Copper in the Ohio River Basin

The Ohio River Watershed Pollutant Reduction Program

The Ohio River Valley Water Sanitation Commission

June 1998

Executive Summary

Copper is a naturally occurring element that is found in its familiar metallic state, as well as a variety of copper compounds. Its physical properties such as high thermal and electrical conductivities, corrosion resistance, and malleability make copper an extremely valuable material for a wide range of applications. Because copper is such a versatile material, copper is widely used in several industries including electrical equipment, construction, transportation, machinery, and chemical manufacturing. The wide use of copper has led to contamination of the atmosphere, soil, and surface waters.

The presence of elevated levels of copper in the environment raises concerns due to the toxicological effects that it can have on humans and wildlife. Copper can cause a wide-range of health effects. These adverse effects can be minor such as nausea and irritation of the mouth, eyes, and nose, or more severe such as liver, kidney, and brain damage in extreme cases. In aquatic environments, elevated in-stream copper concentrations may result in the elimination of aquatic organisms that play an important role in the food chain. Some studies have found that changes in fish and invertebrate community structure can occur in streams polluted with copper (EPA 1987).

In order to protect humans and other organisms from the toxic effects of copper, water quality standards have been established to limit exposure. ORSANCO monitors for copper bimonthly at 17 Ohio River locations and 14 tributary stations. The observed copper levels are compared to acute and chronic aquatic life criteria to determine if water quality standards are being met. From July, 1992 – December, 1997, six Ohio River monitoring stations and six tributary stations reported criteria violations. The Pike Island station on the Ohio River (river mile 84.2) and the Cumberland River station (river mile 16) accounted for over half of all reported violations. In 1992, ORSANCO conducted a trend assessment that found overall copper concentrations decreased from 1980-1990. Seven of the eleven Ohio River stations and 10 of the 12 tributaries sampled revealed a significant decreasing trend for copper. No trends were observed at the other six monitoring stations.

The ultimate concern regarding copper concentrations in the Ohio River is whether or not the biological community is adversely affected at levels present in the water column. Unfortunately, this is extremely difficult to determine considering the numerous variables influencing biological community health. In 1992, ORSANCO conducted a biological assessment of the Ohio River using fish population data from 1968-1990. This study found a steady improvement river-wide in fish community health. This assessment, however, does not allow for conclusions to drawn concerning the specific reason for the improvement. Now while generalizations can be made that copper concentrations are decreasing in the Ohio River, and fish community health is improving, a direct correlation between the two cannot be supported with the available data.

Introduction

Most people recognize copper in its familiar metallic state. The soft, non-magnetic metal has a distinguishing reddish color and is used in common products such as electrical wiring and plumbing. Many, however, are unaware that the wide-spread use of copper has led to the contamination of surface waters throughout the United States.

Copper is a naturally occurring element that is required by living organisms. It is a micronutrient essential for the growth of plants and animals. The adult recommended daily allowance of copper is 2.0 to 3.0 mg/day. Copper is required for hemoglobin formation, carbohydrate metabolism and cross linking of collagen, elastin and hair keratin. (USEPA, 1997)

Physical and Chemical Properties

Copper is a naturally occurring element found in water, soil, sediment, and air. Its distinguishing characteristics that makes it so versatile include: high thermal and electrical conductivity, corrosion resistance, malleability and appearance (USDHHS 1990). Copper can be found in its elemental form, and in a variety of natural and man-made copper compounds. In its familiar metallic state, copper is characterized as a reddish, soft, non-magnetic metal that can be easily shaped and formed.

Copper can occur in four valence states with the Cu(I) and Cu(II) states the most common. The Cu(I) ion is unstable in aqueous solution, and quickly disproportionates to form Cu(II) and copper metal (Cotton and Wilkinson). The cupric or Cu(II) ion is stable in aqueous solution, and is the one of most concern because of its bioavailability. Toxicity from copper exposure is thought to be related to the presence of free Cu(II) ions.

In water, the fate and transport of copper is dependent on a several variables. The pH, redox potential, and the presence of other ions and ligands all influence how copper will behave in aquatic environments. The cupric ion is the most common copper species found in water. The Cu(II) ion can be present in free and complex forms (USEPA 1985). In general, most copper present in water will strongly bind to particulate matter, and is thus not available for uptake by biota. One study on the fate of copper in water found that 74-87% of copper present in river water was found in crystalline sediments (Gibbs 1973).

Very little data exists on the behavior of copper in the atmosphere. It has been estimated, however, that copper aerosols may persist in the atmosphere for 2-10 days in unpolluted areas (EPA 1987). In polluted regions, atmospheric residence times are much shorter. Atmospheric deposition can be a significant source of copper to surface waters and soil (EPA 1987). The removal of copper from the atmosphere occurs through wet and dry deposition. Dry deposition is the process by which compounds in the particulate phase settle to the ground due to gravity. Wet deposition occurs when rain scavenges both particulate and vapor phase compounds from the atmosphere, and deposits them through precipitation. Observed dry deposition rates range from $<0.02\ \mu g/cm^2$-year in isolated areas to >20 μg/cm^2-year in urban areas. Rates for wet deposition are typically in line with that of dry deposition.

In soil, copper binds strongly with organic matter, carbonate and clay minerals, or hydrous iron and manganese oxides. Generally, leaching of copper does not appear to be significant, and tends to remain in the upper few centimeters of soil (USDHHS 1990). Leaching is most likely to occur in sandy soils with low pH.

Environmental and Human Health Concerns

Humans and other organisms all require small amounts of copper in their diet for proper nutrition. Problems arise, however, when excessive exposure occurs. There are three major exposure pathways: ingestion, inhalation, and dermal contact. The major route of exposure for most humans is ingestion. It is estimated that the typical US resident consumes 260 μg/day through drinking water and <2000-4000 μg/day from foods. The National Academy of Science suggests a daily intake of 2000-3000 μg/day. Copper intake through inhalation has been found to be negligible for most humans when compared to ingestion of copper. However, individuals living near and working in certain industries such as copper smelters and refineries can be exposed to significant amounts through inhalation of fumes and dust containing copper. Dermal contact is not a significant route of exposure except for individuals that handle copper products containing soluble cupric salts on a routine basis. These compounds are used frequently in agriculture and water treatment.

It is believed that copper is only bioavailable in the free Cu(II) ion form, and that the toxicological effects of copper are the results of absorption of this ion. Once absorbed into the bloodstream, copper is distributed to all organ systems, with the liver being the primary storage organ (EPA 1987). Copper that is not retained in the body is eliminated through urine and feces.

Many studies have been conducted characterizing the toxicity of copper to humans and other organisms. These studies have reported that copper exposure can produce a wide range of adverse health effects in the liver, kidneys, blood, gastrointestinal tract, brain, and fetus. Acute exposure to elevated levels of copper in drinking water can cause vomiting, diarrhea, stomach cramps, headaches, and dizziness. Prolonged exposure to high concentrations of copper in drinking water has been found to cause liver damage in infants (USDHHS 1990). In some extreme cases, such as suicide attempts, consumption of large quantities of copper has resulted in ulceration of the gastric mucosa, hepatic and renal necrosis, coma, and even death.

A variety of health effects have been observed in workers exposed to copper fumes, mists, and dust particles. Common effects include irritation of the mouth, eyes, and nose, as well as anorexia, nausea, and diarrhea (USDHHS 1990). A condition known as "metal fume fever" has also been observed in these workers. This condition persists for 1-2 days and is characterized by flu-like symptoms such as chills, fever, aching muscles, and headache (USDHHS 1990). Inhalation of airborne copper has also been found to cause lung damage in hamsters and mice.

In aquatic environments, acute toxicity of copper is greatly dependent on water chemistry. Acute toxicity has been found to decrease as hardness and alkalinity increase (EPA 1987). Total organic carbon (TOC) concentrations may also influence the toxicity of copper to aquatic organisms (EPA 1984). Elevated in-stream copper concentrations may result in the elimination of aquatic organisms, such as certain macroinvertebrates, that play an important role in the food chain. Some species of fish are also sensitive to copper. Field studies have indicated changes in fish and invertebrate community structure can occur in streams polluted with copper (EPA 1987).

In order to protect humans and other organisms from the toxic effects of copper, federal and state environmental agencies have established specific criteria to limit exposure. The ambient water quality criteria for the protection of aquatic life in freshwater are hardness based and are as follow:

Chronic - the four-day average concentration should not exceed the value (in µg/L) given by $e^{(0.8545[\ln(\text{hardness})]-1.465)}$ more than once every three years on the average.

Acute – the one hour average concentration (in µg/L) should not exceed the value given by $e^{(0.9422[\ln(\text{hardness})]-1.464)}$ more than once every three years on the average.

A specific Maximum Contaminant Level (MCL) has not been established for copper because most copper contamination in drinking water comes from the corrosion of household plumbing systems. However, a Treatment Technique (TT) has been developed which requires public water treatment systems to follow specific procedures to control the corrosivity of their finished drinking water. A TT is an enforceable set of procedures developed by EPA when it is not economically or technically feasible to determine the level of the contaminant (EPA 1994a). The Maximum Contaminant Level Goal (MCLG) for copper (a non-enforceable goal based solely on toxicity data) has been set at 1.3 mg/L (EPA 1994b).

Formation and Sources

Copper occurs naturally in the environment as a metal, and in several minerals such as cuprite, malachite, azurite, chalcopyrite, chalcocite, and bornite (USDHHS 1990). Most copper is extracted from surface mines, with some additional copper ore obtained from underground mines. Most metallic copper is produced by first smelting sulfide ore, and then converting the molten sulfide of copper and iron to the metal form by a two-step oxidation process. The metal product can then be used in its primary metallic state, in alloys, or to produce copper compounds.

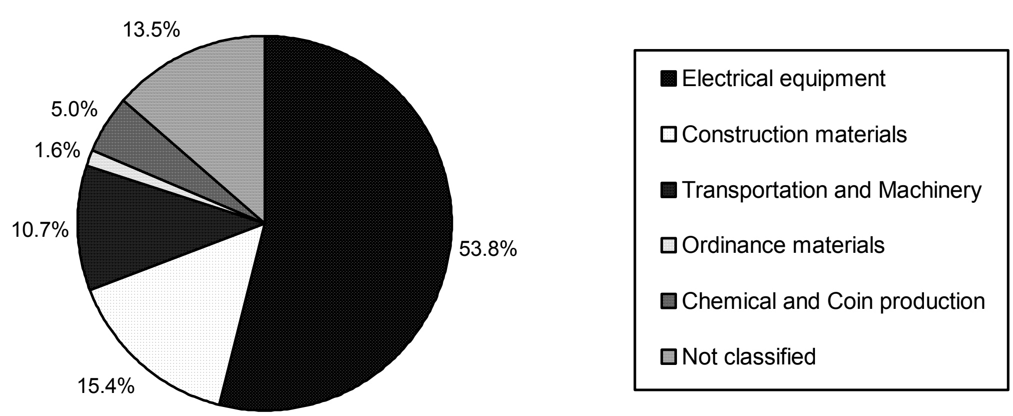
Worldwide, anthropogenic activities release an estimated three times more copper into the atmosphere than do natural sources (EPA 1987). The major anthropogenic sources are nonferrous metal production and wood combustion, while windblown dust is the primary natural source of copper to the atmosphere (see Table 1). Copper in the atmosphere eventually settles to the Earth's surface or precipitates out in the form of snow or rain. Atmospheric deposition is a significant source of copper to soils and surface waters (EPA 1987). Other sources to surface water include stream discharge, soil erosion, and point sources such as industrial and municipal dischargers.

Table 1. Atmospheric Sources of Copper (Nriagu 1979)

Natural Sources	Anthropogenic Sources
Windblown dust	Nonferrous metal production
Volcanoes	Wood combustion
Vegetation	Iron and steel production
Forest fires	Coal combustion
Sea spray	Waste incineration
	Industrial applications
	Nonferrous metal mining
	Oil and gasoline combustion

Most copper is used as the metal and in alloys, with a small amount used to make a variety of copper compounds. The primary uses are electrical equipment and supplies, construction materials, transportation and machinery (see chart 1). Only about 5% of copper goes to the production of copper compounds. Of these compounds, copper sulfate is the most commonly used. Uses for copper compounds include fungicides, algicides, insecticides, fertilizers, metal finishing, wood preservatives, water treatment, mineral froth flotation, petroleum refining (USDHHS 1990), anti-fouling paints, corrosion inhibitors, fabric, flameproofing, fuel additives, glass and ceramics (EPA 1987).

Chart 1. Major Uses of Copper (EPA 1987)

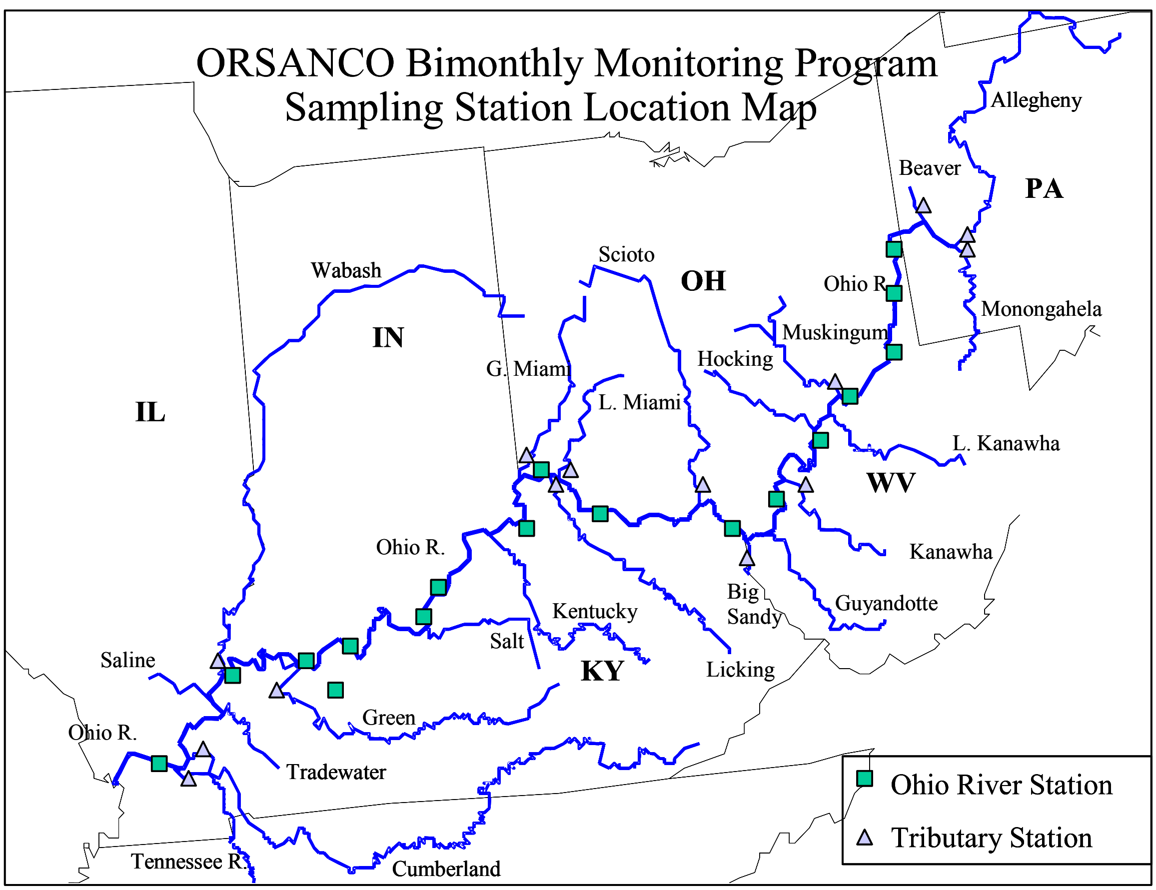


Presence in the Ohio River Basin

Within the Ohio River Basin, at least 4 sites on the U.S. EPA's final National Priorities List (NPL) are contaminated with copper. These facilities include two industrial sites and two military installations. These sites are potential sources of copper to the Ohio River and its tributaries. Nationally, 210 of the 1177 NPL sites have at least some copper contamination (USDHHS 1990). However, this number may increase as more sites are evaluated for copper. The NPL is a list of uncontrolled or abandoned hazardous waste sites identified for possible long-term cleanup under the Superfund Program.

As part of the 1997 Toxics Release Inventory (TRI), 17 of the 19 Original Industries, Standard Industrial Classification (SIC) codes 20-39, reported releases of copper in the six states bordering the Ohio River. For example, 338 individual facilities reported releases of copper in the State of Ohio alone. (TRI, 1999) These incidents include releases to air, land, and water. Facilities are required to report to the TRI if they: 1) have more than ten employees, 2) use more than 10,000 pounds of any designated chemical, and 3) conduct manufacturing operations in the groups specified by the (SIC) Codes 20 through 39 (USEPA, 1999). These releases could all contribute to copper concentrations in the Ohio River and its tributaries.

Map 1. Ohio River Monitoring Points



Copper concentrations are monitored bimonthly by ORSANCO at 17 Ohio River locations and 14 tributary stations (see Map 1). These levels are compared to acute and chronic aquatic life criteria to determine if violations exist. Over a five and one half-year period from July, 1992 - December, 1997, six different stations reported violations on the main stem of the Ohio River (see Table 2). The Pike Island location (Ohio River mile point 84.2) accounted for seven of the 16 main stem chronic violations, and three of the six acute violations. Average concentrations (assuming non-detects are equal to the detection limit of 5 μg/l) for the main stem locations ranged from 5.2 μg/L to 8.7 μg/l, with an overall average for all Ohio River stations of 6.0 μg/L. Over 75 percent of all Ohio River samples collected were below the detection limit.

Table 2. Copper Violations at Ohio River Bimonthly Sampling Stations (July, 1992-December, 1997).

Monitoring Station	**River Mile**	**Acute**	**Chronic**
Pike Island	84.2	3	7
Hannibal	126.4	0	1
Anderson Ferry	477.5	0	1
McAlpine	606.0	1	4
West Point	619.3	2	2
Smithland	918.5	0	1
Totals		6	16

During the same period, six tributary stations reported 17 chronic and eight acute violations (see Table 3). The Cumberland River sampling location (at river mile 16) accounted for over half of these tributary violations, with 10 chronic and four acute. Average concentrations (assuming non-detects are equal to the detection limit of 5 μg/l) for the tributary locations ranged from 5.0 μg/L to 9.6 μg/l, with an overall average for all tributary stations of 6.1 μg/L. Nearly 80 percent of all tributary samples collected were below the detection limit.

Table 3. Copper Violations at Ohio River Tributary Bimonthly Sampling Stations (July, 1992-December, 1997).

Monitoring Station	**River Mile**	**Acute**	**Chronic**
Beaver River	5.3	3	7
Muskingum River	0.8	0	1
Big Sandy River	20.3	0	1
Licking River	4.7	1	4
Cumberland River	16.0	2	2
Tennessee River	5.0	0	1
Totals		6	16

In 1992, ORSANCO conducted an assessment to look at significant trends in water quality for the Ohio River (ORSANCO 1992a). This assessment found that, in general, copper concentrations in the Ohio River and several major tributaries decreased during the period from 1980-1990. Seven of the eleven main-stem sampling locations indicated decreasing copper levels, while the other four sites showed no trend. Data for 10 of the 12 tributaries sampled also revealed a declining trend for copper, while no trend was observed at the other two tributary locations.

The ultimate concern regarding copper concentrations in the Ohio River is whether or not the biological community is adversely affected at levels present in the water column. Unfortunately, this is extremely difficult to determine considering that numerous variables influence biological health. The data necessary to make this type of assessment has simply not been collected.

ORSANCO did conduct a biological assessment of the Ohio River using fish population data from 1968-1990 (ORSANCO 1992b). This study found a steady improvement river-wide in fish community health over the 22-year period. In general, the Modified Index of Well Being (MIwb)values increased in a downstream direction, with depressed values occurring in the New Cumberland/Pike Island area and at McAlpine. Coincidentally, Pike Island and McAlpine are the Ohio River monitoring stations with the most copper criteria violations from 1992-1997. Before jumping to conclusions, however, one must consider that these areas are heavily industrialized. Considering that a whole host of pollutants enter the river at these two locations due to the numerous industries and combined sewer overflows, it is impossible to make any connections between copper violations and depressed MIwb scores in these areas. Copper levels can influence fish community health, but there is no data available that allows one to distinguish the effects resulting from elevated levels copper from the many other controlling factors (e.g. other pollutants, suitable habitat, dams) present in the river.

Conclusion

Copper, being a naturally occurring element, will always be present throughout the environment at low levels. The versatility of copper to be used in a variety of applications, however, has led to widespread use, and has resulted in significant releases of copper to the environment. While minute amounts of copper are required by most organisms, excessive quantities can pose human health and ecological concerns.

Overall, copper concentrations have been improving in the Ohio River, while some localized problem areas do exist. Monitoring by ORSANCO indicates water quality violations at six Ohio River locations and at six tributary sampling sites over the past 5 and one half years. The Pike Island sampling location on the Ohio River at mile 84.2 and the Cumberland River sampling site account for over half of all reported chronic and acute violations.

The main concern with elevated copper concentrations in the river is the effect that it may have on the biological community. Unfortunately, due to the numerous factors influencing biological community health, it is very difficult (maybe even impossible) to ascertain the impact of copper levels in such a complex system as the Ohio River. While generalizations can be made such as copper concentrations are decreasing in the Ohio River and fish community health is improving, a direct connection between the two cannot be supported with the available data.

Recommendations

1. **Conduct intensive sampling program to investigate hot spots**
   - 19 of the 22 criteria violations on the Ohio River from July 1992 – December 1997 occurred at three monitoring stations (Pike Island, McAlpine, and West Point)
   - 19 of the 25 criteria violations at tributary monitoring stations from July 1992 – December 1997 occurred at two locations (Cumberland and Tennessee Rivers)

2. **Continue bimonthly sampling program for copper**
   - The bimonthly sampling program provides an excellent means to assess long-term trends, and to identify localized hot spots.

Literature Cited

Gibbs, R. J. 1973. Mechanisms of trace metal transport in rivers. Science, 180:71-73.

Nriagu, J.O. 1979. Copper in the atmosphere and precipitation. Copper Environment, J.O. Nriagu, Ed. John Wiley and Sons, NY.

Ohio River Valley Water Sanitation Commission (ORSANCO). 1992a. Water quality trends, Ohio River and its tributaries, 1980-1990, A supplement to the 1977-1987 study.

Ohio River Valley Water Sanitation Commission (ORSANCO). 1992b. Assessment of ORSANCO fish population data using the Modified Index of Well Being (MIwb).

Toxic Release Inventory (TRI). 1999. Information Database. U.S. Environmental Protection Agency, Washington, DC.

U. S. Department of Health & Human Services (USDHHS). 1990. Toxicological profile for copper. Agency for Toxic Substance and Disease Registry. ATSDR/TP-90/08.

U. S. Environmental Protection Agency (EPA). 1985. Ambient water quality criteria for copper – 1984. Office of Water Regulations and Standards, Criteria and Standards Division, Washington, D.C. EPA 440/5-84-031.

U. S. Environmental Protection Agency (EPA). 1987. Summary review of the health effects associated with copper. Office of Health and Environmental Assessment, Washington, D.C. EPA/600/8-87/001

U. S. Environmental Protection Agency (EPA). 1994a. Drinking water standard setting and question-and-answer primer. Office of water, Office of Ground Water and Drinking Water, Washington, D.C. EPA 811-K-94-001.

U. S. Environmental Protection Agency (EPA). 1994b. National primary drinking water standards. Office of Water, Washington, D.C. EPA 810-F-94-001.

U. S. Environmental Protection Agency (EPA). 1999. Code of Federal Regulations. 40 CFR 372.22