

Office of Water Programs

# Water Quality Standards
# Aquatic Life Criteria for Copper

Proposed Rulemaking

Agricultural Advisory Committee

October 19, 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

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# 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

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# 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 | 1.21 | 1.831 |

* lower reporting limit = 0.5673 µg/L

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# 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

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# Current Aquatic Life Criteria

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

| | | | *Fish and Aquatic Life Criteria* | |
|---|---|---|---|---|
| *PP NO* | *Chemical Name* | *CAS Number* | *Criteria Continuous Concentration (µg/L)* | *Criteria Maximum Concentration (µg/L)* |
| 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) |

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# 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

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# 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

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# BLM

## BLM Conceptual Framework

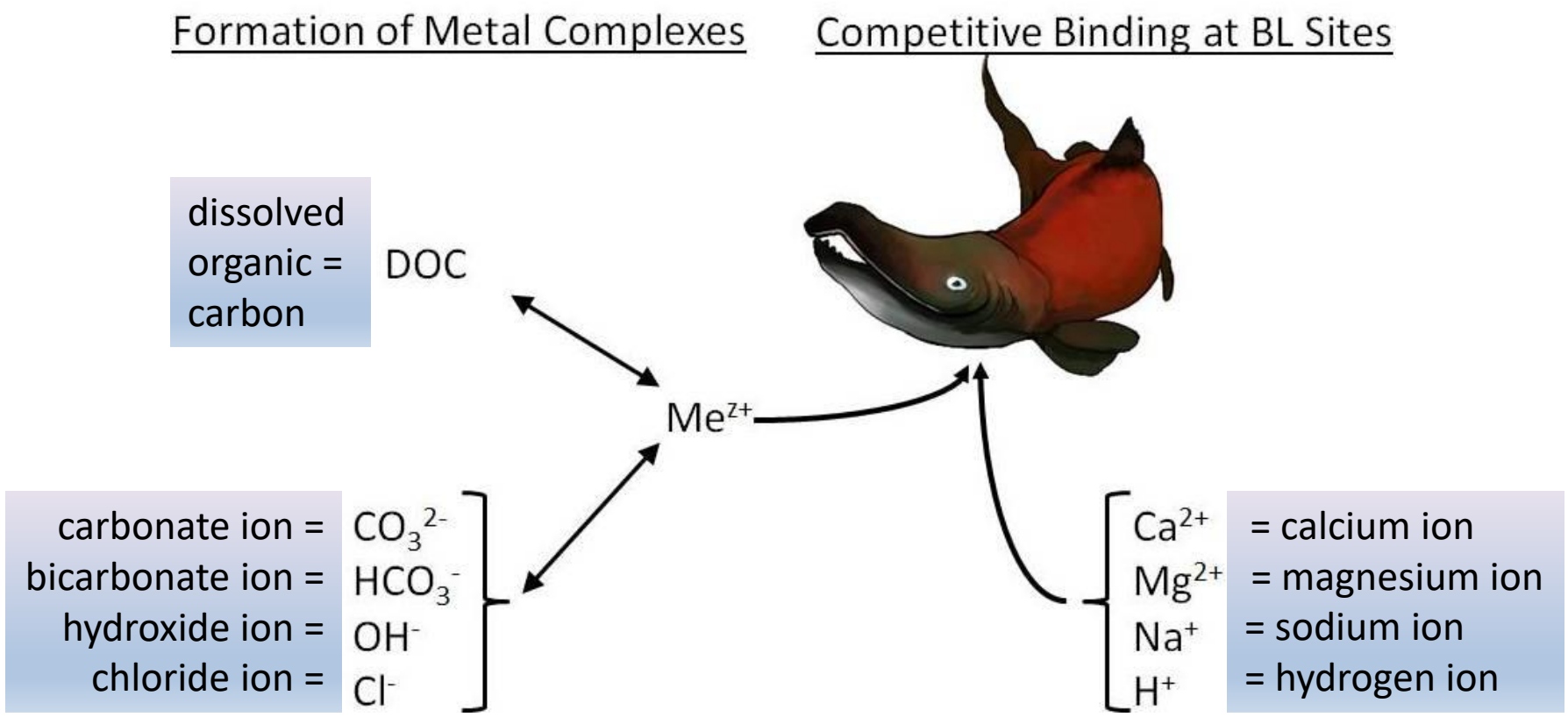


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Image Credit: Windward Environmental LLC

# BLM

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.

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# BLM

Criteria Frequency

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

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# 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** | | | |
|---|---|---|---|
| | *Chronic* | *Acute* | *Source* |
| * * * * * | | | |
| Chromium VI | 0.962 | 0.982 | 1,2 |
| Copper* | 0.960 | 0.960 | 1,2 |
| Lead[*] | 1.46203- (ln[H] x 0.145712) | 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.**

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# Annex

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

**TABLE 5**

**WATER QUALITY CRITERIA FOR TOXIC SUBSTANCES**

| | | | *Fish and Aquatic Life Criteria* | | *Human Health Criteria (ug/L)* | |
|---|---|---|---|---|---|---|
| *PP NO* | *Chemical Name* | *CAS Number* | *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)** | **[*0.960xExp(0.9422xln[H]-1.700)** | N/A | - |
| | | | **(ex: @H=100, CCC=9.0)]** | **(ex: @H=100, CMC=13)]** | | |
| | | | ***BLM** | ***BLM** | | |
| 7M | LEAD | 07439921 | *{1.46203-(ln[H] x0.145712)} x | *{1.46203-(ln[H]x0.145712)} x | N/A | - |
| | | | Exp(1.273xln[H]-4.705) | Exp(1.273xln[H]-1.460) | | |
| | | | (ex: @H=100, CCC=2.5) | (ex: @H=100, CMC=65) | | |
| * * * * * | | | | | | |

**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

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# Annex

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

**TABLE 6**

**GREAT LAKES AQUATIC LIFE AND HUMAN HEALTH CRITERIA**

| | | | *Fish and Aquatic Life Criteria* | | *Human Health Criteria (ug/L)* | |
|---|---|---|---|---|---|---|
| *PP NO* | *Chemical Name* | *CAS Number* | *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)]** | | |
| | | | ***BLM** | ***BLM** | | |
| 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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