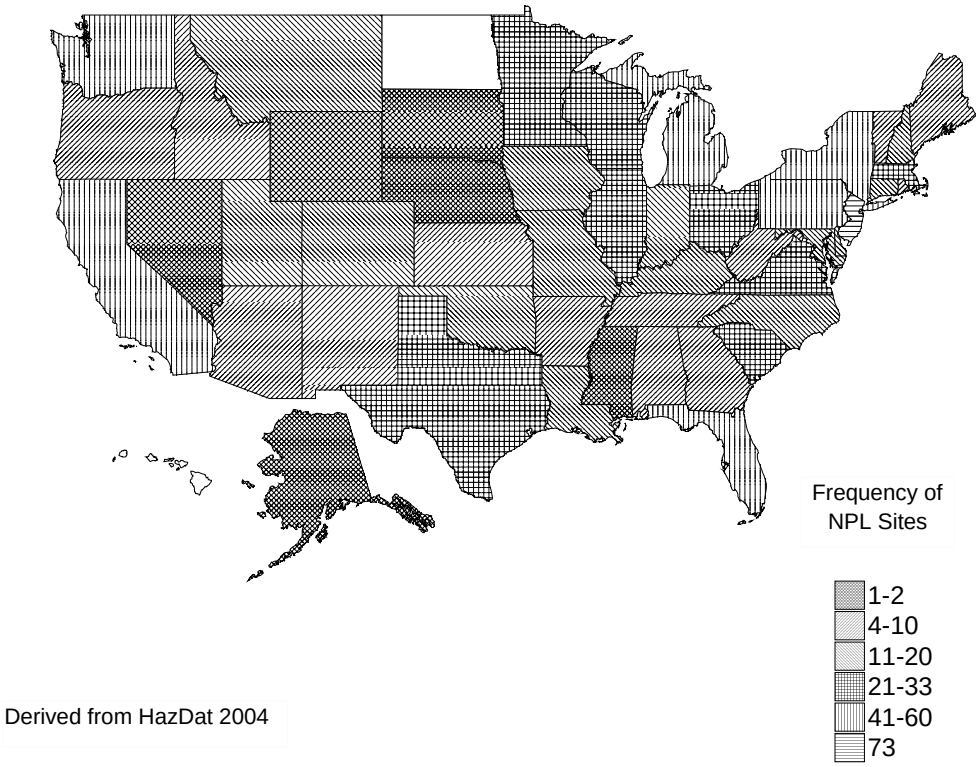
6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Copper has been identified in at least 906 of the 1,647 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2004). However, the number of sites evaluated for copper is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 895 are located within the United States, 2 are located in the Territory of Guam, 8 are located in the Commonwealth of Puerto Rico, and 1 is located in the U.S. Virgin Islands (the sites in the Territory of Guam, the Commonwealth of Puerto Rico, and the U.S. Virgin Islands are not shown).

Copper and its compounds are naturally present in the earth's crust. Natural discharges to air and water, such as windblown dust, volcanic eruptions, etc., may be significant. Therefore, it is important to consider the copper concentrations within a specific environment, geographical region, or human population study site that has been minimally affected by anthropogenic sources of copper in order to accurately assess the contribution of an anthropogenic activity to human exposures to copper. In air, the mean copper concentrations in the atmosphere range between 5 and 200 ng/m^3 in rural and urban locations. Airborne copper is associated with particulates that are obtained from suspended soils, combustion sources, the manufacture or processing of copper-containing materials, or mine tailings. The median concentration of copper in natural water (e.g., rivers, lakes, and oceans) is 4–10 ppb. It is predominantly in the Cu(II) state. Most of it is complexed or tightly bound to organic matter. Little is present in the free (hydrated) or readily exchangeable form. The combined processes of complexation, adsorption, and precipitation control the level of free Cu(II). 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 mean concentration of copper in soil ranges from 5 to 70 mg/kg and is higher in soils near smelters, mining operations, and combustion sources. Sediment is an important sink and reservoir for copper. In relatively clean sediment such as those found in some of the bays and estuaries along the New England Coast, the copper concentration is <50 ppm; polluted sediment may contain several thousand ppm of copper. The form of copper in the sediment also will be site-specific. In aerobic sediments, copper is bound mainly to organics (humic substances) and iron oxides. However, in some cases, copper is predominantly associated with carbonates. In anaerobic sediments, Cu(II) will be reduced to Cu(I) and insoluble cuprous salts will be formed.

Figure 6-1. Frequency of NPL Sites with Copper Contamination



The largest release of copper to the environment by anthropogenic activities is by far to land. The major sources of release 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 as a result of natural weathering of soil and discharges from industries and sewage treatment plants. Copper compounds may also be intentionally applied to water to kill algae.

Copper associated with particulate matter is emitted into the air naturally from windblown dust, volcanoes, and anthropogenic sources, the largest of which are being primary copper smelters and ore processing facilities. The concentration of copper in emissions from copper smelters has been found to range between 7 and 137.8 ng/m^3 (Hutchinson 1979; Romo-Kröger et al. 1994).

In the general population, the highest exposures to copper come from drinking water and food. Of special concern is copper that gets into drinking water from water distribution systems (both from the water treatment plant and in the home). When a system has not been flushed after a period of disuse, the concentration of copper in tap water may exceed 1.3 ppm, the EPA drinking water limit. The estimated intakes of copper in the general population are 0.15 mg/day from drinking water, and approximately 2 mg/day from food. The dietary intake of copper can be increased from the regular consumption of certain foods, such as shellfish, organ meats (e.g., liver and kidney), legumes, and nuts. However, except for shellfish, where an additional intake of 2–150 mg/day is possible for those individuals who regularly consume shellfish, these other sources of higher copper intake are not expected to increase the total daily intake of copper beyond the recommended limit of 10–12 mg/day for adults (WHO 1996). In comparison to intake of copper through ingestion of water and food, the intake of copper through inhalation of copper in dust is much less significant at an estimated rate of 0.1–4.0 µg copper/day. Contact with available copper also may result from the use of copper fungicides and algicides.

Many workers are exposed to copper in agriculture, industries connected with copper production, metal plating, and other industries. Little information is available concerning the forms of copper to which workers are exposed.

At this time, copper has been identified in 906 out of 1,647 NPL hazardous waste sites in the United States (HazDat 2004). The frequency of these sites within the United States is noted in Figure 6-1. Based on the available data, people living close to NPL sites 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 into 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. For example, ingestion of 300 mg of soils near copper smelters by children could result in the intake as high as 0.74–2.1 mg copper per day, based on measurements of copper concentrations in these soils of 2,480–6,912 mg/kg.

6.2 RELEASES TO THE ENVIRONMENT

Industrial manufacturers, processors, and users of copper and copper compounds are required to report the quantities of this substance released to environmental media annually (EPA 1988d). The data compiled in the Toxics Release Inventory (TRI01 2003) are for releases in 2001 to air, water, soil, and transfer of copper and copper compounds for offsite disposal. These data are summarized in Tables 6-1 (copper) and 6-2 (copper compounds). Total releases (rounded to three significant digits) of copper into the environment in 2001 were approximately 11,100,000 pounds (approximately 5,050 metric tons) (TRI01 2003), of which approximately 821,000 pounds (373 metric tons), or 7.4% of the total, were released to air. Another 46,600 pounds (21 metric tons) or approximately 0.4% of the total, were released into water, 0.5% (53,800 pounds, 24 metric tons) was injected underground, and 91.9% (10,200,000 pounds, 4,360 metric tons) was released to land. Total releases (rounded to three significant digits) of copper compounds to the environment in 2001 were approximately 1,000,000,000 pounds (approximately 455,000 metric tons) (TRI01 2003) of which approximately 1,420,000 pounds (645 metric tons), or 0.1% of the total, were released to air. Another 418,000 pounds (190 metric tons), or approximately 0.04% of the total, were released into water, 0.09% (894,000 pounds or 406 metric tons) was injected underground, and 99.8% (998,000,000 pounds or 454,000 metric tons) was released to land. The TRI data should be used with caution because only certain types of facilities are required to report them (i.e., this is not an exhaustive list).

Industrial releases are only a fraction of the total environmental releases of copper and copper compounds. Other sources of copper release into the environment originate from domestic waste water, combustion processes, wood production, phosphate fertilizer production, and natural sources (e.g., wind blown dust, volcanoes, decaying vegetation, forest fires, sea spray, etc.) (Georgopoulos et al. 2001;

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Copper[a]

		Reported amounts released in pounds per year[b]						
State[c]	Number of facilities	Air[d]	Water	Under-ground injection	Land	Total on-site release[e]	Total off-site release[f]	Total on and off-site release
AK	2	0	No data	0	27,324	27,324	0	27,324
AL	51	11,825	1,321	0	14,906	28,052	47,708	75,760
AR	48	5,951	573	0	143,970	150,494	231,861	382,355
AZ	30	978	48	0	227,993	229,019	9,094	238,113
CA	168	9,745	908	0	2,608,971	2,619,624	171,791	2,791,415
CO	18	472	16	0	125,387	125,875	15,991	141,866
CT	63	10,662	904	0	5	11,571	47,415	58,985
FL	35	832	303	51,262	158,561	210,958	40,092	251,050
GA	72	4,473	575	0	135,127	140,175	30,052	170,227
HI	2	0	No data	0	117,010	117,010	0	117,010
IA	39	3,050	566	0	250	3,866	35,144	39,010
ID	5	120	5	0	450,820	450,945	4,000	454,945
IL	160	46,380	4,623	0	1,601,420	1,652,423	658,745	2,311,168
IN	161	42,775	1,239	0	369,664	413,678	2,223,563	2,637,241
KS	24	2,535	251	0	297,190	299,976	24,566	324,542
KY	73	18,633	390	0	269,927	288,950	179,301	468,251
LA	15	126,947	710	2,200	2,426	132,283	690	132,973
MA	69	2,530	77	0	0	2,607	64,821	67,427
MD	12	250	10	0	250	510	89,168	89,678
ME	11	106	321	0	500	927	9,034	9,961
MI	142	35,480	685	0	849	37,014	161,721	198,735
MN	50	16,129	10	0	5	16,144	825,881	842,025
MO	79	9,204	671	0	52,581	62,456	409,753	472,209
MS	35	2,350	657	0	520	3,527	56,712	60,239
MT	1	161	No data	0	1,030,000	1,030,161	No data	1,030,161
NC	83	7,965	1,076	0	193,576	202,617	107,899	310,516
ND	3	23	5	0	0	28	339	367
NE	19	3,638	5	0	47,005	50,648	7,628	58,276
NH	22	1,005	25	0	0	1,030	37,543	38,573
NJ	46	15,584	165	5	22,973	38,727	12,291	51,018
NM	7	500	No data	0	118,680	119,180	23,453	142,633
NV	6	905	No data	0	500	1,405	5,201	6,606
NY	104	11,484	14,198	0	114,462	140,144	894,995	1,035,138
OH	251	55,122	5,424	0	606,137	666,683	481,776	1,148,459
OK	64	8,712	303	0	80,952	89,967	29,726	119,693
OR	23	771	9	0	81,984	82,764	1,495	84,259
PA	222	85,511	2,913	0	43,546	131,970	343,353	475,324

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Copper[a]

		Reported amounts released in pounds per year[b]						
State[c]	Number of facilities	Air[d]	Water	Under-ground injection	Land	Total on-site release[e]	Total off-site release[f]	Total on and off-site release
PR	21	15,944	5	0	0	15,949	9,247	25,196
RI	33	5,093	5	0	0	5,098	22,759	27,857
SC	55	10,018	875	0	76,761	87,654	59,678	147,332
SD	10	4,885	No data	0	750	5,635	280	5,915
TN	89	165,328	567	0	206	166,101	87,117	253,218
TX	117	26,388	4,006	369	574,322	605,085	178,081	783,166
UT	12	1,179	56	0	46,085	47,320	298	47,618
VA	46	21,649	694	5	239,776	262,124	210,846	472,970
VT	5	0	No data	0	250	250	1,025	1,275
WA	28	474	633	0	166,530	167,637	150,773	318,410
WI	159	25,741	617	0	26,845	53,203	257,886	311,089
WV	12	1,951	116	5	30,759	32,831	8,102	40,933
WY	5	381	0	0	60,882	61,263	75	61,338
Total	2,807	821,838	46,559	53,846	10,168,637	11,090,881	8,268,966	19,359,847

Source: TRI01 2003

[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]The sum of fugitive and stack releases are included in releases to air by a given facility.
[e]The sum of all releases of the chemical to air, land, water, and underground injection wells.
[f]Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Copper Compounds[a]

		Reported amounts released in pounds per year[b]						
State[c]	Number of facilities	Air[d]	Water	Under-ground injection	Land	Total on-site release[e]	Total off-site release[f]	Total on and off-site release
AK	6	475	57	670,000	5,193,578	5,864,110	750	5,864,860
AL	66	27,363	28,896	0	2,315,767	2,372,026	66,409	2,438,435
AR	60	17,082	3,277	0	86,510	106,869	173,666	280,535
AZ	27	135,813	584	0	451,467,272	451,603,669	76,083	451,679,752
CA	92	5,374	878	0	111,029	117,281	166,771	284,053
CO	15	720	15,810	0	115,190	131,720	61,086	192,806
CT	24	2,072	635	0	0	2,707	354,565	357,272
DC	1	0	0	0	4,600	4,600	0	4,600
DE	9	3,203	9,196	0	25,029	37,428	30,509	67,937
FL	54	85,273	22,720	0	648,038	756,031	169,746	925,777
GA	69	14,994	48,943	0	776,472	840,409	369,367	1,209,776
IA	52	15,425	3,386	0	156,575	175,386	152,607	327,993
ID	11	1,305	800	0	424,736	426,841	272	427,113
IL	114	46,746	5,233	0	503,051	555,030	1,021,024	1,576,054
IN	88	52,013	20,411	250	1,098,611	1,171,285	1,044,431	2,215,716
KS	20	3,774	0	0	247,277	251,051	112,520	363,571
KY	49	37,298	40,320	0	889,385	967,003	529,758	1,496,761
LA	33	5,626	17,074	7	274,009	296,716	156,664	453,380
MA	27	720	39	0	3	762	104,579	105,341
MD	19	7,471	8,993	0	20,391	36,855	163,428	200,283
ME	5	2,200	485	0	0	2,685	37,187	39,872
MI	68	60,059	14,850	0	643,734	718,643	511,519	1,230,162
MN	46	9,598	882	0	281,020	291,500	2,115,492	2,406,992
MO	55	20,270	2,900	0	4,658,137	4,681,307	248,752	4,930,059
MS	35	45,892	279	12,000	22,708	80,879	54,015	134,894
MT	10	12,595	10	47,757	3,385,422	3,445,784	32,403	3,478,187
NC	88	21,656	15,299	0	758,429	795,384	124,485	919,869
ND	8	632	11,877	0	138,516	151,025	124,852	275,877
NE	21	1,999	155	0	207,272	209,426	21,672	231,098
NH	13	561	12	0	0	573	28,554	29,127
NJ	30	1,187	5,754	0	18,117	25,058	1,869,339	1,894,397
NM	10	11,839	4,005	0	55,651,587	55,667,431	43,010	55,710,441
NV	18	2,034	160	1	27,004,822	27,007,017	3,067	27,010,084
NY	35	9,816	9,830	1	52,320	71,967	161,344	233,311
OH	105	14,459	17,520	8,100	1,158,856	1,198,935	1,555,185	2,754,120
OK	23	2,466	5,082	662	212,835	221,045	48,189	269,234
OR	25	2,160	1,021	0	216,646	219,827	19,130	238,957

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Copper Compounds[a]

		Reported amounts released in pounds per year[b]						
State[c]	Number of facilities	Air[d]	Water	Under-ground injection	Land	Total on-site release[e]	Total off-site release[f]	Total on and off-site release
PA	115	484,099	14,493	0	371,008	869,600	3,121,602	3,991,202
PR	7	44	265	0	0	309	0	309
RI	13	253	608	0	108	969	2,927	3,896
SC	53	32,578	2,664	0	203,101	238,343	309,623	547,966
SD	5	6,150	1,340	0	88,000	95,490	18	95,508
TN	60	17,676	20,876	0	11,178,079	11,216,631	336,292	11,552,923
TX	124	99,287	12,731	155,405	1,302,462	1,569,885	849,639	2,419,524
UT	18	63,960	2,860	0	424,682,491	424,749,311	36,408	424,785,719
VA	50	10,518	19,707	0	390,234	420,459	184,428	604,887
WA	23	6,200	756	0	212,242	219,198	35,097	254,295
WI	56	7,319	13,315	0	59,775	80,409	221,765	302,174
WV	18	4,390	11,557	0	769,830	785,777	199,314	985,091
WY	5	1,470	118	0	235,587	237,175	46,668	283,843
Total	1,978	1,416,114	418,663	894,183	998,260,861	1,000,989,821	17,096,211	1,018,086,032

Source: TRI01 2003

[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]The sum of fugitive and stack releases are included in releases to air by a given facility.
[e]The sum of all releases of the chemical to air, land, water, and underground injection wells.
[f]Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

Harrison 1998). Quantitative information on release of copper to specific environmental media is discussed below. A summary of copper concentrations in environmental media is provided in Table 6-3.

6.2.1 Air

Copper is emitted into the air from both natural and anthropogenic sources. Since copper is a component of the earth's crust, the earth's crust is the primary natural source of copper. Windblown dust has an estimated mean worldwide emission of 0.9–15x10^6 kg/year of copper into the atmosphere (WHO 1998). Other natural sources of copper emitted into air (in terms of estimated ranges of worldwide emissions) are forest fires (0.1–7.5x10^6 kg/year), volcanoes (0.9–18x10^6 kg/year), biogenic processes (0.1–6.4x10^6 kg/year), and sea spray (0.2–6.9x10^6 kg/year) (WHO 1998). Based on these data, the mean total non-crustal sources of copper emitted into the atmosphere is 1.3–38.8x10^6 kg/year. Anthropogenic emission sources include nonferrous metal production, wood production, iron and steel production, waste incineration, industrial applications, coal combustion, nonferrous metal mining, oil and gasoline combustion, and phosphate fertilizer manufacture. It is estimated that only 0.04% of copper released to the environment is released into the air (Perwak et al. 1980). Global atmospheric anthropogenic and natural emissions of copper have been estimated to be 35x10^6 and 28x10^6 kg/year, respectively (Giusti et al. 1993; Nriagu 1989; Nriagu and Pacyna 1988). The estimates for the anthropogenic and natural emissions are based on the sum of copper emissions from various sources as shown in Tables 6-4 and 6-5, respectively.

The EPA conducted a detailed study of the total amount of copper emitted into the atmosphere (Weant 1985). The sources of emissions and the estimated quantities of copper emitted in 10^6 kg/year are: primary copper smelters, 0.043–6; copper and iron ore processing, 0.480–0.660; iron and steel production, 0.112–0.240; combustion sources, 0.045–0.360; municipal incinerators, 0.0033–0.270; secondary copper smelters, 0.160; copper sulfate production, 0.045; gray iron foundries, 0.079; primary lead smelting, 0.0055–0.065; primary zinc smelting, 0.024–0.340; ferroalloy production, 0.0019–0.0032; brass and bronze production, 0.0018–0.036; and carbon black production, 0.013. Using the ranges of copper emitted from these sources, it is estimated that U.S. copper emissions into air are 0.9424–7.974(x10^6) kg per annum. Daily stack emission rates have been reported for three coal-burning power plants on a kg/day/1,000 megawatt basis (Quee Hee et al. 1982); they are 0.3–0.7 and 2.00 kg/day/1,000 megawatt for those using low-sulfur western coal and high-sulfur eastern coal, respectively. This amounts to annual emission rates of 110–260 and 730 kg/1,000 megawatt, respectively. In another report, emission of copper into air from a 650 megawatt electrical power plant,

Table 6-3. Summary of Copper Concentrations in Environmental Media[a]

Environmental media		Concentration	Units
Atmosphere			
Aerosol		0.1–382	ppt
Hydrosphere—water			
Coastal	Dissolved	0.06–4.3	ppb
	Total	0.5–13.8	ppb
	Suspended solids	0.6–370,000	ppm
Estuarine	Dissolved	0.02–4.7	ppb
	Total	1.2–71.6	ppb
	Suspended solids	0.38–72	ppm
Ocean	Dissolved	Not detected–10	ppb
	Total	0.04–10	ppb
	Suspended solids	0.01–2.8	ppm
Lake	Dissolved	0.1–15.6	ppb
	Total	0.1–15.6	ppb
River	Dissolved	0.18–3,000	ppb
	Total	0.5–5,800	ppb
Groundwater	Dissolved	0.003–70	ppb
	Total	1–1,160	ppb
Drinking water	Total	0.3–1,352	ppb
Hydrosphere—sediments			
Coastal	Particulate	0.03–3,789	ppm
	Interstitial water	25.5–32.7	ppb
Estuarine	Particulate	0.3–2,985	ppm
	Interstitial water	0.3–100	ppb
Ocean	Particulate	3.1–648	ppb
	Interstitial water	22–45	ppm
Lake	Particulate	0.4–796	ppm
	Interstitial water	45.6–52	ppb
River	Particulate	5.3–4,570	ppm
Pedosphere			
Soil	Total	0.01–3,138	ppm
	Organic	293–7,634	ppm
Dust	Total	2.9–76	ppm

[a]As reported in the Copper Sourcebook 1998 (Harrison 1998), covering the years 1993–1996.

Source: Georgopoulos et al. 2001

Table 6-4. Global Emissions of Copper from Natural Sources ($x10^6$ kg/year)

	Median	Range
Wind-borne particulates	8.0	0.9–15
Marine spray—seasalt and surface organic microlayers	4.0	0.25–7.7
Volcanoes	9.4	0.9–18
Forest fires	3.8	0.1–7.5
Biogenic—continental particulates and volatiles	2.9	0.11–5.6
Total emissions	28	2.3–54

Source: Nriagu 1989

Table 6-5. Global Emissions of Copper from Anthropogenic Sources ($x10^6$ kg/year)

	Median	Range
Coal combustion	5.15	2.3–8.0
Oil combustion	1.86	0.42–3.3
Pyrometallurgical	23.5	15–32
Secondary nonferrous metal production	0.115	0.06–0.17
Steel and iron manufacturing	1.47	0.14–2.8
Refuse incineration	1.5	1.0–2.0
Phosphate fertilizers	0.415	0.14–0.69
Wood combustion	0.9	0.60–1.2
Total emissions	35	20–51

Source: Nriagu and Pacyna 1988

burning bituminous coal, was estimated at 213 kg/year, based on a summary of reportable TRI releases (Rubin 1999).

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 only control for reducing fugitive dust is the manual use of water sprays (EPA 1980b). The highest concentrations of copper in atmospheric particulate matter were obtained from mining activities, primary and secondary production, and industrial manufacturing (Table 6-6).

Romo-Kröger et al. (1994) were able to show, through the use of radioactive tracers and cluster analysis of interelemental correlations, that Cu, S, Zn, and As 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 ng/m^3 (fine particles) and 131 ng/m^3 (coarse particles) to 22 ng/m^3 (fine particles) and 50 ng/m^3 (coarse particles) during a period of inactivity at the plant, clearly demonstrating the contribution of plant emissions to copper levels in the surrounding area.

The amount of copper and other pollutants in fugitive dust originating from copper production sites, such as from smelter bag houses, or waste sites, is of some concern. 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 meters 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 of 0.04–1.6 mg/kg-month) over the refuse dump and 0.51 mg/kg-month (range of 0.26–0.76 mg/kg-month) in the control area (Lodenius and Braunschweiler 1986).

In a study of automobile exhaust emitted from light duty vehicles conducted in Denver, Colorado, it has been shown that this source of copper emission makes a small local contribution to copper in air. The amount of copper emitted in the 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 (UDDS) of the Federal Test Schedule (FTS) during the summer of 1996 and the winter of 1997 (Cadle et al. 1999).

Table 6-6. Concentrations of Copper in Particulate Matter (<10 μm) Generated from Various Sources[a]

Source	Copper concentration (percent, w/w)
Metal mining	6.17[b]
Secondary metal production	4.6[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 USEPA Speciate 3.0; Shareef, G.S; Radian, September, 1987
[c]Data obtained from KVB Literature Search

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 will be in particulate matter in the elemental form or in the form of an oxide, sulfate, or carbonate. Because copper smelters co-emit SO_X 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 (Graedel 1978; Perwak et al. 1980). Copper associated with fine particles (<1 μm) tends to result from combustion, while that associated with large particles (>10 μm) is likely to originate from wind blown soil and dust (Schroeder et al. 1987).

Copper was detected in air at 39 of the 906 NPL hazardous waste sites where copper has been detected in environmental media (HazDat 2004). Copper was detected in offsite air samples at concentrations ranging from 0.02 to 10 μg/m^3 (median concentration of 0.38 μg/m^3) (HazDat 2002). These copper concentrations in air are generally above the annual atmospheric concentrations of 0.005–0.2 μg/m^3 (EPA 1987a).

6.2.2 Water

Much of the copper that enters environmental waters will be associated with particulate matter. 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. Sixty-eight percent of releases of copper to water is estimated to derive from these processes. Copper sulfate use represents 13% of releases to water and urban runoff contributes 2% (Perwak et al. 1980). In the absence of specific industrial sources, runoff is the major factor contributing to elevated copper levels in river water (Nolte 1988). In the EPA-sponsored National Urban Runoff Program, in which 86 samples of runoff from 19 cities throughout the United States were analyzed, copper was found in 96% of samples, at concentrations of 1–100 μg/L (ppb) with a geometric mean of 18.7 μg/L (Cole et al. 1984). This mean concentration of copper in runoff water is higher than the geometric mean concentration of 4.2 ppb for copper in surface water based on measurements in EPA's STORET database (Eckel and Jacob 1988). Of the 71 priority pollutants analyzed, copper, along with lead and zinc, was the most frequently detected.

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 waste water is the major anthropogenic source of copper in waterways (Isaac et al. 1997; Nriagu and Pacyna 1988). Studies in Cincinnati and St. Louis showed discharges of copper into sewer systems from residential areas to be significant, with an average loading of 42 mg/person/day (Perwak et al. 1980). 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 waste water treatment plants (12,351 observations) were 0.0001–36.5 ppm, and the median value was ~0.4 ppm (Minear et al. 1981). Copper is not entirely removed in POTWs, and releases from these facilities contribute ~8% of all copper released to water (Perwak et al. 1980). 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 1981; Perwak et al. 1980). 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 waste water has been found to make up a substantial fraction of the copper found in POTW influent in the waste water 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 storm water runoff. Copper in storm water 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 storm water runoff have been measured (Georgopoulos et al. 2001). Storm water 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 release from disturbed soils contributes 68% of the copper released to waterways (Georgopoulos et al. 2001).

The best data on typical POTWs using secondary treatment show that 55–90% of copper is removed in these plants with a median and mean removal efficiency of 82% (Perwak et al. 1980). By contrast, those plants using only primary treatment had a 37% median removal efficiency. A more recent study focused on heavy metal removal in three POTWs that received primarily municipal sewage and used activated sludge as a secondary treatment. The study looked at removals in both the primary and secondary treatment stage. The mean removals of soluble copper and total copper after secondary treatment were 49–82 and 83–90%, respectively. The average copper concentration in the final effluent was 17–102 ppb, which would amount to an output of between 0.58 and 3.47 kg of copper into receiving waters per day, based on an effluent volume of 34,000 cubic meters (9 million gallons) per day (Aulenbach et al. 1987; Stephenson and Lester 1987).

Overflow outfalls within combined sewer systems (e.g., combination of domestic and industrial waste water plus storm water) 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 into the Newark Bay estuary. The mass loadings of copper into the estuary as a function of source are (in kg/day): municipal treatment systems, 103.4; industry direct discharge, 8.82; combined sewer overflows, 48.0; storm-water runoff, 62.2; tributary flow, 39.1 and discharges from the Passaic Valley Commission and Middlesex County Sewerage Authority, 126.5.

Discharges to water from active mining and milling are small and most of the western operations do not release any water because water is a scarce resource and is recycled (Perwak et al. 1980). Discharges from electroplating operations are either made directly to the water environment or indirectly via POTWs. Runoff from abandoned mines is estimated to contribute 314 metric tons annually to surface water (Perwak et al. 1980). These discharges are primarily insoluble silicates and sulfides and readily settle out into stream, river, or lake beds. Releases from manufactured products containing copper may be substantial, but are difficult to predict. Corrosion of copper in plumbing or construction may result in direct discharges or runoff into waterways. Copper and brass production releases relatively little copper to water.

Waste water generated from copper mining operations comes from seepage, runoff from tailing piles, or utility water used for mine operation. The amount of waste water generated ranges from 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 1980b). Copper concentrations in waste water from a selected open pit and underground copper mine were 1.05 and 0.87 ppm, respectively. Data regarding copper concentrations in waste water associated with selected concentrating, smelting, and refining operations can be found in EPA (1980b). Drainage from mining operations and abandoned mines has been shown to have an effect on copper content in local surface waters (see Table 6-7) with concentrations as high as 69,000 ppb being measured (Rösner 1998).

Results of an EPA industrial effluent survey show that mean and maximum levels of copper in treated waste water from six industries exceeded 1 and 10 ppm, respectively (EPA 1981). These industries and their mean and maximum discharges in ppm are: inorganic chemicals manufacturing (<1.6, 18); aluminum forming (<160, 2,200); porcelain enameling (1.3, 8.8); gum and wood chemicals (1.4, 3.0); nonferrous metals manufacturing (1.4, 27.0) and paint and ink formulation (<l.0, 60.0). Emission factors in nanograms of copper released per L of water outflow have been estimated for various industries. These factors would enable estimation of an industry's copper releases if the discharge volumes were known (Nriagu and Pacyna 1988).

Effluents from power plants that use copper alloys in the heat exchangers of their cooling systems discharge copper into receiving waters (Harrison and Bishop 1984). The largest discharges occur after start-up and decrease rapidly thereafter. At the Diablo Canyon Nuclear Power Station, a very high start-up discharge containing 7,700 ppb of copper fell to 67 ppb after 24 hours (Harrison et al. 1980). During normal operation at two nuclear power stations 6.5×10^6 cubic meters (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 ranging between 0.6 and 3.3 ppb (Harrison et al. 1980). This amounts to a total output of copper in the discharged seawater of 3.9–42 kg per day or 1,400–15,000 kg/annum 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 (Harrison et al. 1980). During normal operation, <20% of the copper released was in the <1,000 molecular weight fraction, which contains the more available copper species.

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

Table 6-7. Concentrations of Copper in Water

Sample type/ source	Location	Concentration (ppb) Range (mean) [median]	Comments	Reference
Drinking water				
Private wells	Nova Scotia, four communities	40–200	at tap, running water	Maessen et al. 1985
		130–2,450, 53% of samples >1,000 ppm	at tap, standing water	
Private wells	New Bedford, Massachusetts	(330)	at tap, running water	Yannoni and Piorkowski 1995
Not specified	Seattle, Washington	(160)	running water	Maessen et al. 1985
		(450), 24% of samples >1,000 ppm	standing water	
River water	Canada (National Survey)	≤5–530 [≤5]	raw water	Meranger et al. 1979
		≤5–100 [≤5]	treated water	
		≤5–220 [20]	distributed water	
Lake water	Canada (National Survey)	≤5–80 [≤5]	raw water	Meranger et al. 1979
		≤5–100 [≤5]	treated water	
		≤5–560 [40]	distributed water	
Well water	Canada (National Survey)	≤5–110 [≤5]	raw water	Meranger et al. 1979
		≤5–70 [≤5]	treated water	
		10–260 [75]	distributed water	
School drinking water	New Jersey	BD–10,200[a]	first draw	Murphy 1993
		BD–7,800	10-minute flush	
		BD–8,500	mid-day, first draw	
Municipal water supply	Berlin, Germany	0.009–4.2 (0.561)	at tap, running water	Zietz et al. 2003a
Municipal water supply	Lower Saxony, Germany	<0.1–6.40 (0.183)	at tap, standing water	Zietz et al. 2003b
		<0.1–3.00 (0.106)	at tap, running water	
Groundwater				
Representative sample	New Jersey	[5.0]	1,063 samples, 90th percentile 64.0 ppb, maximum 2,783 ppb, groundwater may or may not be used for drinking water	Page 1981
Shallow monitoring well	Denver, Colorado	<1–14 [2]	30 monitoring wells, 22 with PVC casings and 8 with metal casings; samples obtained after purging well 20 minutes	Bruce and McMahon 1996
Surface water				
U.S. Geological Survey stations	United States	(4.2) [4.0]	53,862 occurrences	Eckel and Jacob 1988

Table 6-7. Concentrations of Copper in Water

Sample type/ source	Location	Concentration (ppb) Range (mean) [median]	Comments	Reference
Representative sample	New Jersey	[3.0]	590 samples, 90th percentile 9.0 ppb, maximum 261 ppb	Page 1981
Surface, marine	East Arctic Ocean	(0.126)	26 locations 0.5–1 m depth	Mart and Nurnberg 1984
Surface, marine	Atlantic Ocean	0.0572–0.0210	20 sites, 2 cruises, 0–1 m depth	Yeats 1988
Pond	Massachusetts	<10–105	Low in summer, high in winter	Kimball 1973
Lakes	Canada	1–8 (2)	Acid sensitive lakes	Reed and Henningson 1984
Lakes	Great Lakes	629–834 (756)	Lake Superior	Nriagu et al. 1996
		703–1,061 (870)	Lake Erie	
		540–1,098 (830)	Lake Ontario	
	Representative samples, nearby to acidic mine drainage	32-1,200 (736)	12 samples taken from streams and ponds near abandoned coal mines in Indiana	Allen et al. 1996
	Representative samples from copper mining areas in Arizona	100–69,000 [1,200]	Samples obtained from the Cerbat Mountains mining area; 15 surface water sites with 14 sites downstream from old tailings and adits	Rösner 1998

[a]BD = below detection limit

PVC = Polyvinyl chloride

(Effler et al. 1980; Perwak et al. 1980). 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; Perwak et al. 1980; 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 as a result of agricultural runoff. For example, estimated loading rates of copper into surface water from irrigation water runoff near the Stillwater National Wildlife Refuge ranged from 0.307 to 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 detritial material).

Copper was detected in groundwater and surface water at 558 and 308 of the 906 NPL hazardous waste sites, respectively, where copper has been detected in environmental media (HazDat 2004). Copper was detected at concentrations ranging from 0.006 to 5.6 ppm (median concentration of 0.103 ppm) in offsite groundwater and 0.00025–590 ppm (median concentration of 0.0282 ppm) in offsite surface water (HazDat 2002).

6.2.3 Soil

An estimated 97% of copper released from all sources into the environment is primarily released to land (Perwak et al. 1980). 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 (Perwak et al. 1980). These wastes accumulate in mining states. Other releases to land include sludge from POTWs, municipal refuse, waste from electroplating, iron and steel producers, and discarded copper products (e.g., plumbing, wiring) that are not recycled. 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 (Perwak et al. 1980). However, even though the largest releases of copper are to land, uptake of copper in human populations through ingestion of copper in soil are expected to be minimal in comparison to the primary route of exposure through the ingestion of drinking water (see Section 6.5).

Copper was detected in soil and sediment (e.g., lakes, streams, ponds, etc.) at 528 and 338 of the 906 NPL hazardous waste sites, respectively, where copper has been detected in environmental media (HazDat 2004). Copper was detected at concentrations ranging from 0.01 to 182,000 ppm (median concentration of 0.103 ppm) in offsite soils and 0.022–14,000 ppm (median concentration of 43 ppm) in offsite sediments (HazDat 2002).

6.3 ENVIRONMENTAL FATE

When considering the environmental fate of a metal, it is not always possible to clearly separate the processes related to the transport and partitioning of a metal, its compounds, and complexes from those related to transformation and degradation of these metal species. Because of analytical limitations, investigators do not often identify the form of a metal present in the environment. A change in the transport or partitioning of a metal may result from the transformation of the metal from one form to another. For example, complexation of a metal with small organic compounds may result in enhanced mobility, while formation of a less-soluble sulfide would decrease its mobility in water or soil. Adsorption may be the result of strong bonds being formed (transformation) as well as weak ones. Characterizing weak and strong adsorption is dependent on the analytical method that is used and care should be exercised when comparing results from different studies. Deposition and general adsorption of copper are discussed in Section 6.3.1. Speciation, compound formation, and oxidation-reduction are examined in Section 6.3.2.

6.3.1 Transport and Partitioning

6.3.1.1 Ambient 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 by 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 will depend on a number of factors, including source characteristics, particle size, turbulence, and wind velocity.

Gravitational settling governs the removal of large particles with mass median aerodynamic (MMA) diameters of >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 associated with sub-micron particles. These particles remain in the troposphere for an estimated 7–30 days. In that time, some copper may be carried far from its source (Perwak et al. 1980).

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 decrease between highly urbanized area such as Chicago, Illinois with an average depositional rate of 0.06 mg/m^2/day, to less urbanized areas such as South Haven, Michigan with rate of 0.007 mg/m^2/day or areas with minimal anthropogenic activity such as Lake Michigan (between 6 and 10 km off shore) with a rate of 0.01 mg/m^2/day (Paode et al. 1998). Estimated copper deposition rates in urban areas are 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 reportedly ranges from 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 reportedly is 0.018–0.5 kg/ha/year or 0.0049–0.14 mg/m^2/day, and wet deposition is 0.033 kg/ha/year or 0.009 mg/m^2/day. The washout ratio is 114,000–612,000 (μg/m^3 rain)/(μg/m^3 air) or, expressed on a mass basis, 140–751 (μg/kg rain)/(μg/kg air). In southern Ontario, Canada, where the average concentration of copper in rain was 1.57 ppb during 1982, 1.36 mg of copper was deposited annually per square meter, or 13.6 kg/ha, as a result of wet deposition (Chan et al. 1986). For central and

northern Ontario, the mean concentrations of copper in rain were 1.36 and 1.58 ppb, respectively, and the annual wet depositions averaged in both instances 1.13 mg/m^2 or 11.3 kg/ha.

For the majority of time, the concentration in air of toxic trace elements, like copper, in a study conducted by Sweet et al. (1993) approached levels measured at a rural site (Bondville, Illinois). These rural levels of airborne copper represented regional background levels in urban study sites with only episodic increases, depending on wind speed and direction and location relative to local point sources. In one urban study site (East St. Louis), smelters are the primary source of copper. Copper depositional fluxes follow an exponential decay as one transitions from urban to rural settings (Sweet et al. 1993). Soil is not the major source of copper in cities or nearby rural soils, but is the predominant source for copper in the atmosphere over more remote areas (Fergusson and Stewart 1992). Sources of copper in urban areas include coal combustion, soil, tire wear, and automobile emissions (Kim and Fergusson 1994). Copper emission from combustion processes is typically associated with fine particles; however, there can be instances where the highest concentrations of copper are measured in coarse particles obtained from paved and unpaved roads and industries (Paode et al. 1998).

Estimated 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). These are: urban, 0.25–0.46 cm/second and rural, 0.18–0.25 in (rural) Kankalee, Illinois 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 velocities are due to higher surface roughness and wind velocities in Chicago.

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

6.3.1.2 Ambient Waters

The average concentrations of copper in Lakes Superior, Erie, and Ontario are 760, 870, and 830 ng/L, respectively (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 meters 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 substantial, 330–1,470 ng/m^2/year, which amounts to a total deposition of 8.00–35.6x10^{13} ng/year. This input of copper accounts for 60–80% of the anthropogenic input into Lake Superior and 20–70% into Lakes Erie and Ontario (Georgopoulos et al. 2001; Nriagu et al. 1996). The mean residency times of copper in sediments are estimated to be 15 years in Lake Erie and 101 years in Lake Superior.

Much of the copper discharged into waterways is in 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 water column, a significant fraction of the copper is adsorbed within the first hour of introduction, and in most cases, equilibrium is obtained within 24 hours (Harrison and Bishop 1984). In fact, most of the copper in POTW effluent and surface runoff is already in the form of complexes (Sedlak et al. 1997). Copper in waste water 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 a total of 200 metric tons of copper entered the Cheasapeake Bay from the effluent discharged from waste treatment plants.

Copper binds primarily to organic matter in estuarine sediment, unless the sediment is low in organic matter content. A study evaluated the importance of the absorption properties of different nonlithogenic components of aerobic estuarine sediment to copper binding by determining copper's adsorptivity to model components (phases) in artificial seawater (Davies-Colley et al. 1984). The 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 bound 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 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).

6.3.1.3 Ambient Soils

Most copper deposited on soil from the atmosphere, agricultural use, and solid waste and sludge disposal will be adsorbed with greater concentrations of copper measured in the upper 5–10 centimeters of soil in comparison to lower soil depths, except in sandy soils where the lability of bound copper is greater (Breslin 1999; Giusquiani et al. 1992; Hutchinson 1979; Luncan-Bouché et al. 1997; Keller and Védy 1994; Levy et al. 1992; Perwak et al. 1980). 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 (EPA 1979; Fuhrer 1986; 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) have shown that between 55 and 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 (Elliot et al 1986; Fuhrer 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). 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 Fe, Mn, and Al oxides become important in determining the adsorption of copper. Fuhrer (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 pHs

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 Zn, Cd, and Ni 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). Elliot et al. (1986) investigated at pH-dependent adsorption of the divalent transition metal cations Cd, Cu, Pb, and Zn 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 Cu and Pb were much more strongly retained than Cd and Zn. 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 solubility 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 solubility only in the oxidizing environment. In the reducing environment, solubility was low, possibly due to the formation of sulfides.

The form of copper at polluted and unpolluted sites may affect its leachability, particularly by acid rain. The leaching of heavy metals by simulated acid rain (pH 2.8–4.2) was measured by applying this rainwater to columns containing humus layers obtained from sites in a Swedish spruce forest both near to and far from a brass mill (Strain et al. 1984). Leaching of copper increased considerably when water with a pH <3.4 was applied to soil from polluted sites. Acid rain produced from SO_X emitted from smelters may increase the leachability of copper in areas affected by smelter stack emissions. 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.

Since, in the range of 0.01–1.97 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, it is important to ascertain whether copper in sludge is apt to leach into soil. Where it stands, this does not appear to be the case and leachate collected from the sludge-amended soil contained <12 ppb of copper (Perwak et al. 1980). In laboratory experiments, three sludges containing 51, 66, and 951 ppm (dry weight) of copper were applied to the top of soil columns containing four coastal plain soils. These soils, Sassafras loamy sand, Woodstown sandy loam, Evesboro loamy sand, and Matapeake silt loam, had similar pHs, 5.1–5.8, and contained 0.9, 1.4, 1.6, and 3.5% organic matter (dry weight), respectively. The sludge containing 51 ppm copper was loaded on the soil columns at amounts that approximated field loadings of between 0 and 90 metric tons per hectare; the sludges containing 66 and 951 ppm copper were loaded in amounts that approximated field loadings of between 0 and 180 metric tons per hectare. The columns were subsequently leached with distilled water at a flow rate of 2.5 cm/day for a total column application of 25.4 cm of water. Only small amounts (<0.01–0.87 ppm) of copper were found in the leachate (Ritter and Eastburn 1978). This suggests that hazardous amounts of copper leach only slowly into groundwater from sludge, even from sandy soils. In another study, soil cores taken after sewage sludge were applied to grassland for 4 years showed that 74 and 80% of copper remained in the top 5 cm of a sandy loam and calcareous loam soil (Davis et al. 1988). Similar studies have also shown that copper is typically confined to the upper 5–10 cm of sludge-amended agricultural soils (Breslin 1999; Giusquiani et al. 1992). 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). 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 for copper due to the increased binding capacity provided by the “low metal” organics in the sludge (Petruzzelli et al. 1994).

Similarly, copper remains in the surface layer when it is applied to soil as a liquid. Secondary sewage effluent spiked with 0.83 ppm of copper was applied weekly to four different soils. After 1 year of treatment, the concentration of copper in the surface horizons increased greatly: 50–76% of the applied copper was found in the upper 2.5 cm and 91–138% was found in the upper 12.7 cm (Brown et al. 1983). In a study of accumulation and movement of metal in sludge-amended soils, field plots received massive amounts of sewage over a period of 6 years. Two sludges (one containing industrial waste), with average copper contents of 0.29 and 23 ppm were incorporated into the top 20 cm of soil in the spring. Barley was grown and, after harvest, core samples of soil were taken down to 1 m. Some movement of copper

into the 22.5–25 cm layer of soil was observed, but little, if any, below this zone. However, at this depth, the copper is still within the root zone of many important food crops and, therefore, is available for uptake into these plants. Also, the availability of the copper in soil, as determined by its extractability with diethylenetriamine pentaacetic acid (DTPA) and nitrate, remained constant over a 4-year period at all depths. From the results of other work, the major portion of the copper (40–74%) is expected to be associated with the organic, Fe-Mn-oxide and carbonate fractions of most soils (Ma and Rao 1997).

6.3.1.4 Bioconcentration and Biomagnification

The bioconcentration factor (BCF) of copper in fish obtained in field studies is 10–667, indicating a low potential for bioconcentration (Perwak et al. 1980). The BCF is higher in mollusks, such as oysters, and squid where it may reach 30,000 and 2.1×10^7, respectively, (Perwak et al. 1980) and may present a major dietary source of copper that could be of concern for those individuals who regularly consume oysters, clams, or squid. Due to the fact that molluscs are filter feeders and copper concentrations are higher in particulates than in water, this is to be expected. On the other hand, there are limited data suggesting that there is little biomagnification of copper in the aquatic food chain (Perwak et al. 1980). 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) 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. Similarly, 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).

No evidence of bioaccumulation was obtained from a study of pollutant concentrations 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, 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 and 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).

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 bioconcentration factor 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 (Mn-oxides and amorphous Fe-oxides), organic, and moderately reducible (hydrous Fe-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 in the dissolved manganese oxide phase is now soluble and available for uptake by other organisms.

6.3.2 Transformation and Degradation

6.3.2.1 Air

Few data are available regarding the chemical forms of copper in the atmosphere and their transformations. In the absence of specific information, 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, sulfatization may occur, but only when SO_X gases are present in the atmosphere in sufficient amount. For example, in Arizona, atmospheric copper oxide levels derived from copper smelters was strongly correlated with co-emitted sulfur (Schroeder et al. 1987).

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 ranged between 0.1 and 1 μM or, respectively, 4 and >90% of copper in the Cu(I) state. The reduction of Cu(II) to Cu(I) is pH dependent and occurs rapidly at pHs>6 (Xue et al. 1991).

6.3.2.2 Water

The Cu(I) ion is unstable in aqueous solution, tending to disproportionate to Cu(II) and copper metal unless a stabilizing ligand is present (EPA 1979; Kust 1978). The only cuprous compounds stable in water are insoluble ones such as Cu_2S, CuCN, and CuF. 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. Ammonia and chloride ions are examples of species that form stable ligands with copper. Copper also forms stable complexes with organic ligands such as humic acids, binding to $-NH_2$ and -SH groups and, to a lesser extent, with -OH groups. 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 formation 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 freashwater 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.), salts (OH^-, S^{2-}, PO_4^{3-}, CO_3^{2-}), and anions of insoluble 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, Cu_2O, 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) concentration to extremely low values.

As a result of the aforementioned 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 (e.g., free metal ion, ion pairs, inorganic or organic complexes) to slowly or nonlabile (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) metal (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 (Harrison and Bishop 1984).

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 (Breault et al. 1996; Cao et al. 1995; Gardner and Ravenscroft 1991; Giusti et al. 1993; Lores and Pennock 1998; 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 deceased 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 Ca and Mg ions than to competition of these ions with copper for fulvic acid binding sites. Increasing 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. This water had the highest pH (7.4) and alkalinity (43.5 mg/L as $CaCO_3$) than six other surface waters (e.g., three rivers, two reservoirs, a pond, and a swamp) with pH and alkalinity 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 from 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 ranged from 16.4 and 2.3 μg/kg, respectively, in the Providence River to 0.23 and 0.12 μg/kg, respectively, in Rhode Island Sound. Particulate copper concentrations in Narragansett bay ranged from 2.42 to 0.06 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 may 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 the copper binds to humic material at a number of sites. The binding strength of the sites varied by two 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 (Harrison et al. 1980). Ten to 75% of the discharged copper was in particulate form.

The bioavailability of Cu(I) has been 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 will be 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).

Experiments performed in synthetic seawater and water from Biscayne Bay, Florida, showed that in the reduction of Cu(II) to Cu(I), the rate was first-order in Cl^- and second-order in H_2O_2 (Sharma and Zika 1987). The chloride ion is thought to be required for stabilizing Cu(I) by forming the copper complex $CuClOH^-$, although experimental evidence suggests that the reduction of Cu(II) may also occur through the formation of a complex between Cu(II) and HO_2^-. Experiments have shown that as much as 15% of copper in surface seawater exists as Cu(I). Photochemical reduction by sunlight increases the percentage of free Cu(I). The photochemical reduction mechanism is supported by the observation that the Cu(I) concentration is highest in the surface layer of seawater and that the hydrogen peroxide concentration increases in parallel to that of Cu(I) (Moffett and Zika 1987). In addition, the percentage of free Cu(I) is highest on the surface.

Once Cu(I) is formed, its lifetime is determined by its rate of oxidation to Cu(II). After Biscayne Bay water was exposed to sunlight for 5 hours, the Cu(I) formed was oxidized to Cu(II). The half-life of Cu(I) was 12 hours. Primarily, dissolved oxygen is responsible for this oxidative reaction. Since the oxidation of Cu(I) by O_2 in distilled water occurs in <6 minutes, Cu(I) in seawater apparently is stabilized by the formation of complexes. In the presence of humic acids, the oxidation of Cu(I) occurs very rapidly. In coastal water off the Everglades in Florida, no Cu(I) was detected. This is due to the binding of Cu(II) in organic complexes and the high concentration of radical oxidants in the water. 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 salinity). 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.

6.3.2.3 Sediment and Soil

The adsorption of copper to soil and sediment was discussed in Section 6.3.1 under transport and partitioning, even though adsorption may really be complexation and transformation. Understanding the transport and fate of copper and its compounds in soils and sediments is important because these compartments tend to be large reservoirs of copper and could have an impact on human exposures to copper. 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 the extractability of the copper and soil conditions. There is evidence to suggest that copper binding in soil is correlated with pH, cation exchange capacity, the organic content of the soil, the presence of manganese and iron oxides and even the presence of inorganic carbon such as carbonates (Petruzzelli 1997; Rieuwerts et al. 1998). At pHs above 5, absorption of copper from pore water on to soil components becomes a significant process, whereas at pHs below 5, copper largely remains in pore water and is therefore mobile in soil (Perwak et al. 1980). However, broad generalizations about the lability 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 is given below.

The form of copper in soil is determined by measuring 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 may occur, as well as other transformations. On the other hand, if a mineral form is deposited, it would be unavailable for binding. 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 KCl. 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 coefficient for copper was >64 for mineral soils and >273 for organic soils. Of the eight heavy metals in the study, only Pb and Sb had higher partition coefficients than copper. Most of the copper in Columbia River estuary sediment and soil was correlated with inorganic carbon (e.g., carbonate), but not with the amount of extractable Fe or the organic carbon content of the sediment (Fuhrer 1986).

The amount of ammonium acetate- and 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, between 69 and 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), between 97.6 and 99.6% of the copper was found to be associated with the residual fraction.

Within the estuarine environment, anaerobic sediments are known to be the main reservoir of trace metals. Under anaerobic conditions, cupric salts will reduce to cuprous 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, that is, 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, as opposed to coarse, sediment. Badri and Aston (1984) 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 (Mn and Fe oxides and possibly carbonates); and resistant (lithogenic). In the three sediments, the nonlithogenic 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 and standard

deviation percentages of copper in the various fractions were: exchangeable, 0 (0); carbonate, 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 of 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.

6.3.2.4 Other Media

Copper is an essential nutrient in plant metabolism. Therefore, uptake of copper from soil in plants through the roots is a natural and necessary process, a process that is actively regulated by the plant (Clemens 2001). 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 (Section 6.3.1.3), this is determined by copper concentrations in soil, soil type, soil components, pH, oxidation-reduction potential in the soil, and concentrations of other cations and anions in the soil, etc. (Rieuwerts et al. 1998). Other factors include root surface area, plant genotype, stage of plant growth, weather conditions, interaction with other nutrients in the soil and the water table (Gupta 1979). Liming is another factor that affects copper uptake. For example, liming acidic soils has been shown to increase copper uptake in hay, but to decrease copper uptake in wheat (Gupta 1979). However, the effect that liming has on increasing soil pH does not appear to be the overriding mechanism behind the changes in copper uptake in plants, even though there is evidence that the addition of lime to soil to increase the pH to 7 or 8 reduces copper availability to some plants (Perwak 1980). This is evidenced by the fact that changes in pH (5.4–8.0) have been found to have little effect on copper concentrations in plant tissues (Gupta 1979).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

6.4.1 Air

Human exposure to copper in air comes from both natural and anthropogenic sources. For the general population, exposures to copper concentrations in air average between 5 and 200 ng/m^3. 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.). The results of

several studies in which concentrations of copper in air were reported and described below and are summarized in Table 6-8.

According to the EPA's National Air Surveillance Network report for the years 1977, 1978, and 1979, median copper concentrations were 133, 138, and 96 ng/m^3, respectively, for urban samples and 120, 179, and 76 ng/m^3 for nonurban samples, respectively (Evans et al. 1984). In this study, 10,769 urban and 1,402 nonurban air samples collected for 24 hours were analyzed. For 1977, 1978, and 1979, 1% of urban samples exceeded 1,156, 975, and 843 ng/m^3, respectively, and 1% of nonurban samples exceeded 1,065, 1,396, and 645 ng/m^3, respectively. The maximum urban and nonurban copper concentrations reported were 4,625 and 4,003 ng/m^3, respectively. 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. The concentrations in rural areas are considerably lower than those reported in the EPA survey. 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. The levels reported by Schroeder et al. (1987) are consistent with those obtained in a study of airborne trace elements in national parks (Davidson et al. 1985). In the Smokey Mountain National Park, the copper concentration in air was 1.6 ng/m^3, while in the Olympic National Park, where several locations were monitored, 3.3–6.7 ng/m^3 of copper was measured in the atmosphere. The lower copper concentrations found in Smokey Mountain Park compared with those in the Olympic National Park have been attributed to greater vegetative cover and higher moisture in the former and larger amounts of exposed rock and soil in the latter. Average copper crustal enrichment factors (the concentration of copper in air compared with the average concentration in the earth's crust) were 31 and 76, respectively.

As part of the Airborne Toxic Element and Organic Substances (ATEOS) project for determining patterns of toxic elements in different settings, three urban areas (Camden, Elizabeth, and Newark) and one rural site (Ringwood) in New Jersey were studied during two summers and winters between 1981 and 1983 (Lioy et al. 1987). Each site was sampled every 24 hours for 39 consecutive days. As an example, the geometric mean copper concentrations in the summer of 1983 were 16.0, 21.0, 21.0, and 6.0 ng/m^3 for Camden, Elizabeth, Newark, and Ringwood, respectively. In the winter of 1983, the mean copper concentrations were slightly higher with values of 21.0, 36.0, 33.0, and 63.0 ng/m^3, respectively. The levels of copper measured in these industrial urban areas are considerably higher than the mean values reported in the National Air Surveillance survey where arithmetic means of 0.201 and 0.259 ng/m^3 for copper in air were obtained in1978 and 1979, respectively (Evans et al. 1984). Summer and winter

Table 6-8. Concentrations of Copper in Air

Date/sample	Location	Concentration[a] (ng/m^3) (mean) [median]	Comments	Reference
1977, urban	United States	[133], 433_{90}, $1,156_{99}$ (207.5), $3,296_{max}$	4,648 samples, National Survey	EPA 1984
1978, urban	United States	[138], 430_{90}, 975_{99} (200.8), $4,625_{max}$	3,615 samples, National Survey	EPA 1984
1979, urban	United States	[96], 363_{90}, 519_{99} (259.3), $1,627_{max}$	2,507 samples, National Survey	EPA 1984
1977, nonurban	United States	[120], 450_{90}, $1,065_{99}$ (193.2), $16,706_{max}$	709 samples, National Survey	EPA 1984
1978, nonurban	United States	[179], 607_{90}, $1,396_{99}$ (265.7), $1,396_{max}$	458 samples, National Survey	EPA 1984
1977, nonurban	United States	[76], 322_{90}, 645_{99} (141.7), $4,003_{max}$	235 samples, National Survey	EPA 1984
Urban		20–200, [50]	Representative values	Davies and Bennett 1985
Rural		5–50, [20]		
Remote		0.29–12	Values from literature survey	Schroeder et al. 1987
Rural		3–280		
Urban	Canada	17–500		
Urban	United States	3–5,140		
Urban	Europe	13–2,760		
Urban	Other	2.0–6,810		
1979, remote	Smokey Mountain National Park	(1.6)	Above canopy, crustal enrichment factor 31	Davidson et al. 1985
1980, remote	Olympic National Park	3.3–6.7, (5.6)	Crustal enrichment factor 76	Davidson et al. 1985
1981, 1982, summer	Camden, New Jersey	16.0–18.0[b], 100.0_{max}	Seasonal variations noted; three urban areas and one rural area.	Lioy et al. 1987
	Elizabeth, New Jersey	21.0–29.0, 120.0_{max}		
	Newark, New Jersey	25.0–33.0, 131.0_{max}		
	Ringwood, New Jersey	13.0–63.0, 77.0_{max}		
1982, 1983, winter	Camden, New Jersey	17.0–21.0, 231.0_{max}		
	Elizabeth, New Jersey	28.0–36.0, 493.0_{max}		
	Newark, New Jersey	21.0–27.0, 380.0_{max}		
	Ringwood, New Jersey	6.0–18.0, 29.0_{max}		

[a]Percentile level and maximum indicated as subscripts.
[b]Concentrations in Lioy et al. (1987) are geometric means, unless otherwise noted.

maxima in the four ATEOS study areas were: 100.0 and 131.0 ng/m^3 in Camden, 231.0 and 493.0 ng/m^3 in Elizabeth, 131.0 and 380.0 ng/m^3 in Newark, and 77.0 and 29.0 ng/m^3 in Ringwood, respectively. Copper follows the same pattern as other heavy metals, in that increased copper levels are present in winter in urban areas and in summer in rural areas. No explanation for this pattern has been offered.

Anderson et al. (1988) performed a study of the atmospheric aerosols collected at a site in Chandler, Arizona, over a 12-day period in February and March 1982. 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. Particles containing >0.5% Cu were termed 'Cu-bearing' particles; 5.6% of the fine (0.4 to ~2 μm) particles collected were in this category. The most abundant type of Cu-bearing particle, representing 74% of the total, was associated with sulfur. However, the analysis was not able to specify the form of sulfur present. These particles were often associated with Zn, Fe, Pb, As, and Ca. Sixteen percent of the Cu-bearing particles were associated with silicon and 4% were associated with chloride. The concentration of Cu-S particles was highest when the surface and upper level winds were from the southeast to the east, and reached a maximum 1–2 days after the winds began to blow. Therefore, the smelters to the southeast appear to be the probable source. The particles associated with silicon and chlorine did not show any apparent correlation with wind and were either from a diffuse regional source or a local source.

Mine waste dump sites are a source of airborne copper carried in dust (Table 6-9). Particle size distribution and the concentration of copper in particle size ranges differ depending on the mine waste site (Mullins and Norman 1994). For example, the mean concentrations (ppm, w/w) of copper in dust (<10 μm particle size range) collected at four mine waste dump sites in Butte, Montana, were 3,370 (Gray Rock), 1,950 (Corra), 1,960 (Late Acquisition), and 2,570 (Railroad Bed).

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, 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 standard deviation) ppb during 1982 (Chan et al. 1986). These concentrations showed little spatial variability. Concentration of copper

Table 6-9. Particle Size Distributions and Total Copper Concentrations in Dust Collected at Four Mine Waste Pump Sites in Butte, Montana

Site	Particle size (µm)	Percent in total dust collected	Concentration of copper (ppm, w/w)
Corra	4.7–10	76.6±4.8	1,550
	1.1–4.7	20.9±0.63	3,110
	<1.1	1.9±0.14	4,900
Gray rock	4.7–1.0	84.5±0.93	3,240
	1.1–4.7	13.6±0.82	4,120
	<1.1	1.9±0.14	4,370
Railroad bed	4.7–10	61.5±1.06	2,580
	1.1–4.7	31.3±0.96	2,850
	<1.1	7.2±0.26	1,400
Late acquisition	4.7–10	70.3±1.36	1,560
	1.1–4.7	25.0±1.18	2,730
	<1.1	4.7±0.44	3,330

Source: Mullins and Norman 1994

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).

The concentration of copper in rain samples taken within 2–15 km downwind of the Claremont, New Hampshire, municipal waste incinerator was found to range from 0.11 to 2.12 μg/L with a mean concentration of 0.87 μg/L. The total mean deposition rate of airborne copper from rain was measured to be 4.0 μg/m^2/day for the eight sampling sites used in the study (Feng et al. 2000). However, 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 meters) from an expressway in Montreal, Canada. Mean concentrations of copper in the snow (expressed as mg/L [and standard deviations]) were measured as 0.051 (0.073), 0.065 (0.127), 0.034 (0.027), and 0.044 (0.051) at 15, 20, 15, and 150 meters, respectively (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).

Elevated levels of copper in fog water have been observed 3 km downwind from a refuse incinerator in Switzerland (Johnson et al. 1987). High concentrations of copper were associated with low pH. The maximum concentration, 673 ppb, occurred at pH 1.94; levels >127 ppb were associated with pH values <3.6. Copper(II) concentrations in fog water from the central valley of California ranged from 1.7 to 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.

6.4.2 Water

Copper is widely distributed in water since it is a naturally occurring element. Copper levels in surface water range from 0.5–1,000 ppb, with a median of 10 ppb; seawater contains <1–5 ppb (Davies and Bennett 1985; Mart and Nurnberg 1984; Page 1981; Perwak et al. 1980; Yeats 1988). The results of several studies in which copper was detected in drinking water, groundwater, and surface water are described in this section and summarized in Table 6-7. The information in Table 6-7 demonstrates that copper concentrations in drinking water can vary widely (≤5–10,200 ppb) and can exceed the action limits of 1,300 ppb that have been set for copper in drinking water (EPA 1991). The table also

emphasizes the importance of running tap water before using it and the need to control corrosion of piping in water distribution systems.

Copper concentrations in drinking water vary widely as a result of variations in pH, hardness of the water supply and copper released from the water distribution system (Davies and Bennett 1985; Yannoni and Piorkowski 1995). Copper concentrations in drinking water range from a few ppb to 10 ppm. A Canadian national survey of copper and other metals in drinking water was conducted from November 1976 to January 1977 (Meranger et al. 1979). Supplies from 70 municipalities representing 38% of the Canadian population were included in the survey, including 50 derived from river or lake water and 20 derived from groundwater. Unfiltered raw, treated and distributed drinking waters were analyzed. Whether the water was derived from river, lake, or well water did not significantly affect the copper concentration in the raw water. Only in a few supplies did copper levels in raw water exceed 20 ppb and only one of these was derived from groundwater. The results in groundwater contrast with those of Page (1981) in New Jersey, in which over 100 wells contained copper levels in excess of 64 ppb. However, that study included groundwater that was a source of drinking water, in addition to groundwater that was not. The copper concentration in Canadian treated water was generally ~10 ppb (Meranger et al. 1979). In 20% of the samples, the copper level in distributed water was significantly higher than the treated water. The increase was greater in areas where the water was soft and corrosive, thus enhancing leaching of copper from the distribution system.

Elevated concentrations of copper in drinking water can result as a consequence of leaching processes that occur in water distribution systems. 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 the 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 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–<40 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.

The geometric mean (standard deviation) and median concentration of dissolved copper in surface water based on 53,862 occurrences in EPA's STORET database are 4.2 (2.71) and 4.0 ppb, respectively (Eckel and Jacob 1988). Higher concentrations tend to be found in New England, the western Gulf and the lower Colorado River (Perwak et al. 1980). The finding of high concentrations of copper species in minor river basins reported in EPA's STORET database in 1978 revealed that sources of copper in the Gila, Coeur D'Alene, and Sacramento River Basins appear to be primarily mining activities, especially abandoned sites (Perwak et al. 1980). Generally, the high concentrations (>120 μg/L) were generally observed at localized stations and correlated with low pH of the surface water. However, in another study concerning

75 Canadian headwater lakes sensitive to acid rain, copper values were relatively low (1–8 ppb range, 2 ppb mean) regardless of pH or alkalinity (Reed and Henningson 1984).

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 storm water, measurements of copper concentrations in storm water 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; but were much higher in unfiltered samples (copper bound to particulate matter) with mean values (in μg/L) of 110 (roof areas), 116 (parking areas), 280 (street runoff), 135 (vehicle service 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 waste water 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 a 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 in 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 (Perwak et al. 1980). Copper levels are overall lower in the Pacific Ocean than in the Atlantic Ocean and higher near the continental shelf than in the open ocean. Copper concentrations in surface water at a depth of 1 meter 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 meter of the eastern Arctic Ocean was 93 ppt (Mart and Nurnberg 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.

6.4.3 Sediment and Soil

Copper occurs naturally at levels of ~50 ppm in the earth's crust, which includes soil and parent rock (Perwak et al. 1980). In the United States, copper concentrations in differing soil types can vary over a large range (1–300 mg/kg, dry weight); but the mean values are relatively similar (14–41 mg/kg, dry weight) as a function of soil type (Table 6-10) and land resource region (Table 6-11) (Chen et al. 1999; Fuhrer 1986). These copper levels are similar to those given in a review of soil copper concentrations that reported a median concentration of 30 ppm (dry weight) and a range of 2–250 ppm (Davies and Bennett 1985). In other studies of copper concentrations in U.S. soils, the mean copper concentrations are within the range of 14–41 mg/kg. In the work of Ma et al. (1997), the mean concentration of copper in soils of the United States was determined to be 30 mg/kg, whereas the copper concentration in agricultural surface soils in the United States that had not received an application of sludges from municipal waste treatment plants was found to be 18 mg/kg. In Florida surface soils, the geometric mean of copper concentration in 40 different soil types was 4.10 mg/kg, with a range of 1.89–10.7 mg/kg (Ma et al. 1997). Chen et al. (1999) reported copper concentrations in Florida soils ranging from 0.1 to 318 mg/kg with a geometric mean of 2.21±3.15 mg/kg (arithmetic mean of 6.10±22.1 mg/kg). These investigators also reported geometric means of 24.0 mg/kg in California soils and 17 mg/kg in U.S. soils. In agriculturally productive soils, copper ranges from 1 to 50 ppm, while in soil derived from mineralized parent material the copper levels may be much higher (NRC 1977; Perwak et al. 1980).

Copper concentrations in soil may be much higher in the vicinity of a source of copper emissions, such as a mining operation or smelter. 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.

Table 6-10. Concentration of Copper in Surface Soils of the United States (in ppm-Dry Weight [dw], Equivalent to mg/kg-dw)

Soil	Range	Mean
Sandy soils and lithosols on sandstones	1–70	14
Light loamy soils	3–70	25
Loess and soils on silt deposits	7–100	25
Clay and clay loamy soils	7–70	29
Alluvial soils	5–50	27
Soils over granites and gneisses	7–70	24
Soils over volcanic rocks	10–150	41
Soils over limestones and calcareous rocks	7–70	21
Soils on glacial till and drift	15–50	21
Light desert soils	5–100	24
Silty prairie soils	10–50	20
Chernozems and dark prairie soils	10–70	27
Organic light soils	1–100	15
Forest soils	7–150	17
Various soils	3–300	26

Source: EPA 1995

Table 6-11. Geometric Means of Selected Soil Elements and Associated Soil Parameters in U.S. Surface Soils by Land Resource Regions

Land resource region	mg/kg dry soil
Mineral soils	
Northwestern specialty	34.3
Northwestern wheat	23.2
California subtropical	43.4
Western range and irrigated	26.8
Rocky Mountain	19.1
Northern Great Plains	20.2
Western Great Plains	16.3
Central Great Plains	12.6
Southwest Plateau	10.0
Southwest Prairie	4.9
Northern lake states	15.4
Lake states	18.2
Central feed grains	19.7
East and central farming	8.0
Mississippi Delta	21.1
South Atlantic and Gulf slope	6.3
Northeastern forage	34.0
Northern Atlantic slope	13.5
Atlantic and Gulf coast	7.6
Florida subtropical	31.9
All mineral soils	15.6
Histosols	
Northern lake states	59.6
Lake states	84.7
Northeastern forage	149.0
Florida subtropical	94.3
All histosols	86.9

Source: Holmgren et al. 1993

Copper and its compounds were found at 906 of 1,647 hazardous waste sites on the NPL of highest priority sites for possible remedial action (HazDat 2002). Since copper is commonly found in soil, it should occur at all sites. In past work, data analysis of metal concentrations measured in soil from hazardous waste sites taken from the 1980–1983 Contract Laboratory Program (CLP) Analytical Results Data Base (CARD) was conducted to ascertain whether elemental concentrations at hazardous waste sites were elevated above that which normally would be expected in soil of similar composition and derivation. Of the 1,307 samples in CARD, 10.5 and 7.3% had copper concentrations exceeding the number normally expected in soil at the 95 and 99% confidence intervals, respectively (Eckel and Langley 1988).

In a study in which the copper concentrations of 340 soil samples collected from diverse land-use situations, the average copper concentrations reported were 25 ppm in agricultural land, 50 ppm in suburban/residential land, 100 ppm in mixed industrial/residential land, and 175 ppm in industrial/inner urban areas (Haines 1984). 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.

The concentration of copper in soils and sediments was 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 ranged from 5 to 70 μg/g (dry weight). At nonurban indicator sites, the median concentrations ranged from 13 to 47 μg/g. The same study derived an average crustal abundance of copper of 60 μg/g.

Sediment is an important sink and reservoir for copper. In areas where there is no known input of copper obtained from anthropogenic sources, sediment generally contains <50 ppm copper. The level can reach several thousand ppm in polluted areas (Harrison and Bishop 1984). The mean copper level in surficial sediment of Penobscot Bay, Maine, was 14.1 ppm (dry weight), while that in estuaries or bays in other New England locations ranged from 4.4 to 57.7 ppm (Larsen et al. 1983b). Levels reflect anthropogenic input as well as the mineral content of the regional bedrock. Copper levels in sediment from 24 sites along the New Jersey coast ranged from <1.0 to 202 ppm, with a mean value of 66 ppm (Renwick and Edenborn 1983). The texture of the sediment varied from 94% clay to 100% sand, and the copper level was correlated negatively with the percentage of sand in the sediment.

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 ppm dry weight, over 100 times the concentration in a lake selected as a baseline lake 180 km away.

An analysis of the Coastal Sediment Database (COSED) showed that 73% of coastal waterways had copper concentrations below 42 μg/g; 25% had copper concentrations between 42 and 210 μg/g; and 2% were above 210 μg/g. These higher concentrations are 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 to sediments to depths of 54 cm (Bopp et al. 1993). Combined sewer outflows can also contribute significantly to the copper content in 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 ppm, 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 ppm during a period where untreated industrial effluents and sewage outflows were allowed to enter the bay. However, copper concentrations in surface sediments (0–2 cm) where measured at 208 ppm. 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.

6.4.4 Other Environmental 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. Several studies of copper content in a variety of foods have been conducted as part of the FDA's Total Diet Survey and are described in this section. These data have been used to estimate the average intakes of copper in the human diet within various age groups. For example, in the 25–30-year-old age group, copper intake has been estimated to be 0.93 mg/day for women and 1.24 mg/day for men (Pennington 1983). The levels of copper in other food sources such as mollusks, fish, and agricultural plants have been measured and the results summarized in this section. One highlight in the data is the potential for high dietary intakes of copper for those individuals who regularly consume of mollusks where the daily intake of copper could increase by 5.7–136 mg/day in comparison to the

general population (see Section 6.5). Other media covered in this section are human tissues, cigarette smoke, industrial and municipal waste streams, and agricultural products.

The FDA Total Diet Survey has provided copper concentration in various foods, examples of which are given in Table 6-12 (FDA 2001). The highest concentrations of copper were found in liver, in some oat and bran cereals, in some legumes and nuts, and in raw avocadoes and mushrooms. Coleman et al. (1992) reported copper concentrations in the edible tissues of livestock and poultry with the highest mean concentrations (ppm) found in liver (cow 43.7; 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).

More recent measurements of copper concentrations in 265 foods analyzed from 1991 to 1996 and from 1991 to 1999 have been obtained from the FDA Total Diet Study (Capar and Cummingham 2000; FDA 2000). The copper contents of selected foods provided in the most recent FDA Total Diet Study (FDA 2000) are similar to those obtained from the 1982–1984 FDA study. 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. The results of a 1994–1996 Continuing Survey of Food Intakes (CSFII) found that the daily intakes of copper for men and women ages ≥60 years old are 1.3 and 1.0 mg/day, respectively (Ma and Betts 2000). In a separate study by Ellis et al. (1997), copper intake for male and female African-Americans ages 21–65 years old was determined to be 1.0 mg/day for both sexes.

Daily intakes of copper and other essential minerals were estimated for eight age-sex groups of the United States population as part of the FDA's Total Diet Study (Pennington et al. 1986). By analyzing the mean mineral content of samples of 234 foods obtained in 24 cities from mid-1982 to mid-1984 and by using previously determined daily intakes of each food as determined from data obtained from the National Food Consumption Survey (1977–1978) and the Second National Health and Nutrition Examination Survey (1976–1980) (Pennington 1983), the daily mineral intake for the age-sex groups was determined. The copper intakes in mg/day of the eight age-sex groups were: 6–11-month-old infant, 0.47; 2-year-old child, 0.58; 14–16-year-old girl, 0.77; 14–16- year-old boy, 1.18; 25–30-year-old woman, 0.93; 25–30-year-old man, 1.24; 60–65-year-old woman, 0.86; and 60–65-year-old man, 1.17. All values were low in terms of the estimated safe and adequate daily dietary intake of this nutrient. The food item with the highest copper level was beef/calf liver (61 ppm).

Table 6-12. Copper Content of Selected Foods (mg/kg)[a]

Food description	Mean	SD[b]
Breads		
bagel, plain	1.3	0.2
cracked wheat bread	1.8	0.2
English muffin, plain, toasted	1.3	0.1
graham crackers	1.5	0.3
rye bread	1.5	0.2
saltine crackers	1.4	0.1
white bread	1.1	0.2
white roll	1.3	0.2
whole wheat bread	2.3	0.3
Cereal, rice, and pasta		
corn flakes	0.5	0.1
crisped rice cereal	2.0	0.2
egg noodles, boiled	1.0	0.2
granola cereal	3.0	0.4
macaroni, boiled	0.9	0.1
oatmeal, quick (1–3 minutes), cooked	0.7	0.1
oatring cereal	3.3	0.4
raisin bran cereal	4.4	0.4
shredded wheat cereal	3.7	0.5
wheat cereal, farina, quick (1–3 minutes), cooked	0.3	0.3
white rice, cooked	0.7	0.1
Vegetables		
asparagus, fresh/frozen, boiled	1.0	0.2
beets, fresh/frozen, boiled	0.7	0.2
black olives	1.4	0.4
broccoli, fresh/frozen, boiled	0.2	0.1
Brussels sprouts, fresh/frozen, boiled	0.4	0.1
cabbage, fresh, boiled	0	0
carrot, fresh, boiled	0.3	0.2
cauliflower, fresh/frozen, boiled	0	0
celery	0	0.1
collards, fresh/frozen, boiled	0.5	0.4
corn, fresh/frozen, boiled	0.3	0.2
cream style corn, canned	0.1	0.2
cucumber, raw	0.2	0.2
eggplant, fresh, boiled	0.5	0.2
green beans, fresh/frozen, boiled	0.5	0.3
green peas, fresh/frozen, boiled	1.0	0.2
green pepper, raw	0.7	0.3
iceberg lettuce, raw	0.2	0.2
lima beans, immature, frozen, boiled	1.5	0.2
mixed vegetables, frozen, boiled	0.6	0.2
mushrooms, raw	2.4	0.6
okra, fresh/frozen, boiled	0.8	0.3
onion, mature, raw	0.4	0.1
peas, mature, dry, boiled	2.3	0.3
spinach, fresh/frozen, boiled	0.8	0.3
summer squash, fresh/frozen, boiled	0.5	0.1
sweet potato, fresh, baked	1.4	0.4
tomato, red, raw	0.5	0.2
tomato sauce, plain, bottled	1.2	0.4
tomato, stewed, canned	0.7	0.2
turnip, fresh/frozen, boiled	0	0.1
white potato, baked with skin	1.0	0.4
white potato, boiled without skin	0.6	0.2
winter squash, fresh/frozen, baked, mashed	0.6	0.2
Fruits		
apple, red, raw	0.2	0.2
applesauce, bottled	0.2	0.1
apricot, raw	0.8	0.3
avocado, raw	2.2	0.6
banana, raw	1.1	0.2
cantaloupe, raw	0.3	0.1
fruit cocktail, canned in heavy syrup	0.5	0.1
grapefruit, raw	0.3	0.1
grapes, red/green, seedless, raw	1.1	0.6
orange, raw	0.4	0.1
peach, canned in light/medium syrup	0.3	0.2
peach, raw	0.7	0.2
pear, canned in light syrup	0.4	0.1
pear, raw	0.8	0.1
pineapple, canned in juice	0.5	0.1
plums, raw	0.6	0.1
prunes, dried	2.9	0.3
raisins, dried	3.3	0.4
strawberries, raw	0.5	0.3
watermelon, raw	00.4	0.1

Table 6-12. Copper Content of Selected Foods (mg/kg)[a]

Food description	Mean	SD[b]
Fruit juices		
apple juice, bottled	0	0.1
grape juice, bottled	0	0.1
grapefruit juice, from frozen concentrate	0.3	0.1
orange juice, from frozen concentrate	0.3	0.1
pineapple juice from frozen concentrate	0.4	0.1
prune juice	0.1	0.1
tomato juice, bottle	0.6	0.1
Dairy products		
American, processed cheese	0.1	0.2
cheddar cheese	0.3	0.2
chocolate milk, fluid	0.3	0.2
cottage cheese, 4% milkfat	0	0
cream cheese	0	0
eggs, boiled/fried	0.6	0.1
eggs, scrambled	0.5	0.1
half & half	0	0
lowfat (2%) milk, fluid	0	0
skim milk	0	0
sour cream	0	0
Swiss cheese	0.4	0.4
whole milk	0	0
Meat, poultry, and seafood		
beef chuck roast, baked	1.0	0.1
beef steak, loin, pan-cooked	1.0	0.2
bologna, sliced	0.4	0.2
chicken breast, roasted	0.3	0.1
chicken, fried (breast, leg, and thigh)	0.7	0.1
frankfurters, beef, boiled	0.4	0.1
ground beef, pan-cooked	0.8	0.1
haddock, pan-cooked	0.06	0.13
ham, baked	0.6	0.2
ham luncheon meat, sliced	0.5	0.1
lamb chop, pan-cooked	1.4	0.2
liver, beef, fried	123	57
pork bacon, pan-cooked	1.2	0.4
pork chop, pan-cooked	0.8	0.2
pork roast, baked	0.8	0.1
pork sausage, pan-cooked	0.8	0.1
quarter-pound hamburger on bun, fast-food	0.9	0.1
salami, sliced	1.0	0.2
salmon, steaks or filets, fresh or frozen, baked	0.5	0.1
shrimp, boiled	2.3	0.6
tuna, canned in oil	0.5	0.1
turkey breast, roasted	0.4	0.1
veal cutlet, pan-cooked	1.0	0.3
Legumes, nuts, and nut products		
kidney beans, dry, boiled	2.7	0.5
mixed nuts, no peanuts, dry roasted	15.5	2.6
peanut butter, smooth	5.2	0.6
peanuts, dry roasted	5.8	0.6
pinto beans, dry, boiled	2.4	0.2
pork and beans, canned	1.8	0.2
Fats, oils, condiments, snacks, and sweets		
butter, regular (salted)	0	0
corn chips	1.0	0.2
fruit flavor sherbet	0	0.1
gelatin dessert, any flavor	0	0
honey	0	0
jelly, any flavor	0	0.1
margarine, stick, regular (salted)	0	0
mayonnaise, regular, bottled	0	0
olive/safflower oil	0	0
popcorn, popped in oil	1.7	0.4
potato chips	2.8	0.8
pretzels, hard, salted, any shape	1.6	0.2
vanilla ice cream	0.06	0.24
white sugar, granulated	0	0
Beverages		
coffee, from ground	0	0
cola carbonated beverage	0	0
tea, from tea bag	0	0

[a]Source: FDA 2000
[b]SD = Standard Deviation

A baseline value for the copper content of mother's milk was determined by a survey of literature values. Based on the data obtained from 28 study sets, a baseline copper concentration of 331 ppb was determined from a range of values of 197–751 ppb and a median of 290 ppb (Iyengar and Woittiez 1988). In a separate study of 11 lactating women, it was found that the variability in the copper content of mother's milk was primarily subject-related. The copper concentration in milk declined moderately, from 0.43 μg/mL between 1 and 3 months postpartum to 0.24 μg/mL between 10 and 12 months postpartum (Vaughan et al. 1979). In a study of 82 lactating women, the copper concentration in breast milk ranged between 0.8 and 1.1 ppm and remained relatively constant in individual women over the first 7 days postpartum (Arnaud and Favier 1995).

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). Perwak et al. (1980) reported similar results for mussels (3.9–8.5 ppm) and for clams (8.4–171 ppm). Recent measurements of copper concentrations in zebra and quagga mussels taken from Lakes Erie and Ontario in 1997 ranged from 21 to 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 (*M. edulis*, *M. californianus*, *C. 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.

As a part of the National Contaminant Biomonitoring Program of the U.S. Fish and Wildlife Service, eight species of freshwater fish were collected at 112 stations in the United States in 1978–1979 and 1980–1981 (Lowe et al. 1985). The geometric mean concentrations of copper in ppm (wet weight, whole fish) for these two periods were 0.86 and 0.68, respectively; the 85th percentiles were 1.14 and 0.90, respectively, and the ranges were 0.29–38.75 and 0.25–24.10, respectively. The highest concentration, 38.75 and 24.10 ppm, during both collecting periods was in white perch from the Susquehanna River and the second highest concentration, 19.3 ppm, was found in white perch from the Delaware River near Trenton, New Jersey. However, copper concentrations in common carp and white catfish collected from the same station at the same time were 0.76 and 1.35 ppm, respectively.

In bluefin tuna caught in the northwest Atlantic off Newfoundland, the mean copper concentration in muscle tissue has been measured at 1.0 ppm (dry weight) (Hellou et al. 1992a). In cod caught off the coast of Newfoundland, mean copper concentrations of <1.2–1.5 μg/g (dry weight) in muscle and 5–10 ppm (dry weight) in liver have been determined (Hellou et al. 1992b).

Copper residues in muscle of 268 fish specimens from 17 species were analyzed over a 5-year period in several surface water systems in eastern Tennessee (Blevins and Pancorbo 1986). The mean residue levels in the muscle of different species of fish from nine stations ranged from 0.12–0.86 ppm (wet weight). Maximum levels ranged from 0.14 to 2.2 ppm.

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 bluegill sunfish collected from storm water 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 storm water ponds and controls did not significantly differ, with values of 3.81 and 4.71 mg/kg wet weight, respectively.

Respective mean and median copper concentrations of 127 samples of finfish from Chesapeake Bay and its tributaries were 1.66 and 0.36 ppm in 1978, and 1.85 and 0.61 ppm in 1979 (Eisenberg and Topping 1986). In striped bass taken from Turkey Point in the bay, copper levels were below the detection limit of the study (<0.1 μg/g) in muscle, but were higher in liver tissue ranging from 0.86 to 23.5 μg/g. In gonad tissue obtained from tissue from a different site on the bay, there was also an increase in the mean copper concentration in this tissue (4.25 μg/g) as compared to muscle (0.76 μg/g). The copper content of muscle tissue of several species of fish collected from metal-contaminated lakes near Sudbury, Ontario, ranged from 0.5 to 1.4 ppm (dry weight). No major pattern in variation was evident among species or among the study lakes (Bradley and Morris 1986). The copper concentration in the livers, however, ranged from 5 to 185 ppm (dry weight) and differed significantly among species and among lakes. Unlike muscle tissue, liver tissue is a good indicator of copper availability, although the data indicate that there are other factor(s) that influence the availability and bioaccumulation of copper in these fish.

The copper concentrations in the liver of lake trout and grayling taken from four fresh water 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 statistically significant higher burdens 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.

Although the concentrations of copper in plants vary widely, they usually range from 1 to 50 ppm (dry weight) (Davies and Bennett 1985) and from 1 to 143 ppm (dry weight) in edible plants (Perwak et al. 1980). Concentration ratios of copper in plants relative to soil (concentration factors or CF) demonstrate that copper uptake differs significantly between plants. For example, CF 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 were found to vary among soil types (0.59–3.58) with copper concentrations in rice ranging from 1.7 to 5.1 μg/g (Herawati et al. 2000). Copper concentrations in rice grain have been found to increase significantly from 1.4 to 15.5 μg/g when copper concentrations in waste water 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 50–70 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. Copper concentrations in human tissues are given in Table 6-13 (Georgopoulos et al. 2001). 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).

The mean copper content of tobacco in Finnish cigarettes was 24.7 ppm, with a standard deviation of 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.

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

Table 6-13. Copper Content of Human Tissues and Body Fluids

Tissue	Mean content (µg/g dry weight)	
	Normal	Wilson's disease
Adrenal	7.4	17.6
Aorta	6.7	—
Bone	4.2	—
Brain	—	—
Caudate nucleus	—	212
Cerebellum	—	261
Frontal lobe cortex	—	118
Globus pallidus	—	255
Putamen	—	314
Cornea	—	92.9
Erythrocytes (per 100 mL packed red blood cells)	23.1	—
Hair	89.1	—
Heart	16.5	12.7
Kidney	14.9	96.2
Leukocytes (per 109 cells)	0.9	—
Liver	25.5	584
Lung	9.5	15.5
Muscle	5.4	25.9
Nail	18.1	—
Ovary	8.1	5.2
Pancreas	7.4	4.2
Placenta	13.5	—
Prostate	6.5	—
Skin	2	5.2
Spleen	6.8	5.6
Stomach and intestines	12.6	22.9
Thymus	6.7	—
Thyroid	6.1	—
Uterus	8.4	—
Aqueous humor	12.4	—
Bile (common duct)	1,050	173
Cerebrospinal fluid	27.8	—
Gastric juice	28.1	—
Pancreatic juice	28.4	—
Plasma, Wilson's disease		—
Saliva	50	—

Table 6-13. Copper Content of Human Tissues and Body Fluids

Tissue	Mean content (μg/g dry weight)	
	Normal	Wilson's disease
Serum		
Female	120	—
Male	109	—
Newborn	36	—
Sweat		
Female	148	—
Male	55	—
Tissue		
Synovial fluid	21	—
Urine (24-hour)	18	—

Source: Georgopoulos et al. 2001; Scheinberg 1979; Sternlieb and Scheinberg 1977

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 ranged from 126 to 7,729 ppm (dry weight), with a median value of 991 ppm. Gutenmann et al. (1994) report 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). For comparison, the concentration of copper in cow's manure is ~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 in composts formed from yard waste ranging from 22.7 to 327 ppm, from sewage sludge ranging from 432 to 1,019 ppm and from municipal solid waste ranging from 191 to 1,143 ppm.

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 Landberger (1995) report 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 of 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 have been obtained (Eary et al. 1990).

Agricultural sources of copper contamination in soils has been summarized by EPA (1995) and are shown in Table 6-14. Concentrations of copper in fertilizers, soil amendments and other agricultural materials have been measured by Raven and Loeppert (1997). The materials and mean concentrations: 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).

Table 6-14. Agricultural Sources of Copper Contamination in Soils

Source	Concentration (ppm dry weight)[a]
Sewage sludges	50–3,300
Phosphate fertilizers	1–300
Limestones	2–125
Nitrogen fertilizers	<1–15
Manure	2–60
Pesticides (percent)	12–50

Source: EPA 1995

[a]Equivalent to mg/kg-dry weight

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Due to the ubiquitousness 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 1987a). 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 1987a), the average daily intake by inhalation, would range from 0.1 to 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 1987a), 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, which is usually not the case. The average daily dietary intake of copper from food is ~2 mg/day. 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). 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 (Goldberg 1986; Perwak et al. 1980). Assuming a median copper concentration in drinking water of 75 μg/L, the average daily copper exposure from consumption of 2 L of water per day is 0.15 mg. However, many people may have high levels of copper in their tap water that have been acquired during transport through the water distribution system. If the system is not permitted to flush out, average intakes from water may be >2 mg/day. It is less likely that high dermal exposures will result from bathing in this tap water because the distribution system will flush itself out as the water is drawn. The total exposure of copper for the average person from all sources (e.g., air, drinking water, and food) is estimated to be 2.75 mg/day.

A National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimated that potentially 505,982 workers, including 42,557 women, were occupationally exposed to copper in the United States (NIOSH 1988). The NOES estimate is provisional because all of the data for trade name products that may contain copper have not been analyzed. Of the potential exposures, 1,073 are to pure copper, while in the other cases, the molecular form of copper was unspecified. Additionally, according to the NOES, 125,045 workers, including 38,075 women, were potentially exposed to copper sulfate

(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 exposure limits for copper fume are 0.2 and 1 mg/m^3 for dust and mists (Frazier and Hage 1998).

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7 Children's Susceptibility.

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 kilogram 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 breast milk 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).

With respect to inhalation, exposures of children to copper are not expected to be very different from those of the rest of the general population. However, exposure of copper through oral routes may differ, 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 breast milk 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 for a 6–11-month-old infant and a 2-year-old child were estimated to be 0.47 and 0.58 mg/day, values which are lower than the adult intake of ~1 mg/day. However, one study has provided estimated inhalation and ingestion exposures of copper for children in India (Raghunath et al. 1997). In this work, concentrations of copper in particulates in air 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. In this same work, exposures to copper through ingestion were estimated to be between 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 near a lead smelter, as measured by copper concentration in teeth, increased with decreasing distance from the smelter (Blanuša et al. 1990). 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). 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.

6.7 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) and perhaps some weakly complexed or adsorbed forms of copper. The data indicate that copper in natural water, sediment, and soil mainly exists in bound form. Even so, the free form of copper can be released readily from ingested materials, for example a child's sampling of soil, following exposure to the low pHs encountered in the stomach (Pizarro et al. 2001). Potential for high uptake copper in the general population may exist where people consume large amounts of tap water that has picked up copper from the distribution system, or already has 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 systems is likely to occur where the water is soft and not allowed to run to flush out the system. In such cases, the 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 and industrial workers, such as those in the plating industry, may come into dermal contact with these chemicals. Exposure to high levels of free Cu(II) may occur, for example, from swimming in water that has been recently treated with a copper-containing algicide.

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 which are in close proximity to 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 and workers in these and other industries may 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 more deeply into the lung, thereby evading the mucocilliary escalator.

6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of the ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to pursue assessment of the adequacy of the available information on the health effects of copper. Where adequate information is not available, the ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of copper.

The following categories of possible data needs have been identified by a joint team of scientists from the ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce uncertainties of regarding human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized and a refined substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties. In general, the available data on the physical and chemical properties of elemental copper and copper sulfate are sufficient for estimating their environmental fate. That no numerical value is listed for the water solubility of copper in Table 4-3 is of no special significance. For inorganic salts, the solubility product coupled with stability constants for the ionic species in solution are the factors determining how much of a compound goes into solution (i.e., the concentration). The solubility products and stability constants for copper that are required for determining the copper species in natural water and their concentrations are known (Schnoor et al. 1987; Town and Filella 2000). Although no K_{oc} values are listed, copper binds very strongly to organic matter, and values for the binding constants and solubility products to humic acids are available (Schnoor et al.

1987). Similarly, there are binding constants and solubility products for other species that bind or coprecipitate with copper, such as clay minerals and iron and manganese oxides (Schnoor et al. 1987). Binding constants for copper in specific natural waters are also available (Town and Filella 2000). Other physical and chemical properties in Table 4-3 for which there is no data are not well defined for these copper compounds.

In general, experimental confirmation is required for predicting copper's fate in the environment. The factors which determine the copper species present or the material to which copper may be bound and the strength of the binding can be site specific. If the level of detail requires knowledge of, for example, the percentage of copper associated with iron oxides or that which is easily exchangeable, experimental confirmation is necessary.

Production, Import/Export, Use, Release, and Disposal. Information on the production, use, release, and disposal of copper is used for evaluating the potential for exposure of people to copper who live or work near waste sites and other sources. Copper exposure is widespread; but much of this exposure is to generally benign forms, such as metallic copper. The information available often does not distinguish between these forms and those of greater toxicological significance.

Information on the production, use, release, and disposal of metallic copper and copper sulfate is generally available. These two forms of copper account for most of the copper used. This information is tabulated by the U.S. Geological Survey every year in the Minerals Yearbook and predictions of future trends in production and use are available. Such information is not available for other copper compounds. We also know the major uses of copper and where these uses occur (e.g., the home, workplace, etc.).

According to the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRTKA), (§313), (Pub. L. 99-499, Title III, §313), industries are required to submit release information to the EPA. The TRI contains release information for copper and copper compounds and is updated yearly.

For disposal, industrial waste copper is generally either recycled or landfilled. Data on secondary copper production (i.e., copper produced from scrap) is compiled by the U.S. Geological Survey. Effluent and disposal regulations for copper and its compounds are listed in the Clean Water Act and the Resource Conservation and Recovery Act (RCRA).

Environmental Fate. Reliable information on how copper and its compounds partition in the environment (i.e., to soil and sediment), and the type of transformations that occur in different media, is available from over 35 published studies included in this chapter. We also have data concerning its transport in the environment from over 50 reliable studies. Although information on the fate of copper in air, water, and soil is available, the fate of copper is both species- and site- specific. Information concerning the forms of copper (i.e., specific compound, to what it is bound or complexed, or, in the case of air, the particle size) or the lability of the copper in particular media is available from only a few, -yet reliable, studies. These are sufficient to identify numerous contributors to the fate of copper and its compounds; but are insufficiently comprehensive for developing accurate fate maps. In addition, studies of how fate data relate to human exposures, especially in regard to projecting copper toxicity in children, is inadequate.

Bioavailability from Environmental Media. Copper is found in food, water, ambient air, and soil. The bioavailability of copper from food and water has been investigated in animals and humans. No information on the availability of copper from air was located. Copper in air originating from smelter sites is predominantly associated with sulfur, and presumably exists as the sulfate. Copper dust from soil in general as well as around mining and smelter sites may occur in ore dust or a silicate. No information was located on the bioavailability of copper in air. Copper in soil often is bound to organic molecules. Therefore, the bioavailability of the copper from soil cannot be assessed based on bioavailability information from drinking water or food studies. Studies on the bioavailability of copper from soil and ambient air would be useful in assessing potential toxicity to people living near a hazardous waste site.

The form and lability of copper in the environment is known in only a few site-specific cases. None of these cases include hazardous waste sites. More information on the forms of copper found at industrial sites and hazardous waste sites would be useful, especially since data from the Hazardous Substances Data Bank (HSDB) indicate that concentrations of copper as high as 182,000 ppm in soil and 14,000 ppm in sediments have been measured offsite of listed NPL sites (HazDat 2002). Monitoring groundwater near industries that use highly acid, copper-containing solutions, such as electroplating, electrowinning, and ore leaching industries, is important for the protection of human populations at risk of exposure to their highly mobile and highly bioavailable copper to human risk populations.

Food Chain Bioaccumulation. Because copper occurs in different forms in the environment, its bioaccumulation is expected to vary according to site and species. Data are available on the bioconcentration of copper in aquatic organisms, plants, and animals, as well as biomagnification in food

chains. This information is useful in assessing the potential for exposure from ingesting food originating from contaminated areas. However, little information is available on the potential for intoxication from foodstuffs from apparently nonpolluted areas or where they may have accumulated toxic levels of copper through biomagnification resulting from foraging in polluted areas.

Exposure Levels in Environmental Media. Data are available regarding the concentrations of copper in environmental media, including the concentration of copper in soil at some hazardous waste sites. Since copper is naturally present in soil, trace quantitative analytical and statistical techniques can be used to determine whether the copper found at these sites is elevated above normal levels. Monitoring data are reasonably current and human intake of copper from food, water, and air can be estimated.

Exposure Levels in Humans. There are reasonably current data on levels of copper in human tissue and human milk. Although information on copper concentrations in individuals exposed within specific work settings is increasing (for example, Gerhardsson et al. 1993; Saltzman et al. 1990), none of the studies address specific U.S. populations living around hazardous waste sites. There are some quantitative data relating occupation, level and route of exposure to the form of copper to which people are exposed. There is some limited information correlating copper concentration and form to body burden in the general population. However, more information is needed for occupational and other at-risk populations.

Exposures of Children. Reasonably current data report levels of copper intake in infants and children. Information on copper intake by infants from human milk also is available. Exposure of children to copper in drinking water has been assessed and methods to decrease this exposure have been identified and implemented. However, only limited information on inhalation and ingestion is available. Some information on exposure of children to copper near mining, smelting, refining, manufacture facilities, waste sites and other hazardous sites is available; but not for U.S. populations. This information is needed to better estimate exposures of children in U.S. populations living near these facilities and sites. The use of copper concentrations in toenails and hair has been investigated as a surrogate measure of copper exposure in children and adults and more research into establishing the validity of these surrogates is underway.

Child health data needs relating to susceptibility are discussed in Section 3.12.2 Identification of Data Needs: Children’s Susceptibility.

Exposure Registries. No exposure registries for copper and its compounds were located. No subregistry has currently been established for these chemicals. They will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates epidemiological research needed to assess adverse health outcomes that may be related to the exposure to these chemicals.

6.8.2 Ongoing Studies

Ongoing studies of copper in soils, sediments and aquifers have been identified and are listed in Table 6-15. Also included in Table 6-15 are ongoing investigations of human exposures to copper.

Table 6-15. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Copper

Investigator	Affiliation	Research description	Sponsor[a]
Gardea-Torresdey J	Stanford University	Uptake of copper and lead into creosote bushes in regions with heavy metal contamination	National Center for Research Services
Naqvi SM	Southern University A&M	Bioaccumulation and biomagnification of copper in crayfish	National Institute of General Medical Sciences
Conklin MH	University of Arizona College of Pharmacy	Characterization of abandoned mine sites and mine wastes in Arizona; assess stability of these sites to emission of copper and other metals to surface waters	National Institute of Environmental Health Sciences
Sparks DL	University of Delaware	Influence of aging and competitive sorption on stabilization of metals through surface precipitates in soils	CSREES Delaware
Reeve AS	University of Maine	Use of stable isotope tracing techniques to determine the source of salts in Maine groundwater, including copper	CSREES Maine
Welch RM	Agricultural Research Service, Ithaca, New York	Study the soil chemistry, distribution, and bioavailability to crops of health-related elements (e.g., Fe, Zn, Ca, Se, Cd, B) and their movement into edible plant parts.	ARS
Ahner BA	Cornell University	Determine the nature and source of organic ligands in marine waters to better understand the cycling and bioavailability of Cu and Fe.	SAES New York
Hesterberg DL	North Carolina State University	Determine the significance of heavy-metal sulfides (and other stable chemical species) for reducing the mobility and bioavailability of potentially-toxic metals in complex clay-organic systems.	CSREES North Carolina

Table 6-15. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Copper

Hunt JR	Agricultural Research Center, Grand Forks, North Dakota	Determine how changes in the U.S. diet may affect nutritional status, with emphasis on intakes and bioavailabilities of iron, zinc, copper, and selenium	ARS
Zelazny LW	Virginia Polytechnic Institute	Determine and compare the quantity, chemical forms, and plant available levels of P, Cu, and Zn from manures treated with phytase after reacting with selected soils for various time periods	CSREES Virginia

Source: CRIS 2003; FEDRIP 2003

[a]ARS = Agricultural Research Service; CSREES = Cooperative State Research, Education, and Extension Service; SAES = State Agricultural Research Station–Multistate Research Projects