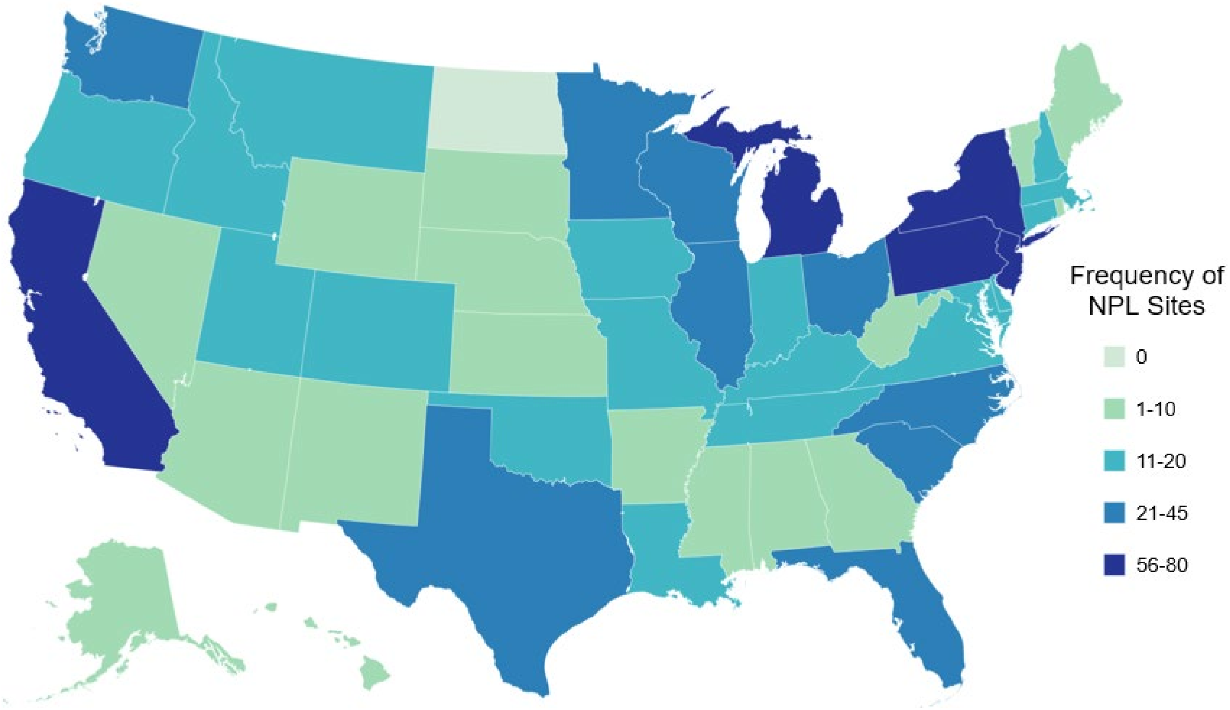
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Copper and copper compounds have been identified in at least 934 of the 1,868 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2022). However, the number of sites evaluated for copper and copper compounds is not known. The number of sites in each state is shown in Figure 5-1. Of these sites, 924 are located within the United States, 1 is located in Guam, 1 is located in the Virgin Islands, and 8 are located in Puerto Rico (not shown).

Figure 5-1. Number of NPL Sites with Copper Contamination



Source: ATSDR 2022

- Copper occurs naturally both in many minerals and in the metallic state. The top 10 applications for copper in the United States, in order of percentage of total use, are building wire, plumbing, and heating, automotive, air conditioning, refrigeration and natural gas, power utilities, telecommunications, in-plant equipment, ordnance, business electronics, and lighting and wiring devices.

- Industrial effluents, mining, and production of copper and other metals, municipal solid waste management, and fossil fuel combustion account for a large portion of the total environmental releases of copper and copper compounds. Natural sources of copper releases include windblown dust, volcanoes, decaying vegetation, forest fires, and sea spray.

- Copper is an essential micronutrient present in many foods. Copper gluconate and copper sulfate are direct food additives generally recognized as safe by the U.S. Food and Drug Administration (FDA).
- The general population is expected to be exposed to copper daily via inhalation of ambient air, ingestion of foods and drinking water, and to a lesser extent dermally to materials containing copper.
- People living near copper smelters and refineries and workers in these and other industries may be exposed to high levels of dust-borne copper by both inhalation and ingestion.

Copper and its compounds are naturally present in the Earth's crust and can be discharged naturally to air and water during weathering. Mean copper concentrations in the atmosphere were 0.0182–0.0238 $\mu g/m^3$ at 13 U.S. locations from 2020 to 2021 (EPA 2022a). For 10 U.S locations reporting data for 2022, the mean value was 0.021 $\mu g/m^3$ and the maximum value was 0.0640 $\mu g/m^3$ (EPA 2022a). Airborne copper is associated with particulates that are derived from suspended soils, combustion sources, the manufacture or processing of copper-containing materials, and mine tailings. Copper associated with particulate matter is emitted into the air naturally from windblown dust, volcanoes, and anthropogenic sources, the largest of which are primary copper smelters and ore processing facilities. The major sources of releases to water are mining operations, agriculture, sludge from publicly owned treatment works (POTWs), and municipal and industrial solid waste. Mining and milling contribute the most waste. Copper is released to water because of natural weathering of soil and discharges from industries and sewage treatment plants. Copper compounds may also be intentionally applied to water as an aquatic herbicide to kill algae. Copper concentrations in groundwater vary widely from 0.2 to 98.4 µg/L (USGS 2020b). Copper is predominantly found in the Cu(II) ($^+$2 oxidation) state under environmental conditions, and most of it is complexed or tightly bound to organic matter. A small amount of copper is present as the free (hydrated) or readily exchangeable form. The combined processes of complexation, adsorption, and precipitation control the level of free Cu(II) in the environment. The chemical conditions in most natural water are such that, even at relatively high copper concentrations, these processes will reduce the free Cu(II) concentration to extremely low values. The USGS reported the median level of copper in soil and sediment as 30 ppm (USGS 2016). Copper concentrations will be higher in soils that are close to sources of copper emissions and mining activities.

In the general population, the highest exposures to copper come from the ingestion of drinking water and foods. Copper is found in organ meats, shellfish, and nuts, as well as some whole grains, chocolate, and leafy vegetables like spinach (see Section 5.5.4 and Table 5-22). Copper can leach into drinking water from contact surfaces within water distribution systems, water treatment plants, and in-home plumbing systems. When a system has not been flushed after a period of disuse, the concentration of copper in tap water can exceed 1.3 mg/L, the EPA drinking water action level. Copper-contaminated water may have a light blue or blue-green color with a metallic, bitter taste (WHO 2004).

Many workers are exposed to copper in agriculture, industries connected with copper production, metal plating, and other industries. Based on the available data, people living close to NPL sites contaminated with copper may be at greater risk for exposure to copper than the general population with respect to inhalation of airborne particulates from the NPL sites, ingestion of contaminated water or soil, and/or uptake of copper by fruits and vegetables raised in gardens of residents living near NPL sites. People living near copper smelters and refineries and workers in these and other industries may be exposed to high levels of dust-borne copper by both inhalation and ingestion routes.

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

Copper occurs naturally in many minerals, such as cuprite (Cu_2O), tenorite (CuO), malachite ($CuCO_3{\cdot}Cu(OH)_2$), azurite ($2CuCO_3{\cdot}Cu(OH)_2$), antlerite ($CuSO_4{\cdot}2Cu(OH)_2$), brochantite ($CuSO_4{\cdot}3Cu(OH)_2$), chrysocolla ($CuO{\cdot}SiO_2{\cdot}2H_2O$), chalcopyrite ($CuFeS_2$), chalcocite ($Cu_2S$), covellite ($CuS$), and bornite ($Cu_5FeS_4$). It also occurs as copper metal (Davenport 2001). Copper is most commonly present as copper-iron-sulfide and copper sulfide minerals (Schlesinger et al. 2011a). The copper content of ores ranges from 0.5 to 1 or 2% copper (Schlesinger et al. 2011a). Most copper is obtained from copper-iron-sulfur ores, such as chalcopyrite and chalcocite, and the principal copper ore mineral is chalcopyrite, which yields a matter of approximately 50% copper (Morris and Wadsley 2001; Schlesinger et al. 2011a). The most common process to produce copper is via pyrometallurgical technology, accounting for about 80% of global processes; production of pure copper metal typically involves concentrating, smelting, and electrolytic refining of low-grade ores containing copper-sulfide minerals (Adrianto et al. 2022; Haynes et al. 2015; USGS 2022).

Domestic mine production of recoverable copper in the United States totaled 1.3 million tons in 2019, 1.2 million tons in 2020, and 1.23 million tons in 2021 (USGS 2022). The average daily mine production in January of 2022 increased by 14% compared to production in January 2021. In 2015, the recoverable copper content per unit of ore mined was 0.47% (USGS 2017b). The United States is the world's fourth leading copper producer, along with Congo and following Chile, China, and Peru (USGS 2020a). Based on data from S&P Global Market Intelligence, annual global production of copper in 2019 equaled 20.5 Mt (Adrianto et al. 2022). In 2021, copper was actively mined in seven states with Arizona accounting for 71% of U.S. copper production, and active operations in Utah, New Mexico, Nevada, Montana, Michigan, and Missouri (USGS 2020a). There were 25 copper-producing U.S. mines in 2021, with 19 mines accounting for 99% of production in the United States.

Tables 5-1 and 5-2 summarize information on companies that reported the production, import, or use of copper and copper compounds, respectively, for the Toxics Release Inventory (TRI) in 2022 (TRI22 2024). TRI data should be used with caution since only certain types of industrial facilities are required to report. This is not an exhaustive list.

Table 5-1. Facilities that Produce, Process, or Use Copper

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AK	3	1,000	99,999	12
AL	72	0	999,999,999	1, 5, 7, 8, 9, 10, 11, 12, 13, 14
AR	46	0	49,999,999	2, 3, 6, 7, 8, 9, 10, 11, 12, 14
AZ	24	0	9,999,999	1, 4, 5, 7, 8, 11, 12, 13
CA	94	0	9,999,999	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 14
CO	9	0	999,999	2, 3, 4, 8, 11, 12, 14
CT	40	1,000	9,999,999	2, 3, 4, 8, 9, 12, 14
DE	2	1,000	9,999	7, 8, 11
FL	33	100	999,999	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
GA	61	0	49,999,999	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 14
HI	3	0	999,999	9, 12
IA	50	1,000	9,999,999	1, 2, 3, 5, 7, 8, 9, 11, 12, 14
ID	10	0	999,999	1, 8, 9, 11, 12, 13, 14
IL	122	0	99,999,999	1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 14
IN	132	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 14
KS	43	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 14
KY	55	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
LA	19	0	9,999,999	1, 2, 5, 7, 8, 9, 10, 12, 13, 14
MA	44	1,000	9,999,999	1, 3, 6, 7, 8, 9, 11, 12, 14
MD	5	1,000	999,999	2, 3, 4, 8, 12
ME	8	1,000	999,999	7, 8, 9, 12
MI	117	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
MN	54	0	9,999,999	2, 3, 7, 8, 11, 12, 13, 14
MO	66	0	9,999,999	1, 5, 7, 8, 9, 11, 12, 14
MS	31	1,000	49,999,999	2, 3, 7, 8, 12

Table 5-1. Facilities that Produce, Process, or Use Copper

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
MT	1	1,000	9,999	1, 5, 12
NC	79	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 14
ND	3	1,000	99,999	8
NE	17	10,000	9,999,999	7, 8, 11, 14
NH	17	100	9,999,999	2, 3, 7, 8, 9, 11, 12
NJ	29	100	49,999,999	1, 2, 3, 4, 5, 7, 8, 9, 12
NM	3	10,000	99,999	8, 12
NV	13	1,000	9,999,999	1, 2, 3, 4, 5, 8, 9, 11, 12
NY	79	0	9,999,999	1, 2, 3, 4, 5, 7, 8, 9, 11, 12, 14
OH	185	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
OK	58	100	499,999,999	6, 7, 8, 9, 11, 12, 14
OR	12	0	999,999	1, 5, 7, 8, 12, 14
PA	198	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14
PR	10	100	9,999,999	7, 8, 9, 11
RI	16	1,000	9,999,999	1, 3, 4, 7, 8, 9, 12, 14
SC	64	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14
SD	13	1,000	999,999	1, 5, 7, 8, 14
TN	72	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
TX	118	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 14
UT	13	1,000	9,999,999	2, 3, 7, 8, 12
VA	36	0	9,999,999	7, 8, 11, 12, 14
VT	4	1,000	99,999	2, 3, 8, 9, 11, 12
WA	20	0	999,999	1, 2, 3, 5, 6, 7, 8, 9, 11, 12, 14
WI	149	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14
WV	5	10,000	9,999,999	2, 3, 7, 8
WY	3	100	99,999	1, 2, 4, 9, 12, 13

[a] Post office state abbreviations used.
[b] Amounts on site reported by facilities in each state.
[c] Activities/uses:

1. Produce
2. Import
3. Used Processing
4. Sale/Distribution
5. Byproduct
6. Reactant
7. Formulation Component
8. Article Component
9. Repackaging
10. Chemical Processing Aid
11. Manufacture Aid
12. Ancillary
13. Manufacture Impurity
14. Process Impurity

Source: TRI22 2024 (Data are from 2022)

Table 5-2. Facilities that Produce, Process, or Use Copper Compounds

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AK	7	1,000	9,999,999	1, 5, 6, 8, 10, 12, 13, 14
AL	57	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
AR	48	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13, 14
AZ	27	100	10,000,000,000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
CA	67	0	999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14
CO	21	0	999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
CT	17	1,000	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13
DC	1	10,000	99,999	12
DE	6	10,000	99,999	8
FL	42	100	9,999,999	1, 2, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
GA	61	100	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
IA	37	0	999,999	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
ID	16	1,000	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
IL	75	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
IN	63	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
KS	13	100	999,999	1, 3, 4, 5, 6, 8, 9, 10, 12, 13, 14
KY	40	1,000	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
LA	30	0	49,999,999	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13
MA	8	1,000	999,999	1, 2, 4, 5, 7, 8, 11, 14
MD	14	100	9,999,999	1, 3, 4, 5, 7, 8, 9, 12, 13
ME	3	100	999,999	1, 5, 7, 14
MI	59	1,000	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
MN	40	100	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
MO	52	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
MS	28	1,000	49,999,999	1, 2, 3, 4, 5, 8, 10, 13, 14
MT	9	100	49,999,999	1, 3, 4, 5, 6, 8, 9, 10, 12, 13, 14
NC	61	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13, 14
ND	6	1,000	999,999	1, 3, 5, 10, 12, 13, 14
NE	22	100	49,999,999	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
NH	7	1,000	999,999	1, 3, 5, 6, 8, 9, 11, 14
NJ	12	1,000	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 14
NM	7	1,000	49,999,999	1, 3, 4, 5, 8, 9, 11, 12, 13, 14
NV	16	0	49,999,999	1, 4, 5, 10, 12, 13, 14
NY	22	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 13, 14
OH	76	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
OK	22	0	999,999	1, 2, 3, 4, 5, 8, 9, 10, 12, 13, 14
OR	23	0	9,999,999	1, 2, 3, 5, 6, 8, 10, 11, 12, 14
PA	82	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
PR	8	10,000	9,999,999	1, 5, 8, 12, 14

Table 5-2. Facilities that Produce, Process, or Use Copper Compounds

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
RI	7	1,000	999,999	7, 8, 11, 12, 14
SC	34	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
SD	8	0	0	0
TN	54	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
TX	119	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
UT	19	1,000	10,000,000,000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
VA	32	100	999,999	1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 14
VI	1	10,000	99,999	10
VT	2	0	0	0
WA	19	100	49,999,999	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
WI	48	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14
WV	18	1,000	999,999	1, 3, 4, 5, 7, 8, 9, 11, 12, 13, 14
WY	6	0	999,999	1, 2, 3, 4, 5, 12, 13, 14

[a] Post office state abbreviations used.
[b] Amounts on site reported by facilities in each state.
[c] Activities/uses:

1. Produce
2. Import
3. Used Processing
4. Sale/Distribution
5. Byproduct
6. Reactant
7. Formulation Component
8. Article Component
9. Repackaging
10. Chemical Processing Aid
11. Manufacture Aid
12. Ancillary
13. Manufacture Impurity
14. Process Impurity

Source: TRI22 2024 (Data are from 2022)

Copper from oxidized minerals is usually produced by leaching, solvent extraction, and electrowinning (Schlesinger et al. 2011b). Since most copper comes from Cu-Fe-S ores that are not easily dissolved by aqueous solutions, most extraction occurs by concentration, smelting, and refining (Schlesinger et al. 2011b). This extraction occurs by crushing and grinding the ore and then isolating mineral particles to a concentrate by froth flotation, smelting the concentrate to a matte, oxidizing the matte to impure molten copper, and then fire- and electrorefining the copper (Schlesinger et al. 2011b).

Production of copper in the United States includes not only the processing of both domestic and foreign ores, but also the recovery of scrap. Scrap is a significant part of the U.S. copper supply. There are three types of scrap: home scrap (copper that primary producers cannot further process or sell), old scrap (metal that has been used in products), and new scrap (generated during manufacturing) (Schlesinger et al. 2011c). In 2015, smelting was performed in the United States by three smelters, with a combined production of 527,000 metric tons per year (USGS 2017b). During 2015, three refineries produced

1,090,000 metric tons of copper from primary sources and 48,800 from secondary materials (scrap), for a combined total refinery production in the United States of 1,140,000 tons (USGS 2017b). Production of secondary copper amounted to 805,000 metric tons in 2015 (USGS 2017b). In 2019, 3 smelters, 3 electrolytic refineries, 4 fire refineries, and 14 electrowinning facilities operated in the United States (USGS 2020a). Refineries produced 1,000,000 metric tons from ore and 45,000 metric tons from scrap, for a total refinery production of 1,045,000 metric tons.

Copper sulfate is also produced as a byproduct of copper production by ore-leaching with sulfuric acid as the solvent. Production of copper sulfate in the United States increased from 22,800 metric tons in 2011 to 23,000 metric tons in 2013 but decreased to 18,497 metric tons in 2015 (USGS 2017b). Production figures for other copper compounds are not reported by the USGS.

5.2.2 Import/Export

In 2021, 13,000 metric tons of unmanufactured copper and 920,000 metric tons of refined copper were imported into the United States (USGS 2022). Chile, Canada, and Mexico were the principal sources of imported refined copper. Imports of copper sulfate amounted to 43,900 metric tons in 2015 and were primarily obtained from Mexico (USGS 2017b).

In 2021, the United States exported 360,000 metric tons of unmanufactured copper and 50,000 metric tons of refined copper (USGS 2022). In 2015, copper scrap was the leading U.S. copper export at 426,000 metric tons (USGS 2017b). Exports of copper sulfate amounted to 6,170 metric tons in 2015 (USGS 2017b).

5.2.3 Use

Copper is one of the most important metals used in industries because of its resistance to corrosion, antimicrobial properties, durability, ductility, malleability, and electrical and thermal conductivity. It is used primarily as copper metal or in alloys. Copper alloys, including brass and bronze, are important commodities (USGS 2009a). Currently, American coins are copper alloys (USDT 2018). A small percentage of copper production goes into the manufacture of copper compounds, primarily copper sulfate.

After accounting for production, imports, and exports, 1,800,000 metric tons of copper were available for use in 2019 (USGS 2020a). The Copper Development Association estimated that the end-use distribution of copper and copper alloy products in 2019 were: building construction, 43%; electrical and electrical products, 20%; transportation equipment, 20%; consumer and general products, 10%; and industrial machinery and equipment, 7% (USGS 2020a). The top 10 applications for copper in the United States, in order of percentage of total use, are building wire, plumbing and heating, automotive, air conditioning, refrigeration and natural gas, power utilities, telecommunications, in-plant equipment, ordnance, business electronics, and lighting and wiring devices (Schlesinger et al. 2011b). Copper plumbing is used in water distribution systems (Edwards et al. 2001; EPA 1995; Grace et al. 2012; Knobeloch et al. 1998; Lagos et al. 2001; Rajaratnam et al. 2002; Schock and Sandvig 2009; Turek et al. 2011). Copper and its salts are also used in cookware, kitchen utensils, and mugs; marine antifouling paints; animal feed supplements; fertilizers, fireworks; brake pads; water pipes; roofs; gutters; shingles; wood preservatives; and tires (Banavi et al. 2020; Koo et al. 2020; Lifset et al. 2012; Ni and Li 2008).

EPA has registered about 300 copper compounds and alloys as antimicrobial agents (Vincent et al. 2016). Copper-silver ionization filters have been used in hospital water systems to control waterborne pathogens (Huang et al. 2008; Rohr et al. 1999), and copper sulfate is used as an algaecide and bactericide in drinking water in the United States (NSF 2021). Since copper's antimicrobial properties make it useful for drinking water treatment and distribution, it also has potential uses for reducing microbial contamination and health care-associated infections by controlling microorganisms in heating ventilation and air-conditioning systems (Arendsen et al. 2019; Vincent et al. 2016). Aside from possible use for controlling contamination and infections, copper has some other uses in medicine and health care. Copper-containing ointments are used in anthroposophical medicine (Gorter et al. 2004). Copper IUDs are commonly used forms of birth control (Gu et al. 2012; Wildemeersch et al. 2014). Copper is also available in multivitamins, dietary supplements, and fortified foods.

Copper and copper compounds have many applications in agriculture, food processing, and production. Copper and copper compounds are registered as fungicides, bactericides, algaecides, herbicides, insecticides, and molluscicides for use on almost all food and feed crops (EPA 2009b). Copper can be present in growth stimulants and fertilizers for plants. Copper sulfate is used in land-applied pesticides in United States agriculture, primarily as a fungicide and bactericide for fruits and vegetables, and as an algaecide in reservoirs and waterways (Lifset et al. 2012). Industrial applications of copper sulfate include use as an activator in froth flotation of sulfide ores, production of chromated copper arsenate (CCA) wood preservatives, electroplating, azo dye manufacturing, mordant for textile dyes, petroleum refining and in the manufacture of other copper salts such as copper hydroxide and copper carbonate (Mannsville Chemical Products 1984).

USGS estimates annual agricultural pesticide use in U.S. counties as part of the Pesticide National Synthesis Project. Estimated use for copper and copper compounds pesticides is presented in Table 5-3.

Table 5-3. Estimated Pesticide Use (kg) in the United States from 2013 to 2017

	Range				
Compound	2013	2014	2015	2016	2017
Copper	345,176–391,165	393,407–435,968	416,161–478,510	528,201–540,102	435,373–531,312
Copper hydroxide	2,218,149–2,378,077	1,867,194–1,951,160	1,952,598–2,129,077	1,989,599–2,101,067	2,063,632–2,204,163
Copper sulfate	924,911–1,017,101	1,014,369–1,077,501	969,716–1,026,607	931,604–958,736	1,135,793–1,270,874
Copper sulfate tribasic	465,364	456,608	601,444	603,385	638,114
Copper oxychloride	142,874–144,116	116,065–120,032	214,475–247,904	206,268–217,275	257,866–290,005
Copper oxychloride	50,723–136,649	67,750–114,027	67,025–107,164	61,052–100,496	10,535–16,516
Copper octanoate	4,439–4,463	7,730–7,938	10,056–10,179	11,184–11,230	12,117–12,448

Source: USGS 2017a

Copper is widely used in many applications, and demand is projected to increase. However, as ore grades and natural deposits are depleted, more emphasis may be put on a circular economy of copper and secondary production (Ciacci et al. 2020; Schipper et al. 2018). Under different models to explore the impacts of different futures on global copper supply/demand, demand is estimated to increase by 300–2,100% through 2100, depending on population, welfare, and renewable energy development (Schipper et al. 2018). All scenarios result in increased demand that would deplete copper resources (Schipper et al. 2018). While increasing secondary flows and recycling could meet increasing demands and result in a circular economy, most scenarios analyzed by Ciacci et al. (2020) for Europe would not meet greenhouse gas reduction targets unless green technology and equitable lifestyles are emphasized.

5.2.4 Disposal

Based on a review of several papers, it is estimated that 40–84% of copper in waste materials is recovered, depending on the country (Schlesinger et al. 2011c). The recycling rate in the United States is estimated to be between 29 and 49% (Lifset et al. 2002, 2012). In 2019–2021, copper in scrap was estimated to contribute about 32–35% of the U.S. copper supply (USGS 2020a, 2022). There are several recycling processes depending on the copper content of scrap material, other metals present in the scrap, and size. Clean, high-grade copper scrap can be re-melted and recovered without further refining, while scrap of lower grade must be refined, often through electrorefining (Samuelsson and Björkman 2014). Copper is removed from industrial wastewaters using a variety of processes, including chemical precipitation, ion exchange, membrane filtration, flotation, electrochemical treatment, coagulation/ flocculation, and adsorption (Bilal et al. 2013). Copper and copper compounds that are not recycled are disposed of in landfills (Cui and Zhang 2008).

In case of a solid copper sulfate spill on land, the solids should be protected from rain and fire-fighting water by covering the material with plastic sheeting (NLM 2024). In the event of a water spill, the copper sulfate should be neutralized with crushed limestone, slaked lime, or sodium bicarbonate, and the solidified masses should be removed (NLM 2024).

Liquid spills containing copper should be cleaned up via adsorption using vermiculite, dry sand or earth, or a similar adsorbent. Copper dusts or mists and copper compounds can be disposed of in sealed containers in secure landfills (EPA 1986).

Disposal and use of sewage sludge containing heavy metals such as copper must be monitored in accordance with regulations found in EPA (1993).

5.3 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2022b). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ ≥10 full-time employees; if their facility's North American Industry Classification System (NAICS) codes is covered under EPCRA Section 313 or is a federal facility; and if their facility manufactures (defined to include importing) or processes any TRI chemical in excess of 25,000 pounds, or otherwise uses any TRI chemical in excess of 10,000 pounds, in a calendar year (EPA 2022b). TRI releases of copper and copper compounds to the environment are provided in Tables 5-4 and 5-5, respectively.

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Copper[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AL	72	6,974	34,865	0	246,905	15,194	40,047	263,891	303,938
AK	2	0	240	0	34,077	0	34,077	240	34,316
AZ	24	18,238	314	0	25,123	45	43,305	416	43,720
AR	45	5,267	236	0	215,825	56,918	194,717	83,529	278,246
CA	92	1,310	408	0	1,148,918	27,124	1,124,544	53,216	1,177,760
CO	9	272	113	0	139,681	23,754	130,423	33,397	163,820
CT	40	66	168	0	1,075	261	95	1,476	1,571
DE	2	10	75	0	5	0	10	80	90
FL	33	102	34,355	36,877	111,892	44,892	148,495	79,624	228,118
GA	61	2,524	1,981	0	522,783	3,991	475,216	56,064	531,280
HI	3	2	0	0	86,237	0	86,239	0	86,239
ID	10	57	7	0	306,293	729	305,808	1,278	307,086
IL	122	11,424	20,972	924	375,595	6,494,632	55,382	6,848,165	6,903,547
IN	131	19,338	4,350	4,089	1,099,100	5,775,408	65,033	6,837,250	6,902,283
IA	50	4,337	722	0	39,330	2,766	5,056	42,099	47,155
KS	43	886	1,078	0	53,259	5	24,334	30,894	55,228
KY	55	38,376	387	0	246,046	5,736	173,495	117,052	290,547
LA	19	319	1,070	1,100	82,891	4	54,665	30,718	85,383
ME	8	8	36	0	1,552	5,738	12	7,321	7,333
MD	5	602	42	0	0	0	602	42	644
MA	44	1,005	1,440	0	22,491	15,418	1,011	39,344	40,354
MI	114	9,706	1,444	7,923	215,535	28,883	45,725	217,765	263,490
MN	54	5,430	134	0	75,711	46,097	64,095	63,277	127,373
MS	31	28,823	3,455	0	63,843	20,601	83,893	32,829	116,723
MO	66	3,856	459	0	265,391	16,740	236,029	50,417	286,446
MT	1	148	0	0	2,806	0	148	2,806	2,953
NE	17	1,456	36	0	527	1,720	1,456	2,283	3,739
NV	12	23	3	0	535,359	37	535,248	173	535,421
NH	17	38	131	0	85,413	22,582	137	108,027	108,164
NJ	29	9,609	135	0	79,805	202,408	35,820	256,137	291,957
NM	3	0	0	0	147,622	0	147,622	0	147,622
NY	79	2,181	22,775	0	123,771	16,915	112,172	53,470	165,642

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Copper[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
NC	77	5,088	21,546	0	566,974	9,955	518,777	84,786	603,563
ND	3	21	25	0	0	0	45	1	46
OH	185	24,056	1,232	206,314	336,353	76,751	302,273	342,433	644,706
OK	58	5,133	515	0	428,637	140	418,180	16,245	434,425
OR	12	360	20	0	82,463	3,024	82,821	3,046	85,867
PA	198	25,765	2,066	418	456,691	23,981	162,600	346,323	508,922
RI	16	234	42	0	821	5,845	239	6,702	6,941
SC	64	2,597	1,241	0	212,265	29,784	149,697	96,190	245,887
SD	13	5,055	42	0	460	24	5,249	332	5,581
TN	72	2,771	8,629	0	520,107	37,797	293,143	276,161	569,304
TX	118	6,510	1,419	19,349	312,848	87,179	299,856	127,448	427,304
UT	12	40	12	0	11,973	0	11,995	30	12,026
VT	4	0	1	0	17,786	4	17,381	410	17,791
VA	35	12,098	2,440	0	155,932	6,602	162,032	15,040	177,072
WA	20	1,340	1,228	0	154,992	244,565	149,510	252,615	402,125
WV	4	795	442	0	0	51	824	464	1,289
WI	148	4,486	932	0	162,047	60,354	54,839	172,980	227,819
WY	3	55	1	0	90,830	0	90,886	0	90,886
PR	10	22	46	0	10	576	22	632	654
Total	2,345	268,816	173,311	276,994	9,866,050	13,415,227	6,945,279	17,055,117	24,000,396

[a] The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b] Data in TRI are maximum amounts released by each facility.
[c] Post office state abbreviations are used.
[d] Number of reporting facilities.
[e] The sum of fugitive and point source releases are included in releases to air by a given facility.
[f] Surface water discharges, wastewater treatment (metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g] Class I wells, Class II-V wells, and underground injection.
[h] Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i] Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.
[j] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k] Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI22 2024 (Data are from 2022)

Table 5-5. Releases to the Environment from Facilities that Produce, Process, or Use Copper Compounds[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AL	57	1,919	4,345	0	3,133,832	11,189	2,966,114	185,172	3,151,286
AK	7	13,481	42	0	5,902,493	0	5,911,816	4,200	5,916,016
AZ	27	108,628	22,597	0	17,721,038	2,851	17,569,851	285,262	17,855,114
AR	48	2,088	1,461	0	599,036	39,743	558,819	83,509	642,328
CA	67	1,815	7,426	0	1,307,293	19,533	947,345	388,722	1,336,067
CO	21	5,042	46	0	231,332	0	196,158	40,262	236,421
CT	17	436	1,718	0	159,251	16,349	544	177,210	177,755
DE	6	0	0	0	0	213	0	213	213
DC	1	0	0	0	7,407	0	7,407	0	7,407
FL	42	939	7,002	0	142,139	29,874	71,193	108,761	179,954
GA	61	8,235	14,505	0	148,326	11,852	48,308	134,609	182,918
ID	16	502	412	0	702,605	10,569	480,604	233,483	714,088
IL	72	16,450	28,271	86	753,277	121,193	318,713	600,564	919,277
IN	62	30,931	15,096	484	845,960	199,021	569,785	521,708	1,091,492
IA	36	7,747	1,812	0	163,359	5	68,285	104,638	172,923
KS	13	646	296	28	95,205	11,133	95,701	11,607	107,309
KY	40	7,809	49,423	2	1,262,017	8,117	635,343	692,026	1,327,369
LA	30	8,458	2,925	25	1,415,050	13,197	1,258,466	181,189	1,439,654
ME	3	91	149	0	30,935	0	240	30,935	31,175
MD	14	14	4	0	23,649	3,600	18	27,249	27,267
MA	8	19	1,716	0	617	19,359	21	21,691	21,712
MI	58	6,502	20,099	0	1,603,420	16,102	1,367,108	279,015	1,646,123
MN	40	1,146	1,141	0	368,718	7,798	182,503	196,299	378,802
MS	28	4,918	386	23,938	178,557	11,222	69,600	149,421	219,021
MO	52	8,825	2,173	0	3,424,958	16,119	3,284,653	167,421	3,452,074
MT	9	13,674	10	0	18,808,090	0	18,746,910	74,864	18,821,774
NE	22	2,041	564	0	140,888	1,886	122,844	22,535	145,378
NV	13	2,590	0	260	5,165,860	1,692	5,168,099	2,303	5,170,402
NH	7	0	179	0	20	6,542	0	6,741	6,741
NJ	12	11,804	8,698	0	5,479	138,315	11,805	152,491	164,297
NM	7	4,318	1,059	0	162,753	23,658	167,840	23,948	191,788
NY	22	18,565	7,098	0	29,864	40,198	34,643	61,081	95,724
NC	61	11,793	1,218	0	201,412	21,770	195,683	40,509	236,192
ND	5	851	81	0	191,546	1,640	154,109	40,009	194,118
OH	76	8,357	30,474	0	956,021	175,820	451,193	719,479	1,170,672
OK	22	3,800	31	0	314,333	88	288,813	29,438	318,251

Table 5-5. Releases to the Environment from Facilities that Produce, Process, or Use Copper Compounds[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
OR	23	8,729	13,532	0	423	8,859	9,195	22,347	31,543
PA	82	10,002	4,535	0	777,519	129,742	310,793	611,006	921,799
RI	7	28	8,214	0	0	25,130	128	33,245	33,373
SC	34	1,419	5,047	0	623,482	14,124	558,992	85,080	644,072
SD	8	0	0	0	0	0	0	0	0
TN	54	2,125	16,670	85,981	1,718,996	13,271	1,486,714	350,328	1,837,042
TX	118	28,739	38,040	98,966	992,879	142,800	929,651	371,774	1,301,424
UT	19	90,816	771	0	53,110,614	4,440	53,181,512	25,130	53,206,642
VT	2	0	0	0	0	0	0	0	0
VA	32	5,150	5,292	0	86,341	28,040	33,862	90,960	124,823
WA	19	6,929	496	0	23,696	332,659	8,429	355,350	363,779
WV	18	3,979	401	0	732,674	1,568	593,563	145,059	738,622
WI	48	2,473	7,923	1,274	208,843	7,431	40,023	187,922	227,944
WY	6	1,625	20	0	185,489	0	154,298	32,836	187,134
PR	8	1,326	57	0	36,382	0	1,383	36,382	37,765
VI	1	0	5	0	0	0	5	0	5
Total	1,561	477,776	333,462	211,044	124,694,079	1,688,708	119,259,083	8,145,986	127,405,069

[a] The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b] Data in TRI are maximum amounts released by each facility.
[c] Post office state abbreviations are used.
[d] Number of reporting facilities.
[e] The sum of fugitive and point source releases are included in releases to air by a given facility.
[f] Surface water discharges, wastewater treatment (metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g] Class I wells, Class II-V wells, and underground injection.
[h] Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i] Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.
[j] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k] Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI22 2024 (Data are from 2022)

Industrial releases such as industrial effluents, mining and production of copper and other metals, municipal solid waste management, and fossil fuel combustion account for a portion of the total environmental releases of copper and copper compounds. Other sources of copper released into the environment include pesticides, marine paints, animal feeds, fertilizers, fireworks, brake pad wear, copper pipe corrosion, leaching from architectural surfaces, releases from treated wood, vehicle fluid leaks, tire wear, wood combustion, biomass burning, and sewage sludge (Lifset et al. 2012; Rauch and Graedel 2007). Natural sources of copper releases include windblown dust, volcanoes, decaying vegetation, forest fires, and sea spray (Georgopoulos et al. 2001; Rauch and Graedel 2007).

5.3.1 Air

Estimated releases of 268,816 pounds (~122 metric tons) of copper to the atmosphere from 2,345 domestic manufacturing and processing facilities in 2022, accounted for about 1.1% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). These releases are summarized in Table 5-4.

Estimated releases of 477,776 pounds (~217 metric tons) of copper compounds to the atmosphere from 1,561 domestic manufacturing and processing facilities in 2022, accounted for about 0.38% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). These releases are summarized in Table 5-5.

Copper is emitted into the air from both natural and anthropogenic sources. Global atmospheric concentrations and releases of copper from manmade and natural sources have been estimated (Rauch and Graedel 2007). Estimates for the natural and anthropogenic emissions copper from various sources in the mid-1990s are shown in Tables 5-6 and 5-7. Based on these data, 6.9×10^7 kg/year of copper from natural sources is estimated to be emitted to the atmosphere.

Table 5-6. Global Emissions of Copper from Anthropogenic Sources in the mid-1990s

Source	Emissions (Gg[a] Cu/year)
Metal production	18
Nonferrous metal production	18
Iron and steel production	0.14
Fossil fuel combustion	7.1

Table 5-6. Global Emissions of Copper from Anthropogenic Sources in the mid-1990s

Source	Emissions (Gg[a] Cu/year)
Metal fabrication	1.4
Metal discard management	0.62

[a]One Gg is one billion (10^9) g. It is the same as one million (10^6) kg.

Source: Rauch and Graedel 2007

Table 5-7. World Total Copper Emissions into the Atmosphere in 1995

Source	Emissions (tonnes/year)
Primary copper production	17,708
Secondary copper production	160
Primary lead production	23
Secondary lead production	2
Primary non-ferrous metals production	17,909
Secondary non-ferrous metals production	162
Primary and secondary zinc production	177
Stationary fossil fuel combustion	7,081
Pig iron and steel production[a]	142
Municipal waste incineration[b]	547
Sewage sludge incineration[b]	74

[a]In 1994.
[b]In the mid-1990s.

Source: Pacyna and Pacyna 2001

Windblown dusts account for an estimated global emission of 5.0×10^7 kg/year of copper into the atmosphere (Rauch and Graedel 2007). Other natural sources of copper emitted into air (in order of highest to lowest worldwide emissions) are sea salt spray, biomass burning, and volcanoes. Anthropogenic emission sources include nonferrous metal production, fabrication, and use; fossil fuel combustion; metal production; and mining. Lifset et al. (2012) estimates the following emissions to the atmosphere in the United States: fireworks (2.2×10^5 kg/year), copper primary production (4.7×10^5 kg/year), copper waste management (1.9×10^5 kg/year), coal combustion (1.36×10^6 kg/year), oil combustion (4.5×10^5 kg/year), metals production (2.0×10^4 kg/year), and wood combustion (4.0×10^4 kg/year).

Daily stack emission rates have been reported for three coal-burning power plants on a kg/day/1,000-megawatt basis (Que Hee et al. 1982); they were 0.3–0.7 and 2.00 kg/day/1,000 megawatts for those using low-sulfur western coal and high-sulfur eastern coal, respectively. This amounted to annual emission rates of 110–260 kg/1,000 megawatts for the low-sulfur western coal and 730 kg/1,000 megawatts for the high-sulfur eastern coal.

Emission factors in grams of copper released to the atmosphere per ton of product have been estimated for various industries (Nriagu and Pacyna 1988). These factors would enable estimation of an industry's copper emissions from its production volume. Missing from these emission estimates is fugitive dust arising from drilling, blasting, loading, and transporting operations associated with copper mining. The most common control for reducing fugitive dust is the manual use of water sprays (EPA 1980a). The highest concentrations of copper in atmospheric particulate matter were obtained from mining activities, primary and secondary production, and industrial manufacturing (Table 5-8).

Table 5-8. Concentrations of Copper in Particulate Matter (<10 μm) Generated from Various Sources

Source[a]	Median
Metal mining	6.17[b]
Secondary metal production	4.60[b]
Primary metal production	3.50[b]
Industrial manufacturing	2.16[b]
Steel production	0.55[b]
Gray iron foundries	0.19[b]
Steel foundry, general	0.17[b]
Solid waste	0.09[b]
Food and agriculture	0.05[b]
Chemical manufacturing	0.03[b]
Petroleum industry	0.03[b]
Gasoline vehicle exhaust	0.05[c]
Paved road dust	0.0162[c]
Construction dust	0.0102[c]
Landfill dust	0.0102[c]
Unpaved road dust	0.0087[c]
Agricultural lands, dust	0.0067[c]
Diesel vehicle exhaust	0.003[c]

[a] Values obtained from CEIDARS 2000.
[b] Data obtained from EPA Speciate 3.0; Shareef, G.S; Radian, September 1987.
[c] Data obtained from KVB literature search.

Romo-Kröger et al. (1994) were able to show, through the use of radioactive tracers and cluster analysis of inter-elemental correlations, that copper, arsenic, sulfur, and zinc measured near a copper smelter in Chile were derived from the plant and not from the surrounding soil. The concentration of copper in air near the plant decreased from 66 to 22 ng/m^3 of fine particles and from 131 to 50 ng/m^3 of coarse particles during a period of inactivity at the plant, demonstrating the contribution of plant emissions to copper levels in the surrounding area.

Copper and other pollutants are present in fugitive dust originating from copper production sites or from waste sites. In one study, the amount of airborne copper and other heavy metals deposited near a large refuse dump that received municipal and industrial waste and sewage sludge was determined by first measuring the amount of the metal accumulated in moss bags suspended 1–3 m above the ground. The deposition rate was then determined from the amount of copper in the moss bags accumulated over the summer of 1985 and compared with that for an agricultural control area. The mean copper deposition rates in the two areas were about the same: 0.55 mg/kg-month (range 0.04–1.6 mg/kg-month) over the refuse dump and 0.51 mg/kg-month (range 0.26–0.76 mg/kg-month) in the control area (Lodenius and Braunschweiler 1986). Lodenius and Braunschweiler (1986) concluded that the refuse dump did not contribute to copper concentrations in urban air above normal values.

A study of automobile exhaust emitted from light-duty vehicles conducted in Denver, Colorado showed that this source of copper emission makes a small local contribution to copper in air. The amount of copper emitted in exhaust from automobiles powered by regular gasoline has been measured to be 0.001–0.003 mg/mile driven using the Urban Dynamometer Driving Schedule of the Federal Test Schedule during the summer of 1996 and the winter of 1997 (Cadle et al. 1999). Diesel-powered vehicles were also studied and found to emit 0.005–0.039 mg of copper per mile driven for vehicles using #2 diesel fuel.

Only in a few cases has the form of copper released into the air been determined. Copper released into the atmosphere can be in particulate matter in the elemental form or in the form of an oxide, sulfate, or carbonate, or other compound depending on the source material and conditions under which it is emitted. Because copper smelters co-emit sulfur oxides gases, copper is expected to be released largely as the sulfate in particulate matter from these facilities. Combustion processes are reported to release copper into the atmosphere as the oxide, elemental copper, and adsorbed copper. Cupric oxide has been identified in emissions from steel manufacturing and in fly ash from oil-fired power plants and open-hearth steel mills (EPA 1980b). Copper associated with particles (≤10 μm) has been suggested to originate from windblown soil and dust (Schroeder et al. 1987). Generally, aerosols from sea spray, dust, and volcanic mineral emissions tend to be larger than particles formed by condensation of gases in the troposphere (Buseck and Pósfai 1999). Skeaff et al. (2011) collected and analyzed particulates from the interior walls of primary stacks, enabling the quantitative chemical speciation of particulate releases from three copper smelters. Emissions from smelter stacks included copper species such as copper sulfate, copper arsenate as $(Cu_{0.94}Zn_{0.06})_2(AsO_4)(OH)$, $(Cu_{0.98}Zn_{0.02})_3(AsO_4)_2 \cdot 2H_2O$, or $(Cu_{0.84}Zn_{0.16})(AsO_3OH)$, and cuprite (Skeaff et al. 2011).

In a study of particulate matter emitted by fireworks, Hickey et al. (2020) sampled 10 types of fireworks and found that 4 of the 12 samples contained copper at concentrations of 12,000–53,000 ppm in the PM_{10} size range. Using an emission factor of 3,000 ppm developed by the European Copper Institute, Lifset et al. (2012) estimated that releases from fireworks in the United States increased from 40 metric tons in 1975 to 220 metric tons in 2000.

5.3.2 Water

Estimated releases of 173,311 pounds (~79 metric tons) of copper to surface water from 2,345 domestic manufacturing and processing facilities in 2022, accounted for about 0.72% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). This estimate includes releases to waste water treatment and POTWs (TRI22 2024). These releases are summarized in Table 5-4.

Estimated releases of 333,462 pounds (~151 metric tons) of copper compounds to surface water from 1,561 domestic manufacturing and processing facilities in 2022, accounted for about 0.26% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). This estimate includes releases to waste water treatment and POTWs (TRI22 2024). These releases are summarized in Table 5-5.

Sources of copper releases to water include algaecides, marine paints, corrosion of metallic copper, architectural uses, CCA wood management, industrial effluent, and copper mining leachate (Lifset et al. 2012).

Copper is a natural constituent of soil and will be transported into streams and waterways in runoff either due to natural weathering or anthropogenic soil disturbances (Rader et al. 2018). Sixty-eight percent of releases of copper to water is estimated to derive from soil runoff and weathering, while copper sulfate use represents 13% of releases to water and urban runoff contributes 2% (EPA 1980b). In the absence of specific industrial sources, runoff is the major factor contributing to elevated copper levels in river water (Nölte 1988). In the previous EPA National Urban Runoff Program, 86 samples of runoff from 19 cities throughout the United States were analyzed, and copper was found in 96% of samples, at concentrations of 1–100 μg/L (equivalent to ppb) with a geometric mean of 18.7 μg/L (Cole et al. 1984).

Giusti et al. (1993) provided estimates of global anthropogenic and natural copper inputs into oceans that are derived from two sources: atmospheric deposition and riverine input. Atmospheric input has been estimated at 14–45x10^6 kg/year for copper in a dissolved form (e.g., rainwater) and 2–7x10^6 kg/year for copper in a particulate form (e.g., aerosols). Riverine input is estimated to be 10x10^6 kg/year as dissolved copper and 1,500x10^6 kg/year as copper bound to particulates.

Domestic wastewater is the major anthropogenic source of copper in waterways (Isaac et al. 1997; Nriagu and Pacyna 1988). Studies in Cincinnati, Ohio and St. Louis, Missouri showed discharges of copper into sewer systems from residential areas to be significant, with an average loading of 42 mg/person/day (EPA 1980b). In a more comprehensive review, Jenkins and Russell (1994) reported a range of average copper loadings derived from residential and some small industrial contributions of 2.8–83 mg/person/day. Concentrations of copper in influents to 239 wastewater treatment plants (12,351 observations) were 0.0001–36.5 ppm and the median value was ~0.4 ppm (EPA 1981a). Copper is not entirely removed in POTWs, and releases from these facilities contribute ~8% of all copper released to water (EPA 1980b). Inputs into the Narraganset Bay, Rhode Island, in decreasing order of importance, are sewage effluent, rivers, urban runoff, and atmospheric fallout (Mills and Quinn 1984; Santschi et al. 1984). Ninety percent of both dissolved and particulate copper was from the effluent of sewage treatment plants that discharged into the Providence River.

While some copper is removed from the waste stream by sewage treatment facilities, considerable copper remains in the effluent and is released into receiving waters (EPA 1980b, 1981b). Because removal efficiencies for copper from waste streams tend to remain constant rather than proportional to influent copper concentrations, increases in copper concentrations in POTW influent streams will also result in increased copper concentrations in the effluent streams (Isaac et al. 1997). The copper in domestic wastewater has been found to make up a substantial fraction of the copper found in POTW influent in the wastewater systems of four Massachusetts municipalities. The range of removal efficiencies reported for pilot and full-scale plants suggests that removal depends strongly on plant operation or influent characteristics.

A source of copper released into waterways is from urban stormwater runoff. Copper in stormwater runoff originates from the sidings and roofs of buildings, various emissions from automobiles, and wet and dry depositional processes (Davis et al. 2001). Concentrations of between 1 and 100 µg/L of copper in stormwater runoff have been measured (Georgopoulos et al. 2001). Stormwater runoff normally contributes approximately 2% to the total copper released to waterways. In contrast, copper in runoff that is obtained from the natural weathering of soil or is released from disturbed soils contributes 68% of the copper released to waterways (Georgopoulos et al. 2001).

Experimental wastewater treatment technologies have been investigated with the goal to minimize copper contamination in finished water (Biswas and Mishra 2016; Shahin et al. 2019). Effluent guidelines set forth by the EPA are national wastewater discharge standards that are developed by EPA on an industry-by-industry basis. Copper limitations for 16 point-source categories are listed in the Effluent Limitations Guidelines and Standards Database. Values for copper limitations are 0.02–5 mg/L for daily maximums, 0.014–1.45 mg/L for the maximum range for monthly averages, and 0.15–2.07 mg/L for the monthly average range (EPA 2022c).

Overflow outfalls within combined sewer systems (e.g., combination of domestic and industrial wastewater plus stormwater) are the primary sources of copper pollutants entering estuaries and other coastal areas of the United States (Crawford et al. 1995; Georgopoulos et al. 2001; Huh 1996; Iannuzzi et al. 1997). For example, Crawford et al. (1995) compiled a summary of the sources of various metals and other contaminants in the Newark Bay estuary. The mass loadings of copper into the estuary as a function of source are (in kg/day): discharges from the Passaic Valley Commission and Middlesex County Sewerage Authority, 126.5; municipal treatment systems, 103.4; stormwater runoff, 62.2; combined sewer overflows, 48.0; tributary flow, 39.1; and industry direct discharge, 8.82.

Wastewater generated from copper mining operations comes from seepage, runoff from tailing piles, or utility water used for mine operation. The amounts of wastewater generated were 0–300 L water/metric ton of ore mined for open pit copper mines and 8–4,000 L water/metric ton of ore mined underground (EPA 1980a). Copper concentrations in wastewater from a selected open pit and underground copper mine were 1.05 and 0.87 ppm, respectively. Data regarding copper concentrations in wastewater associated with selected concentrating, smelting, and refining operations can be found in EPA (1980a).

Drainage from mining operations and abandoned mines has been shown to influence copper content in local surface waters with concentrations as high as 69,000 ppb being measured (Rösner 1998). An assessment of the life cycle of global sulfidic copper mine waste indicted that copper tailings, from large- and medium-sized copper deposits contribute to >75% of the global ecotoxicity impacts of copper tailings via leaching and infiltration. Analysis of data from 431 global active copper mine sites revealed concentrations of $Cu(OH)_2$ (mole/Kg) ranging from ~0.001%wt to ~0.09%wt in tailings from porphyry deposits, volcanic massive sulfide deposits, skarn deposits, sediment hosted deposits, magmatic sulfide deposits, iron oxide deposits, intrusion related deposits, and epithermal deposits (Adrianto et al. 2022).

Studies from the 1980s reported that effluents from power plants that use copper alloys in the heat exchangers of their cooling systems discharge copper into receiving waters (U.S. NRC 1984). The largest discharges occur after startup and decrease rapidly thereafter. At the Diablo Canyon Nuclear Power Station, a very high startup discharge containing 7,700 ppb of copper fell to 67 ppb after 24 hours (U.S. NRC 1980). During normal operation at two nuclear power stations 6.5×10^6 m^3 (1,700 million gallons) of seawater per day is used as cooling water for these facilities and discharged into the ocean, with copper levels in the effluent of 0.6–3.3 ppb (U.S. NRC 1980). This amounts to a total output of copper in the discharged seawater of 3.9–42 kg/day or 1,400–15,000 kg/year from these two power plants. Except for after start-up of the cooling system, most of the soluble copper (that which passes through a 0.45-µm filter) discharged was in bound forms (U.S. NRC 1980). During normal operation, <20% of the copper released was in the <1,000 molecular weight fraction, which contains the more available copper species. More recent data on these releases were not located.

Copper sulfate is added directly to lakes, reservoirs, and ponds for controlling algae. However, the copper concentration in the water column generally returns to pretreatment levels within a few days (Effler et al. 1980; EPA 1980b). The reduction in dissolved copper during this period was accompanied by an increase in particulate copper (e.g., sorption to algae or other organic matter, which settles into the sediments of these bodies of water). The copper in the settled particulates is in equilibrium with the water column, which greatly favors copper in a bound state.

A potential source of copper release into waterways is leachate from municipal landfills. Copper concentrations in leachate obtained from waste sites have been found to vary widely. For example, copper concentrations in leachate from municipal landfills have been found to range from 0.005 to 1,110 ppm (Christensen et al. 1994; EPA 1980b; Roy 1994). Although copper was measured in these leachates, its origin may not be from copper contained within the waste site, but from the surrounding soils. Cyr et al. (1987) reported that leachate from three municipal landfills in New Brunswick, Canada, did not contain copper concentrations significantly above those in control samples representing the surrounding soil types. Therefore, the emissions of copper from landfills into leachates should be made relative to the contribution of copper from surrounding soils, as determined from appropriately selected control samples.

Copper can enter surface waters because of agricultural runoff. For example, estimated loading rates of copper into surface water from irrigation water runoff near the Stillwater National Wildlife Refuge were 0.307–8.34 mg/hour, depending on what period of the irrigation season samples were taken (Kilbride et al. 1998). The highest loading rates were obtained during the middle period (August through mid-September) of the irrigation season. The copper in the runoff water was found to be predominantly bound to drift material in the water (e.g., algae, vascular plants, invertebrates, vertebrates, and detrital material).

5.3.3 Soil

Estimated releases of 9,866,050 pounds (~4,475 metric tons) of copper to soil from 2,345 domestic manufacturing and processing facilities in 2022, accounted for about 41.11% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). An additional 276,994 pounds (~126 metric tons), constituting about 1.15% of the total environmental emissions, were released via underground injection (TRI22 2024). These releases are summarized in Table 5-4.

Estimated releases of 124,694,079 pounds (~56,560 metric tons) of copper compounds to soil from 1,561 domestic manufacturing and processing facilities in 2022, accounted for about 97.87% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). An additional 211,044 pounds (~96 metric tons), constituting about 0.17% of the total environmental emissions, were released via underground injection (TRI22 2024). These releases are summarized in Table 5-5.

TRI data show that the largest release of copper compounds come from Utah and Arizona (TRI22 2024). Both states have active mining operations and the majority of the reported releases result from on-site disposal of tailings that are typically placed in secure holding areas. Facilities such as Kenncott Utah Copper Mine and Copper Smelter Refinery in Utah and Freeport-Mcmoran Copper & Gold and Pinto Valley Mine in Arizona account for the largest sources of copper released, both reporting release to onsite facilities (TRI22 2024).

An estimated 97% of copper released from all sources into the environment is primarily released to land (EPA 1980b). These include primarily tailings and overburdens from copper mines and tailings from mills. The copper in tailings represents the portion of copper that could not be recovered from the ore and is generally in the form of insoluble sulfides or silicates (EPA 1980b). These wastes accumulate in mining states. Other releases to land include sludge from POTWs, municipal refuse, waste from electroplating, iron, and steel producers, discarded copper products (e.g., plumbing, wiring) that are not recycled, fungicides, animal feed, fertilizers, brake pads, vehicle leaks, and tire wear, and CCA-treated wood (EPA 1980b; Lifset et al. 2012; Tang et al. 2023). The copper content of municipal solid waste is ~0.16%. Much of this waste is landfilled directly or is in the form of residues following incineration. Emission factors in milligrams of copper released per gram of solid waste have been estimated for various industries. These factors would enable estimation of an industry's copper releases in terms of total quantity of solid waste discharged. Sludge from sewage treatment plants is a major source of copper released to land (Nriagu and Pacyna 1988). Agricultural products are believed to constitute 2% of the copper released to soil (EPA 1980b).

Some animal feeds contain trace metals including copper; excess copper from animal diets ultimately ends up in manure (Chesapeake Bay Foundation 2004). The land application of biosolids such as manure may result in a buildup of heavy metals such as copper in soils (Mahdy et al. 2007; Raven and Loeppert 1997). In Arkansas, daily production of poultry manure has been reported to contain 540 pounds (0.24 tonnes) of copper (United Poultry Concerns 2022). In accordance with 40 CFR Part 503, concentrations and loading rates of copper in sewage sludge are regulated as follows: ceiling concentration, 4,300 mg/kg; cumulative pollutant loading rate, 1,500 kg/hectare; monthly average concentration, 1,500 mg/kg; and annual pollutant loading rate, 75 kg/hectare per 365-day period (EPA 2018a).

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

Air. Copper is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter. It is removed by gravitational settling (bulk deposition), dry deposition (inertial impaction characterized by a deposition velocity), in-cloud scavenging (attachment of particles to rain droplets within clouds), and washout (collision and capture of particles by falling raindrops below clouds)

(Schroeder et al. 1987). The removal rate and distance traveled from the source depend on several factors, including source characteristics, particle size, turbulence, and wind velocity.

Gravitational settling governs the removal of large particles with mass median aerodynamic diameters >5 μm, whereas smaller particles are removed by the other forms of dry and wet deposition. The importance of wet to dry deposition generally increases with decreasing particle size. The scavenging ratio (ratio of the copper concentration in precipitation [ppm] to its air concentration [μg/m^3]) for large particles displays a seasonal dependence that reflects more effective scavenging by snow than by rain (Chan et al. 1986). Copper from combustion sources is often adsorbed to sub-micron particulate matter. Thermal process may also release copper oxide or elemental copper as a vapor or copper adsorbed to larger particulates (EPA 1980b). Copper adsorbed to sub-micron particles remains in the troposphere for an estimated 7–30 days. In that time, some copper may be carried far from its source (EPA 1980b).

Rates of metal deposition (e.g., depositional fluxes) vary between dry and wet depositional processes and show spatial variability. Dry depositional fluxes of copper tend to be higher in highly urbanized areas and lower in less urbanized areas or areas with minimal anthropogenic activity. For example, average depositional rates were 0.06 mg/m^2/day in Chicago, Illinois, 0.007 mg/m^2/day in South Haven, Michigan, and 0.01 mg/m^2/day 6–10 km offshore of Lake Michigan (Paode et al. 1998). Estimated copper deposition rates in urban areas were 0.119 and 0.164 kg per hectare per year (kg/ha/year) or 0.0326 and 0.0449 mg/m^2/day for dry and wet deposition, respectively (Schroeder et al. 1987). Bulk deposition was 0.002–3.01 kg/ha/year or 0.0005–0.825 mg/m^2/day (Golomb et al. 1997; Landing et al. 1995; Schroeder et al. 1987). For rural areas, the range of bulk deposition was 0.018–0.5 kg/ha/year or 0.0049–0.1 mg/m^2/day and wet deposition was 0.033 kg/ha/year or 0.0090 mg/m^2/day. The washout ratio was 140–751 (Schroeder et al. 1987).

Levels of airborne copper measured at a rural site in Bondville, Illinois were comparable to regional background levels in other urban study sites with variations, such as episodic increases, depending on wind speed, direction, and location relative to local point sources, observed. Sources of copper in urban areas include coal combustion, soil, tire wear, and automobile emissions (Kim and Fergusson 1994). In one urban study at a site in East St. Louis, smelters were the primary source of copper. From this site, it was observed that copper depositional fluxes followed an exponential decay as one transitioned from the urban site to more rural settings (Sweet et al. 1993). In contrast, it has been observed that at more remote sites, atmospheric copper is derived from source points in nearby cities and depositional fluxes of airborne, windblown dust and soil containing this trace metal (Fergusson and Stewart 1992).

Furthermore, high copper concentrations in snow and aerosols from polar snowfields and remote locations have been attributed to airborne pollution and long-range transport (Annibaldi et al. 2007; Dinu et al. 2020).

Long-range transported emissions from combustion processes are typically associated with fine particles; however, there can be instances where the highest concentrations of copper are measured in coarse particles near point sources (Paode et al. 1998). Estimates of depositional velocities for fine particles (<2.5 µm) and coarse particles (2.5–10 µm) in urban (Chicago) and rural (Kankalee, Illinois) areas have been made (Pirrone and Keeler 1993). The estimated depositional velocities are urban, 0.25–0.46 rcm/second and rural, 0.18–0.25 cm/second for fine particles; and urban, 1.47–2.93 cm/second and rural, 0.87–1.71 cm/second for coarse particles. The differences in depositional velocities are thought to be due to higher surface roughness and wind velocities in Chicago.

Copper concentrations in particulates formed in a controlled study of waste oil combustion were: 687±11 µg/g (10-µm diameter), 575±8 µg/g (50-µm diameter), 552±12 µg/g (100-µm diameter), 568±9 µg/g (300-µm diameter), and 489±8 (500-µm diameter). Approximately 25% of copper was in the 10-µm fraction and ~18% was in each of the larger fractions (e.g., 50-, 100-, 300-, and 500-µm diameter) (Nerín et al. 1999).

Water. Copper in aqueous environments exists primarily in ionic form as Cu(II) and is weakly associated with water molecules. Copper may also be adsorbed or associated with suspended particles or various organic and inorganic chemicals in aqueous systems (EPA 2007). Free copper ions have the greatest bioavailability in water (Wapnir 1998). The mobility and bioavailability of copper in water and sediments depend on the physical and chemical form, which is a function of environmental conditions such as temperature, pH, and redox conditions; copper speciation and solubility of the copper form; and types of complexes that may be formed with other chemicals present (both organic and inorganic) (Adams et al. 2020; Ankley et al. 1996; Harmesa et al. 2023).

The average concentrations of copper in Lakes Superior, Erie, and Ontario were 760, 870, and 830 ng/L, respectively, in studies from the late 1990s and early 2000s (Georgopoulos et al. 2001; Nriagu et al. 1996). These values were derived from measurements taken from 11, 11, and 9 nearshore and offshore sampling sites at different points in the water column up to depths of 251, 55, and 145 m for Lakes Superior, Erie, and Ontario, respectively (Nriagu et al. 1996). In Lake Ontario, the highest copper concentrations were found at nearshore sampling sites neighboring Buffalo, New York (887–1,051 ng/L), Rochester, New York (1,041–1,098 ng/L), and Kingston, Ontario (921–1,026 ng/L). The lowest concentrations of copper in Lake Ontario were measured in an offshore sampling site (540–710 ng/L) that was approximately 40 km from the Buffalo sampling site.

The atmospheric input of copper into the Great Lakes is 330–1,470 ng/m^2/year, which amounts to a total deposition of 8.00–35.6x10^{13} ng/year (80.0–356 kg/year). This input of copper accounts for 60–80% of the anthropogenic input into Lake Superior and for 20–70% of the anthropogenic input into Lakes Erie and Ontario (Georgopoulos et al. 2001; Nriagu et al. 1996).

Much of the copper discharged into waterways is bound to particulate matter and settles out. In the water column and in sediments, copper adsorbs to organic matter, hydrous iron and manganese oxides, and clay. In the open water column, a significant fraction of the copper is adsorbed within the first hour of introduction, and in most cases, a steady state is obtained within 24 hours (U.S. NRC 1984). Most dissolved copper in POTW effluent and surface runoff is mostly already in complexed form (Sedlak et al. 1997). Copper in wastewater discharged into Back River leading into Chesapeake Bay, Maryland contained 53 ppb of copper, of which 36 ppb (based on weight) were in the form of settleable solids (Helz et al. 1975). The concentration of copper rapidly decreased downstream of the outfall so that 2–3 km from the outfall, the copper concentration had fallen to 7 ppb. The concentration of copper in sediment 2–3 km downstream from the outfall was about a factor of 10 higher than in uncontaminated areas (e.g., Rappahannock River). Based on their data and the results from other studies, Helz et al. (1975) estimated that approximately 200 metric tons of copper entered the Chesapeake Bay from the effluent discharged from waste treatment plants annually. Whitall et al. (2010) concluded that copper released from antifouling paint on boats was a likely source of copper measured in the Choptank River estuary, a tributary of the Chesapeake Bay.

Copper binds primarily to organic matter in aerobic estuarine sediment unless the sediment is low in organic matter content. Davies-Colley et al. (1984) determined copper's absorptivity to model phases in artificial seawater to estimate copper distributions between estuarine sedimentary phases and water. The model phases included hydrous iron and manganese oxides, clay, aluminosilicates, and organic matter. The binding affinities varied by over a factor of 10,000 and were in the following order: hydrous manganese oxide > organic matter > hydrous iron oxide > aluminosilicates > clay (montmorillonite). The partition coefficients at pH 7 for the more strongly binding phases (manganese oxide, iron oxide, and estuarine humic material) were 6,300, 1,300, and 2,500, respectively. The affinity increased somewhat with pH but did not vary appreciably when the salinity was reduced from 35 to 5%. Considering the typical compositional characteristics of estuarine sediment in terms of binding capacity, the results indicate that copper binds predominantly to organic matter (humic material) and iron oxides. Manganese oxide contributes only 1% to the binding because of its generally low concentration in sediment; the other phases are usually unimportant. These findings concur with results of selective extraction experiments (Badri and Aston 1983) and studies of the association of copper with humic material (Raspor et al. 1984). Copper will bind with acid-volatile sulfide to form very insoluble sulfur precipitates in sulfidic anoxic sediments, which is an important environmental fate process in marine sediments that are often anaerobic (Ankley et al. 1996; Di Toro et al. 1996; Rader et al. 2019). Copper has been reported to have a higher affinity for sulfide than other trace metals such as nickel, cadmium, and zinc (Rader et al. 2019).

Sorption capacity of copper to aquatic microplastics was evaluated in a review using experimental data and artificial neural networks modeling (Guo and Wang 2021). The study authors found that sorption capacity was influenced by the concentration of metal ions in the surrounding waters and increased as levels of the ion increased; predicted sorption capacities for copper based on concentrations in South Asia, South Africa, and China were 270–280 μg/g. Furthermore, sorption capacity is related to salinity and pH, where increased salinity decreases the sorption capacity, and values of <0.3 μg/g are predicted for the Pacific Ocean, Arctic Ocean, and Southern Ocean; along the China coastline, sorption of copper onto polypropylene microplastics was ~0.117–0.174 μg/g. Findings also indicated that aged microplastics demonstrate a sorption capacity for metal ions 1–5 times higher than virgin microplastics.

Soil. Most copper deposited on soil from the atmosphere, agricultural use, and solid waste and sludge disposal is retained in the upper 5–10 cm of soil in comparison to lower soil depths, except in sandy soils where the lability of bound copper is greater (Breslin 1999; EPA 1980b; Giusquiani et al. 1992; Hutchinson 1979; Luncan-Bouché et al. 1997; Levy et al. 1992). Copper was evaluated in soil samples at constructed wetlands on the Savannah River, South Carolina receiving storm runoff and industrial effluent generated from the Tritium Facility. Sediment core samples were collected twice a year from 2007 to 2013. Concentrations in surface sediments fluctuated over the study period and ultimately increased from 6.0±2.8 to 139.6±87.7 mg/kg dry weight. Concentrations of copper were lower in the middle and bottom layers of sediment at 5.2±5.8–19.7±43.0 and 4.4±1.4–7.4±7.5 mg/kg, respectively (Elhaj Baddar et al. 2021). Copper's movement in soil is determined by a host of physical and chemical interactions of copper with the soil components. In general, copper will adsorb to organic matter, carbonate minerals, clay minerals, or hydrous iron and manganese oxides (DOI 1986; EPA 1979; Janssen et al. 1997; Petruzzelli 1997; Tyler and McBride 1982). Sandy soils with low pH have the greatest potential for leaching. In a laboratory study, Luncan-Bouché et al. (1997) demonstrated that 55–85% of copper bound to sand (with no other soil components added) is remobilized upon reduction of the pH from 9 to 4. In most temperate soils, the pH, organic matter, concentrations of metal oxyhydroxides, and ionic strength of the soil solutions are the key factors affecting adsorption (DOI 1986; Elliott et al. 1986; Gerritse and Van Driel 1984; Janssen et al. 1997; Rieuwerts et al. 1998; Tyler and McBride 1982). The ionic strength and pH of the soil solution affect the surface charge of soils and thereby influence ionic interaction (Rieuwerts et al. 1998). Soil microorganisms also affect the absorption of copper in soils due to the uptake and assimilation of the metal by these microorganisms (Rieuwerts et al. 1998). Tang et al. (2023) demonstrated that in CCA-polluted soils, the levels of water extractable copper and bioavailable copper, free copper ion activity, and microbial inhibition decreased with increased cation exchange capacity, decreased the carbon to nitrogen ratio, and increased total nitrogen and total phosphorus in tested systems. However, it is not known how the rate of uptake and absorption capacity of the microorganisms for copper compares with the binding capacity and affinities of copper by organic matter in soils, such as humic and fulvic acids. When the amount of organic matter is low, the mineral content or iron, manganese, and aluminum oxides become important in determining the adsorption of copper. DOI (1986) reported that, in oxidized estuarine sediment, adsorption of copper is dominated both by amorphous iron oxide and humic material.

Copper binds strongly to soils with high organic content (14–34% organic matter, dry weight), and the distribution of copper in the soil solution is less affected by changes in pH (within the range of pH normally encountered in the environment) than other metals are (Gerritse and Van Driel 1984). In a laboratory study of competitive adsorption and leaching of metals in soil columns of widely different characteristics, copper eluted in a 0.01-M $CaCl_2$ leaching solution much more slowly and in much lower quantities than zinc, cadmium, and nickel from a low-pH and a high-pH mineral soils and not at all from peat soil, which contained the greatest amount of organic matter (Tyler and McBride 1982). Elliott et al. (1986) investigated pH-dependent adsorption of the divalent transition metal cations cadmium, copper, lead, and zinc in two mineral soils (silty clay loam, 0.5 g/kg organic dry weight, and sandy clay, 1.6 g/kg organic) and two soils containing considerable organic matter (loamy sand, 20.5 g/kg organic, and silt loam, 42.5 g/kg organic). Adsorption increased with pH, and copper and lead were much more strongly retained than cadmium and zinc. Reduction in absorptivity after removal of the organic matter demonstrated the importance of organic matter in binding copper. In a study of clay soils, Wu et al. (1999) observed preferential copper binding to organic matter but found higher binding affinities to fine (<0.2 μm) clay fractions once the organic matter had been removed.

To determine the factors affecting copper leachability in soil, Hermann and Neumann-Mahlkau (1985) performed a study in the industrial Ruhr district of West Germany, which has a high groundwater table (10–80 cm from the surface) and a history of heavy metal pollution. Groundwater samples were taken from six locations and two soil horizons, an upper oxidizing loam, and a lower reducing loam. Total copper concentrations were high in the upper soil horizons and low in the lower horizons. Copper showed a pronounced leachability only in the oxidizing environment. In the reducing environment, the mobility was low, possibly due to the formation of sulfides.

The mobility of copper from soils was also found to increase following the introduction of 10–100 mM sodium chloride or calcium magnesium acetate deicing salts into soil (Amrhein et al. 1992). The concentration of sodium chloride or calcium magnesium acetate used in the study approximate those in runoff water produced from the melting of snow along salted roadways.

For concentrations up to 2 mg of copper per liter of water, 25–75% of copper entering POTWs is removed in sludge, much of which is disposed of by spreading on land. Thus, it is useful to ascertain whether copper in sludge is apt to leach into soil. This did not appear to be the case: leachate collected from sludge-amended soil contained <12 ppb of copper (EPA 1980b). Older studies found that small amounts of copper were found in leachate from soils treated with copper-containing sludge, and copper is typically confined to the upper 5–10 cm of soil (Breslin 1999; Davis et al. 1988; Giusquiani et al. 1992; Ritter and Eastburn 1978). In soils receiving long-term, heavy applications of sludge, high copper concentrations (471 mg/kg in comparison to 19.1 mg/kg in unamended control soils) were reported to depths of up to 25 cm (Richards et al. 1998). Brown et al. (1983) found that copper remained in the upper 12.7 cm of soil treated with sewage sludge for a year. The mobility of copper into soil from sludge was found to be determined mainly by the amount of soil organic carbon and soil surface area (Domergue and Védy 1992; Gao et al. 1997). In addition, soils amended by sludge with low metal content were found to have increased sorption of copper due to the increased binding capacity provided by the “low metal” organics in the sludge (Petruzzelli et al. 1994). From the results of other work, the major portion of the copper (40–74%) is expected to be associated with the organic iron-manganese-oxide and carbonate fractions of most soils (Ma and Rao 1997).

Recent studies on the long-term effects of soil treated with organic amendments, such as sludge, manure, and compost, on copper availability have been published. Models to predict copper bioavailability in soils have been developed to characterize potential toxicity to ecological species under certain environmental conditions (Smolders et al. 2009). It has been observed that abiotic soil properties, including the cation exchange capacity, pH, and composition, are significant factors in determining the available concentration of copper. The availability of copper species from freshly amended soils and aged field-contaminated, naturally leached soils is dependent on ionic strength and pH. Toxicity to ecological species was observed to be lower in experimentally aged or field-contaminated soils. Higher ionic strength and lower pH of freshly amended soils may create a more favorable environment both abiotically and biotically and increase metal bioavailability (Smolders et al. 2012). Smolders et al. (2012) found that copper availability in soil treated long-term with organic amendments was lower than that in soil that had been freshly spiked with Cu^{2+} salts due to its lower availability in the original matrix and to aging reactions. Cagnarini et al. (2021) simulated long-term metal concentrations in soil treated with organic amendments in Switzerland. Copper concentrations have decreased over time and are projected to remain nearly constant or in decline through 2100 (Cagnarini et al. 2021). The model suggests that although concentrations of copper in soil treated with sewage sludge are expected to decrease, historic inputs of sewage sludge would result in exceedances of the threshold concentration that would persist through 2100. Copper availability in soil to which stabilized sewage sludge or biosolids were applied has also been studied; concentrations of copper in biosolid treated clay, calcareous, and sandy soil were significantly higher than in control samples (Mahdy et al. 2007).

Other Media. Accumulation of copper in biota is inversely related to exposure concentrations (McGeer et al. 2003). Low potential for bioaccumulation is likely the result of natural homeostatic controls in organisms. Homeostatic regulation in a marine thornfish, *Terapon jarbua*, exposed to waterborne (10.6±1.2 μg/L copper) and dietary copper (162±10.4 μg/g dry weight) was investigated using a PBPK model (Wang and Wang 2016). Results from the study found that concentrations in the blood were lowest and increased minimally during exposure, while concentrations in the liver were highest and increased to levels as high as 10.1 and 8.4 μg/g fresh weight for dietary and waterborne exposures, respectively.

In multiple studies conducted prior to 1980, bioconcentration factors (BCFs) of copper in fish obtained in field studies were 667 in marine fish and 50–200 in freshwater fish, suggesting a low potential for bioconcentration (EPA 1980b). The BCF is higher for mollusks such as hard-shell clams and squid, with BCFs of 30,000 and 2.1×10^7, respectively; it was noted that the high levels found in squid may be a result of copper requirements for metabolic processes (EPA 1980b). This may present a major dietary source of copper that could be of concern for those individuals who regularly consume oysters, clams, or squid. Since mollusks are filter feeders and copper concentrations are higher in particulates than in water, this is to be expected (EPA 1980b). For example, a study was conducted with white suckers and bullheads, both bottom-feeding fish, in two acidic Adirondack, New York, lakes (Heit and Klusek 1985). These lakes were known to have received elevated loadings of copper, but the suckers and bullhead had average copper levels of only 0.85 and 1.2 ppm (dry weight), respectively, in their muscle tissue. The biomagnification ratio (the concentration of copper in fish compared to that in their potential food sources on a wet weight/wet weight basis) was <l, indicating no biomagnification in the food chain. The copper content of muscle tissue of fish from copper contaminated lakes near Sudbury, Ontario, did not differ significantly from that of the same fish species in lakes far from this source (Bradley and Morris 1986). In a commercial catfish pond where copper was applied as an algaecide, only 0.01% of the copper applied was taken up by the fish (Liu et al. 2006). Similarly, the copper concentration in shrimp in a shrimp farm with high copper bioavailability did not differ from other shrimp populations (Lacerda et al. 2009).

Copper ions have the greatest bioavailability in water; however, chemical speciation of copper is contingent on aqueous conditions, which may lead to differences in bioavailability (Erickson et al. 1996; Wapnir 1998). The bioavailability and uptake of copper in aquatic species vary with the physiochemical conditions present in the aquatic environment as well as the copper species present. For example, copper and copper monohydroxide binding capacity with dissolved organic matter in aqueous systems varies with the composition of the dissolved organic matter, which affects the bioavailable concentrations present (Davies-Colley et al. 1984; EPA 2007; Hollis et al. 1997). Models such as the Biotic Ligand Model and others have been developed to predict the uptake and aquatic toxicity of copper by considering parameters that affect the bioavailability of copper (e.g., dissolved organic carbon, hardness, and pH) (Adams et al. 2020; Brix et al. 2017; Di Toro et al. 2001; EPA 2007). De Schamphelaere et al. (2009) evaluated the composition of dissolved organic matter and corresponding aquatic toxicity (48-hour EC_{50}) values of copper for the aquatic invertebrate, *Daphnia magna*. Dissolved organic carbon concentrations varied between 2 and 18 mg/L, with corresponding EC_{50} values of between 51 and 638 μg Cu/L. These results suggested that lower dissolved organic carbon results in an increase in bioavailable copper (De Schamphelaere et al. 2009).

As with water, the bioavailability of copper in food sources and other environmental media is a function of the conditions, solubility, copper speciation, and types of complexes that may result. Possible ligands in foods may include amino acids and other organic acids that can act as strong or weak complexing ligands affecting the bioavailability of copper in the complex formed. Soil and sediment composition and characteristics are also factors in determining the copper complexes that may be formed; for example, humic and fulvic acids are potential ligands (Adams et al. 2020; NRC 2000; Tipping 1994; Wapnir 1998).

The bioavailability of copper from different compounds has been studied in chickens. Baker et al. (1991) compared copper bioavailability from copper oxide, cuprite, and copper-lysine complex to that of $CuSO_4 \cdot H_2O$ and found that accumulation of copper in the liver from cuprite and copper-lysine complex is comparable to $CuSO_4 \cdot H_2O$, while copper in copper oxide was not readily bioavailable (Baker et al. 1991).

No evidence of bioaccumulation was obtained from a study of various pollutants in the muscle and livers of 10 mammal species in Donana National Park in Spain (Hernandez et al. 1985). The park is impacted by organochlorine compounds and heavy metals emitted from anthropogenic activities that surround the park. For example, the Guadalquivir River that flows through the park first flows through a major mining region in addition to a large urban area and industrial areas, potentially carrying with it contaminants acquired from these sites. The animal species in the study were classified into three categories (herbivorous, omnivorous, and carnivorous) to ascertain if the pollutants were showing biomagnification in higher trophic levels of animals. No evidence of copper biomagnification in the food chain was observed. Likewise, in a study of a food web in a beech tree forest in Northern Germany, there was no evidence of biomagnification in tertiary consumers (e.g., vole, shrew, and mouse) compared to secondary consumers (e.g., earthworm, snail, beetle, and isopod) (Scharenberg and Ebeling 1996). A study of heavy metals in cottontail rabbits on mined land treated with sewage sludge showed that, while the concentration of copper in surface soil was 130% higher than in a control area, the elevation was relatively little in foliar samples. No significant increase in copper was observed in rabbit muscle, femur, kidney, or liver. Apparently, copper was not bioaccumulating in the food chain of the rabbit (Dressler et al. 1986).

Trophic transfer factors (TTFs), which are similar to biomagnification factors, were investigated for copper in freshwater and marine food chains (Cardwell et al. 2013). Copper TTFs in freshwater were 0.1 for cladocera, 1.0 for insects, 6 for gastropods, and 27 for bivalves. Copper TTFs in marine studies were 0.3 for amphipods, 1.4 for bivalves, and 0.1 for fish. TTFs for accumulator species in marine systems ranged from ~0.2 for *Perna viridis* to ~8.1 for *Saccostrea glomerata*. The relationship between the presence or absence of adverse effects, calculated TTFs, and dietary exposure concentration from laboratory studies for copper showed that only one of the nine data points associated with effects had a TTF >1.0, the value in which, if exceeded, suggests the potential for trophic transfer and biomagnification (Cardwell et al. 2013).

At the lowest levels of the food chain, there is little evidence of copper bioaccumulation. In a study of copper uptake in earthworms as a function of copper concentration (6–320 mg/kg dry weight) in sludge-amended soils, a BCF of <1 (0.67) was obtained (Neuhauser et al. 1995). In another example, a study of earthworms and soil from 20 diverse sites in Maryland, Pennsylvania, and Virginia, copper concentrations in earthworms showed a poor correlation with that in soil (Beyer and Cromartie 1987). These results are consistent with the results of another study that also showed no clear correlation between copper concentrations in earthworm tissues and two soils that were heavily contaminated with heavy metals (copper concentrations of 242 and 815 mg/kg dry weight) (Marinussen et al. 1997).

However, there is some evidence in one study for bioconcentration of copper at low copper concentrations in soil. Even though Scharenberg and Ebeling (1996) showed that there was no evidence for biomagnification of copper in a forest food web, their results did show that the total concentrations of copper in the secondary (18.3–192.0 mg/kg dry weight) and tertiary consumers (9.9–17.4 mg/kg dry weight) were higher than the concentrations of the metal in the dominant vegetation (5.3–10.9 mg/kg dry weight) and soil (1.8–5.8 mg/kg dry weight) in the ecosystem.

Diks and Allen (1983) added copper to four sediment/water systems and studied the distribution of copper among five geochemical phases, namely, absorbed/exchangeable, carbonate, easily reducible (manganese oxides and amorphous iron oxides), organic, and moderately reducible (hydrous iron oxides). The investigators then attempted to correlate the concentration in each phase with the copper uptake by tubificid worms. Only copper extracted from the manganese oxide/easily reducible phase correlated with the copper content of worms at the 95% confidence level. This result suggests that the redox potential and pH in the gut of the worm is such that manganese oxide coatings are dissolved. The copper derived from the dissolved manganese oxide phase in the gut of the tubificid worms appeared to be soluble and available for uptake.

5.4.2 Transformation and Degradation

Air. Data are available on the speciation of copper in airborne particulates. It is generally assumed that metals of anthropogenic origin, especially those from combustion sources, exist in the atmosphere as oxides because metallic species are readily attacked by atmospheric oxidants. As these oxides age, sulfurization may occur, but only when SO_X gases are present in the atmosphere in sufficient amount. For example, in Arizona, atmospheric copper oxide levels near copper smelters were strongly correlated with co-emitted sulfur (Schroeder et al. 1987). Copper was primarily bound to organics and sulfides in dry deposition near a smelter in China, and dust from the smelter and in deposition samples showed sulfides and oxides (Liu et al. 2021c). Copper has been observed bound to fine aerosol particles as the sulfate and nitrate (Osán et al. 2010). The form of copper in the coarse fraction could be used to trace its source to soil resuspension or brake pad wear erosion (Osán et al. 2010).

In fog water, Cu(II) is reduced to Cu(I) by sulfite, which becomes enhanced by the fact that sulfite is also a ligand of and binds to Cu(I) (Xue et al. 1991). Concentrations of Cu(I) in fog water were 0.1–1 μM, or 4–>90%, respectively, of copper in the Cu(I) state. The reduction of Cu(II) to Cu(I) is pH-dependent and occurs rapidly at pH >6 (Xue et al. 1991).

Water. Free Cu(I) (Cu^+) ion is unstable in aqueous solution, tending to disproportionate to Cu(II) (Cu^{2+}) and copper metal unless a stabilizing ligand is present (EPA 1979; Kust 1978; Tipping 1994). The only cuprous compounds stable in water are insoluble ones such as copper (I) sulfide, copper (I) cyanide, and copper (II) fluoride. Therefore, human exposures to copper will predominately be in the form of Cu(II). Copper in its Cu(II) state forms coordination compounds or complexes with both inorganic and organic ligands. Ammonium and chloride ions can form stable ligands with copper. Copper also forms stable complexes with organic ligands such as humic acids, binding to $-NH_2$ and -SH functional groups and, to a lesser extent, with -OH functional groups. Copper binding to humic and fulvic substances appears as both ionic binding and chelation. Natural waters contain varying amounts of inorganic and organic species. This affects the complexing and binding capacity of the water and the types of complexes formed. In seawater, organic matter is generally the most important complexing agent (Coale and Bruland 1988). In water, the presence of ligands may affect other physicochemical processes such as adsorption, precipitation, and oxidation-reduction (EPA 1979). More specific information on the transformation and degradation of copper in its cupric [Cu(II)] and cuprous [Cu(I)] states is given below.

At the pH values and carbonate concentrations characteristic of fresh surface waters, most dissolved Cu(II) exists as carbonate complexes rather than as free (hydrated) cupric ions (Stiff 1971).

Based on the results of a theoretical model, the major species of soluble copper found in freshwater, seawater, and a 50:50 combination of the freshwater and seawater over a pH range of 6.5–7.5 is Cu^{2+}, $Cu(HCO_3)^+$, and $Cu(OH)_2$ (Long and Angino 1977).

The concentration of dissolved copper depends on factors such as pH, the oxidation-reduction potential of the water, and the presence of competing cations (Ca^{2+}, Fe^{2+}, Mg^{2+}, etc.), anions (OH^-, S^{2-}, PO_4^{3-}, CO_3^{2-}), and soluble cupric-organic and -inorganic complexing agents. If the combination of a particular anion with copper forms an insoluble salt, precipitation of that salt will occur. The most significant precipitate formed in fresh surface waters is malachite ($Cu_2[OH]_2CO_3$) (Sylva 1976). Other important precipitates are $Cu(OH)_2$ (and ultimately CuO) and azurite ($Cu_3[OH]_2[CO_3]_2$). In anaerobic waters, Cu_2S, cuprite, and metallic copper forms and settles out (EPA 1979). The combined processes of complexation, adsorption, and precipitation control the level of free Cu(II) in water. The chemical conditions in most natural water are such that, even at relatively high copper concentrations, these processes will reduce the free Cu(II) ion concentration to extremely low values.

As a result of the previously described physico-chemical processes, copper in water may be dissolved or associated with colloidal or particulate matter. Copper in particulate form includes precipitates, insoluble organic complexes, and copper adsorbed to clay and other mineral solids. In a survey of nine rivers in the United Kingdom, 43–88% of the copper was in the particulate fraction (Stiff 1971). A study using suspended solids from the Flint River in Michigan found that the fraction of adsorbed copper increased sharply with pH, reaching a maximum at a pH of 5.5–7.5 (McIlroy et al. 1986).

The soluble fraction of copper in water is usually defined as that which will pass through a 0.45-µm filter. It includes free copper and soluble complexes as well as fine particulates and colloids. The soluble fraction may be divided according to the lability (e.g., the relative ability of the copper to dissociate from the bound form to the free ion) of the copper forms in the water. Categories range from the very labile metal (e.g., free metal ion, ion pairs, inorganic or organic complexes) to slowly or nonlabile metal (e.g., colloidally bound to inorganic colloidal phases of other metals such as $Fe(OH)_3$ or FeOOH, or bound to high molecular weight organic material) (Tan et al. 1988). For example, in a typical study, 18–70% of dissolved copper in river water was labile and 13–30% was slowly labile (Tan et al. 1988). Various techniques may be used to classify the lability of different fractions of soluble copper; these techniques include solvent extraction, ion-specific electrodes, ion exchange, ultrafiltration, electrochemical methods such as anodic stripping voltammetry, and gel filtration chromatography (U.S. NRC 1984). Newer technologies include hyphenated inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent Technologies 2012). The resulting classification depends on the specific procedure employed. Therefore, a comparison of the results of different researchers should be done in general terms.

The nature of copper's association with inorganic and organic ligands will vary depending on the pH, copper concentration, concentration of competing ligands, binding capacity of the ligands, and hardness or salinity of the water (Adams et al. 2020; Breault et al. 1996; Cao et al. 1995; Gardner and Ravenscroft 1991; Giusti et al. 1993; Lores and Pennock 1998; Tipping 1994; Town and Filella 2000). In river water from the northwestern United States that had a relatively high pH (7.0–8.5) and alkalinity (24–219 ppm as

$CaCO_3$), inorganic species like CO_3^{2-} and OH^- were the most important ligands at high copper concentrations (McCrady and Chapman 1979). However, other species such as organic compounds were important at low copper concentrations. On the other hand, copper in samples from surface water of lakes and rivers in southern Maine with a relatively low pH (4.6–6.3) and alkalinity (1–30 ppm as $CaCO_3$) was largely associated with organic matter (Giesy et al. 1978). The binding of copper to dissolved organics was found to be dependent on the specific organic chemical species (e.g., fulvic acid) and their concentrations in the surface water, the number of available binding sites per fulvic acid carbon, and the hardness of the water (Breault et al. 1996). Increasing water hardness results in decreased fulvic acid binding sites. This effect is due more to the depression of the solubility of high molecular weight fulvic acid in the presence of calcium and magnesium ions than to competition of these ions with copper for fulvic acid binding sites. Changing pH from 8 to 6 resulted in a 7-fold increase in the binding constant for Cu(II) with humic acid (Cao et al. 1995).

The extent to which copper binds to inorganic and organic ligands can be altered by materials carried in runoff. For example, after a period of rain in southeastern New Hampshire, inorganic constituents contributed more to copper binding in lakes and rivers than did dissolved organic matter (Truitt and Weber 1981). A green precipitate, confirmed to be malachite ($Cu_2[OH]_2CO_3$), was formed in river water in Exeter, New Hampshire. The water had a high alkaline pH (7.4) with 43.5 mg/L $CaCO_3$ as a buffering agent that was higher than six other surface waters (e.g., three rivers, two reservoirs, a pond, and a swamp) with pH values of 5.7– 7.4 and 1.7–41 mg/L, respectively. A computer simulation of the copper species in water of a pond and water obtained from an artesian well that fed the pond predicted that 98% of the copper in the artesian well water would exist as the free copper ion (Cu^{+2}), whereas 88 and 63% of the copper in pond water would be bound to organics in the spring and fall, respectively (Giesy et al. 1983). These estimates were based on experimentally determined binding capacities of the organic matter in the two water sources and stability constants for the copper-organic matter complexes.

Seawater samples obtained in a transect of the uppermost Narragansett Bay in August 1980 were analyzed for dissolved, particulate, and organically bound copper to investigate the geochemistry of copper-organic complexes (Mills and Quinn 1984). Narragansett Bay is a partly mixed estuary in Massachusetts and Rhode Island that receives organic matter and metals from rivers, municipal and industrial effluents, and runoff. The Fields Point waste treatment facility accounts for 90% of the copper input into the bay through the Providence River, with dissolved copper representing 60% of the total copper input. The concentrations of dissolved and organic copper were 16.4 and 2.3 μg/kg, respectively, in the Providence River and 0.23 and 0.12 μg/kg, respectively, in Rhode Island Sound. Particulate copper concentrations in Narragansett Bay were 0.06–2.42 μg/kg and generally comprised 40% of the total copper in the bay. Analysis of the data indicated that ~75% of the dissolved copper that enters the bay from the Providence River is removed within the bay.

Organic ligands can contain a variety of binding sites, and the strength of the resulting copper complexes will vary accordingly. Over 99.7% of the total dissolved copper in ocean surface water from the northeast Pacific was associated with organic ligands (Coale and Bruland 1988). The dominant organic complex, limited to surface water, was a strong ligand of biological origin. A second, weaker class of organic ligand was of geologic origin. An independent study showed that copper binds to humic material at several sites. The binding strength of the sites varied by 2 orders of magnitude (Giesy et al. 1986). The humic material in this study was derived from nine surface waters in the southeastern United States. Soluble copper in water discharged from a nuclear power station was primarily complexed with organic matter in the 1,000–100,000 molecular weight range (U.S. NRC 1980). Ten to 75% of the discharged copper was in particulate form. Chemical speciation in environmental media where the binding of copper to organic ligands depends on organic matter in the system may be estimated using models such as WHAM (Windermere Humic Aqueous Model) (Tipping 1994).

The bioavailability of Cu(I) is difficult to access due to its thermodynamic instability in the environment (Xue et al. 1991). Cu(I) is a reactive reducing agent, and its concentrations in the environment is typically determined both by its reaction with oxygen and other oxidants in the aqueous environment to form Cu(II) and its rate of production through the reaction of Cu(II) with reducing agents (Sharma and Millero 1988). Investigators have shown the presence of Cu(I) in seawater, which is thought to occur through the reduction of Cu(II) to Cu(I) by photochemical processes (Moffett and Zika 1987; Xue et al. 1991). The detection of Cu(I) in seawater is likely the result of the stabilization of Cu(I) through complex formation with chloride ions. Cu(II)-organic complexes absorb radiation at wavelengths >290 nm and can undergo charge transfer reactions where the Cu(II) is reduced and a ligand is oxidized. Photochemically-generated reducing agents such as O^{2-} and H_2O_2 in the surface water of oceans and possibly other natural waters (e.g., lakes) may contribute to the reduction of Cu(II) to Cu(I) in these waters (Moffett and Zika 1987; Sharma and Millero 1988).

Melake et al. (2023) measured the average concentration of copper in water (176.43 μg/L) and fish tissues (*Oreochromis niloticus*, *Clarias gariepinus*, and *Bacteroides intermedius*) and calculated bioaccumulation factor (BAF) values of 0.0002–0.004.

Cu(I) was measured in sunny waters off the Florida coast at depths up to 90 m. Cu(I) concentration was highest in the surface layer of seawater, accounting for ~15% of the total copper (~$4x10^{10}$ mol/L), and the hydrogen peroxide concentration increased in parallel to that of Cu(I) (Moffett and Zika 1987). Concentrations of Cu(I) were ~$1.2\ x10^{10}$ mol/L at 25 m and decreased to below the detection limit at 90 m (<$0.1x10^{10}$ mol/L). In addition, the percentage of free Cu(I) is highest on the surface. Sharma and Millero (1988) measured the rate of Cu(I) oxidation in seawater as a function of pH, temperature, and salinity. The rate of reaction increased with pH and temperature and decreased with increasing ionic strength (or higher salinity) (Sharma and Millero 1988). The results suggested that the rates are controlled by Mg^{2+}, Ca^{2+}, Cl^-, and HCO_3 through their involvement in complex formation and ligand exchange (Sharma and Millero 1988).

Sediment and Soil. The adsorption of copper to soil and sediment was discussed in Section 5.4.1 under transport and partitioning. It is important to understand the transport and fate of copper and its compounds in soils and sediments because these compartments tend to be large reservoirs of copper and could have an impact on human exposures. Copper concentrations in drinking water obtained from groundwater can be affected by the leaching of copper from soil. Reservoir sediments have been shown to be sources of copper in drinking water (Georgopoulos et al. 2001). Although much of the copper is bound to inorganic or organic matrices in soils and sediments, there is the potential for release of copper into pore water within soils and sediments depending on soil conditions and the forms of the copper present. There is evidence to suggest that copper binding in soil is correlated with pH, cation exchange capacity, organic content of the soil, presence of manganese and iron oxides, and even presence of inorganic carbon such as carbonates (Petruzzelli 1997; Rieuwerts et al. 1998). At pH levels >5, absorption of copper from pore water onto soil components becomes a significant process, whereas at pH levels <5, copper largely remains in pore water and is, therefore, mobile in soil (EPA 1980b). However, broad generalizations about the mobility of copper in soils are not possible since the situation will differ among different soil types and environmental conditions. More specific information on the lability (e.g., extractability) of copper from differing soils and conditions follows.

There are several ways for determining the forms of copper in soil, the most common method being measuring of the extractability of the copper with different solvents. Extractability is a function of the nature of the soil and the form of copper deposited in the soil. If a relatively labile form of copper is applied, binding to inorganic and organic ligands can occur, as well as other transformations. The capacity of soil to remove copper and the nature of the bound copper were evaluated by incubating 70 ppm of copper with 5-g samples of soil for 6 days (King 1988). Twenty-one samples of soils

(10 mineral and 3 organic) from the southeastern United States were included in the study. Some soil samples were taken from the subsoil as well as the surface. The amount of adsorbed copper ranged from 36 to 100%, of which 13–100% was nonexchangeable when extracted with potassium chloride. Removal of copper from solution was much higher with surface soils than with subsurface sandy soils; 95–100% of the copper was removed by five of the mineral surface soils and all three organic soils. The percentage of copper that was nonexchangeable was relatively high in all but some of the acid subsoils. While the fraction of exchangeable copper was not dependent on pH in surface soils, 96% of the variation in exchangeability was correlated with pH in subsoils. The soil/water partition coefficients for copper were >64 for mineral soils and >273 for organic soils. Of the eight heavy metals in the study, only lead and antimony had higher partition coefficients than copper. Most of the copper in Columbia River estuary sediment and soil was associated with inorganic carbon (e.g., carbonate), but not with the amount of extractable iron or the organic carbon content of the sediment (DOI 1986).

The amount of ammonium acetate- and diethylenetriaminepentaacetic acid (DTPA)-extractable copper in wetland soil/sediment resulting from atmospheric deposition from smelters in Sudbury, Ontario showed the same pattern as total copper, despite random variations in soil pH, redox potential, and organic carbon (Taylor and Crowder 1983). Therefore, in this case, soil characteristics were not the dominant factors determining extractability and availability, but rather the form of copper that was deposited. The median concentrations of total copper, ammonium acetate-extractable copper, and DTPA-extractable copper at 25 sample sites were 371, 49, and 98 ppm, respectively.

In another study of copper partitioning in nine different contaminated soils, sequential extractions were used to operationally define six soil fractions in decreasing order of copper availability: water soluble > exchangeable > carbonate > Fe-Mn oxide > organic > residual (Ma and Rao 1997). The results of this study showed that the distribution of copper in these six soil fractions differed depending on the total copper concentration in the soil. As the copper concentration increased above 240 mg/kg, 69–74.4% of the total copper was found in the water-soluble, carbonate, Fe-Mn oxide, and organic fractions. In relatively uncontaminated soils (<240 mg/kg copper), 97.6–99.6% of the copper was found to be associated with the residual fraction.

In estuarine environments, anaerobic sediments are known to be the main reservoir of trace metals. Under anaerobic conditions, Cu(II) salts will reduce to Cu(I) salts. The precipitation of cupric sulfide and the formation of copper bisulfide and/or polysulfide complexes determine copper's behavior in these sediments (Davies-Colley et al. 1985). In the more common case where the free sulfide concentration is low due to the controlling coexistence of iron oxide and sulfide, anaerobic sediment acts as a sink for copper (i.e., the copper is removed from water and held in the sediment as an insoluble cuprous sulfide). However, in the unusual situation where the free sulfide concentration is high, soluble cuprous sulfide complexes may form, and the copper concentration in sediment pore water may then be high.

In sediment, copper is generally associated with mineral matter or tightly bound to organic material (Kennish 1998). As is common when a metal is associated with organic matter, copper generally is associated with fine sediment, as opposed to coarse sediment. Badri and Aston (1983) studied the association of heavy metals in three estuarine sediments with different geochemical phases. The phases were identified by their extractability with different chemicals and termed easily or freely leachable and exchangeable; oxidizable-organic (bound to organic matter); acid-reducible (manganese and iron oxides and possibly carbonates); and resistant (lithogenic). In the three sediments, the non-lithogenic fraction accounted for ~14–18% of the total copper and the easily exchangeable component was 5% of the total copper. In addition, the compositional associations of copper in sediment samples taken from western Lake Ontario were analyzed employing a series of sequential extractions (Poulton et al. 1988). The mean (±standard deviation) percentages of copper in the various fractions were exchangeable, 0±0; carbonate salt, 0.1±0.3; iron or manganese oxide-bound, 0.2±0.3; organic-bound, 40±11; and residual, 60±8. Another study found that 10–20% of the copper in Lake Ontario sediment samples was bound to humic acids, with virtually all the copper bound to organic matter (Nriagu and Coker 1980). The concentration of copper associated with humic acids was 21–40 times greater than in the sediment as a whole.

Melake et al. (2023) measured the average concentration of copper in sediment (32.93 mg/kg dry weight) and in fish tissues (*O. niloticus*, *C. gariepinus*, and *B. intermedius*) and calculated biota-sediment accumulation factor (BSAF) values of 0.001–0.02.

Other Media. Copper is an essential nutrient for plant growth and metabolism. Therefore, uptake of copper from soil by plants through the roots is a natural and necessary process, actively regulated by the plant (Clemens 2001). However, loss of biodiversity has been reported in environments contaminated with copper. Naveed et al. (2014) found that increasing copper pollution resulting from a former wood preservation plant had a negative impact on plant growth and species. Earthworms, bacteria, nematodes, and fungi showed a similar response to increasing copper concentrations. Results of this study showed that there was a 10% loss in soil biodiversity within a copper concentration range of 110–800 mg/kg (Naveed et al. 2014). Cao et al. (2020) observed a reduction in soil enzyme activity and both microbial and fungal diversity in copper-amended soils (measured concentrations of 19.8, 173.7, and 468.9 mg/kg) under flooded and non-flooded conditions over a 60-day period; high concentrations of copper showed significant decreases in the number and diversity of the communities. Furthermore, fungal communities were more sensitive than bacteria under flooding conditions (Cao et al. 2020).

The uptake of copper into plants is dependent on the concentration and bioavailability of copper in soils. The bioavailability of copper is determined largely by the equilibrium between copper bound to soil components and copper in soil solution. As noted in the discussion of copper binding in soils, this is determined by copper concentrations in soil, soil type, soil components, pH, oxidation-reduction potential of the soil, concentrations of other cations and anions in the soil, etc. (Rieuwerts et al. 1998). Other factors involved root surface area, plant genotype, stage of plant development, weather conditions, interaction with other nutrients in the soil, and the water table (Gupta 1979). Using lime (calcium carbonate) to adjust soil pH is another factor that affects copper uptake. For example, liming acidic soils can increase copper uptake in hay, but decrease copper uptake in wheat (Gupta 1979). However, the effect of liming on increasing soil pH does not appear to be the overriding factor behind the changes in copper uptake by plants, even though there is evidence that the addition of lime to soil to increase the pH to 7 or 8 reduces copper bioavailability to some plants (EPA 1980b). This is evidenced by the fact that changes in pH (5.4–8.0) have little effect on copper concentrations in plant tissues (Gupta 1979).

It appears that microorganisms can transform copper and affect the copper bioavailable for plant uptake (Mulder and van Veen 1968). Hydrogen sulfide (H_2S)-forming microorganisms may be involved in soil copper precipitation as nearly insoluble sulfide salts. Bacteria of the genera, *Thiobacillus* and *Ferrobacillus*, can oxidize CuS to copper sulfate. Johnson et al. (2017) carried out experiments to study the redox transformation of copper by acidophilic bacteria and found that oxidation and reduction of copper were mediated by acidophilic bacteria indirectly. Copper (I) accumulated in aerobic cultures of sulfur-grown *Acidithiobacillus* spp. More copper (I) was produced by *Acidithiobacillus caldus* than by the other species. Reduction of copper (II) by aerobic cultures of sulfur-grown *Acidithiobacillus* spp. was more pronounced as culture pH declined. *Acidithiobacillus* grown anaerobically on hydrogen and *Acidiphilium cryptum* grown micro-aerobically on glucose only reduced copper (II) when iron (III) was included. Copper (I) was only oxidized by growing cultures of *Acidithiobacillus* spp. when iron (II) was included.

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to copper depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of copper in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on copper levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

Table 5-9 shows the lowest limit of detections that are achieved by analytical analysis in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-10.

Table 5-9. Lowest Limit of Detection for Copper Based on Standards[a]

Media	Detection limit	Reference
Metal and nonmetal dust on mixed cellulose ester membrane (MCE) filters in workplace	0.07 μg/sample[b]	NIOSH 2014a; Method 7302, Issue 1
Metal and nonmetal dust on polyvinyl chloride (PVC) filters	0.08 μg/sample[b]	NIOSH 2014b; Method 7304, Issue 1
Biological tissues (nail, liver, lungs, etc.)	6 μg/g[c]	NIOSH 2018; Method 8200, Issue 1
Water, wastewater, and solid wastes	5.4 mg/L[d]	EPA 1994a; Method 200.7
Drinking water	0.2 μg/L[e]	EPA 2003; Method 200.5
Groundwaters, surface waters, and drinking water	0.01–0.5 μg/L 0.2 mg/kg[f]	EPA 1994b; Method 200.8
Groundwater, surface water, drinking water, storm runoff, industrial and domestic wastewater	0.7 μg/L[g]	EPA 1994c; Method 200.9
Air	0.00001 μg/L[h]	EPA 2020a
Food	6.02 μg/kg[f]	FDA 2020
Serum	2.5 μg/dL[i]	CDC 2018

[a] Detection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.
[b] Inductively coupled argon plasma-atomic emission spectroscopy.
[c] Inductively coupled plasma-atomic emission spectroscopy.
[d] Inductively coupled plasma-atomic emission spectrometry.
[e] Axially viewed inductively coupled plasma-atomic emission spectrometry.
[f] Inductively coupled plasma-mass spectrometry.
[g] Graphite furnace atomic absorption.
[h] Inductively coupled plasma-mass spectrometry or x-ray fluorescence.
[i] Inductively coupled plasma dynamic reaction cell mass spectrometry.

Table 5-10. Summary of Environmental Levels of Copper

Media	Low	High	For more information
Outdoor air (ppbv)	0.002	5.14	Table 5-13 or Section 5.5.1
Indoor air (ppbv)	0.008	0.012	Section 5.5.1
Surface water (ppb)	1	123,000	Tables 5-14 and 5-16 or Section 5.5.2
Groundwater (ppb)	<1	520,000	Tables 5-14 and 5-16 or Section 5.5.2
Drinking water (ppb)	<5	10,200	Table 5-15 or Section 5.5.2
Food (ppb)	0	135	Table 5-22 or Section 5.5.4
Soil and sediments (ppb)	0.001	310,000,000	Section 5.5.3
Biota (ppb)	0	171,000	Section 5.5.4

Detections of copper in air, water, and soil at NPL sites are summarized in Table 5-11.

Table 5-11. Copper Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median[a]	Geometric mean[a]	Geometric standard deviation[a]	Number of quantitative measurements	NPL sites
Water (ppb)	235	368	16.2	360	197
Soil (ppb)	411,000	435,000	17.1	468	250
Air (ppbv)	0.113	0.332	80.5	28	20

[a]Concentrations found in ATSDR site documents from 1981 to 2022 for 1,868 NPL sites (ATSDR 2022). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

Human exposure to copper in air comes from both natural and anthropogenic sources. The concentrations of copper in air can be higher in the proximity of major sources such as smelters, mining operations, and combustion sources (e.g., power plants, incinerators, automobiles, etc.). Yearly mean data from EPA's Air Quality System (AQS) for the years 2012–2022 are reported in Table 5-12. The AQS database contains ambient air pollution data collected by EPA, state, local, and tribal air pollution control agencies from monitors throughout the country. Most monitoring sites reporting sampling for copper were located in California and a few others have been located in Michigan in some years (including three in 2016, six in 2017, two in 2018, and two in 2019). Based on the most up-to-date data in Table 5-12 (2020–2022), in areas where copper is present in ambient air, the general population is expected to be exposed to average copper concentrations in air of ≤0.0238 $\mu g/m^3$ and maximum concentrations of ≤0.160 $\mu g/m^3$

Table 5-12. Summary of Annual Concentration of Copper (μg/m^3) Measured in Ambient Air Samples at Locations Across the United States[a]

Year	Number of monitoring locations	Number of samples	Average of the arithmetic mean at all locations	Maximum concentration
2022[b]	10	63	0.0219	0.0640
2021	13	331	0.0182	0.1600
2020	13	212	0.0238	0.0745
2019	8	353	0.0255	0.3970
2018	13	495	0.0283	0.4090
2017	14	578	0.0964	3.4400
2016	2	107	0.0363	0.4020
2015	25	785	0.1476	4.1400
2014	25	1,226	0.1109	3.6100
2013	28	1,400	0.1265	3.8400
2012	28	1,479	0.9019	1.8500

[a] 24-hour sampling period.
[b] As of October 24, 2022.

Source: EPA Air Quality System (AQS) annual summaries (EPA 2022a)

One study found that the mean concentration of copper in ambient air from 13 U.S. cities was 0.005 μg/m^3; concentrations ranged from 0.002 to 0.006 μg/m^3 (Chen and Lippmann 2009). The results of several studies in which concentrations of copper in air were reported are described below and summarized in Table 5-13. It should be noted that older data may not be representative of current concentrations, given the reduction of ambient air pollution in the United States.

Table 5-13. Outdoor Air Monitoring Data for Copper

Location(s)	Geographic type	Date(s)	Mean concentration (ng/m^3)	Notes	Reference
United States	Urban	1977	207.5	4,648 samples[a]	EPA 1984
United States	Urban	1978	200.8	3,615 samples[a]	
United States	Urban	1979	259.3	2,507 samples[a]	
United States	Nonurban	1977	193.2	709 samples[a]	
United States	Nonurban	1978	265.7	458 samples[a]	
United States	Nonurban	1979	141.7	235 samples[a]	
Smokey Mountain National Park	Remote	1979	1.6	Above canopy, crustal enrichment factor 31	Davidson et al. 1985
Olympic National Park	Remote	1980	5.6	Crustal enrichment factor 76	

Table 5-13. Outdoor Air Monitoring Data for Copper

Location(s)	Geographic type	Date(s)	Mean concentration (ng/m^3)	Notes	Reference
Camden, New Jersey	Urban	Summer 1981 and 1982	16.0–18.0[b]		Lioy et al. 1987
Elizabeth, New Jersey	Urban	Summer 1981 and 1982	21.0–29.0[b]		
Newark, New Jersey	Urban	Summer 1981 and 1982	25.0–33.0[b]		
Ringwood, New Jersey	Rural	Summer 1981 and 1982	13.0–63.0[b]		
Camden, New Jersey	Urban	Winter 1982 and 1983	17.0–21.0[b]		
Elizabeth, New Jersey	Urban	Winter 1982 and 1983	28.0–36.0[b]		
Newark, New Jersey	Urban	Winter 1982 and 1983	21.0–27.0[b]		
Ringwood, New Jersey	Rural	Winter 1982 and 1983	6.0–18.0[b]		

[a] Samples from National Survey.
[b] Concentrations reported by Lioy et al. (1987) are geometric means.

Davies and Bennett (1985) reported average atmospheric copper concentrations of 5–50 ng/m^3 in rural areas and 20–200 ng/m^3 in urban locations. Data from many urban locations in the United States show concentrations of copper associated with particulate matter ranging from 3 to 5,140 ng/m^3 (Schroeder et al. 1987). Remote and rural areas have concentrations of 0.029–12 and 3–280 ng/m^3, respectively (Schroeder et al. 1987). In remote areas such as national parks, differences in copper concentrations have been attributed to greater vegetative cover and higher moisture and larger amounts of exposed rock and soil (Davidson et al. 1985). Copper follows the same pattern as other heavy metals, in that increased copper levels are present in urban areas in winter and in rural areas in summer (Evans et al. 1984; Lioy et al. 1987.

Anderson et al. (1988) performed a study of the atmospheric aerosols collected at a site in Chandler, Arizona. Several major copper smelters are located ~120 km to the southeast, which were upwind of the sampling site during approximately 50% of the study period. The most abundant type of copper-bearing particle, representing 74% of the total, was associated with sulfur. However, the analysis was not able to specify the form of sulfur present. Anderson et al. (1988) concluded that the smelters to the southeast were the probable source. Mine waste dump sites are another source of airborne copper (Mullins and

Norman 1994). Particle size distribution and the concentration of copper in particle size ranges differ depending on the mine waste site (Mullins and Norman 1994).

Mean concentration ranges of copper in remote (any area of lowest copper concentration such as the Antarctic or Arctic) and rural (any site that represents a regional background that is not directly influenced by local anthropogenic emissions) precipitation ranges were 0.013–1.83 and 0.68–1.5 ppb, respectively, based on a weight per unit volume basis (Barrie et al. 1987). Although an earlier survey referred to by these investigators (Galloway et al. 1982) yielded much higher values of 0.060 and 5.4 ppb, these were ascribed to sample contamination. The mean concentration of copper in rain reported in an extensive study in southern Ontario, Canada was 1.57±0.36 ppb during 1982 (Chan et al. 1986). These concentrations showed little spatial variability. Concentration of copper in cloud water over Olympic Peninsula in Washington State has been measured at 1.7±1.6 μg/L (air equivalent mean concentration of 0.5 ng/m^3) (Vong et al. 1997). Copper concentrations in precipitation may be affected by proximity to industry, but concentrations do not appear to be affected by proximity to automobile emissions. Elevated levels of copper in fog water were observed 3 km downwind from a refuse incinerator in Switzerland (Johnson et al. 1987). The concentration of copper in rain samples taken within 2–15 km downwind of the Claremont, New Hampshire municipal waste incinerator was 0.11–2.12 μg/L, with a mean concentration of 0.87 μg/L (Feng et al. 2000). Cu(II) concentrations in fog water from the central valley of California were 1.7–388 ppb (Miller et al. 1987). The source of the copper was not investigated. The highest values were recorded just as the fog was dissipating.

Copper deposition from automobile emissions, as measured by the concentration of copper in snow, did not vary significantly as a function of distance (15–150 m) from an expressway in Montreal, Canada (Loranger et al. 1996).

Airborne concentrations of copper in the indoor atmosphere within homes located in Suffolk and Onondaga counties in New York average between 8 and 12 ng/m^3 (Koutrakis et al. 1992). The concentration was significantly affected by the use of kerosene heaters, which were found to emit copper into the indoor air at a rate of 15,630 ng/hour (Koutrakis et al. 1992).

5.5.2 Water

Copper is widely distributed in water since it is a naturally occurring element. The results of several studies in which concentrations of copper in water were reported are described below and summarized in

Tables 5-14, 5-15, and 5-16. Data from older studies may have been analyzed with instrumentation with high detection limits, and samples were often contaminated during collection, treatment, and analysis.

Table 5-14. Surface Water and Groundwater Monitoring Data for Copper

Location(s)	Type	Date(s)	Range (μg/L)[a]	Mean concentration (μg/L)	Notes	Reference
Surface water						
United States	USGS survey stations	Not specified	Not reported	4.2	53,862 occurrences	Eckel and Jacob 1988
New Jersey	Representative sample	1977–1979	Maximum 261.0	Not reported	1,603 samples taken from 600 sites; median of 3.0	Page 1981
East Arctic Ocean	Ocean water	1980	32–489 ng/kg	93±38 ng/kg	26 locations 0.5–1 m depth; mean concentration at depth was 400 ng/kg; unfiltered samples	Mart et al. 1984
Atlantic Ocean	Ocean water	Not specified	0.79–3.9 nM	Not reported	20 sites, 2 cruises, 0–1 m depth; unfiltered samples	Yeats 1988
Massachusetts	Pond water	April 1971–March 1972	<10–105	Not reported	Low in summer, high in winter	Kimball 1973
Canada	Lake water	November 1976–January 1977	1–8	2	Acid sensitive lakes	Reed and Henningson 1984
Lake Superior	Lake water	August–September 1991	629–834	756	3 samples; filtered samples	Nriagu et al. 1996
Lake Erie	Lake water	August 1993	703–1,061	870	9 samples; filtered samples	Nriagu et al. 1996
Lake Ontario	Lake water	May–June 1993; October 1993	540–1,098	830	14 samples; filtered samples	Nriagu et al. 1996
Indiana	Stream and pond water, near acidic mine drainage		32–1,200	736	12 samples taken from streams and ponds near abandoned Cerbat Mountain coal mines; filtered samples	Allen et al. 1996

Table 5-14. Surface Water and Groundwater Monitoring Data for Copper

Location(s)	Type	Date(s)	Range (µg/L)[a]	Mean concentration (µg/L)	Notes	Reference
Cerbat Mountains, northwestern Arizona	Surface water in a copper mining area	March 1995, September 1995	100–69,000	Not reported	Samples obtained from the Cerbat Mountains mining area; 15 surface water sites with 14 sites downstream from old tailings and adits; median of 1,200	Rösner 1998
Groundwater						
New Jersey	Representative sample	1977–1979	Maximum 2,783.0	5.0	1,063 samples, 90th percentile 64.0 ppb, groundwater may or may not be used for drinking water	Page 1981
Denver, Colorado	Shallow monitoring well	1993	<1–14	2.0	30 monitoring wells, 22 with PVC casings and 8 with metal casings; samples obtained after purging well 20 minutes; filtered pesticide samples and unfiltered VOC samples	Bruce and McMahon 1996

[a]Range is µg/L unless otherwise stated

USGS = United States Geological Survey; PVC = polyvinyl chloride; VOC = volatile organic compound

Table 5-15. Copper Concentrations in Drinking Water Monitoring Data

Location(s)	Type	Date(s)	Range (µg/L)	Mean (µg/L)	Notes	Reference
Nova Scotia, four communities	Running tap water from private wells	NS	40–200	NR	53% of homes exceeded Canada's maximum permissible limit for copper (1.0 mg/L)	Maessen et al. 1985
	Standing tap water from private wells	NS	130–2,450	NR		
New Bedford, Massachusetts	Running tap water from private wells	April 1987, 1992, 1993 July 1992	NR	230–560	24 sample areas included	Yannoni and Piorkowski 1995

Table 5-15. Copper Concentrations in Drinking Water Monitoring Data

Location(s)	Type	Date(s)	Range (μg/L)	Mean (μg/L)	Notes	Reference
Canada (National Survey)	Raw, treated, and distributed water	November 1976–January 1977	≤5.0–620	NR	Sampled raw, treated, and distributed water from 70 municipalities; median concentration was 20; noted differences based on source and type of water; filtered samples	Meranger et al. 1979
New Jersey	School drinking water	1991–1992	BD (50) – 10,200	NR	Sampled two water fountains in each of 50 schools. Median concentration ranged from 68 to 260 μg/L depending on time of day; noted differences based on time of day and corrosivity of samples	Murphy 1993
California	School drinking water	2017–2022	1,302–2,140	224 (first draw); 158 (second draw)	Three (4%) school drinking fountains had copper levels that exceeded the EPA action level (1.3 mg/L) on the first draw; the three schools had a greater proportion of students eligible for free/reduced priced meals compared to the average California public school	Garvey et al. 2023
Michigan, Massachusetts, Maryland, Virginia	Public schools and childcare facilities drinking water	2016–2020	Range of maximum values: 7,730–53,200	NR	Samples from 133 schools in Michigan; 84,153 water fixtures in 2,000 schools and childcare facilities in Massachusetts: 40 schools in Maryland; and 25 schools in Virginia	Montagnino 2022
Berlin, Germany	Running tap water from municipal water supply	June 1998–March 2001	9–4,200	436–561	2,619 samples from 2,944 households	Zietz et al. 2003a

Table 5-15. Copper Concentrations in Drinking Water Monitoring Data

Location(s)	Type	Date(s)	Range (µg/L)	Mean (µg/L)	Notes	Reference
Lower Saxony, Germany	Tap water from municipal water supply	January 1997–November 1999	>10–6,400	106–183	1,619 stagnated water samples and 1,660 random daytime samples	Zietz et al. 2003b

BD = below detection; EPA = U.S. Environmental Protection Agency; NR = not reported

Table 5-16. Summary of Concentrations of Copper (µg/L) Measured in Surface and Groundwater Samples Across the United States

Year range	Average	Maximum concentration	Number of samples[a]	Percent detected
Surface water				
2020–2022[b]	21.9	25,490	33,645	74%
2015–2019	47.8	23,600	90,360	78%
2010–2014	83.7	123,000	62,180	71%
Groundwater				
2020–2022[a]	31.5	10,400	2,309	68%
2015–2019	41.7	43,000	6,672	76%
2010–2014	279.3	520,000	7,711	79%

[a] Samples collected from the U.S. Geological Survey S Water Science Center monitoring sites and other state environmental departments in over 37 U.S. states.
[b] As of October 24, 2022.

Source: WQP 2022

Groundwater collected from wells from 2013 to 2016 by USGS for the National Water-Quality Assessment Project show copper concentrations of 0.2–98.4 µg/L (USGS 2020b). Copper concentrations in drinking water can vary widely (≤5–53,200 ppb) and can exceed the action level of 1,300 ppb (1.3 mg/L) that is the regulatory Maximum Contaminant Level Goal (MCLG) for copper in drinking water (EPA 1991, 2021b). Copper was found at concentrations greater than EPA's Treatment Technology Action Level of 1.3 mg/L in 0.06% of domestic wells sampled by USGS from 1991 to 2004 (USGS 2009b). An action level is the concentration of a contaminant in potable water, which, if exceeded in 10% of monitoring systems, requires treatment for corrosion control and public notification (EPA 2018b).

A national water quality study was done for contaminants including copper over the period of 1991–2010 (USGS 2014). The study evaluated frequency of copper concentrations greater than the human-health benchmark of 1,300 μg/L (1.3 mg/L) and concentrations outside of recommended non-health guidelines for drinking water in principal aquifers in the United States. For the 37 aquifers used for drinking water and sampled for copper, the percentage of all samples containing copper at ≥1.3 mg/L was 0.03%. For the 17 shallow groundwater aquifers beneath agricultural land and 21 shallow groundwater aquifers beneath urban land, 0% of samples contained copper at ≥1.3 mg/L (USGS 2014).

Elevated concentrations of copper in drinking water can result from leaching processes from source materials such as piping, tanks, and valves in water distribution systems. Copper in tap water is related to Cu(II) mineralogy and solubility, which have been shown to be affected by age, pH, and dissolved inorganic carbon within the system (Montagnino et al. 2022). Data from 208 U.S. households indicates that about a third of U.S. homes have drinking water containing more than 0.1 ppm copper (Brewer 2010). A study of 1,000 water samples from random households in Ohio found that ~30% contained copper levels >1 ppm (Strain et al. 1984). The highest copper level in the study was 18 ppm. In a study of private water wells in four communities in Nova Scotia, Maessen et al. (1985) found that the concentrations of copper increased in water that remained in the distribution system overnight, indicating that copper was mobilized from the distribution system. Whereas the level of copper in running water was generally very low, that in standing water was variable and exceeded 1.0 ppm in 53% of the homes. Similar results were reported for U.S. cities (Maessen et al. 1985; Schock and Neff 1988; Strain et al. 1984). In a study in Seattle, Washington, the mean copper concentrations in running and standing water were 0.16 and 0.45 ppm, respectively, and 24% of the standing water samples exceeded 1.0 ppm (Maessen et al. 1985). The difference in copper level between standing and flushed systems became evident at pH 7 and increased with decreasing pH (Strain et al. 1984). Copper levels in school drinking water were found to differ by 3-fold between first draw and 10-minute flush water samples, irrespective of the corrosiveness of the water (Murphy 1993). However, the concentration of copper in both first draw and 10-minute flush samples decreased by approximately 10-fold as the corrosiveness of the water decreased. Increasing pH in water distribution lines has been found to result in an overall decrease in metal concentrations. For example, increasing the pH of water from 7.5 to 8.5 in distribution lines decreased copper concentration by 50% (Yannoni and Piorkowski 1995). In a review of copper in drinking water at schools (n=12,193) and childcare centers (n=5,460) using public water systems as of July 2020, it was estimated that a total of 6,419 (13.2%) copper action level exceedances were reported since 1992. Voluntary testing for copper in drinking water conducted in 2016 at 133 schools in Michigan, ~2,000 schools in Massachusetts, and 40 schools in Maryland found that 11, 351, and 4 schools/childcare facilities, respectively, had copper levels above the EPA action limit. The maximum levels of copper found were 15.5 mg/L (15.5 ppm) in Detroit at a kitchen faucet, 10.2 mg/L (10.2 ppm) in Maryland at a kitchen sink, and 53.2 mg/L (53.2 ppm) in Massachusetts at a kitchen faucet. In 2019 and 2020, voluntary testing in Virginia identified nine and six instances, respectively, of public school exceedances, with maximum values reported at a kitchen sink of 7.73 mg/L (7.73 ppm) in 2019 and 11.4 mg/L (11.4 ppm) in 2020 (Montagnino et al. 2022).

In homes with copper piping, the mean concentration of copper in tap water has been shown to decline with the age of the home. In a sampling of tap water of 2,619 households in Berlin, Germany that are supplied with municipal drinking water, the mean concentration of copper decreased from 0.77 ppm in homes with stated ages of 0–<5 years to 0.23 ppm in homes with stated ages of 35–<40 years (Zietz et al. 2003a). In another study of 1,619 homes in Lower Saxony, Germany, the mean concentration of copper in first draw tap water decreased from 0.37 ppm in homes with stated ages of 0–<5 years to 0.05 ppm in homes with stated ages of 35–<45 years (Zietz et al. 2003b). These decreases of copper concentration with age were attributed to a buildup of a surface layer on the piping that reduced corrosion. However, in these same two studies, it was found that the concentration of copper in tap water began to increase with increasing age in homes with stated ages of >45 years. This increase in copper concentration was attributed to the increased probability of repair or partial placement (or unknown total replacement) of piping in these homes.

In a study of groundwaters and surface waters throughout New Jersey in which >1,000 wells and 600 surface sites were sampled, the median copper levels in groundwater and surface water were 5.0 and 3.0 ppb, respectively (Page 1981). The respective 90th percentile and maximum levels were 64.0 and 2,783.0 ppb for groundwater and 9.0 and 261.0 ppb for surface water. The pattern of contamination in surface water correlates with light hydrocarbons, while that in groundwater correlates with heavy metals. This suggests that the sources of contamination of surface water and groundwater are different. The nature of the sites with elevated levels of copper was not indicated.

Several studies reported copper levels in surface water with a range of 0.5–1,000 ppb and a median of 10 ppb; seawater contained <1–5 ppb (EPA 1980b; Davies and Bennett 1985; Mart et al. 1984; Page 1981; Yeats 1988). The geometric mean, standard deviation, and median concentration of dissolved copper in surface water based on 53,862 occurrences in the Water Quality Portal (WQP) are 4.2±2.71 and 4.0 ppb, respectively (WQP 2020). Higher concentrations tend to be found in New England, the western Gulf, and the lower Colorado River.

Copper concentrations were measured in surface water obtained from sampling sites in the Spearfish Creek, Whitewood Creek, and Bear Butte Creek watersheds. These watersheds are affected by water leaching from tailings and acid mine drainage from gold mining operations in the Black Hills of South Dakota. Copper concentrations of <0.24–28 μg/L were measured in surface water, whereas concentrations in sediments were much higher, ranging from 7.8 to 159 mg/kg (May et al. 2001).

In a survey of sources of copper in stormwater, measurements of copper concentrations in stormwater samples were taken from various urban locations in Birmingham, Alabama. Copper concentrations were generally low in filtered samples (dissolved copper), ranging between 1.4 and 20 μg/L; however, they were much higher in unfiltered samples (copper bound to particulate matter) with mean values (in μg/L) of 280 (street runoff), 135 (vehicle service areas), 116 (parking areas), 110 (roof areas), 81 (landscaped areas), 50 (urban creeks), and 43 (retention ponds) (Pitt et al. 1995).

As a result of improvements in controlling the quality of discharges from municipal and industrial wastewater treatment plants mandated in the Clean Water Act, copper concentrations have been declining in surface waters. For example, median copper concentrations in the Hudson River estuary have fallen 36–56% between the mid-1970s and the mid-1990s (Sañudo-Wilhelmy and Gill 1999).

The copper concentration in some bodies of water evidently varies with season. In a study of a small pond in Massachusetts from April of 1971 to March 1972, the concentration of copper was found to vary, decreasing during the spring and early summer to lows of <10–30 ppm in early August and then increasing when the pond was under the cover of ice to maximum values of 80–105 ppb in late January and early February (Kimball 1973). Similar seasonal variations were noted in the epilimnion of the offshore waters of the Great Lakes (Nriagu et al. 1996). In both examples, the cycling of copper concentrations is thought to be a response to biological need and copper uptake during the growing season and its subsequent release from seasonal die-off and decay of biota.

Copper concentrations in seawater usually are in the 1–5 ppb range (EPA 1980b). Copper levels are overall lower in the Pacific Ocean versus the Atlantic Ocean and higher near the continental shelf than in the open ocean. Copper concentrations in surface water at a depth of 1 m transected on a cruise from Nova Scotia to the Sargasso Sea ranged from 57.2 to 210 parts per trillion (ppt) (Yeats 1988). The mean value in surface water sampled at a depth of 1 m of the eastern Arctic Ocean was 93 ppt (Mart et al.

1984). As noted in a review by Kennish (1998), concentrations of copper in estuarine and coastal waters in the United States were 0.3–3.8 and 0.1–2.5 ppb, respectively.

5.5.3 Sediment and Soil

Copper occurs naturally in the Earth's crust at a mean concentration of approximately 50 ppm (Henckens and Worrell 2020). Rauch and Graedel (2007) estimated that 9.9 $x10^{11}$ Gg ($9.9x10^8$ kg) of copper exists in the Earth's crust. Several databases report copper levels in soil and sediment in the United States. The National Geochemical Database by USGS (2016) reported that copper occurs in soils at levels of 0.005–200,000 ppm and in sediment at levels of 0.001–150,000 ppm. The median level of copper in soils and sediments reported to the National Geochemical Database was 30 ppm in soils and sediments (USGS 2016). The National Water Information System by USGS reported copper in soil at levels of 0.84–9.8 mg/kg (WQP 2020). Copper occurs in sediments at levels of 0.12–35,700 mg/kg (WQP 2020). EPA reported levels in soil of 0.58–334 mg/kg (WQP 2020). In 2007, USGS conducted a geochemical and mineralogical survey of soils of the conterminous United States. The mean concentration of copper calculated from the 4,841 samples taken was 17.9 mg/kg, with values ranging from <0.5 to 996 mg/kg (USGS 2013). Data as of October 2022 from USGS monitoring systems across the United States are reported in Tables 5-17, 5-18, and 5-19 (WQP 2022).

Table 5-17. Summary of Concentrations of Copper (µg/kg) Measured in Soil Samples at Superfund Sites

Year range	Average	Maximum concentration	Number of samples	Percent detected
2020–2022[a]	–	–	–	–
2015–2019	–	–	–	–
River Mile 11 East Supplemental Remedial Investigation/Feasibility Study, Portland Harbor Superfund Site, Oregon				
2010–2014	48,994	146,000	17	100%

[a] As of October 24, 2022.

Source: WQP 2022

Table 5-18. Summary of Concentrations of Copper (ppb) Measured in Soil Samples Across the United States

Year range	Average	Maximum concentration	Number of samples	Percent detected
2020–2022[a]	2,545,044	82,500,000	76[b]	100%
2015–2019	168,933	3,830,000	1,463[c]	78%
2010–2014	387,270	310,000,000	3,542[d]	61%

[a] As of October 24, 2022.
[b] Samples collected from monitoring sites in Arizona, Kansas, South Dakota, and Wisconsin.
[c] Samples collected from monitoring sites in Louisiana, Montana, New York, North Carolina, South Dakota, Texas, and Virginia.
[d] Samples collected from monitoring sites in Alabama, Alaska, Arizona, Florida, Hawaii, Montana, New Mexico, Oklahoma, South Dakota, Texas, Utah, and Wisconsin.

Source: WQP 2022

Table 5-19. Summary of Concentrations of Copper (ppb) Measured in Sediment Samples Across the United States

Year range	Average	Maximum concentration	Number of samples	Percent detected
2020–2022[a]	396,843	160,000,000	990[b]	87%
2015–2019	114,339	42,200,000	10,801[c]	89%
2010–2014	85,326	17,500,000	15,305[d]	92%

[a] As of October 24, 2022.
[b] Samples collected from monitoring sites in Alabama, Arizona, Florida, Hawaii, Illinois, Mississippi, Montana, New Jersey, Texas, and Wisconsin.
[c] Samples collected from monitoring sites in over 27 U.S. States.
[d] Samples collected from monitoring sites in over 36 U.S. States.

Source: WQP 2022

Anthropogenic and industrial sources can contribute to copper concentrations in soils (Bassetti et al. 2023). Copper concentrations in soil may be much higher in the vicinity of a source of copper emissions, such as a mining operation or smelter activity. Concentrations in the top 5 cm of soil near the boundary of a secondary copper smelter were 2,480±585 ppm (Davies and Bennett 1985). Maximum wetland soil/sediment copper concentrations were 6,912 ppm in the immediate vicinity of a Sudbury, Ontario smelter but the concentration decreased logarithmically with increasing distance from the smelter (Taylor and Crowder 1983). The observation that the copper concentrations were highest in soils within 1–2 km from the smelter and decreased exponentially with increasing distance from the plant suggests that copper in the soil from the study area was primarily derived from particulate emissions from the smelter. In urban surface soils used for community gardens in Pennsylvania, concentrations of copper were greater in areas where smelting activities were identified as a contamination source (59.4–388.8 mg/kg) compared to areas with anthropogenic source contamination (11.6–110.1 mg/kg) (Bassetti et al. 2023).

In 2021, elemental copper concentrations were measured in urban forest soils at 460 locations in Hartford, Connecticut (n=140), Lexington, Massachusetts (n=152), and Springfield, Massachusetts (n=168), which represent multiple land uses including single-family residential, multi-family residential, commercial, industrial, education, lands, and parks (including vacant lots), and all other or unknown land uses. The study reported mean copper concentrations of 17–35 mg/kg (maximum, 106.8–117.2 mg/kg) and there were no significant differences for copper among the land uses evaluated (Sirkovich et al. 2023). Soil samples collected from August to September 2021 in Grand Forks, North Dakota, characterized as poorly drained clay and silt with relatively low permeability, had measured concentrations of copper of 12.58–21.84 mg/kg in park soils and 13.17–22.53 mg/kg in residential soils (Saleem et al. 2023).

From an analysis of the spatial distribution of the copper concentrations in soils where lowest copper soil concentrations are observed for rural (agricultural) soils and highest in soils obtained from industrialized urban areas, it was concluded that most of the contamination was a result of airborne deposition from industrial sources. Concentrations of copper were 16.9–171 mg/kg in soil samples from urban gardens in New York and 19.7–62.8 mg/kg in soil samples from an orchard (Cai et al. 2016). At an abandoned wood impregnation site in Denmark, copper concentrations of 1,300 mg/kg dry weight were measured in CCA-polluted soils in March of 2020 (Tang et al. 2023).

The concentrations of copper in soils and sediments were assessed as part of the National Water-Quality Assessment Program (Rice 1999). The median concentrations of copper at 541 sites throughout the conterminous United States were 5–70 μg/g (dry weight). At nonurban indicator sites, the median concentrations were 13–47 μg/g. The same study derived an average crustal abundance of copper of 60 μg/g (60 ppm).

Sediment is an important sink and reservoir for copper. Surficial sediment in lakes in the Sudbury region of northeastern Ontario, where several smelters operate, decreased rapidly with increasing distance from the smelters (Bradley and Morris 1986). Three lakes, 10 km from the Sudbury smelters, contained copper concentrations in sediment approaching 2,000 mg/kg dry weight, over 100 times the concentration in a baseline lake 180 km away.

An analysis of the Coastal Sediment Database (COSED) showed that 73% of coastal waterways had copper concentrations <42 µg/g; 25% had copper concentrations between 42 and 210 µg/g; and 2% were >210 µg/g. These higher concentrations were associated with locations of high ship traffic, industrial activity, and relatively poor water flushing (Daskalakis and O'Connor 1995). In coastal areas receiving persistently high influxes of contaminants, high concentrations of copper (151 ppm) have been measured in sediments to depths of 54 cm (Bopp et al. 1993). Combined sewer outflows can also contribute significantly to the copper content of sediments. For example, mean (arithmetic) copper concentrations of 180, 208, 280, and 284 mg/kg were measured in sediment samples obtained near four sewer outflows in the lower Passaic River, New Jersey (Iannuzzi et al. 1997). In Jamaica Bay, New York, copper concentrations in sediments were 151–406 mg/kg, with a concentration of 151 ppm in sediment core samples obtained at a depth of 52–54 cm (Bopp et al. 1993). The highest concentrations were found in the middle depths (16–44 cm), ranging from 280 to 406 mg/kg during a period when untreated industrial effluents and sewage outflows entered the bay. However, copper concentrations in surface sediments (0–2 cm) were measured at 208 mg/kg. The decrease in copper concentration in the surface sediments suggests that efforts to reduce metal contaminants from sewage outflows have been making an impact on the copper concentrations in receiving waters and their sediments.

5.5.4 Other Media

In addition to the ingestion of drinking water, the consumption of food is the other primary route for copper intake in the general population. Copper is an essential nutrient present in many plant and animal foods and available as a dietary supplement. The RDAs and Tolerable Upper Intake Levels (ULs) by life stage group are presented in Table 5-20. Copper intake per day based on NHANES data is provided in Table 5-21. Voluntary food fortification in the United States increases the probability of consuming copper and has been associated with copper intakes exceeding the UL for children ages 1–3 years (Sacco et al. 2013).

Table 5-20. Dietary Reference Intakes for Copper

Life stage group[a]	RDA (µg/day)	UL (µg/day)
1–3 years	340	1,000
4–8 years	440	3,000
9–13 years	700	5,000
14–18 years	890	8,000
≥19 years	900	10,000

Table 5-20. Dietary Reference Intakes for Copper

Life stage group[a]	RDA (µg/day)	UL (µg/day)
Pregnant females, ≤18 years	1,000	8,000
Pregnant females, 19–50 years	1,000	10,000
Lactating females, ≤18 years	1,300	8,000
Lactating females, 19–50 years	1,300	10,000

[a] RDAs are not estimated for ages 0–12 months. Adequate intake at this life stage is 220 µg/day.

RDA = Recommended Dietary Allowance; UL = Tolerable Upper Intake Level

Source: IOM 2006

Table 5-21. Mean Amount of Copper Consumed per Individual by Gender and Age

Gender and age (years)	Amount consumed (mg)	Standard error
Males		
2–5	0.8	0.02
6–11	0.9	0.05
12–19	1.1	0.03
20–29	1.2	0.05
30–39	1.4	0.06
40–49	1.4	0.07
50–59	1.5	0.07
60–69	1.3	0.05
≥70	1.3	0.05
Females		
2–5	0.7	0.02
6–11	0.9	0.03
12–19	0.9	0.04
20–29	1.1	0.04
30–39	1.1	0.04
40–49	1.0	0.03
50–59	1.1	0.06
60–69	1.2	0.05
≥70	1.1	0.03

Source: USDA 2020

The FDA Total Diet Survey provides copper concentration in various foods, examples of which are given in Table 5-22 (FDA 2017). The copper content in baby food is given in Table 5-23. The highest concentrations of dietary copper were found in liver; some oat and bran cereals; some legumes and nuts;

and chocolate syrup, candy, and some desserts. Coleman et al. (1992) reported copper concentrations in the edible tissues of livestock and poultry with the highest mean concentrations (mg/kg) found in liver (cow 3.7; lamb 89.8; chicken 4.60; turkey 7.14), followed by kidney (cow 8.15; lamb 5.39; chicken 3.07; turkey 3.68), and muscle (cow 1.41; lamb 1.47; chicken 0.67; turkey 0.83) (Coleman et al. 1992).

Table 5-22. Copper Content of Selected Foods (mg/kg)

Food description	Mean±SD	Food description	Mean±SD
Liver (beef/calf), pan-cooked with oil	135.00±40.78	Pear, canned in light syrup	0.55±0.22
Sunflower seeds (shelled), roasted, salted	19.23±0.40	Pepper, sweet, green, raw	0.55±0.28
Walnuts, shelled	11.70±0.00	Beef with vegetables in sauce, from Chinese carry-out	0.54±0.24
Peanut butter, creamy	4.94±0.38	Cornbread, homemade	0.54±0.03
Peanuts, dry roasted, salted	4.82±0.16	Meatloaf, beef, homemade	0.54±0.08
Raisin bran cereal	4.32±0.31	Pie, pumpkin, fresh/frozen	0.54±0.04
Syrup, chocolate	3.82±0.26	Salmon, steaks/fillets, baked	0.53±0.12
Candy bar, milk chocolate, plain	3.67±0.33	Cream of wheat (farina), enriched, cooked	0.52±0.17
Shredded wheat cereal	3.66±0.38	Tomato, raw	0.52±0.22
Potato chips	3.57±0.35	Chicken potpie, frozen, heated	0.51±0.03
Oat ring cereal	3.55±0.23	Corn flakes cereal	0.51±0.04
Brownie	3.43±0.17	Frankfurter (beef/pork), boiled	0.51±0.08
Raisins	3.30±0.35	Tomato juice, bottled	0.51±0.06
Pinto beans, dry, boiled	3.18±0.39	Chicken breast, fried, fast-food (with skin)	0.50±0.07
Avocado, raw	2.96±0.59	Pineapple, canned in juice	0.50±0.05
Granola with raisins	2.90±0.38	Chicken nuggets, fast-food	0.49±0.10
Bread, whole wheat	2.77±0.02	Pie, apple, fresh/frozen	0.48±0.07
White beans, dry, boiled	2.71±0.58	Pineapple juice, frozen concentrate, reconstituted	0.48±0.05
Chocolate chip cookies	2.70±0.70	Collards, fresh/frozen, boiled	0.47±0.06
Bread, multigrain	2.64±0.16	Potatoes, mashed, prepared from fresh	0.47±0.23
Granola bar, with raisins	2.47±0.85	Orange juice, frozen concentrate, reconstituted	0.46±0.06
Cake, chocolate with icing	2.38±0.17	Blueberries, raw	0.45±0.00
Mushrooms, raw	2.34±0.50	Tuna, canned in water, drained	0.45±0.05
Sweet potato, baked, peel removed	2.31±0.00	Beets, canned	0.44±0.12
Candy bar, chocolate, nougat, and nuts	2.25±0.11	Brussels sprouts, fresh/frozen, boiled	0.43±0.04
Popcorn, microwave, butter-flavored	2.23±0.21	Fruit cocktail, canned in light syrup	0.43±0.02
Pork and beans, canned	2.10±0.14	Watermelon, raw/frozen	0.43±0.33
Lima beans, immature, frozen, boiled	2.08±0.20	Orange (navel/Valencia), raw	0.42±0.07

Table 5-22. Copper Content of Selected Foods (mg/kg)

Food description	Mean±SD	Food description	Mean±SD
Sandwich cookies with filling	2.06±0.42	Orange juice, bottled/carton	0.42±0.02
Ice cream, chocolate	1.85±0.00	Strawberries, raw/frozen	0.40±0.13
Refried beans, canned	1.85±0.13	Turkey breast, oven-roasted	0.40±0.07
Crisped rice cereal	1.82±0.14	Peach, canned in light/medium syrup	0.39±0.03
Crackers, graham	1.79±0.20	Carrot, fresh, peeled, boiled	0.36±0.09
Meal replacement, liquid RTD, any flavor	1.70±0.62	Green beans, canned	0.36±0.08
Pretzels, hard, salted	1.66±0.15	Onion, mature, raw	0.36±0.06
Black olives	1.63±0.37	Soup, tomato, canned, condensed, prepared with water	0.36±0.03
Tomato catsup	1.55±0.17	Chicken breast, oven-roasted (skin removed)	0.35±0.05
Rice, brown, cooked	1.52±0.00	Eggplant, fresh, peeled, boiled	0.34±0.25
Chili con carne with beans, canned	1.51±0.03	Applesauce, bottled	0.33±0.06
Lamb chop, pan-cooked with oil	1.51±0.10	Bologna (beef/pork)	0.33±0.02
Bagel, plain, toasted	1.48±0.14	Cantaloupe, raw/frozen	0.33±0.22
Bread, rye	1.46±0.29	Cheese, Swiss, natural	0.33±0.05
French fries, fast-food	1.43±0.33	Corn, fresh/frozen, boiled	0.33±0.24
Shrimp, boiled	1.40±0.56	Grapefruit, raw	0.33±0.04
Crackers, saltine	1.38±0.14	Carrot, baby, raw	0.32±0.23
English muffin, plain, toasted	1.35±0.14	Apricots, canned in heavy/light syrup	0.30±0.06
Noodles, egg, enriched, boiled	1.34±0.29	Soup, vegetable beef, canned, condensed, prepared with water	0.30±0.06
Soup, bean with bacon/pork, canned, condensed, prepared with water	1.28±0.02	Broccoli, fresh/frozen, boiled	0.29±0.22
Spaghetti, enriched, boiled	1.25±0.34	Dill cucumber pickles	0.27±0.03
Bread, white, enriched	1.23±0.16	Grapefruit juice, bottled	0.27±0.06
Beef steak, loin/sirloin, broiled	1.18±0.46	Cod, baked	0.26±0.00
Pineapple, raw/frozen	1.16±0.00	Sweet & sour sauce	0.26±0.23
Spaghetti with meat sauce, homemade	1.16±0.10	Cheese, cheddar, natural (sharp/mild)	0.25±0.18
Bread, white roll/bun (hamburger/hotdog)	1.15±0.00	Lettuce, leaf, raw	0.23±0.46
Beef stroganoff with noodles, homemade	1.14±0.25	Milk, chocolate, low-fat, fluid	0.21±0.14
Fruit-flavored cereal, presweetened	1.13±0.20	Grape juice, frozen concentrate, reconstituted	0.20±0.03
Crackers, butter-type	1.12±0.11	Prune juice, bottled	0.20±0.01
Burrito with beef, beans, and cheese, from Mexican carry-out	1.11±0.21	Cucumber, peeled, raw	0.16±0.18
Pizza, cheese, fast-food	1.11±0.00	Cake, yellow with icing	0.15±0.17

Table 5-22. Copper Content of Selected Foods (mg/kg)

Food description	Mean±SD	Food description	Mean±SD
Quarter-pound hamburger on bun, fast-food	1.09±0.04	Cream substitute, non-dairy, liquid/frozen	0.13±0.23
Tortilla, flour	1.08±0.11	Wine, dry table, red/white	0.12±0.04
Turkey, ground, pan-cooked	1.08±0.00	Cheese, American, processed	0.11±0.20
Peas, green, fresh/frozen, boiled	1.05±0.19	Corn, canned	0.11±0.18
Pizza, cheese and pepperoni, regular crust, from pizza carry-out	1.03±0.05	Apple juice, bottled	0.10±0.03
Corn/tortilla chips	1.02±0.10	Sour cream dip, any flavor	0.10±0.17
Fried rice, meatless, from Chinese carry-out	1.02±0.18	Turnip, fresh/frozen, boiled	0.10±0.17
Quarter-pound cheeseburger on bun, fast-food	1.02±0.12	Catfish, pan-cooked with oil	0.09±0.18
Doughnut, cake-type, any flavor	1.00±0.28	Clam chowder, New England, canned, condensed, prepared with whole milk	0.09±0.15
Salami, luncheon-meat type (not hard)	0.96±0.12	Cottage cheese, creamed, low-fat (2% milk fat)	0.09±0.15
Asparagus, fresh/frozen, boiled	0.93±0.15	Luncheon meat (chicken/turkey)	0.09±0.16
Pork bacon, oven-cooked	0.93±0.22	Sorbet, fruit-flavored	0.09±0.15
Tortilla, corn	0.92±0.00	Soup, chicken noodle, canned, condensed, prepared with water	0.09±0.15
Potato, baked (with peel)	0.89±0.15	Lettuce, iceberg, raw	0.08±0.15
Banana, raw	0.87±0.15	Cabbage, fresh, boiled	0.07±0.14
Beef roast, chuck, oven-roasted	0.87±0.09	Fruit juice blend (100% juice), canned/bottled	0.05±0.05
Biscuits, refrigerated-type, baked	0.86±0.01	Cranberry juice cocktail, canned/bottled	0.03±0.05
Rice, white, enriched, cooked	0.85±0.15	Milk, low-fat (2%), fluid	0.03±0.04
Chicken leg, fried, fast-food (with skin)	0.84±0.12	Lemonade, frozen concentrate, reconstituted	0.02±0.04
Pork sausage (link/patty), oven-cooked	0.84±0.05	Tea, from tea bag	0.02±0.03
Sweet potatoes, canned	0.84±0.17	Milk, skim, fluid	0.01±0.03
Iced cinnamon roll	0.83±0.08	Milk, whole, fluid	0.01±0.03
Lasagna with meat, frozen, heated	0.83±0.07	Apple (red), raw (with peel)	0.00±0.00
Tomato sauce, plain, bottled	0.83±0.05	Beer	0.00±0.00
Fish sticks or patty, frozen, oven-cooked	0.82±0.19	Bottled drinking water (mineral/spring), not carbonated or flavored	0.00±0.00
Salami, dry/hard	0.82±0.00	Brown gravy, canned or bottled	0.00±0.00
Mustard, yellow, plain	0.81±0.06	Butter, regular (not low-fat), salted	0.00±0.00
Egg, cheese, and ham on English muffin, fast-food	0.80±0.13	Candy, hard, any flavor	0.00±0.00
Oatmeal, plain, cooked	0.77±0.20	Carbonated beverage, cola, low-calorie	0.00±0.00
Peach, raw/frozen	0.77±0.18	Carbonated beverage, cola, regular	0.00±0.00

Table 5-22. Copper Content of Selected Foods (mg/kg)

Food description	Mean±SD	Food description	Mean±SD
Tomato salsa, bottled	0.77±0.06	Carbonated beverage, fruit-flavored, regular	0.00±0.00
Chicken filet (broiled) sandwich on bun, fast-food	0.75±0.13	Cauliflower, fresh/frozen, boiled	0.00±0.00
Chicken leg, fried, fast-food (with skin)	0.75±0.00	Celery, raw	0.00±0.00
Macaroni salad, from grocery/deli	0.74±0.15	Cheese, Monterey jack	0.00±0.00
Biscuits, fast-food	0.73±0.00	Cheese, mozzarella	0.00±0.00
Potato salad, mayonnaise-type, from grocery/deli	0.71±0.27	Coffee, decaffeinated, from ground	0.00±0.00
Potato, boiled (without peel)	0.71±0.26	Coffee, from ground	0.00±0.00
Tuna noodle casserole, homemade	0.71±0.09	Coleslaw, mayonnaise-type, from grocery/deli	0.00±0.00
Chicken thigh, oven-roasted (skin removed)	0.70±0.15	Corn/hominy grits, enriched, cooked	0.00±0.00
Fish sandwich on bun, fast-food	0.69±0.06	Cream cheese	0.00±0.00
Okra, fresh/frozen, boiled	0.69±0.03	Cream, half & half	0.00±0.00
Taco/tostada with beef and cheese, from Mexican carry-out	0.69±0.08	Fruit drink (10% juice), canned or bottled	0.00±0.00
Pancakes, frozen, heated	0.68±0.05	Fruit drink, from powder	0.00±0.00
Pear, raw (with peel)	0.68±0.07	Gelatin dessert, any flavor	0.00±0.00
Breakfast tart/toaster pastry	0.67±0.08	Honey	0.00±0.00
Soup, Oriental noodles (ramen noodles), prepared with water	0.67±0.04	Ice cream, light, vanilla	0.00±0.00
Squash, winter (Hubbard or acorn), fresh/frozen, boiled	0.67±0.15	Ice cream, regular (not low-fat), vanilla	0.00±0.00
Beef, ground, regular, pan-cooked	0.66±0.09	Jelly, any flavor	0.00±0.00
Pork roast, loin, oven-roasted	0.64±0.02	Margarine, regular (not low-fat), salted	0.00±0.00
Eggs, boiled	0.63±0.18	Mayonnaise, regular, bottled	0.00±0.00
Eggs, scrambled with oil	0.63±0.10	Milk shake, vanilla, fast-food	0.00±0.00
Pork chop, pan-cooked with oil	0.62±0.06	Olive oil	0.00±0.00
Sugar cookies	0.62±0.06	Popsicle, fruit-flavored	0.00±0.00
Summer squash, fresh/frozen, boiled	0.62±0.23	Pudding, ready-to-eat, flavor other than chocolate	0.00±0.00
Grapes (red/green), raw	0.60±0.13	Salad dressing, creamy/buttermilk type, low-calorie	0.00±0.00
Green beans, fresh/frozen, boiled	0.60±0.18	Salad dressing, creamy/buttermilk type, regular	0.00±0.00
Spinach, fresh/frozen, boiled	0.60±0.14	Salad dressing, Italian, regular	0.00±0.00
Ham, cured (not canned), baked	0.59±0.11	Sour cream	0.00±0.00
Milk shake, chocolate, fast-food	0.59±0.35	Sugar, white, granulated	0.00±0.00
Mixed vegetables, frozen, boiled	0.58±0.12	Syrup, pancake	0.00±0.00

Table 5-22. Copper Content of Selected Foods (mg/kg)

Food description	Mean±SD	Food description	Mean±SD
Chicken with vegetables in sauce, from Chinese carry-out	0.57±0.13	Tea, decaffeinated, from tea bag	0.00±0.00
Muffin, blueberry	0.56±0.12	Tilapia, baked	0.00±0.00
Luncheon meat, ham	0.55±0.07	Vegetable oil	0.00±0.00
Macaroni and cheese, prepared from box mix	0.55±0.15	Yogurt, frozen, vanilla	0.00±0.00
Pear, canned in light syrup	0.55±0.22	Yogurt, low-fat, fruit-flavored	0.00±0.00

SD = standard deviation

Source: FDA 2017

Table 5-23. Copper Content of Selected Baby Foods (mg/kg)

Food description	Mean	SD
Teething biscuits	1.60	0.53
Sweet potatoes	1.24	0.22
Arrowroot cookies	1.08	0.08
Cereal, mixed, dry, prepared with water	1.01	0.18
Cereal, oatmeal with fruit, prepared with water	0.96	0.10
Pears	0.95	0.08
Peaches	0.92	0.14
Turkey and rice	0.92	0.22
Cereal, oatmeal, dry, prepared with water	0.91	0.21
Mixed vegetables	0.90	0.10
Peas	0.89	0.07
Infant formula, soy-based, ready-to-feed	0.86	0.06
Bananas	0.84	0.22
Macaroni and cheese with vegetables	0.70	0.27
Chicken noodle dinner	0.67	0.09
Pears and pineapple	0.67	0.08
Plums/prunes with apples or pears	0.65	0.18
Apricots with mixed fruit	0.64	0.20
Carrots	0.64	0.17
Macaroni, tomato, and beef	0.64	0.08
Chicken with rice	0.61	0.06
Vegetables and turkey	0.61	0.16
Apples with fruit other than berries	0.57	0.14
Green beans	0.57	0.05
Infant formula, milk-based, iron fortified, ready-to-feed	0.56	0.07
Vegetables and beef	0.56	0.10

Table 5-23. Copper Content of Selected Baby Foods (mg/kg)

Food description	Mean	SD
Squash	0.55	0.09
Fruit yogurt dessert	0.53	0.23
Vegetables and chicken	0.51	0.14
Cereal, rice, dry, prepared with water	0.46	0.04
Beef and broth/gravy	0.39	0.10
Applesauce	0.36	0.06
Juice, pear	0.34	0.04
Chicken and broth/gravy	0.33	0.02
Apples with berries	0.26	0.23
Turkey and broth/gravy	0.15	0.26
Juice, apple	0.11	0.03
Juice, grape	0.02	0.04

SD = standard deviation

Source: FDA 2017.

The contribution of food groups to copper intake varies depending on the age group (Pennington and Schoen 1996). For example, animal flesh only contributes to 18% of the copper intake for a 2-year-old child but contributes to 38% of the copper intake for a 60–65-year-old male.

Wu et al. (2018) conducted a review of the literature to determine nutrient composition in human milk in the United States and Canada from 1980 to 2017. Average copper levels were 0.02–0.08 μg per 100 g of human milk in women 1–6 months postpartum and 0.017–0.02 μg per 100 g of human milk in women 7–12 months postpartum.

Concentrations of copper in biota sampled across the United State are reported in Table 5-24 (WQP 2022). High concentrations of copper have been measured in shellfish and crustacean species such as shrimp and prawns, which use a copper-containing protein, hemocyanin, as an oxygen-transport molecule (Olmedo et al. 2013; Venugopal and Gopakumar 2017). Median copper concentrations ranged from 0 mg/kg wet weight in canned frigate to 6.865 mg/kg wet weight in frozen prawn (Olmedo et al. 2013). The calculated intake of copper from fish and shellfish is 0.117 mg/day, which is not expected to pose a risk to the average consumer (Olmedo et al. 2013). Shellfish provide between 7 and 378% of percent daily values of copper, with the highest contributions from oysters, squid, and lobster (Venugopal and Gopakumar 2017). The concentrations of copper in the soft tissue in mussels and oysters collected as part of the U.S. Mussel Watch Program in 1976–1978 were 4–10 ppm (dry weight) for mussels and 25–

600 ppm for oysters (Goldberg 1986). Copper concentrations in mussels collected from 11 sites near Monterey Bay, California were 4.63–8.93 ppm (dry weight) (Martin and Castle 1984). EPA (1980b)reported similar results for mussels (3.9–8.5 ppm) and for clams (8.4–171 ppm). Measurements of copper concentrations in zebra and quagga mussels taken from Lakes Erie and Ontario in 1997 were 21–41 ppm (dry weight) (Rutzke et al. 2000). In the National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Project, copper concentrations were quantified in mollusks (*Mytilus edulis*, *Mytilus californianus*, *Crassostrea virginica*, and *Ostrea equestris*) from 113 sites around the United States in 1993 and compared to copper concentrations measured in mollusks taken from the same site in the EPA2 Mussel Watch Program, 1976–1978 (Lauenstein and Daskalakis 1998). The results of the comparison indicate that the decreasing and increasing trends in copper concentrations in mollusks were approximately equal among the sites, except in California, where increasing trends were noted at five sites.

Table 5-24. Summary of Concentrations of Copper (µg/kg) Measured in Biota Samples Across the United States

Year range/ organism	Average	Maximum concentration	Number of samples	Percent detected
2020–2022[a]	4,404	126,000	338	100%
Mylocheilus caurinus	194	4,980	48	14%
Catostomus macrocheilus	7,023	35,900	40	12%
Micropterus salmoides	198	342	39	12%
Ptychocheilus oregonensis	2,108	4,140	30	9%
Ictalurus punctatus	256	410	28	8%
Oncorhynchus mykiss	4,493	22,100	21	6%
Micropterus dolomieu	354	943	19	6%
2015–2019[b]	5,651	1,219,000	3,567	88%
M. salmoides	4,402	1,070,000	507	14%
I. punctatus	836	26,900	217	6%
M. dolomieu	967	84,830	163	5%
2010–2014[c]	4,642	394,000	2,871	91%
M. salmoides	2,932	76,000	495	17%
I. punctatus	1,212	27,000	208	7%
Mytilus edulis	4,920	58,600	194	7%
M. dolomieu	516	4,800	173	6%

[a] As of October 24, 2022; all organism (n=33) data regardless of detection frequency.
[b] All organism (n=179) data regardless of detection frequency.
[c] All organism (n=116) data regardless of detection frequency.

Source: WQP 2022

Concentrations of copper in three species of fish living in storm treatment ponds have been compared to copper concentrations in controls collected from surrounding surface waters near Orlando, Florida (Campbell 1994). In redear sunfish and bluegill sunfish collected from stormwater ponds, the mean whole-body copper concentrations were 6.37 and 2.08 mg/kg wet weight, respectively, and were significantly higher than the mean concentrations of copper, 0.879 and 1.07 mg/kg wet weight, respectively, measured in controls collected in natural lakes or ponds. However, in largemouth bass, the mean copper concentrations in fish collected from stormwater ponds and controls did not significantly differ, with values of 3.81 and 4.71 mg/kg wet weight, respectively.

The copper concentrations in the liver of lake trout and grayling taken from four freshwater lakes in Alaska did not correlate well with the concentrations of copper in the sediments of these lakes (Allen-Gil et al. 1997). Lake trout were found to have significantly higher burdens ($p<0.05$) of copper in their livers than grayling, and the concentrations of copper in the livers of trout varied considerably depending on the lake from which they were collected. The species and site differences in copper concentrations in fish livers have been attributed to differences in diet (grayling consume mainly insects, whereas trout consume a mix of snails, insects, and small fish) and time spent at various depths of the water column.

Concentration ratios of copper in plants relative to soil (concentration factors) demonstrate that copper uptake differs significantly between plants. For example, concentration factor values have been found to vary from 0.02 (onion), 0.13 (celery), 0.21 (lettuce), and 0.30 (potato) to 2 (grapes), 4.5 (alfalfa), and 6.8 (grass) (Pinochet et al. 1999). Concentration factors in rice grown in Japan were found to vary among soil types (0.59–3.58), with copper concentrations in rice of 1.7–5.1 µg/g (Herawati et al. 2000). Copper concentrations in rice grain from the Yangtze delta in China have been found to increase significantly from 1.4 to 15.5 µg/g when copper concentrations in wastewater irrigated soils increased from 17.0 mg/kg (wet weight) to 101.2 mg/kg (wet weight) (Cao and Hu 2000).

Studies of copper in human tissues suggest that copper content in a 70-kg adult ranges from 50 to 70 mg (Davies and Bennett 1985). Wise and Zeisler (1984) reported an average copper concentration of 10 ppm in the human liver in 36 samples. Despite the wide variation in copper concentrations in the environment, the copper concentration in the liver only varied by a factor of 2–3.5. The concentration of copper in blood is not expected to be predictive of the total body burden of copper. Saltzman et al. (1990) found that the correlation between copper concentrations measured in blood and total body burden was poor ($r=0.54$).

Copper content in 25 tea samples from China ranged from 7.73 to 63.71 mg/kg (Zhong et al. 2015). In a study of copper release from the inner surface of copper teapots, Ni and Li (2008) found that cuprite was a main mineral component of the corrosion byproducts.

The range of copper concentrations in the filler tobacco of 10 cigarette brands manufactured by British American Tobacco and International Tobacco Company were 18.26–34.94 µg/cigarette (Benson et al. 2017). The range in the filters after smoking was 1.77–36.48 µg/g. The mean copper content of tobacco in Finnish cigarettes was 24.7±10.8 ppm (Mussalo-Rauhamaa et al. 1986). However, only 0.2% of this copper passes into mainstream smoke. This translates to a daily exposure of approximately 1 µg of copper in a pack of 20 cigarettes. Copper levels of 15.4–447 ng/10 puffs were reported for four nicotine-based e-cigarette or vaping product (EVP) aerosols and 16.08 ng/10 puffs in one cannabinoid-based EVP aerosol (Gonzalez-Jimenez et al. 2021).

In an EPA-sponsored study conducted to determine the metal concentration in sewage sludge (Feiler et al. 1980), copper concentrations in primary sludge at seven POTWs were reported to be 3.0–77.4 ppm, with a median concentration of 20.5 ppm. The plant with the highest copper concentrations received wastes from plating industries, foundries, and coking plants. In a comprehensive survey of heavy metals in sewage sludge, 30 sludges from 23 American cities were analyzed (Mumma et al. 1984). The copper concentration in the sludges was 126–7,729 ppm (dry weight), with a median value of 991 ppm. Gutenmann et al. (1994) reported similar concentrations (217–793 ppm, dry weight) in sewage sludge obtained from 16 major cities in the United States. The proposed limit for copper in sludge spread on agricultural land is 1,000 ppm (Mumma et al. 1984). The concentration of copper in cow's manure was ~5 ppm (Mumma et al. 1984).

In municipal solid waste compost obtained from nine sites in the United States, a mean copper concentration of 281 mg/kg (dry weight) was obtained, with range of 36.4–424 mg/kg (He et al. 1995). Lisk et al. (1992) reported copper concentrations of 22.7–327 ppm in composts formed from yard waste, 432–1,019 ppm from sewage sludge, and 191–1,143 ppm from municipal solid waste.

Bolan et al. (2003) analyzed copper in farm effluent and sludge samples at dairy and pig farms that utilized copper hydroxide and at farms that did not use copper hydroxide. The concentration of total copper was higher at farms that used the compound. Copper concentrations were higher in the sludge samples than the effluent. At dairy farms utilizing copper hydroxide, the copper concentrations were 52–

105 mg/kg in sludge and 2.5–10.5 mg/L in effluent. At pig farms utilizing copper hydroxide, copper concentrations were 12.5–526 mg/kg in sludge and 0.1–1.55 mg/L in effluent.

Copper concentrations in waste from the combustion of municipal solid waste and other combustion processes have been reported. Copper in incinerator bottom ash and fly ash has been measured at mean concentrations of 1,700 and 1,000 mg/kg, respectively (Goldin et al. 1992). Buchholz and Landsberger (1995) reported concentrations of copper of 390–530 μg/g in fly ash, 1,560–2,110 μg/g in bottom ash, and 1,140–1,540 μg/g in combined ash. In sewage sludge incineration process steams, copper concentrations were 4,561 mg/kg in sludge cake, 3,465 mg/kg in bottom ash, 3,707 mg/kg in cyclone ash, 3,684 mg/kg in scrubber particulate matter, and 6,666 mg/kg in stack particulate matter (Balogh 1996). In fossil fuel wastes, copper concentrations were 33–2,200 mg/kg in fly ash, 4–930 mg/kg in bottom ash, 6–340 mg/kg in flue gas desulfurization sludge, 10–130,000 mg/kg oil ash, and 2–190 mg/kg in coal (Eary et al. 1990).

Copper concentrations have been measured in several types of electronic and e-waste. The concentrations of copper were 276,186–423,727 mg/kg in discarded basic phones and 268,945–434,628 mg/kg in discarded smartphones (Singh et al. 2019). The average concentrations in basic phones and smartphones were 378,406 and 357,560 mg/kg, respectively. The average weights of copper in different electronic devices were 700,300 mg in plasma televisions, 625,600 mg in color cathode-ray tube (CRT) televisions, 206,000 mg in liquid-crystal-display (LCD) televisions, 102,800 mg in laptop computers, 59,500 mg in LCD monitors, and 18,800 mg in cell phones (Woo et al. 2016). In an assessment of hazardous chemicals in a market-representative set of waste printed circuit boards (WPCBs) originating from computers manufactured from 1996 to 2010, copper was found ranging from 177,000 to 268,000 mg/kg and was the most abundant metal in the WPCBs (Chen et al. 2016). In WPCBs, copper is used to transmit electric signals and is fundamental, but results from the study showed that technological innovation modeled by three types of Intel chipsets correlates with an overall decrease in copper concentration (Chen et al. 2016).

Copper may also be found in clothing. Herrero et al. (2020) analyzed 39 swimsuits made in Vietnam, China, Cambodia, Albania, Sri Lanka, Bangladesh, Tunisia, Spain, Morocco, and Myanmar. Copper was detected in 64% of the samples at concentrations of <0.15–328 mg/kg, with an average concentration of 27.9 mg/kg. Although Herrero et al. (2020) did not specifically discuss the origins of copper in swimsuits, the study authors do note that many swimsuits were made of artificial fibers so that they may be water repellant or fast drying. Metals may be used in the textile industry as dyes, antimicrobials, and water repellants (Herrero et al. 2020).

An assessment of trace metals in lip balms, lip glosses, and lipsticks found that copper was one of the three major trace metals found in lip cosmetics (Gao et al. 2018). Copper concentrations were 11.07–136.73 mg/kg in the products sampled; the mean concentrations were 61.96 (lip balms), 81.28 (lip glosses), and 93.93 mg/kg (lipsticks).

Copper has been detected in pigments in American tattoo ink (Liszewski and Warshaw 2019). Of 44 distinct pigments identified, 4 contained copper. All four pigments were phthalocyanine. The most frequently used pigment containing copper is found in 13 tattoo ink brands and in 562 inks; the least frequently used is found in 1 brand and 1 ink.

Concentrations of copper in fertilizers, soil amendments, and other agricultural materials have been measured by Raven and Loeppert (1997). The materials and mean concentrations are urea (<0.6 μg/g), ammonium nitrate (<0.6 μg/g), ammonium sulfate (<0.6 μg/g), ammonium phosphate (<2– 41.8 μg/g), potassium chloride (<2–3.5 μg/g), potassium-magnesium-sulfate (1.4–5 μg/g), North Carolina rock phosphate (9.6 μg/g), calcite (2.3 μg/g), corn leaves (9.4 μg/g), manure (17.5 μg/g), and austinite (300 μg/g). Copper was measured in cement dust from the United States at an average concentration of 23.66±7.23 μg/g (Ogunbileje et al. 2013).

5.6 GENERAL POPULATION EXPOSURE

Due to the ubiquity of copper in the environment and the general occurrence of copper in airborne particulates, exposure to copper through inhalation is commonplace. Estimates of atmospheric copper concentrations from different source categories (e.g., smelters, ore processing, steel production, and combustion) yielded a maximum annual concentration of 30 μg/m^3 (EPA 1987). If a person is assumed to inhale 20 m^3 of air/day, this would amount to an average daily intake of 600 μg of copper. For the reported range of annual atmospheric copper concentrations, 5–200 ng/m^3 (EPA 1987), the average daily intake by inhalation, would be 0.1–4.0 μg. At the maximum reported ambient air concentration, 100 μg/m^3 for a 24-hour period at a location within one-half mile of a major source (EPA 1987), the average daily intake would rise to 2,000 μg. These estimates assume that all of the copper is attached to particles of inhalable size, <10 μm in diameter.

For adult men and women in the United States, the median intake of copper from food sources has been approximated as 1.0–1.6 mg/day (IOM 2001). Based on NHANES data in the 2020 pre-pandemic survey titled *What We Eat in America*, for all individuals aged ≥2 years, the average daily dietary intake of copper from food is 1.1 mg/day (USDA 2020). According to the NHANES survey of all individuals aged ≥20 years, 18% reported using supplements containing copper. For individuals consuming supplements, the average daily intake from food plus supplement was 2.4 mg/day (USDA 2020). The mean nutrient intake of copper for all males aged ≥20 years from foods was 1.3 mg, and intake from foods plus supplements was 1.5 mg. The mean nutrient intake of copper from foods for all females aged ≥20 years was 1.1 mg, and intake from foods plus supplements was 1.3 mg. For those participants who were supplement users, the mean nutrient intakes of copper for males aged ≥20 years were 1.5 mg from foods and 2.6 mg from foods plus supplements and the mean nutrient intakes of copper for female supplement users aged ≥20 years were 1.1 mg from foods and 2.3 mg from foods plus supplements (USDA 2020). The dietary intake of copper is expected to be above this average for those individuals who regularly consume organ meats (e.g., liver and kidney), nuts, seeds (including cocoa powder), legumes, and bran and germ portions of grains; these intakes are not expected to exceed the maximum recommended limits of 10–12 mg/day (WHO 1996). Mammalian liver, nuts, oilseeds, cocoa powder, and chia seeds contained the highest copper concentrations in a German total diet study (Kolbaum et al. 2023). Copper concentrations appeared to be greater in organically produced foods compared to conventionally produced food, and copper intake was about 10% higher in consumers selecting organic foods. The dietary exposure for children was between 0.04 and 0.07 mg/kg body weight per day, and for adults, exposure ranged between 0.02 and 0.04 mg/kg body weight per day (Kolbaum et al. 2023). In the United States, Tolerable Upper Intake Levels (ULs) vary by life stage, ranging from 1 mg/day for 1-year-old children and 10 mg/day for adults and pregnant and lactating females ≥19 years old (Table 5-17). Those individuals who regularly consume oysters or clams may increase their dietary intake of copper by 2–150 mg/day when consuming 250 g of edible tissue per day, based on copper concentrations of 25–600 and 8.4–171 ppm in oysters and clams, respectively (EPA 1980b; Goldberg 1986).

Assuming a median copper concentration in drinking water of 75 μg/L, the average daily copper exposure from consumption of 2 L water/day would be 0.15 mg. However, people may have high levels of copper in their tap water due to transport through the water distribution system. While corrosion can occur in plumbing of any age, new copper plumbing is a potential source of exposure as copper leaches into drinking water. In the presence of certain water qualities, copper levels in excess of the EPA action level (1.3 mg/L) are most likely to occur in newly constructed homes and buildings with copper plumbing, or at sites that have been recently renovated with new copper plumbing (Edwards et al. 2001; EPA 1995; Grace et al. 2012; Knobeloch et al. 1998; Lagos et al. 2001; Rajaratnam et al. 2002; Schock and Sandvig 2009; Turek et al. 2011). If the system is not permitted to flush out, average intakes from water may be >2 mg/day. Exposure to copper via drinking water has declined significantly since the implementation of

1991 EPA Lead and Copper Rule; exceedances of the action level in the nation's water systems has decreased by over 90% (EPA 2019, 2020b). It is less likely that high dermal exposures will result from bathing in contaminated tap water because the distribution system will flush itself out as the water is drawn.

Exposure to copper compounds may occur through inhalation of aerosols from electronic cigarettes. The potential for exposure depends on the design and materials used in the construction of the aerosol devices, the liquid contents, and the number of puffs that an individual takes per day (generally between 10 and several hundred puffs per day). Copper content in aerosols from first-, second-, and fourth-generation devices ranged from <0.2 to 614 ng per 10 puffs (Halstead et al. 2020). In aerosols from fourth-generation, pod-type devices, copper levels ranged from <0.2 to 209 ng per 10 puffs (Gray et al. 2022); the range was <1.00–104 ng per 10 puffs in aerosols from first- and fourth-generation devices, depending on the specific nicotine salt used in the respective liquids (Pappas et al. 2024).

Data on serum copper for the U.S population from NHANES survey years 2013 to 2016 are presented in Table 5-25. In a 2019 cross-sectional study in China of 3,285 participants with an average age of 72.7 years, a median whole-blood copper concentration of 751.68 μg/L was reported (Guo et al. 2022b).

Table 5-25. Geometric Mean and Selected Percentiles of Serum Copper (in μg/L) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) (CDC 2016, 2018)

	Survey years	Geometric mean (95% CI)	Selected percentiles 50th	75th	90th	95th	Sample size
Total	13–14	1,148.34 (1,122.60–1,174.68)	1,135	1,319	1,547	1,710	2,520
	15–16	1,146.60 (1,124.94–1,168.68)	1,130	1,314	1,538	1,692	2,436
Age group							
12–19 years	13–14	1,055.83 (1,033.20–1,078.96)	1,036	1,197	1,414	1,641	418
	15–16	1,055.03 (1,012.29–1,099.57)	1,031	1,232	1,408	1,534	371
20–59 years	13–14	1,161.59 (1,129.35–1,194.75)	1,138	1,343	1,607	1,787	1,221
	15–16	1,152.32 (1,129.72–1,175.38)	1,124	1,315	1,600	1,794	1,165
≥60 years	13–14	1,149.31 (1,117.16–1,182.39)	1,165	1,310	1,472	1,599	542
	15–16	1,161.35 (1,123.66–1,200.31)	1,150	1,327	1,479	1,617	579
Sex							
Male	13–14	1,032.39 (1,001.14–1,064.63)	1,032	1,173	1,308	1,414	1,235
	15–16	1,042.57 (1,021.11–1,064.49)	1,043	1,171	1,332	1,422	1,201
Female	13–14	1,271.39 (1,246.35–1,296.93)	1,244	1,453	1,677	1,908	1,285
	15–16	1,254.96 (1,221.69–1,289.15)	1,241	1,429	1,672	1,903	1,235

Table 5-25. Geometric Mean and Selected Percentiles of Serum Copper (in µg/L) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) (CDC 2016, 2018)

	Survey years	Geometric mean (95% CI)	Selected percentiles				Sample size
			50th	75th	90th	95th	
Race/ethnicity							
Mexican American	13–14	1,163.47 (1,132.65–1,195.12)	1,157	1,353	1,567	1,738	431
	15–16	1,147.80 (1,118.65–1,177.70)	1,131	1,294	1,534	1,747	464
Other Hispanic	13–14	1,181.15 (1,126.79–1,238.13)	1,156	1,375	1,587	1,656	235
	15–16	1,142.06 (1,115.41–1,169.35)	1,133	1,323	1,493	1,741	334
Non-Hispanic white	13–14	1,131.74 (1,104.19–1,15997)	1,111	1,300	1,504	1,679	975
	15–16	1,134.14 (1,107.51–1,161.40)	1,117	1,295	1,476	1,652	764
Non-Hispanic black	13–14	1,250.99 (1,217.36–1,285.56)	1,242	1,469	1,653	1,763	516
	15–16	1,270.74 (1,228.30–1,314.63)	1,245	1,452	1,705	1,959	494
Other race	13–14	1,105.52 (1,075.40–1,136–49)	1,082	1,292	1,455	1,659	363
	15–16	1,091.44 (1,053.23–1,131.04)	1,095	1,231	1,486	1,653	380

CI = confidence interval

A National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimated that potentially 920,449 workers, including 72,821 women, were occupationally exposed to copper in the United States (NIOSH 1989). The NOES estimate is provisional because all of the data for tradename products that may contain copper have not been analyzed. An estimated 11,889 workers, including 421 women were potential exposed to pure copper and an estimated 53,282 workers, including 8,758 women were potential exposed to copper powder. Additionally, according to the NOES, 16,759 workers, including 9,684 women, were potentially exposed to copper chloride and 17,248 workers, including 4,024 women, were potentially exposed to copper oxide (NIOSH 1988). The NOES was based on field surveys of 4,490 facilities and was designed as a nationwide survey based on a statistically valid sample of virtually all workplace environments in the United States where eight or more persons are employed in all standard industrial codes (SIC) except mining and agriculture. The exclusion of mining and agriculture is significant for estimating exposure to copper since there is a high potential for exposure in these industries. Current Occupational Safety and Health Administration (OSHA) occupational exposure limits for copper fume are 0.1 and 1 mg/m3 for dust and mists (OSHA 2023).

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kg of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breastmilk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

In a cross-sectional study, including 3,982 children and adolescents participating in NHANES survey years 1999–2006, the reported median copper dietary intake estimated for individuals aged 6–18 years was 0.98 (0.71–1.32) mg/day (Shi et al. 2023).

Children could be exposed to copper through contact with wood treated with alkaline copper quaternary (ACQ) (Cushing et al. 2007). ACQ, which contains copper oxide, is used to treat residential decks and playsets. Children might ingest ACQ from dislodged wood residues via hand to mouth contact or be exposed via dermal contact.

Exposure of copper through oral routes may differ between children and adults, due to differences in the consumption of various food groups between children and adults and ingestion of dust and soils. The dietary copper intake for infants who receive the major portion of their nutritional requirements from breastmilk is likely to be different from infants whose nutritional needs are either supplemented or entirely received through the consumption of formula. Estimates of copper intake from inhalation and ingestion in children in the United States are limited. From the work of Pennington et al. (1986), the copper intakes from food consumption for a 6–11-month-old infant and a 2-year-old child were estimated to be 0.47 and 0.58 mg/day, respectively, values that are lower than the adult intake of ~1 mg/day. One study provided estimated inhalation and ingestion exposures of copper for 6–10-year-old children in India (Raghunath et al. 1997). In this work, mean daily concentrations of copper in particulates in air from six locations were measured at 0.01–0.26 μg/m^3. Based on these measurements, estimated inhalation exposures of children to copper were calculated to be 0.1–3.2 μg/day; exposures to copper through ingestion were estimated to be 684–1,732 μg/day.

Exposures of children to copper are likely to increase in areas where copper concentrations in air are expected to be high, such as mining sites, waste dump sites, smelters, and foundries. For example, copper burdens in children living in a polluted area near a lead smelter in Yugoslavia, as measured by copper concentration in teeth, increased in children living closer to the smelter (Blanuša et al. 1990). A study conducted in an industrial area of Northwest China in which concentrations of copper were measured in street dust samples collected from a commercial area, residential area, scientific and educational area, and an industrial and mining area demonstrated higher concentrations of copper in the industrial and mining area posed a noncarcinogenic risk to preschool children in the area (Zhang et al. 2023b). Children are also at risk for increased copper intake through consumption of drinking water where leaching of copper from the distribution system has occurred (Murphy 1993; Yannoni and Piorkowski 1995). Copper-contaminated drinking water has been reported to create a light blue or blue-green color to water, and may result in a metallic, bitter taste (WHO 2004). This route of copper exposure can be minimized through the flushing of drinking water supply lines or increasing the pH of the water in the distribution system.

Arcega-Cabrera and Fargher (2016) measured copper in blood and urine samples of children in Mexico and found that 79.4% had copper detected in urine and 100% had copper detected in blood. The ranges of median copper were 723.02–1,143.7 µg/dL in blood at nine elementary schools and from below detection limit to 20.62 µg/dL in urine. Using ethnographic data, Arcega-Cabrera and Fargher (2016) identified potential sources and pathways of exposure to metals. They concluded that children from poor or marginalized families tended to be exposed to copper while children from wealthier families tended to be exposed to inorganic copper (copper sulfate). There was a positive correlation between the frequency that children ate fresh fish and copper in blood, while there was a negative correlation between the frequency and copper in urine. This is likely due to the copper in fish being protein-bound. Since copper sulfate is used as a preservative in fresh fish and as a water treatment in ponds and other freshwater surfaces, children who eat fresh fish more often may be exposed to it. Piped or well water in the study was found to contain higher levels of copper than purified water, and children of poorer or more marginalized families who cooked with piped or well water had higher levels of copper in urine. Children from households cooking over open food fires also had higher levels of copper in urine than households cooking with gas.

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In discussing exposure to copper, the important question is whether individuals are exposed to readily available copper, which in general means free (hydrated) Cu(II) ions and perhaps some weakly complexed or adsorbed small particulate copper ions. The data indicate that copper in natural water, sediment, and soil mainly exists in bound form. Even so, the free form of copper may be released from ingested materials due to the acidic pH encountered in the stomach. Potential for high uptakes of copper in the general population may exist in situations where people consume large amounts of tap water that contains dissolved copper that come from corrosion of copper in the distribution system, or already have a high copper background due to natural or anthropogenic activities (e.g., close proximity to mining activities or mine drainage). Leaching of copper from water distribution system materials is likely to occur where the water is soft and not flushed out of the system by running the water down the drain before collecting some of it for use. In such cases, the initial concentration of copper frequently exceeds 1 ppm. A large fraction of the copper may be in the form of free cupric ion, and uptake will result by ingestion and, perhaps, dermal contact. Soluble cupric salts are used extensively in agriculture and in water treatment. Workers engaged in the formulation and application of these chemicals along with industrial workers, such as those in the plating industry, may come into dermal contact with absorbable copper ions. Exposure to high levels of free Cu(II) can occur, for example, from swimming in water that was recently treated with a copper-containing algaecide.

Exposure to environmental tobacco smoke may contribute to increased copper exposure in children. Gatzke-Kopp et al. (2023) identified a positive correlation of salivary levels of copper in children and exposure to environmental tobacco smoke.

In a study in Nigeria, serum concentrations of copper were significantly elevated in users of skin-whitening agents (Iyanda et al. 2011). Copper concentrations were 2.27–8.48 mg/kg in toning and skin lightening creams sold in Nigeria (Sani et al. 2016; Theresa et al. 2011), and higher concentrations (8.8–17.85 mg/kg) were detected in moisturizing creams (Theresa et al. 2011). Thus, in some countries, consumers who use moisturizers, toning creams, or skin-whitening agents could be at risk of higher exposure to copper.

Based on the available data, people living close to NPL sites may be at greater risk for exposure to copper than the general population. In this case, exposure can occur through inhalation of airborne particulates from the NPL sites, ingestion of water from private wells near the sites, ingestion of contaminated soil, and/or uptake of copper into fruits and vegetables raised in gardens of residents living near NPL sites.

People living near copper smelters and refineries, as well as workers within these and other industries, can be exposed to high levels of dust-borne copper by both inhalation and ingestion. In some industries, workers may be exposed to fumes or very fine dust that may be more hazardous than coarse-grained dust, because it can be inhaled and penetrate more deeply into the lung, thereby evading the mucociliary escalator.

A health surveillance assessment conducted at a copper smelter, using historical monitoring data of inhalable copper dust collected between 1982 and 2018, found that smelter workers can be exposed via inhalation to copper at exposure levels averaging 4.61±2.13 mg/m^3-years (Haase et al. 2021). Occupational exposure of foundry workers via inhalation was evaluated in 197 male employees from a Brazilian ferrous foundry plant (Freire et al. 2021). Airborne concentrations of copper ranged between below the detection limit of 0.00003 and 8.8 µg/m^3, with a mean value of 1.9±2.1 µg/m^3. Biological monitoring of the workers found concentrations of 0.6–295 µg/L (mean 13.1±21.3) and 674–1,221 µg/L (mean 962±114) in urine and blood samples, respectively. In a 2011 study, urinary metal concentrations and estimated airborne exposure were analyzed to determine occupational exposure in both men and woman employed in welding and electrical trades. Copper was found at concentrations >4.527 µg/L in 18.7% of welders and 15.0% of electricians (Galarneau et al. 2022). Mean urinary concentrations were 13.24±12.52 (log-transformed concentration 2.37±0.61) and 13.07±8.48 (log-transformed concentration 2.41±0.57) in samples from welding trades and electrical trades, respectively.

Exposure to ultrafine particles of copper poses a risk to human health due to their smaller size, larger surface area, surface material, and physical characteristics (Schraufnagel 2020). Traffic exhaust is a common source of exposure, although homes near a trash burning site, bedrooms with burning coils for mosquito abatement, homes with smokers, and kitchens during domestic cooking are also sources of exposure to ultrafine particles (Schraufnagel 2020). Particles created by brake wear, including copper particles, are in the range of 2.8 µm (Wåhlin et al. 2006). Copper has been identified in ultrafine particles leading to metal fume fever among welders (Schraufnagel 2020).