

Metals

Metals are elements present in all waterbodies with natural concentrations corresponding to local geology. Types of metals found in waterbodies may include aluminum, arsenic, copper, manganese, mercury, nickel, selenium, and zinc.

Why do we measure metals?

All metals can be toxic at high concentrations, even those that are nutritionally essential for sustaining life in aquatic ecosystems in small amounts (such as copper and manganese). Metal toxicity negatively affects the health of aquatic organisms. For example, metal toxicity:

- Decreases abundance and diversity of species
- Changes reproduction, juvenile growth, and behavior
- Causes spinal abnormalities, gill damage, and death

In a waterbody, metals are either dissolved or in particulate form. Dissolved metals are small enough to pass through a 0.45 micron (μm) filter and are more easily absorbed by organisms. Metals can bind to particulates such as clay, sand, or organic matter. Particulate metals are larger and typically less bioavailable than dissolved metals, but organisms can still uptake particulate metals through their gut.

Over time, dissolved and particulate metals in the water can build up in the tissue of fish and other aquatic organisms. This process, called bioaccumulation, occurs when an organism absorbs or uptakes metals more quickly than their body can eliminate them. Biomagnification of some metals (such as mercury) can also occur in an aquatic ecosystem. Biomagnification

occurs when concentrations of metals increase from transfer up through the food chain as larger organisms feed on many smaller organisms who have each bioaccumulated metals in their bodies (see Figure 1). Biomagnification and bioaccumulation can cause concentrations of metals in larger aquatic organisms to be toxic to the humans, and to the birds and other wildlife, that consume them.

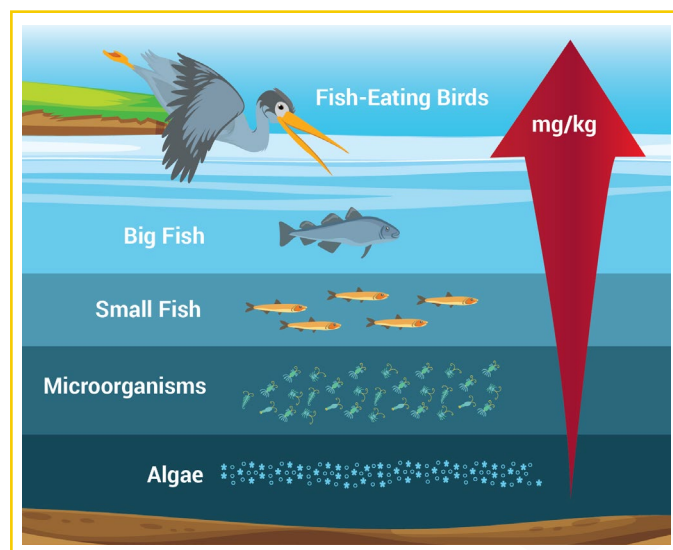


Figure 1. Example of biomagnification of metals in wildlife

What affects levels of metals?

Metals occur naturally and are released into waterbodies when flowing water erodes rocks, minerals, and soil particles. Because different rock types contain different metals, and because some rock types are more susceptible to erosion and erode more quickly, the types and amounts of metals deposited in waterbodies depend on the local geology.

There are also many human-caused sources of metals in waterbodies:

- Mines and smelters (see Figure 2)
- Firing ranges
- Municipal wastewater treatment effluent
- Industrial point sources (specific discharge points)
- Urban and agricultural runoff
- Landfills
- Junkyards
- Dredging
- Coal-burning power plants and atmospheric deposition

pH is a primary factor in determining how much of a metal is dissolved in water. For example, arsenic, copper, lead, and mercury are generally more soluble (or “dissolvable”) at a lower pH.



Figure 2. Abandoned mine site along Galena Creek in Barker Mining District, Montana. Credit: Photo courtesy of USGS

What are EPA's recommended water quality criteria for metals?

EPA has two sets of nationally recommended criteria that include metals. One set protects aquatic life and the other protects human health. Generally, the metals criteria to protect aquatic life are more stringent than those to protect human health because aquatic life is more sensitive to metals absorption.

EPA's *National Recommended Water Quality Criteria – Aquatic Life Criteria Table* specifies the highest concentration of metals that are unlikely to harm aquatic life. Aquatic life criteria for most metals include both an acute criterion or Criterion Maximum Concentration

(CMC) and a chronic criterion or Criterion Continuous Concentration (CCC). The CMC is used for acute exposure (short-term, 1-hour average) and the CCC is used for chronic exposure (long-term, 4-day average). EPA recommends expressing both the CMC and CCC criteria as the micrograms of the dissolved metal per liter of water ($\mu\text{g/L}$) in the water column. The dissolved metal concentration is generally a better approximation of the concentration that is bioavailable to aquatic organisms. (The total recoverable concentration, which is the dissolved plus particulate concentration, accounts for particulate metals that may dissolve later downstream.)

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EPA recommends an exceedance frequency of not more than once every three years on average for most aquatic life criteria. More frequent exceedances could cause recurring stress on aquatic life and not allow time for recovery. Table 1 lists examples of EPA's recommended aquatic life criteria for three metals.

Other water quality parameters such as dissolved organic carbon (DOC), hardness (calcium carbonate), pH, and temperature affect the toxicity of some metals. Therefore, the toxicity criteria for these metals are

calculated with equations that use water quality data. Criteria that vary by hardness are included in EPA's *National Recommended Water Quality Criteria – Aquatic Life Criteria Table*. Hardness generally reduces metal toxicity, so as hardness increases, the criteria also increase because it takes more of the metal to be toxic. Criteria that vary by multiple parameters, including for aluminum, copper, and selenium, rely on a more complex equation. See EPA's *Aquatic Life Criteria* pages on aluminum, copper, and selenium for more information on these complex equations.

Table 1. EPA-recommended national aquatic life criteria for three metals dissolved in freshwater.

Dissolved Metal	Freshwater CMC in µg/L	Freshwater CCC in µg/L
Arsenic	340	150
Nickel ¹	470	52
Zinc ¹	120	120

¹ These criteria vary with hardness. The values presented here are calculated at a hardness value of 100 mg/L (moderately hard waters). EPA's *National Recommended Water Quality Criteria – Aquatic Life Criteria Table* has equations to convert the CMC and CCC when hardness values are not 100 mg/L.

Source: USEPA (Nd)

How do we measure metals?

The concentrations of metals in waterbodies can be measured by collecting water samples from a site and sending them to a laboratory to be processed and analyzed (Figure 3). Because dissolved metals are more easily absorbed by organisms than particulate metals, water samples are typically filtered so that the results represent dissolved metal concentrations. It is also important to measure DOC, hardness, pH, and temperature when the aquatic life toxicity criteria for the metals being measured depend on those parameters.

Bottom sediment and tissue samples can also be collected at the site for processing and analysis. Metals in bottom sediment samples are typically measured in micrograms per kilogram of dried sediment (µg/kg dry weight), and metals in tissue samples are typically measured in mg/kg dry weight of tissue. Tissue samples from muscle, fat, or other tissue indicate the level of bioaccumulation in aquatic organisms.



Figure 3. Collecting a water sample to be analyzed for metals. Credit: Photo courtesy of USGS

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While sediment and tissue sampling can help identify relative metal concentrations in aquatic systems, no metals have corresponding nationally recommended sediment criteria, and few metals have corresponding tissue criteria. EPA has guidance on how to establish sediment criteria in Chapter 3 of EPA's *Water Quality Standards Handbook*.

The concentrations of metals in water, bottom sediment, and tissues can be compared to better understand how metals impact ecosystems. Metal concentrations in tissue samples can reflect exposure to metals in water and in sediment. Even minimal concentrations of certain metals, especially heavy metals like mercury, in water and sediment can bioaccumulate in fish and shellfish tissue to levels that are toxic to both the wildlife and humans that consume them, which can trigger consumption advisories.

What are the challenges of using metals as a water quality parameter?

Because the types and concentrations of metals vary naturally according to local geology, and because a variety of human activities can cause metals to end up in a waterbody, it can be challenging to pinpoint the sources of elevated metal concentrations. Monitoring water chemistry throughout a watershed can help identify the sources of elevated metal concentrations.

There are many different metals that can be analyzed in a waterbody, which also presents challenges:

- Each type of metal has a unique level of toxicity. There is no universal threshold for toxicity, so each metal should be evaluated separately. However, evaluating metals separately ignores the effect of aggregate (or cumulative) toxicity.

- The toxicity of some metals varies with water chemistry. Thus, in addition to metals, DOC, hardness, pH, and temperature should also be assessed to understand the complete picture of metal toxicity.

Because it can be expensive to analyze all types of metals, it may be more cost-effective and strategic to identify a smaller group of high-interest or high-risk metals for analysis, or to ask the laboratory about their pricing to analyze multiple metals per water sample.