be acceptable at all levels of regulatory authority.
4) It is imperative that more toxicity testing for all AWQC be conducted with species resident to arid West streams.
   - Concentrate on criteria of interest to arid West rivers and criteria with more limited databases (e.g., aluminum, daizinon).
   - Funding for these tests could come from interested parties,
     - USEPA
     - AWWQRP
     - WESTCAS
     - others?

APPENDIX 1
DATA COLLECTION USED FOR DEVELOPING RESIDENT SPECIES LIST

APPENDIX 2
UPDATED TOXICITY DATABASES FOR CRITERIA DEVELOPMENT

APPENDIX 3
RECALCULATION WORKSHEETS