



pennsylvania
DEPARTMENT OF ENVIRONMENTAL PROTECTION



Office of Water Programs

Water Quality Standards Aquatic Life Criteria for Copper

Draft Proposed Rulemaking

Water Resources Advisory Committee

September 21, 2023

Josh Shapiro, Governor

Richard Negrin, Secretary

Statutory Authority

Water Quality Standards

- Implement Sections 5 and 402 of The Clean Streams Law and Sections 101 and 303 of the Federal Clean Water Act.
 - Protected water uses, water quality criteria and an antidegradation policy.
 - 25 Pa. Code Chapter 93
 - 25 Pa. Code Chapter 16

Copper in Surface Waters

Sources of Copper in the Environment

Natural Sources:

- Weathering of geological deposits
- Erosion

Anthropogenic (human) Sources:

- Industrial activities
- Wastewater treatment systems
- Groundwater remediation systems
- Stormwater

Copper in Surface Waters

Naturally-occurring concentrations of copper in Pennsylvania surface waters

	Minimum (µg/L)	Maximum (µg/L)	Median (µg/L)	Mean (µg/L)
Dissolved Copper*	0.577	23.5	0.854	1.469
Total Copper*	0.588	22.6	1.210	1.831

* lower reporting limit = 0.5673 µg/L

Aquatic Life Criteria Development

- Established to protect aquatic life from toxic substances.
- U.S. Environmental Protection Agency (EPA) Section 304(a) criteria recommendations.
- *Guidelines for Deriving Numeric National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (EPA, 1985).
- Chapters 93 and 16

Current Aquatic Life Criteria

TABLE 5 (Toxics Criteria) and TABLE 6 (Great Lakes Criteria)

Fish and Aquatic Life Criteria

<i>PP NO</i>	<i>Chemical Name</i>	<i>CAS Number</i>	<i>Criteria Continuous Concentration (µg/L)</i>	<i>Criteria Maximum Concentration (µg/L)</i>
6M	COPPER	07440508	*0.960xExp(0.8545xln[H]-1.702)	*0.960xExp(0.9422xln[H]-1.700)
			(ex: @H=100, CCC=9.0)	(ex: @H=100, CMC=13)

Biotic Ligand Model (BLM)

- Current Section 304(a) recommendation.
- Developed in accordance with the 1985 Guidelines.
- Reflects the latest science (300+ toxicity studies for 27 genera).
- BLM is metal bioavailability model.
- Requires data for 10 water quality parameters, including:
 - pH
 - Dissolved organic carbon (DOC)
 - Magnesium
 - Potassium
 - Chloride
 - Temperature
 - Calcium
 - Sodium
 - Sulfate
 - Alkalinity

BLM

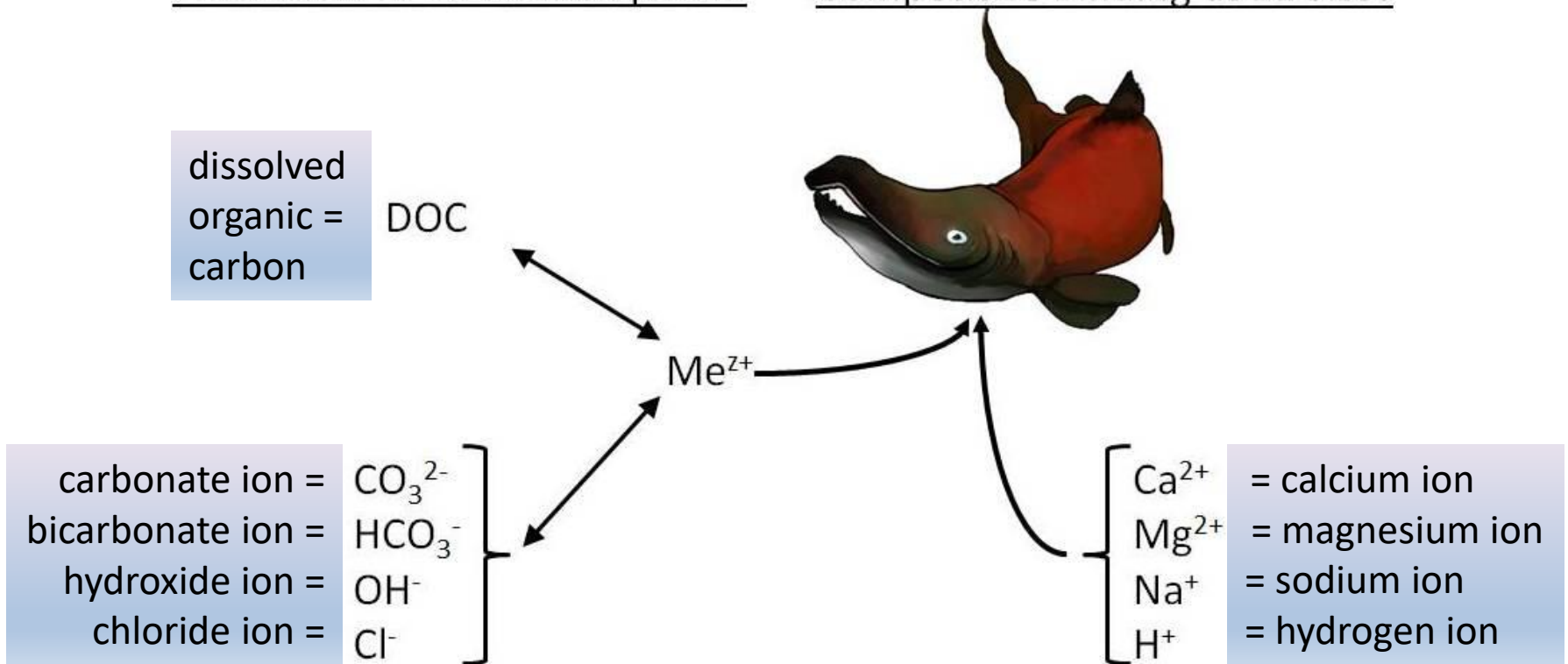
- **Ligand** – an ion, molecule or molecular group that binds to a metal to form a larger complex.
- **Biotic Ligand** – a ligand on an organism.
- **Bioavailability** – the amount of copper that is available for uptake by organisms.
- **Chemical Speciation**
 - pH and alkalinity affect metal speciation
 - At equilibrium in oxygenated waters, free (dissolved) copper = cupric ion (Cu^{2+})
 - Most dissolved Cu is complexed with other ligands

BLM

BLM Conceptual Framework

Formation of Metal Complexes

Competitive Binding at BL Sites



Criteria Duration

- EPA's 2007 recommendations include a 24-hour duration period for the acute criterion.
- Department is recommending a 1-hour duration.
 1. Delayed reaction to acute exposure.
 2. EPA re-evaluated the 24-hour recommendation.
 3. Available science and EPA's 1985 guidelines do not support an extended acute duration.
 4. Recreationally and commercially important fisheries.

Criteria Frequency

- EPA and the Department both recommend a frequency of no more than once every three years on the average.

Annex

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§ 93.8b. Metals criteria.

Dissolved criteria are footnoted in Table 5 **and Table 6**, and have been developed by applying the most current EPA conversion factors to the total recoverable criteria, **except for copper**. The EPA factors are listed in the following Conversion Factors Table.

Conversion Factors Table			
	<i>Chronic</i>	<i>Acute</i>	<i>Source</i>
* * * * *			
Chromium VI	0.962	0.982	1,2
Copper*	0.960	0.960	1,2
Lead[*]	<u>1.46203- (ln[H] x 0.145712)</u>	1.46203- (ln[H] x 0.145712)	2
Mercury	0.85	0.85	1,2
* * * * *			

*** [Conversion factor applies to both acute and chronic criteria.] Conversion factor is included for NPDES permitting purposes only. The dissolved BLM criteria in Table 5 and Table 6 should be divided by the conversion factor to determine the total recoverable copper criteria.**

Annex

§ 93.8c. Human health and aquatic life criteria for toxic substances.

TABLE 5

WATER QUALITY CRITERIA FOR TOXIC SUBSTANCES

PP NO	Chemical Name	CAS Number	Fish and Aquatic Life Criteria		Human Health Criteria (ug/L)	
			Criteria Continuous Concentrations (ug/L)	Criteria Maximum Concentration (ug/L)		
* * * * *						
5M	CHROMIUM VI	18540299	*11	*16	N/A	-
6M	COPPER	07440508	[*0.960xExp(0.8545xln[H]-1.702) (ex: @H=100, CCC=9.0)]	[*0.960xExp(0.9422xln[H]-1.700) (ex: @H=100, CMC=13)]	N/A	-
			*BLM	*BLM		
7M	LEAD	07439921	*{1.46203-(ln[H] x0.145712)} x Exp(1.273xln[H]-4.705) (ex: @H=100, CCC=2.5)	*{1.46203-(ln[H]x0.145712)} x Exp(1.273xln[H]-1.460) (ex: @H=100, CMC=65)	N/A	-
* * * * *						

Acronyms and Footnotes to Table 5

* Indicates dissolved metal criterion; others are total recoverable metals. Each listed dissolved criterion in Table 5 is equal to the corresponding total recoverable criterion before rounding (from the EPA National Ambient Water Quality Criteria Documents) multiplied by the conversion factor (from the Conversion Factors Table), **except for copper**; a criterion that is expressed as a hardness (H)-based equation is shown in Table 5 as the conversion factor (listed) multiplied by the hardness criterion equation; an example criterion at hardness=100mg/L is included.

† Indicates criterion based on the exposure inputs of 2 liters per day of drinking water and consumption of 17.5 grams of fish per day, for protection of a 70 Kg person.

BLM—Biotic Ligand Model

CAS—Chemical Abstract Service number

* * * * *

Annex

§ 93.8e. Special criteria for the Great Lakes System.

TABLE 6

GREAT LAKES AQUATIC LIFE AND HUMAN HEALTH CRITERIA

PP NO	Chemical Name	CAS Number	Fish and Aquatic Life Criteria		Human Health Criteria (ug/L)	
			Criteria Continuous Concentrations (ug/L)	Criteria Maximum Concentration (ug/L)		
* * * * *						
5M	Chromium, VI	18540299	*10.56	*15.73	N/A	-
6M	Copper	07440508	[*0.960xExp(0.8545xln[H]-1.702)	[*0.960xExp(0.9422xln[H]-1.700)	N/A	-
			(ex: @H=100, CCC=8.96)]	(ex: @H=100, CMC=13.44)]		
			<u>*BLM</u>	<u>*BLM</u>		
8M	Mercury	07439976	* 0.77	*1.44	0.0031	H
* * * * *						

Acronyms and Footnotes to Table 6

* Indicates dissolved metal criterion; others are total recoverable metals. Each listed dissolved criterion in Table 6 is equal to the corresponding total recoverable criterion before rounding (from the EPA National Ambient Water Quality Criteria Documents) multiplied by the conversion factor (from the Conversion Factors Table), **except for copper**; a criterion that is expressed as a hardness (H)-based equation is shown in Table 6 as the conversion factor (listed) multiplied by the hardness criterion equation; an example criterion at hardness=100mg/L is included.

BLM—Biotic Ligand Model

CAS—Chemical Abstract Service number

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Recommendation

The Department requests WRAC's concurrence on this draft proposed rulemaking.



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