Heavy Metals in the Mississippi River

John R. Garbarino, Heidi C. Hayes, David A. Roth, Ronald C. Antweiler,
Terry I. Brinton, and Howard E. Taylor

Introduction

Metals in the Mississippi River come from natural as well as artificial sources. Metals that are naturally introduced into the river come primarily from such sources as rock weathering, soil erosion, or the dissolution of water-soluble salts. Naturally occurring metals move through aquatic environments independently of human activities, usually without any detrimental effects. However, as the valleys of the Mississippi River and its tributaries were settled and industrialized, the metals added by human activities have affected the water quality of the Mississippi River and ultimately the Gulf of Mexico. Some of these metals are essential for proper metabolism in all living organisms yet toxic at high concentrations; other metals currently thought of as non-essential are toxic even at relatively low concentrations.

Sources and Sinks of Heavy Metals

(Click on image for a larger version, 83K)

Figure 21.--Heavy metals are released to the Mississippi River from numerous sources. Typical sources are municipal wastewater-treatment plants, manufacturing industries, mining, and rural agricultural cultivation and fertilization. Heavy metals are transported as either dissolved species in water or as an integral part of suspended sediments. Heavy metals may be volatilized to the atmosphere or stored in riverbed sediments. Toxic heavy metals are taken up by organisms; the metals dissolved in water have the greatest potential of causing the most deleterious effects.
Health Significance of Metals in the Environment

The metallic elements can be categorized into two groups. The heavy metals are those having densities five times greater than water, and the light metals, those having lesser densities. Well-known examples of heavy metallic elements are iron, lead, and copper. Examples of light metals are sodium, magnesium, and potassium. Humans consume metallic elements through both water and food. Some metals such as sodium, potassium, magnesium, calcium, and iron are found in living tissue and are essential to human life—biological anomalies arise when they are depleted or removed. Probably less well known is that currently no less than six other heavy metals including molybdenum, manganese, cobalt, copper, and zinc, have been linked to human growth, development, achievement, and reproduction (Vahrenkamp, 1979; Friberg and others, 1979). Even these metals, however, can become toxic or aesthetically undesirable when their concentrations are too great. Several heavy metals, like cadmium, lead, and mercury, are highly toxic at relatively low concentrations, can accumulate in body tissues over long periods of time, and are nonessential for human health. Table 1 lists metals according to their toxicities.

No specific health guidelines for heavy metals associated with suspended or bed sediments have been established by the U.S. Environmental Protection Agency. This lack of national guidelines based on concise scientific criteria causes difficulty when evaluating the environmental effects of heavy metals in sediments. Several different criteria have been defined, primarily on the basis of observed effects on aquatic life (Lyman and others, 1987). Table 2 (page 57) lists criteria for open-water disposal of polluted sediments that can be used for comparison purposes.

Table 1. Classification of naturally occurring metals according to their toxicity and availability in the hydrologic environment (from Wood, 1974)

<table>
<thead>
<tr>
<th>Non-toxic</th>
<th>Low toxicity</th>
<th>Moderate to high toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Magnesium</td>
<td>Barium</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Manganese</td>
<td>Cerium</td>
</tr>
<tr>
<td>Calcium</td>
<td>Molybdenum</td>
<td>Dysprosium</td>
</tr>
<tr>
<td>Cesium</td>
<td>Potassium</td>
<td>Erbium</td>
</tr>
<tr>
<td>Iron</td>
<td>Strontium</td>
<td>Europium</td>
</tr>
<tr>
<td>Lithium</td>
<td>Rubidium</td>
<td>Gadolinium</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Gallium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Germanium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gold</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Holmium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Neodymium</td>
</tr>
</tbody>
</table>
Sources of Metals in the Mississippi River

Heavy metals in the Mississippi River originate from either natural processes or human activities. Natural erosion and weathering of crustal materials take place over long periods of time and the amount of heavy metals released is small. However, the potential for contamination is increased when mining exposes metal-bearing ores. When compared to the natural exposure of ore bodies through erosion, the exposure rate through mining is over ten times faster for lead and zinc (Massachusetts Institute of Technology, 1970). Leaching of mine tailings and drainage from mined areas can introduce substantial amounts of metals into the river.

Two of the largest lead-zinc mining areas in the world are located along the Mississippi River. The reach of the Mississippi River between Prairie du Chien, Wisconsin, and Galena, Illinois, passes through the Upper Mississippi Valley lead-zinc district of southwest Wisconsin, northwest Illinois, and northeast Iowa. The New Lead Belt lies in southeast Missouri adjacent to the Mississippi River downriver of St. Louis, Missouri.
Figure 22. --Like most of the heavy metals in the Mississippi River, lead is transported largely in association with the suspended sediments. The areas of the dots and pie diagrams on the left side of the figure are proportional to the quantities of lead that were being transported down the Mississippi River at 12 sites sampled during July-August 1991; the dots and pie diagrams on the right side of the figure show the inputs from four main tributaries (complete tabulations of the data are given by Hayes, 1993). The lead loads transported by suspended sediment, both silt and colloid, were larger than the dissolved loads because lead is a strongly "hydrophobic" element—that is, it adsorbs onto sediment particles more readily than remaining in solution by a factor of thousands to one. The suspended silt loads are greater than the colloidal loads because the river transports much more silt than colloid. The quantities of colloid in suspension, for example, were so low at the two most downstream sites sampled during this trip that not enough could be collected for chemical analysis.

Both the silt and colloid fractions were analyzed further to determine in detail how the lead is associated with the sediments. More than one-half the lead in the sediment phases is designated "inorganic," which means that it is an inorganic salt or a component of the iron and manganese hydroxides that coat the surfaces of the sediment particles. The second largest percentage of the lead is called "residual," meaning lead sulfide (galena) or other minerals that contain lead. Usually less than 10 percent of the lead is associated with organic material in the suspended sediment. The blank pie diagrams for St. Anthony Falls and Hastings indicate that there was not enough material to obtain the distribution of lead in the suspended colloid. However, enough colloid was available to determine the total amount of lead present and therefore calculate the corresponding load.

Cadmium is distributed in suspended sediment in much the same way as lead, with the largest proportion being inorganic. Chromium and copper, on the other hand, have much greater residual than inorganic components.

Mercury in River Waters and Sediments
Figure 23. -- The transport of mercury in the Mississippi River differs from that of lead in three important respects. First, there is considerably less mercury than lead in the river; notice the difference in the scales between this and the preceding figure. Second, a greater proportion of mercury is transported in the dissolved phase. Third, most of the mercury in the sediment phases is residual, most likely as mercury sulfides, and the remainder is associated with the organic matter in suspension. The dots and pie diagrams in the figure represent samples collected during the downriver cruise of October-November 1991 at 12 sites on the Mississippi River (left) and in 4 major tributaries (right). Complete tabulations of the data are given by Roth (1994). The percentage of mercury in the organic phase of the silt increased downriver of Thebes. Toxicological implications of this increase are strong because the human body absorbs organic forms of mercury 14 times more readily than inorganic forms (Task Group on Metal Accumulation, 1973). Mercury concentrations in both silts and colloids at Trempealeau, Lock & Dam 9, and Keokuk were not determined; therefore, loads could not be calculated.

Major sources of toxic metals arising from human activities are domestic and industrial wastewaters and their associated solid wastes. On the average, the USEPA estimates that 81 percent of the metals introduced into wastewater treatment plants comes from various regulated industries that dispose of their wastes into municipal sewer systems and that about 19 percent comes from consumer households in the form of common household products (U.S. Environmental Protection Agency, 1986). Cadmium, chromium, copper, lead, and mercury are used extensively in industries along the Mississippi River (table 3). The two main by-products of municipal treatment plants are solid wastes and treated wastewater. In the most common form of treatment, 70 to 90 percent of cadmium, chromium, copper, lead, and zinc are removed as solid wastes (Lester, 1983). The other 10 to 30 percent of these heavy metals remain dissolved in the water that is released back into the river. The concentration and transport of several heavy metals in treated effluent from a wastewater- treatment plant are shown in table 4. Note that, in undiluted wastewater, the concentrations of cadmium, chromium, copper, and mercury exceed USEPA aquatic life standards, and concentrations of cadmium, chromium, lead, and mercury exceed the USEPA drinking water standards listed in table 2. The solid waste or sewage sludge is commonly disposed in landfills or sold as fertilizer. Heavy metals can be released through leaching of sewage sludge in landfills. Sewage sludge also contains plant nutrients and compares favorably to other fertilizers in crop production. The amount of sewage sludge that can be applied to cropland is regulated by the USEPA and depends on the concentration of heavy metals in the sludge and the soil chemistry of the cropland. Some toxic heavy metals, especially cadmium, have been found at elevated concentrations in corn kernels harvested from soils fertilized with sewage sludge (Kiemnec and others, 1990).
Table 3. Selected heavy metals presently or formerly used in major industries along the Mississippi River (from Boyer, 1984, and Dean and others, 1972)

<table>
<thead>
<tr>
<th>Industry</th>
<th>Cadmium</th>
<th>Chromium</th>
<th>Copper</th>
<th>Lead</th>
<th>Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>Machinery products</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Paint pigment and ink</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Electroplating</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Textile mill</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood, pulp and paper</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Organic chemicals</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Inorganic chemicals</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Rubber manufacturing</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Iron and steel foundries</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonferrous metal foundries</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Leather processing</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petroleum refining</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam-generation powerplants</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Average releases of heavy metals into the Mississippi River from a large metropolitan wastewater-treatment plant in St. Paul, Minnesota (from Costner and Thornton, 1989)

[μg/L, microgram per liter]

<table>
<thead>
<tr>
<th></th>
<th>Cadmium</th>
<th>Chromium</th>
<th>Copper</th>
<th>Lead</th>
<th>Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration in μg/L</td>
<td>36</td>
<td>470</td>
<td>280</td>
<td>69</td>
<td>2.8</td>
</tr>
<tr>
<td>Daily transport in kilograms per day</td>
<td>2.2</td>
<td>29</td>
<td>17</td>
<td>4.3</td>
<td>0.17</td>
</tr>
<tr>
<td>Annual transport in metric tons per year</td>
<td>0.8</td>
<td>11</td>
<td>6.2</td>
<td>1.6</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Rural cropland and pasture land abound along the Mississippi River and its tributaries. Soil cultivation accounts for at least 90 percent of the soil erosion in the more humid areas of the United States, and it increases the amount of sediment introduced into the streams and rivers (McElroy and others, 1975). Millions of tons of fertilizers and pesticides are applied to croplands every year. Cultivated soils can become enriched with toxic metals associated with...
these applications. Although the concentrations may vary between specific formulations, many of these fertilizers contain chromium, copper, iron, manganese, nickel, and zinc. Selected pesticides use heavy metals such as mercury as an integral component. During the late spring and early summer, after fertilizers and pesticides have been applied, the runoff from rain flushes these contaminants into the Mississippi River. For example, the uranium concentration in the Mississippi River is 20 times that found in the Amazon River, a result linked to the specific use of phosphate fertilizers (Spalding and Sackett, 1972).

The atmosphere is also a source of metal contamination to aquatic environments. Metal-containing particulates that are washed from the atmosphere by rain and snow are deposited in drainage basins and find their way into lakes and rivers. As of 1973, the total nationwide airborne particulate emissions were distributed basically among three sources: 51 percent from industrial processes, 29 percent from fossil-fuel combustion, and 20 percent from miscellaneous burning practices (Magee and others, 1973). Since 1973, vehicle emissions (and perhaps other emissions as well) have decreased. Stone and rock crushing, iron and steel foundries, grain-handling operations, and cement production emit the greatest percentage of the particulates. Coal, used extensively for power generation, often contains significant concentrations of metals such as vanadium, copper, nickel, chromium, zinc, lanthanum, cobalt, molybdenum, gallium, germanium, tin, and mercury (Magee and others, 1973). Automobile fuels have historically contained lead additives for valve lubrication, but their usage is slowly being phased out.

---

**Lead in Silts and Colloids**

__(Click on image for a larger version, 66K)__

**Figure 24.**-- Concentrations of lead in suspended sediments are greater and more variable in the Upper Mississippi than in the Lower Mississippi River. Lead concentrations shown in these graphs are the totals of inorganic, organic, and residual (see fig. 22). Complete data are tabulated by Hayes (1993).

A Lead concentration in colloidal sediments is generally greater than or equal to the concentration in silts. Data shown in this graph are from suspended sediments collected during the down-river cruise of July-August 1991. Lead concentrations in colloids decrease markedly downriver; concentrations in silts also decrease downriver, but less markedly. Concentrations of lead at some sites in the uppermost river exceed the guideline of 60 micrograms per gram (\(\mu g/g\)) for heavily polluted sediments. Cadmium, chromium, and copper concentrations were similar to those of lead in that they were greater in the colloidal fraction, decreased downriver, and reached a fairly constant level downriver of Winfield, Missouri. Suspended sediment was heavily polluted with chromium and copper at 75 percent of all the locations sampled on the Mississippi River main stem.
The variability of concentrations of lead in suspended silts in the Mississippi River main stem decreases markedly downriver. Shown in this graph are the concentrations of lead in suspended silts collected during the three downriver cruises of July-August 1991, October-November 1991, and April-May 1992. Concentrations in the upper river differed seasonally by factors of two or more; those in the lower river registered seasonal differences of only 10 to 15 percent. The greater variability in the upper river probably reflects a diversity of sediment sources and the impoundment of sediment behind the navigation dams. The downriver increase in the uniformity of the concentration probably reflects the progressive homogenization of the suspended sediment by repeated episodes of deposition and resuspension. The concentrations of 27 to 34 $\mu$g/g that were measured during 1991-92 in the lowest reaches of the Mississippi River are similar to the 32 $\mu$g/g measured by Trefry and others (1985) in samples collected there during 1982-83.

**Figure 25.** -- None of the concentrations of dissolved heavy metals that were measured in the Mississippi River during 1987-92 exceeded the USEPA standards for drinking water or the standards for aquatic life. Shown in the graph are the concentrations of dissolved lead measured in depth-integrated composite samples collected during 1987-92 between Minneapolis and New Orleans (complete tabulations of the data are given by Brinton and others, 1995, and Garbarino and others, 1995). All the concentrations shown here were less than the drinking-water standard by a factor of at least 100. More than one-half of the samples collected had dissolved lead concentrations too small to be measured; in the fraction given at the lower end of each bar, the denominator is the total number of samples analyzed from that site, and the numerator is the number of analyses in which the concentration of lead was less than the detection limit of 0.06 $\mu$g/L. The principal tributaries sampled generally contained metal concentrations greater than the main stem Mississippi River. However, these concentrations decreased downstream from the confluences through simple dilution, precipitation, or adsorption onto sediments. The concentrations of heavy metals are controlled by the volume of the flow of the Mississippi River and are greater during the late fall and winter when freezing temperatures decrease river flow and sediment concentrations than in the spring and early summer when runoff is high. Some fluctuations in concentrations can be attributed to seasonal releases of metals from specific sources.
The numerous studies of the heavy-metal water quality of the Mississippi River that have been conducted over the last several decades have emphasized mostly the water quality in specific regions of either the lower reaches of the river (Everett 1971; Hartung, 1974; Presley and Trefry, 1980; Shiller and Boyle, 1983; Newchurch and Kahwa, 1984; Trefry and others, 1986) or the upper reaches of the river (Eisenreich and others, 1980; Water Quality Work Group of the Great River Environmental Action Team, 1980a, 1980b; Bailey and Rada, 1984; Buhl and McConville, 1984; Wiener and others, 1984). The water quality of the Mississippi River at selected locations has also been reported (Briggs and Ficke, 1978; DeLeon and others, 1986; Smith and others, 1987; Costner and Thornton, 1989; Taylor and others, 1990). However, our study assesses the heavy-metal contamination through the full length of the Mississippi River from Minneapolis, Minnesota, to the Gulf of Mexico. Over the 5-year assessment period, the effects of seasonal variation and changes in the river flow rate could be evaluated. The water and sediment samples were collected by the same group of scientists during the entire study using proven sampling protocols. In addition, all samples were analyzed by one group of scientists in a single laboratory using state-of-the-art instrumentation and methodology. Heavy metals released into the Mississippi River, by both natural processes and human activities, can be distributed among several different forms within the water environment as shown in figures 22 and 23. Metals can be either transported with the water and suspended sediment or stored within the riverbed bottom sediments. Heavy metals are transported as (1) dissolved species in the water, (2) suspended insoluble chemical solids, or (3) components of the suspended natural sediments. Metals dissolved in the water can exist as hydrated metal ions or as aqueous metal complexes with other organic or inorganic constituents. Water-insoluble inorganic (non-carbon-containing, except for carbonates) chemical solids such as metal hydroxides may be formed, as may organic (carbon-containing) chemical solids, such as those associated with compounds derived from the decay of living organisms. Both inorganic and organic solids can be transported with the water as individual entities or as chemical coatings on suspended sediments. In addition, mineral components of suspended sediments themselves can contain heavy metals. Heavy-metal solids can also be stored in river-bottom sediments. Suspended sediments and metallic chemical solids are stored in riverbed sediment after they aggregate to form large, denser-than-water particles that settle from the water when the river's flow is not sufficient to keep them in suspension.

**Uranium and Copper Dissolved in River Waters**

(Click on image for a larger version, 83K)

**Figure 26.** -- Although they are well within drinking-water standards, concentrations and loads of dissolved heavy metals in the Mississippi River give clues to their sources. The data for dissolved uranium and dissolved copper shown here were collected during the downriver sampling cruise of April-May 1992. Represented in the figure are depth-integrated composite samples of the flowing main stem (circles) and four tributaries (the Minnesota, Illinois, Missouri, and Ohio Rivers: squares and bars), areally composited samples of backwaters in the navigation pools (triangles), and samples of water dipped from surfaces of tributaries other than the four listed above (squares and bars). The complete data are tabulated by Garbarino and others (1995).
A

Uranium dissolved in the Mississippi River comes, in large part, from phosphate fertilizers applied to croplands. Uranium occurs naturally in phosphate rock that is mined for fertilizer. Rain falling on fertilized croplands washes some uranium-containing fertilizer from the fields into streams and rivers. Concentrations of dissolved uranium are greatest in the Upper Mississippi River. Tributaries like the Minnesota and Des Moines Rivers, which drain areas that are farmed intensively for corn and other grains, have high concentrations of dissolved uranium that increase the concentrations in the Mississippi River downstream from their confluences.

B

Copper dissolved in the Mississippi River comes mostly from industrial and municipal wastewaters. Concentrations of dissolved copper generally increase in the downriver direction, especially near urban centers. Some tributaries carry greater concentrations of copper than the main stem Mississippi, but their influences on main stem concentrations seem to be minimal.

C

The transport of dissolved uranium downriver depends on water discharge as well as on the concentration of the element in solution. Transports usually are greater during high-flow periods such as spring runoff (shown here) than during periods of lower flow. For example, the transport of dissolved uranium measured at Vicksburg during the spring sampling trip shown here was twice the transport measured at the same site the previous November—even though the dissolved concentrations were virtually the same. During the sampling trip shown here, the Mississippi River was receiving high loads of dissolved uranium from the Minnesota and Des Moines Rivers (because of their high concentrations) and from the Missouri and Ohio Rivers (because of their high water discharges). The abrupt decrease in uranium transport near river kilometer 500 represents the Old River Outflow where about one-fourth of the flow of the Mississippi River is diverted into the Atchafalaya River.

D

The transport of dissolved copper in the Mississippi River, like that of dissolved uranium, varies directly with the water discharge. The most significant increases in the transport of dissolved copper occur at the confluences of the Mississippi with the Missouri and Ohio Rivers.

Mercury Dissolved in River Waters

Click on image for a larger version, 50K

Figure 27. -- Mercury dissolved in the Mississippi River is derived (like copper) from municipal and industrial sources. The distribution of dissolved mercury in the Mississippi can be shown in more detail than that of other heavy metals (such as uranium and copper, shown in the previous figure)
because samples were collected specifically for mercury analyses during upriver transects. Shown in the graph are the concentrations of dissolved inorganic mercury in samples collected from the river surface at 15- to 20-kilometer intervals between New Orleans and Minneapolis during the upriver cruise of September 25-October 4, 1991 (a complete tabulation of the data is given by Roth, 1994). The line in the graph represents the average of the concentrations of each three adjacent samples (that is, a 3-point moving average) over 45- to 60-kilometer reaches of the river. Mercury concentrations were lowest in the upper reaches and gradually increased downriver. Large concentrations were measured downstream from tributaries such as the Des Moines, Illinois, and Missouri Rivers and near large metropolitan and industrial centers, specifically St. Louis, Missouri, Vicksburg, Mississippi, and below Baton Rouge, Louisiana. Farther downstream from each of these inputs, the concentration of dissolved mercury appears to have decreased; these decreases may be due to transformations of inorganic mercury to organic forms or to its adsorption onto sediment rather than to a decrease in the overall concentration of mercury in the river.

The different chemical forms of heavy metals in the river influence their availability and toxicity to organisms. Heavy metals are readily available to aquatic organisms and pose a significant health hazard when they are present as dissolved inorganic or organic species in the water or loosely adsorbed to particulate surfaces. When heavy metals are present as components of particulates, such as inorganic metal-hydroxide coatings or metal-organic compounds, some chemical alterations are required before they can be released and become biologically available. Even stronger chemical reactions are required to release heavy metals that are integral parts of the minerals composing river sediments.

The water chemistry of the Mississippi River, the aqueous chemistry of individual heavy metals, the type and surface area of the particulates present in the Mississippi River, and other hydrologic factors control where the metals will be found. The water chemistry is controlled by many complex factors such as water acidity and the type and concentration of the major inorganic compounds, organic compounds, and suspended sediment. Many of these factors are also influenced by seasonal variation in river flow and temperature, and the decomposition of vegetation. The Mississippi River, like the majority of natural waters in the United States, can be described as having bicarbonate-type water because bicarbonates, especially calcium bicarbonate, predominate as the dissolved salt (Water Quality Work Group of the Great River Environmental Action Team, 1980b). Bicarbonate water is slightly alkaline rather than acidic. An aqueous solution of baking soda is a good example of an alkaline solution, whereas orange juice is an acidic solution. The major fraction of heavy metals released into alkaline natural waters becomes associated with either the suspended particulates or the bed sediments. This association reduces or eliminates dissolved heavy metals, which are usually the most toxic form. For example, dissolved lead and zinc compounds from mine wastes tend to be adsorbed onto natural silt and clay sediments or organic matter, rather than staying dissolved in the water of the Mississippi River (Jennett and others, 1973). In contrast, most of the light metals tend to remain as dissolved species in the water.

**Heavy-Metal Water Quality of the Mississippi River**

The brief glimpse at the heavy metals in the Mississippi River described in this chapter generally was based on data collected during the summer and autumn of 1991 and the spring of 1992. Data that were collected in the Lower Mississippi River during 1987-90 (Brinton and others, 1995) reinforce the findings presented here. Concentrations of toxic heavy metals dissolved in the water in the 2,900 km reach of the Mississippi River from Minneapolis, Minnesota, to Belle Chasse, Louisiana, are well below USEPA guidelines for drinking water and water that supports aquatic life. However, heavy metals associated with suspended sediments exceeded the pollution guidelines at many of the main-stem sampling locations. Heavy-metal concentrations in the suspended sediments were generally greater in the small colloidal-sized particles than the larger silt-sized particles. Even though the colloids compose a significantly lower percentage of the total suspended sediment, their heavy-metal concentrations are greater, and they are small enough to pass through some of the filtering systems used in water-treatment facilities. Sediments stored in pools upstream from every lock and dam of the Upper Mississippi
River also have elevated heavy-metal concentrations. The biological accessibility to heavy metals associated with suspended and stored sediment also depends on the chemical form in which the metal exists. A high percentage of the heavy metals in all the sediment sizes exist in chemical forms that can be dissolved if appropriate conditions driven by chemical or biological processes are present.

Concentrations of dissolved heavy metals and those associated with suspended sediment vary seasonally. Dissolved heavy-metal concentrations are generally greater during periods when the river flow is low, during droughts and winter months, because the decrease in water volume decreases dilution effects and the decrease in suspended sediment concentrations decreases metal-scavenging processes. Conversely, the increases in river flow during the warmer months either dilute heavy metal concentrations with greater volumes of water or decrease dissolved metal concentrations through increased scavenging processes resulting from higher suspended-sediment concentrations. As a result, heavy-metal transport on suspended sediment increases during high-flow periods. Wastewater treatment, agricultural practices, and mining activities all influence the water quality. Crop fertilization periodically introduces specific heavy metals into the hydrologic system after spring applications and spring runoff. Discharges from wastewater-treatment facilities and industrial manufacturing activities cause increases in heavy-metal concentrations near major urban areas.

Whether the loads and concentrations of heavy metals in the Mississippi River have increased or decreased in recent years is difficult to determine. Although most of the heavy metals in the river are associated with sediment, most of the previous studies have focused on the dissolved metals. Even for the dissolved metals, comparisons are difficult to draw between earlier and more recent data because analytical laboratory techniques have become markedly more sensitive in the last decade and field sampling techniques have not been adequately standardized. Specific conclusions about increases or decreases in heavy metals with time in the Mississippi River are tenuous at best.

---

**Metals Dissolved in River Waters**

*(Click on image for a larger version, 33K)*

**Figure 28.** Statistical analysis of dissolved heavy-metal concentrations measured at all main-stem locations of the Mississippi River during the July-August 1991, October-November 1991, and April-May 1992 cruises indicate that cadmium, chromium, copper, lead, and uranium varied little with season. Of 36 samples collected during this period only one cadmium concentration was greater than the detection limit of 0.1 ug/L. In 11 of the 36 samples, concentrations of chromium were less than the detection limit of 0.2 ug/L. In 20 of the 36 samples, lead concentrations were less than the detection limit of 0.06 ug/L. Dissolved mercury was less than the detection limit of 0.004 ug/L in 15 of the 36 samples. All the samples contained measurable concentrations of copper and uranium.
**Lead and Mercury in Bed Sediments**

(Click on image for a larger version, 83K)

**Figure 29.** -- The bed sediments stored in the nonchannel (backwater) areas of the navigation pools of the Upper Mississippi River contain substantial quantities of heavy metals. However, the concentrations of lead and mercury in these bed sediments are generally less than those measured in the suspended sediments in transport; and, in the case of lead, the concentrations usually are less than the criterion value of 40 \( \mu g/g \) for moderately polluted sediment. Data used in this figure are the concentrations measured in a composite sample derived from 15-20 bed samples collected from the lower reaches of each navigation pool. The difference between lead and mercury concentrations measured in the bed sediments and in suspended sediments is mostly due to the differences in sediment particle size. Bed sediment samples were composed of a wide variety of particle sizes that ranged from coarse sand to colloid (see fig. 7B), markedly different than the suspended sediment. In addition, bed sediment samples were not separated into individual particle-size fractions prior to analysis, as was the case for suspended sediment, but rather were analyzed as a whole. As a result, the heavy-metal concentrations measured in the bed sediments would be expected to be lower because of the presence of less metal-laden sand particles. Complete data are tabulated in the reports by Hayes (1993) and Roth and others (1995).

**A**

The distribution of bed-sediment particle sizes in navigation pools of the Upper Mississippi River depends on factors such as pool size and configuration. More than 80 percent of the bed sediment collected from Lake Pepin, Pool 9, Pool 12, Pool 13, and Pool 26 was composed of silt and colloid particles (shown here as percent finer than 63 micrometers); more than 70 percent of the sediment collected in Pools 2, 3, 11, and 19 was silt and colloid.

**B**

The bed sediments collected from the rest of the pools contained significantly lower percentages of silt and colloid. In bed sediments collected from 25 navigation pools of the Upper Mississippi River between July 1991 and April 1992, the greatest concentrations of lead were in Lake Pepin, Pool 12, Pool 19, and Pool 26. Lake Pepin, a large and narrow natural lake, is known to trap large proportions of the suspended sediment that the Mississippi River delivers to it from the north. Pool 12 receives inflow from the Galena River, which drains a lead and zinc mining district. Lead leaching from the lead mines has an affinity for sediment. However, the relation of the high lead concentration in Pool 12 to the nearby mining district has not been confirmed. The high lead concentrations could simply be a result of the large proportion of fine bed-sediment material present in the pool. Pool 19 is the largest of the artificial pools, not as large as Lake Pepin, but more likely than the other smaller pools to trap and retain sediments and their associated contaminants. Elevated lead concentrations in the bed sediment of Pool 26 suggest a link to the input of lead-laden sediment from the Illinois River. Grab samples of the bed sediment collected from the Illinois River near Hardin, Illinois, contained 25 \( \mu g/g \) of lead, or about twice the concentration found in the bed sediments from Pool 25. Cadmium, chromium, copper, nickel, and...
zinc followed nearly the same trend as lead, with bed-sediment concentration maximums at Lake Pepin, Pool 12, Pool 19, and Pool 26. Only bed sediments from Lake Pepin, and possibly from Pool 12, can be described as moderately polluted in lead. In most pools, approximately 50 percent of the lead in the bed sediment was associated with the inorganic component, 40 percent with the residual component, and 10 percent with the organic component. The greatest proportions of the inorganic component were found where the lead concentrations were highest. Therefore, most of the lead in the pool bed-sediment environment may be readily accessible and could be released if the proper conditions existed. Other heavy metals-cadmium, chromium, and copper-had their greatest percentages in the residual component. Except for cadmium, the proportions of heavy metals designated as inorganic, organic, and residual were similar to those in the main-stem suspended sediments. The concentrations shown in the figure are similar to earlier data collected by Bailey and Rada (1984), who reported the following average concentrations of lead in bed sediments: 40 \mu g/g in Lake Pepin, 13 \mu g/g in Pool 5, and 14 \mu g/g in Pool 9.

C and D

Mercury concentrations in pool bed sediments of the Upper Mississippi River can be correlated to the organic carbon content of the sediments. Mercury concentrations in the bed sediments of most pools, except for Lake Pepin, were not large enough to cause adverse toxicological effects. Bed-sediment mercury concentrations in Lake Pepin exceeded 0.18 \mu g/g, a level that has been shown to increase the mortality rates in fish embryos, eggs, and larvae (Birge and others, 1977). Mercury can bioaccumulate in many aquatic organisms, especially fish, by direct ingestion of suspended or bed-sediment particles. High organic-carbon concentrations in the presence of mercury in the bed sediments increase the methylation rate of mercury and subsequently increase the absorption and retention of mercury in fish and human tissues. Lake Pepin, Pools 2, 3, 12, 19, and 26 are the most likely areas in which this might occur because of the high percent organic carbon in their bed sediments.

REFERENCES

Bailey, P.A., and Rada, R.G., 1984,


Boyer, H.A., 1984,

Briggs, J.C., and Ficke, J.F., 1978,


Buhl, K.J., and McConville, D.R., 1984,

Costner, Pat, and Thornton, Joe, 1989,
We all live downstream-The Mississippi River and the national toxics crisis: Washington, D.C., Greenpeace USA, 120 p., 1 app. (61 p.).

Trace organic and heavy metal pollutants in the Mississippi River: Chemosphere, v. 15, no. 6, p. 795-805.

Eisenreich, S.J., Hoffmann, M.R., Rastetter, D., Yost, E., and Maier, W.J., 1980,

Everett, D.E., 1971,

Friberg, L., Nordberg, G.F., and Vouk, V.B., eds., 1979,


Great Lakes Water Quality Board, Dredging Subcommittee, 1982,

Hartung, R., 1974,

Hayes, H.C., 1993,
Metal associations in suspended sediments and bed sediments from the Mississippi River: Golden, Colorado School of Mines, Department of Chemistry and Geochemistry, M.S. thesis, 131 p.

Transport mechanisms of lead industry wastes, in Proceedings of Industrial Waste Conference, 28th, Purdue University: Boston, Butterworth Publishers, p. 496-512.

Kiemnec, G.L., Hemphill, D.D., Hickey, M., Jackson, T.L., and Volk, V.V., 1990,

Lester, J.N., 1983,

Lyman, W.J., Glazer, A.E., Ong, J.H., and Coons, S.F., 1987,

Magee, E.M., Hall, H.J., and Varga, G.M., Jr., 1973,
Potential pollutants in fossil fuels: U.S. Environmental Protection Agency Publication EPA-R2-73-249, p. 54-56.

Massachusetts Institute of Technology, 1970,

McElroy, A.D., Chiu, S.Y., Nebgen, J.W., Aleti, A., and Vandergrift, E., 1975,

Newchurch, E.J., and Kahwa, I.A., 1984,

Presley, B.J., and Trefry, J.H., III, 1980,

Roth, D.A., 1994,

Roth, D.A., Garbarino, J.R., and Taylor, H.E., 1995,


Shiller, A.M., and Boyle, Edward, 1983,
Trace metals in the plume of the Mississippi River [abs.]: EOS American Geophysical Union Transactions, v. 64, p. 1021.

Smith, R.A., Alexander, R.B., and Wolman, M.G., 1987,

Spalding, R.F., and Sackett, W.M., 1972,
Uranium in runoff from the Gulf of Mexico distributive province: anomalous concentrations: Science, v. 175, p. 629-631.

Task Group on Metal Accumulation, 1973,
Accumulation of toxic metals with special reference to their absorption, excretion, and biological half-times: Environmental Physiology and Biochemistry, v. 3, p. 65-107.

Taylor, H.E., Garbarino, J.R., and Brinton, T.I., 1990,

Mississippi River methods comparison study-Implications for water quality monitoring of dissolved trace elements: Environmental Science and Technology, v. 29, p. 1313-1317.


Trefry, J.H., III, Metz, S., and Trocine, R.P., 1985,

Trace metal fluxes through the Mississippi River delta system, in Kullenberg, G., ed., Contaminant fluxes through the coastal zone: Rapports et
Contaminants in the Mississippi River

U.S. Environmental Protection Agency, 1982,
Maximum contaminant levels (subpart B of part 141, National interim primary water regulations): U.S. Code of Federal Regulations, Title 40, Parts 100 to 149, revised as of July 1, 1982, p. 315-318.

___ 1986,

___ 1992,

Vahrenkamp, H., 1979

___ 1980b,
Water quality work group appendix: GREAT II, Study of the Upper Mississippi River (Guttenberg, Iowa, to Saverton, Missouri), 216 p.


Wood, J.M., 1974,