

Copper and Aquatic Life Criteria

Water Quality Standards
Division of Water
Alaska Dept. of Environmental
Conservation

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PART 1. INTRODUCTION

- **Introduce Water Quality Standards**
- **Alaska Water Quality Criteria for Copper**
- **EPA Guidelines for Deriving Water Quality Criteria for Aquatic Organisms**
- **Site Specific Criteria**

WHAT ARE WATER QUALITY STANDARDS?

Use + Criteria = Standard

- **Designated water uses**
 - Drinking, recreation, aquatic life & other uses
 - In Alaska, all waters protected for all uses
- **Criteria are pollutant limits**
 - can be either narrative or numeric
- **The most stringent criteria becomes the WQS**

PART 2. COPPER CRITERIA FOR AQUATIC LIFE

- EPA, *Ambient Water Quality Criteria for Copper – 1984, 1985*
- EPA, *1995 Updates: Water Quality Criteria Documents for the Protection of Aquatic Life, 1996*
- EPA, **California Toxics Rule, 1997**
- EPA, *Nationally Recommended WQ Criteria, 2006*
- DEC, *Alaska Water Quality Criteria Manual For Toxic and Other Deleterious Organic and Inorganic Substances, December 28, 2008*

COPPER CRITERIA FOR AQUATIC LIFE

Freshwater

Acute Criterion = $e^{(0.9422 (\ln \text{Hardness}) - 1.700)} * 0.960$
(dissolved)

Hardness (mg/L)	Equation	Criteria Value (µg/L)
50	$e^{(0.9422 (\ln 50) - 1.700)} * 0.960$	7.0
100	$e^{(0.9422 (\ln 100) - 1.700)} * 0.960$	13
200	$e^{(0.9422 (\ln 200) - 1.700)} * 0.960$	26

COPPER CRITERIA FOR AQUATIC LIFE

Freshwater

Chronic Criterion = $e^{(0.0.8545 (\ln \text{Hardness}) - 1.702)} * 0.960$
(dissolved)

Hardness (mg/L)	Equation	Criteria Value (µg/L)
50	$e^{(0.8545 (\ln 50) - 1.702)} * 0.960$	5.0
100	$e^{(0.8545 (\ln 100) - 1.702)} * 0.960$	9.0
200	$e^{(0.8545 (\ln 200) - 1.702)} * 0.960$	16

COPPER CRITERIA FOR AQUATIC LIFE

Marine Water

- Acute Criterion = 4.8 $\mu\text{g/l}$ (dissolved)
- Chronic Criterion = 3.1 $\mu\text{g/l}$ (dissolved)

COPPER CRITERIA FOR AQUATIC LIFE

- **Acute toxicity - 43 genera @ 50 $\mu\text{g/l}$ hardness**
- **Chronic toxicity - 16 species**
- **Toxicity decreases with increases in hardness, alkalinity and total organic carbon**
- **Fish and invertebrates seem equally sensitive**
- **Plants also tested, not much bioconcentration**
- **Sensitivity in saltwater species varies widely**
- **Oysters can bioaccumulate up to 28,200 times**

PART 3. DERIVING AQUATIC LIFE CRITERIA

- EPA, *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*, 1985

WATER QUALITY CRITERIA COMPONENTS

EPA Criteria are Composed of

- Magnitude,**
- Duration, and**
- Frequency**

FRESHWATER CRITERIA STATEMENT FOR COPPER

The procedures described in the methodology indicate that, except possibly where a locally important species is very sensitive, freshwater aquatic organisms should not be affected unacceptably if the **four-day average** concentration of copper does not exceed the **numerical value (in µg/L) given by the equation**

$$CCC = e^{(0.08545 (\ln \text{Hardness}) - 1.702)} * 0.960$$

more than **once every three years** on the average and if the one-hour average concentration does not exceed numerical value (in µg/L) given by the equation

$$CMC = e^{(0.9422 (\ln \text{Hardness}) - 1.700)} * 0.960$$

more than once every three years on the average.

THE CMC AND CCC

Acute Criterion: The criterion maximum concentration (**CMC**) is the highest instream concentration of a toxicant to which organisms can be exposed for a brief period of time without causing an unacceptable adverse acute effect.

Chronic Criterion: The criterion continuous concentration (**CCC**) is the highest instream concentration of a toxicant to which organisms can be exposed for longer time periods without causing an unacceptable adverse effect.

AQUATIC TOXICITY DATA CONSIDERED

Toxicity data on aquatic animals, plants, bioconcentration/ bioaccumulation studies are considered, however almost all criteria are based on animal studies.



ACUTE TOXICITY DATA

96-hour LC50

Concentration:

0.0 $\mu\text{g/L}$

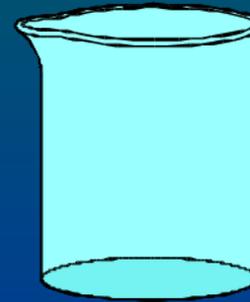
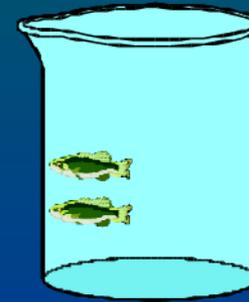
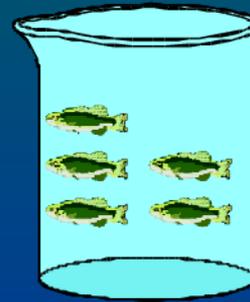
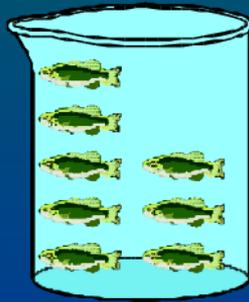
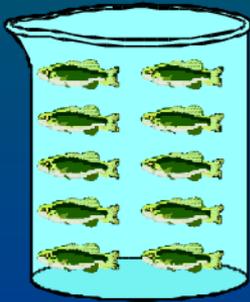
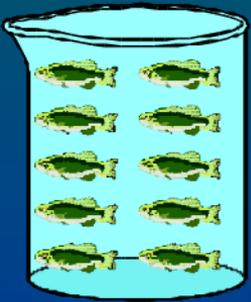
13 $\mu\text{g/L}$

25 $\mu\text{g/L}$

50 $\mu\text{g/L}$

100 $\mu\text{g/L}$

200 $\mu\text{g/L}$



Control

1

2

3

4

5

96-hr LC50 = 50 $\mu\text{g/L}$

CHRONIC TOXICITY DATA

Fathead Minnow Early Life Stage Test Growth Measured as Length

Concentration:

Control

0.0 $\mu\text{g/L}$

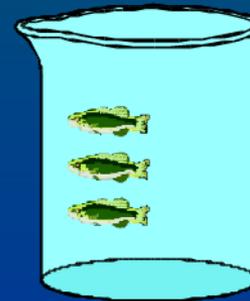
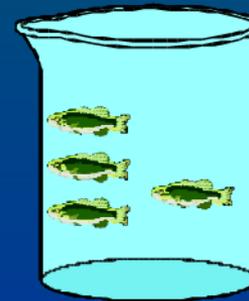
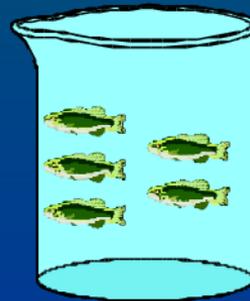
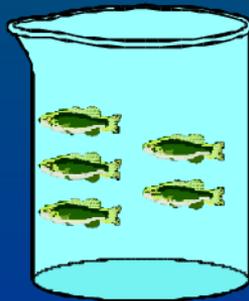
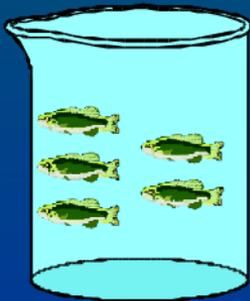
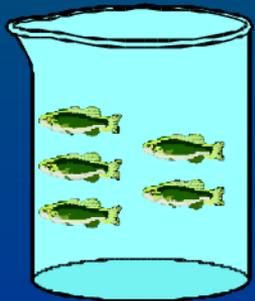
3.8 $\mu\text{g/L}$

7.5 $\mu\text{g/L}$

15 $\mu\text{g/L}$

30 $\mu\text{g/L}$

60 $\mu\text{g/L}$



Length:

40 mm

41 mm

38 mm

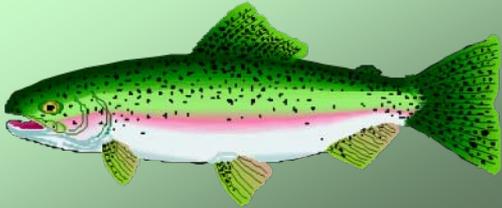
37 mm

25 mm

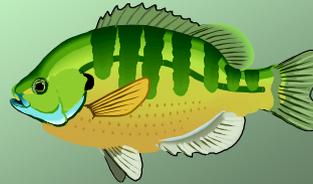
5 mm

MINIMUM DATASET FOR FRESHWATER CRITERIA DERIVATION

SALMONID



**SECOND
FISH
FAMILY**



CHORDATA



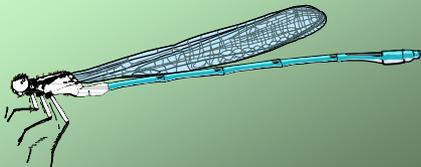
**PLANKTONIC
CRUSTACEAN**



**BENTHIC
CRUSTACEAN**



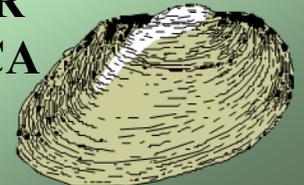
INSECT



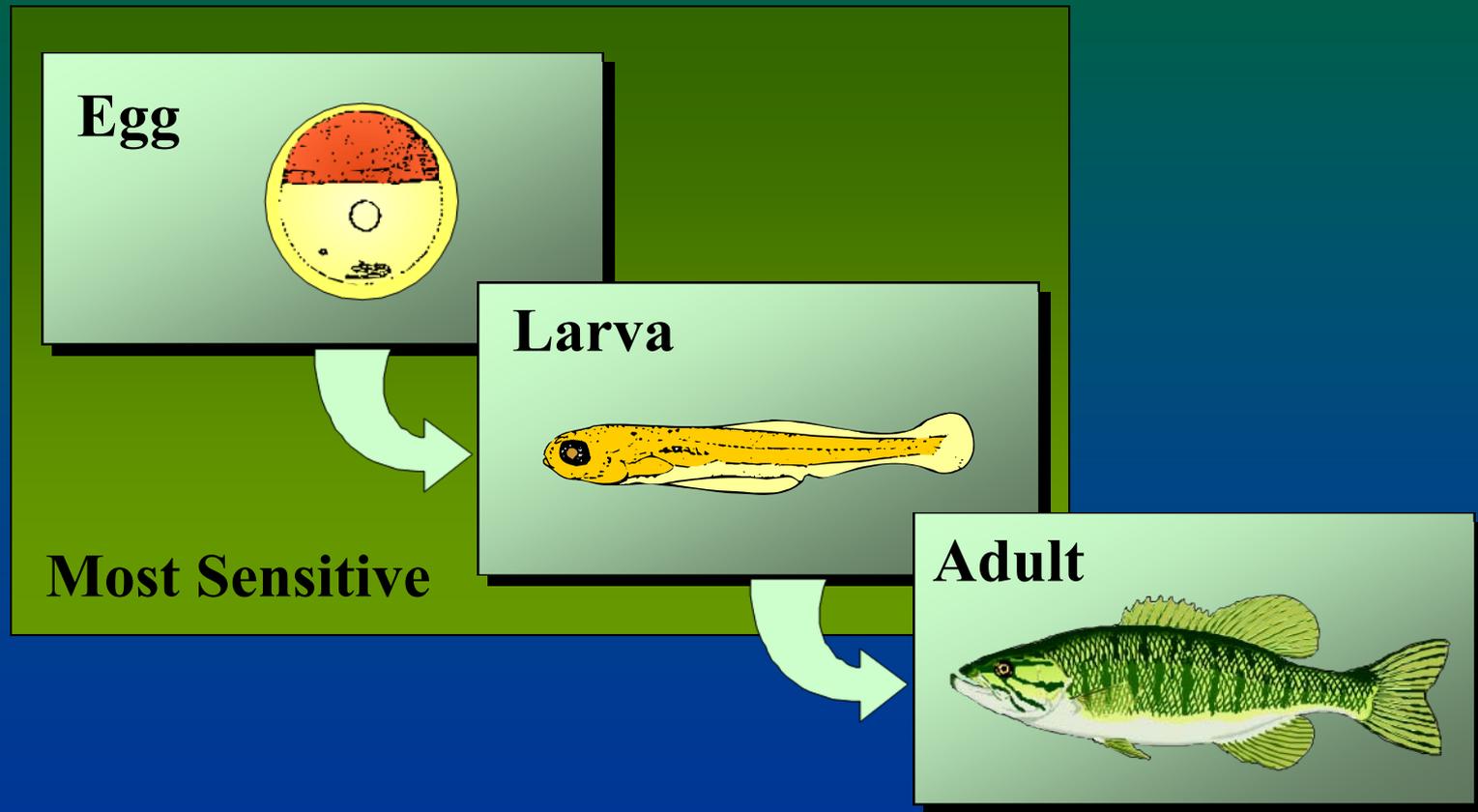
**ROTIFERA,
ANNELIDA,
MOLLUSCA**



**OTHER
INSECT OR
MOLLUSCA**



DATA FROM THE MOST SENSITIVE LIFE STAGES SHOULD BE USED



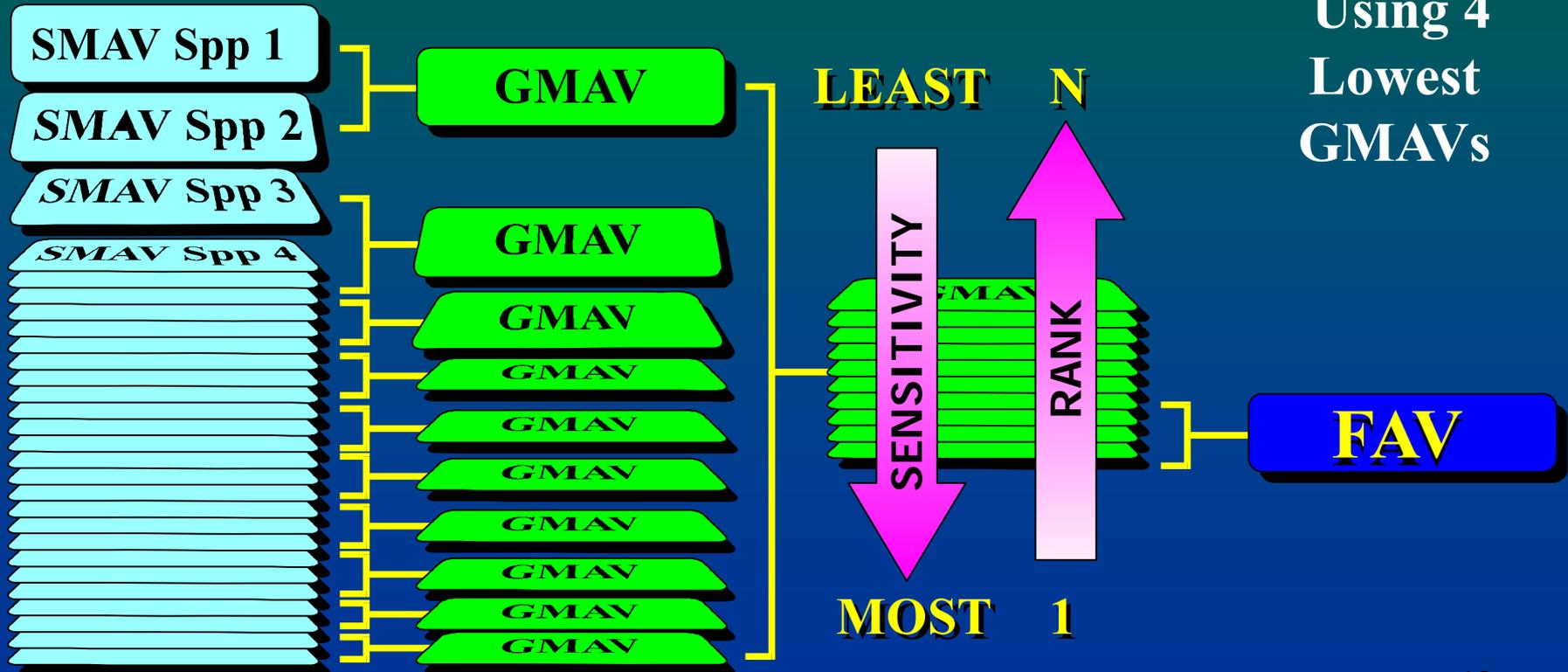
FAV CALCULATION

Step 1.
Calculate
SMAVs

Step 2.
Calculate
GMAVs

Step 3.
Rank
GMAVs

Step 4.
Calculate
FAV
Using 4
Lowest
GMAVs



SPECIES MEAN ACUTE VALUE (SMAV)

Daphnia magna EC50 25 µg/L

Daphnia magna EC50 30 µg/L

Daphnia magna EC50 35 µg/L

Daphnia magna EC50 28 µg/L

SMAV = 29 µg/L

GENUS MEAN ACUTE VALUE (GMAV)

<i>Daphnia magna</i>	SMAV	29 µg/L
<i>Daphnia pulex</i>	SMAV	38 µg/L
<i>Daphnia ambigua</i>	SMAV	42 µg/L

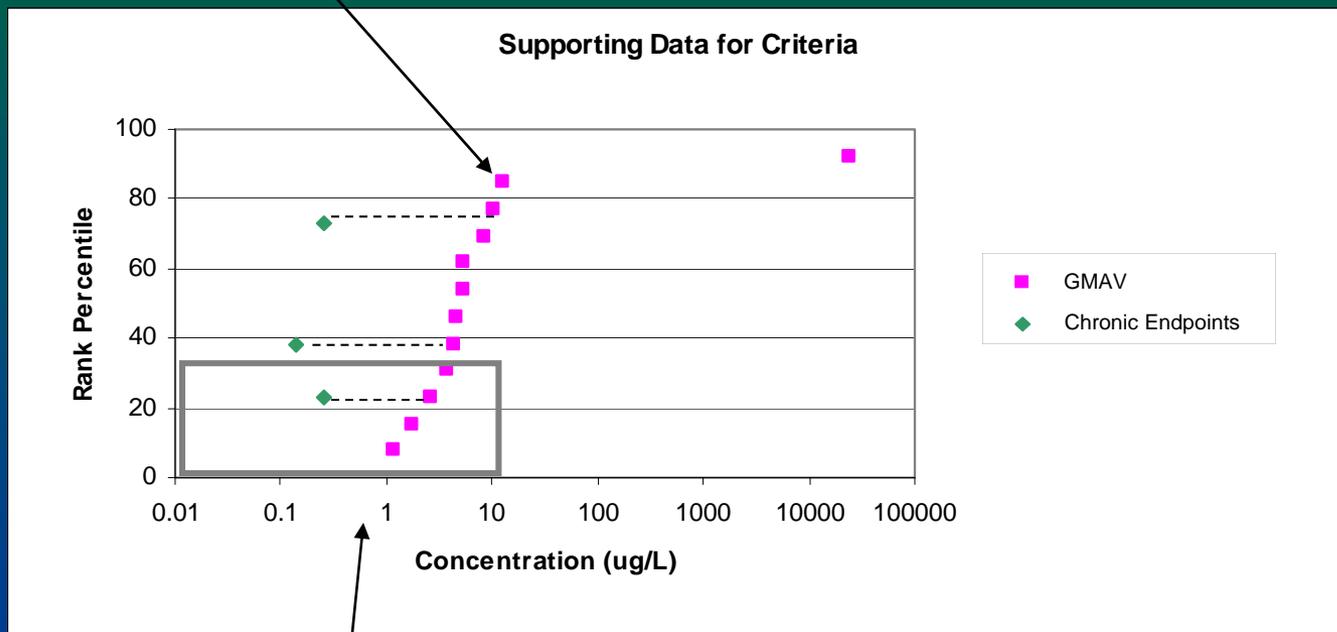
GMAV = 36 µg/L

TABLE 3 - RANK GMAVS

<u>RANK</u>	<u>GMAV</u> <u>(µg/L)</u>	<u>Species</u>	<u>SMAV</u> <u>(µg/L)</u>
4	100	Rainbow Trout, <i>Oncorhynchus mykiss</i>	100
3	36	Cladoceran, <i>Daphnia ambigua</i>	42
		Cladoceran, <i>Daphnia pulex</i>	38
		Cladoceran, <i>Daphnia magna</i>	29
2	25	Amphipod, <i>Gammarus pseudolimnaeus</i>	25
1	19	Amphipod, <i>Hyalella azteca</i>	19

Aquatic Life WQC Calculation

Rank Genus Mean Acute Values (GMAV) and Calculate the Percentile of Each Rank ($100 R/(N+1)$)



Using the 4 Most Sensitive Genera, perform a Least Squares Regression of the $GMAV^2$ (log values) on the Percentile Ranks (square roots)

CALCULATE CMC

- **Toxicity Related to WQ Characteristic?**
Copper - Hardness, alkalinity, TOC
- **Check Agreement within Species**
- **Check Sensitive Life Stages**
- **Calculate Species Mean Acute Values**
- **Calculate Genus Mean Acute Values**
- **Rank GMAVs**
- **Calculate Cumulative Probability**
 - **5th percentile concentration, or**
 - **lowest 4 GMAV**
- **Calculate Final Acute Value**
- **Divide by 2 for CMC**

ACUTE-CHRONIC RATIO (ACR)

The Acute-Chronic Ratio Is Used To Quantify the Difference in the Toxicities Observed in an Acute Test and a Chronic Test.

CALCULATION OF FINAL CHRONIC VALUE FROM ACUTE-CHRONIC RATIO

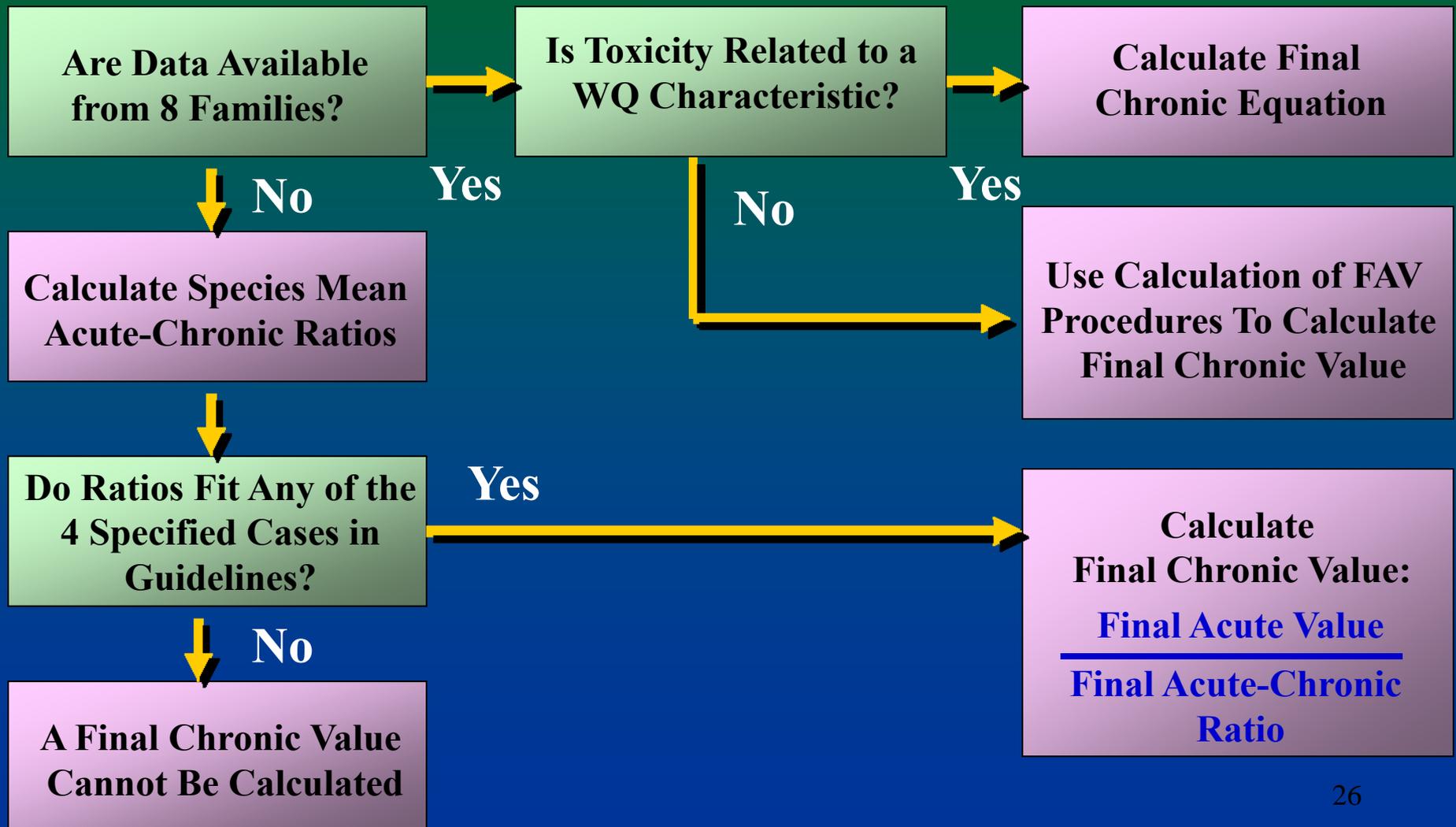
1. Perform Acute and Chronic Testing Using Same Species in Same Dilution Water
2. Use Results to Calculate Acute-Chronic Ratios (ACR)

$$\text{ACR} = \frac{\text{Acute Value}}{\text{Chronic Value}}$$

3. Develop a Final Acute-Chronic Ratio (FACR) by taking a Geometric Mean of the appropriate Acute-Chronic Ratios
4. Calculate the Final Chronic Value (FCV) using the Final Acute-Chronic Ratio

$$\text{FCV} = \frac{\text{Final Acute Value}}{\text{FACR}}$$

CALCULATE FINAL CHRONIC VALUE



DEFAULT AVERAGING PERIOD

**For Both Freshwater and Saltwater
Aquatic Life Criteria:**

CCC	4-Day Average
CMC	1-Hour Average

FINAL REVIEW

- **Are All Required Data Available?**
- **For Any Commercially or Recreationally Important Species, Is the Species Mean Acute Value Lower than the Final Acute Value?**
- **Are Chronic Values Available for Acutely Sensitive Species?**
- **Are There Any Deviations from the Guidelines?**
- **Are They Acceptable?**

AQUATIC LIFE CRITERIA: REVISIONS TO GUIDELINES

Near Term Products (2007):

- Kinetic modeling for addressing duration of exposure.
- Reevaluation of the allowable frequency recommendations.

Longer Term Efforts:

- Extract more information from available data.
- Address priority mechanisms of action (e. g., EDCs).
- Inject more realism into the evaluation of species sensitivity distributions composed of a diversity of species and life-stages.

PART 4. SITE-SPECIFIC CRITERIA

**The Sensitivities of the Site-Species Differ
from the National Data Base**

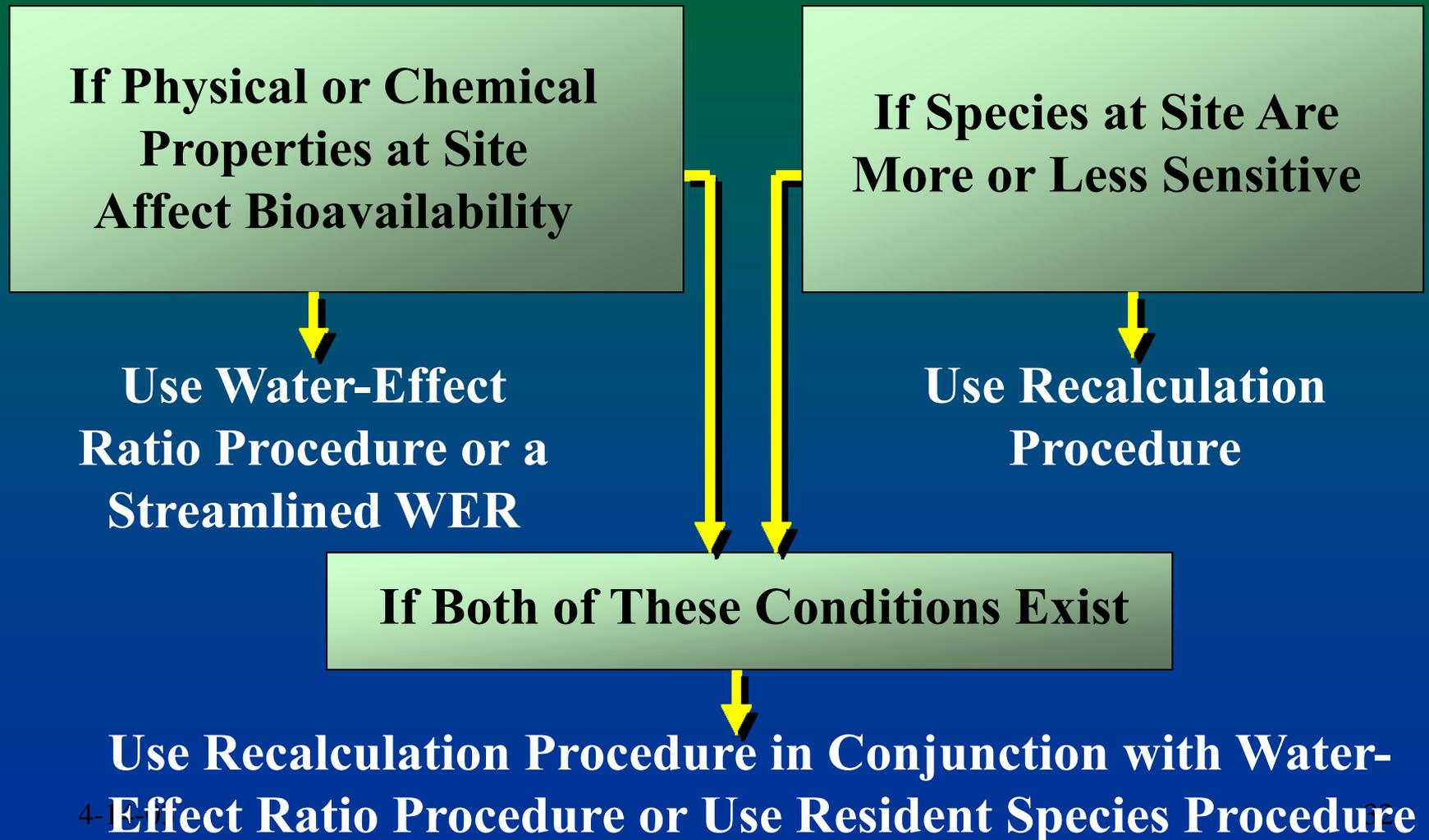
and/or

**The Physical/Chemical Characteristics of
the Site Alter the Bioavailability/Toxicity
of the Pollutant**

THREE PROTOCOLS FOR DEVELOPING SITE-SPECIFIC CRITERIA

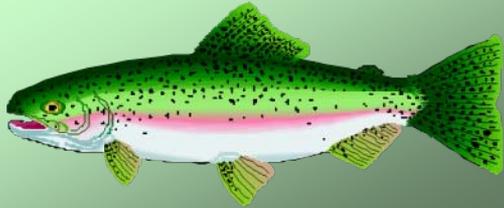
1. Recalculation Procedure
2. Water-Effect Ratio Procedure
 - Streamlined WER for Copper
3. Resident Species Procedure

SITE-SPECIFIC CRITERIA PROCEDURES

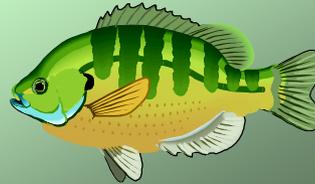


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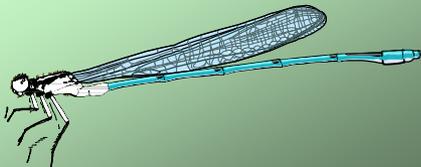
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WATER EFFECT RATIOS

Quantification of the Difference in Toxicities of the Test Material in Site Water as Compared To Lab Water

$$\text{WER} = \frac{\text{Site Water Toxicity Concentration}}{\text{Lab Water Toxicity Concentration}}$$

Site-Specific Criteria = WER x National Criteria

EPA 2007 COPPER CRITERIA BIOTIC LIGAND MODEL (BLM)

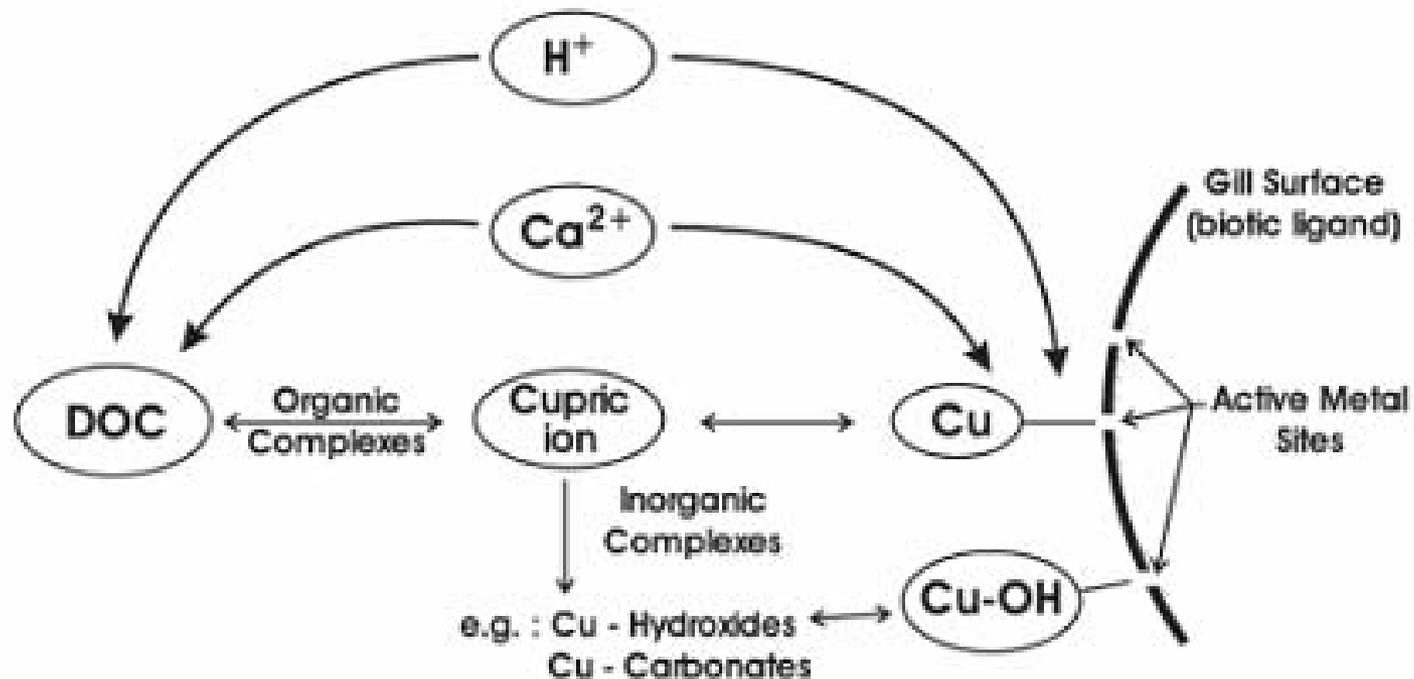


Figure 1. Conceptual Diagram of Copper Speciation and Copper-Gill Model (after Pagenkopf, 1983)

BIOTIC LIGAND MODEL: WHAT DOES IT DO?

- Complements the existing Guideline procedures.
- Provides a way to account for the effect of water chemistry, in addition to hardness, on metal bioavailability and toxicity, i.e. hardness, pH and dissolved organic carbon are used for BLM.
- Should lead to an improved capability to assess the potential for adverse effects to aquatic biota.
- Limited data available for BLM may make this type of criteria derivation difficult to implement.