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Guidelines for Interpretation of the Biological Effects of Selected Constituents in Biota, Water, and Sediment

Copper

Participating Agencies:

Bureau of Reclamation
U.S. Fish and Wildlife Service
U.S. Geological Survey
Bureau of Indian Affairs

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Copper

Description

Copper (Cu) is one of the most familiar metals, having been used for thousands of years to make tools, ornaments, utensils, and coins. The earliest metal workers found copper very easy to work with, owing to its malleability, ductility, and moderate melting point (1,083 °C). Copper is also one of the best conductors of both heat and electricity, which makes it useful in cookware and invaluable in electrical circuits. Native copper is shiny and brown to reddish-brown, but its many salts and minerals take on a variety of hues ranging from bright green to purple to indigo blue to yellowish-brown. Chemically it has two oxidation states, forming either cuprous (Cu^+) or cupric (Cu^{+2}) compounds. The cuprous compounds are not common in natural waters, though, as they oxidize readily to the bivalent form.

Occurrence

Copper is widespread in the environment, having an overall crustal abundance of about 50 mg/kg. It is present in both seawater and fresh water at concentrations generally in the range of 1–20 µg/L (Irwin 1996). Its most common ores include the sulfides chalcopyrite, bornite, chalcocite, and covellite, and the carbonates azurite and malachite. In the Western United States, large copper mining operations are found in Arizona, New Mexico, Utah, and Montana. Most of these are exploiting low-grade porphyry deposits (<1% Cu, mostly as chalcopyrite). Veins of native copper are rare in the Western States.

Copper is one of the most common contaminants found in urban runoff: it is present in the leachate from municipal landfills and in sludges generated by sewage treatment plants, and it is commonly leached from drinking water pipes, particularly in areas where the drinking water is somewhat acidic (Irwin 1996). Significant amounts of copper are produced in wastes from textile mills and cosmetics plants, and in sludge from hardboard production, mining, smelting, and the burning of coal in powerplants (Brown et al. 1983, Furness and Rainbow 1990, Kabata-Pendias and Pendias 1992).

Background Concentrations.—Background copper levels in soil range from 13 to 24 mg/kg in uncontaminated areas (Kabata-Pendias and Pendias 1992). The average concentration for water in lakes and streams is reported to be 2 µg/L (Nriagu 1979), and average freshwater fish concentration is 0.65 mg/kg wet weight (ww) (or about 2.60 mg/kg dry weight [dw]); the 85th percentile concentration in fish was 1 mg/kg ww (4 mg/kg dw) (Schmitt and Brumbaugh 1990). Copper concentrations in plants are generally in the range of 2 to 20 mg/kg dw (Thompson et al. 1991). Whole-body concentrations in small mammals collected from various uncontaminated sites ranged from 8.3 to 13.4 mg/kg dw (Talmage and Walton 1991). Whole-body concentrations of copper in amphibians vary from 8 to 845 mg/kg dw, but extremely high copper concentrations (up to 2,091 mg/kg dw) have been observed in livers of some amphibians from uncontaminated areas (Hall and Mulhern 1984).

Summary of Effects

Copper is an essential element for all living organisms, but elevated levels of copper in the environment may be harmful at or near copper-contaminated sites. Both deficient and excess amounts of copper cause adverse effects in all species. Copper is generally more toxic to aquatic organisms than to birds or mammals. This is reflected by the relatively low ambient water quality criteria for copper and by the rarity of toxic effects through excess dietary exposure in birds and mammals under field conditions. However, some ungulates, such as sheep (NAS 1980; Puls 1988), are more sensitive to copper than other mammals. Nevertheless, copper concentra-tions in the bodies of aquatic birds and mammals are generally well regulated (Furness and Rainbow 1990), and copper toxicity is more likely to affect aquatic plants, invertebrates, and fish. A summary of biotic effect levels is presented in table 8.

Suter and Mabrey (1994) evaluated a series of toxicological benchmarks for screening various contaminants for their potential effects on aquatic biota. In addition to the national ambient water quality (NAWQ) criteria, they provided secondary acute and chronic values, lowest chronic values (including those for fish, daphnids, nondaphnid invertebrates, aquatic plants, and all organisms), test EC20s, sensitive species test EC20s, and population EC20s. The values for water in table 8 are as follows: "No effect" is the lowest chronic value for all organisms; "Toxicity threshold" is the NAWQ chronic criterion (if established) or the secondary chronic value; and "Level of concern" is the range between the two other values.

Field Cases

Three examples illustrate the potential impacts of copper-contaminated mine drainage on the aquatic environment:

(1) Acid mine drainage from the Iron Mountain Mine near Redding, California, containing high concentrations of copper and zinc caused numerous fish kills in the upper Sacramento River (Finlayson and Ashuckian 1979, Finlayson and Verrue 1980). Some of these occurred as far back as the early 1900's, but they became more frequent and more serious following the construction of Shasta Dam in 1944 and Keswick Dam in 1950. Finlayson and Ashuckian (1979) hypothesized that these dams had effectively diminished the "dilution effect" in the Sacramento River. Yet, the outflows from these dams have also been used to purposely dilute elevated concentrations that are detected at downstream monitoring stations.

(2) Similarly, toxic concentrations of copper and zinc from the Penn Mine area in the Sierra Nevada of California caused sizable fish kills in the lower Mokelumne River Basin (Finlayson and Rectenwald 1978). During a fish kill in the Mokelumne River in 1958, copper was elevated to 3.8 mg/L a short distance downstream from the mine.

(3) In Canada, the effects of mixed mining wastes on fish were examined through integrated field sampling of water, sediment, invertebrates, and fish (Munkittrick et al. 1991, Miller et al. 1992). Miller et al. (1992), in particular, made an extensive study of the relationships between concentrations of zinc and copper in all these media in the Manitouwadge chain of lakes in northern Ontario. They found a correlation between zinc concentrations in invertebrates and in sediment but observed no such relationship with water concentrations. Neither did they find any relationship between zinc concentrations in fish tissue and those in invertebrates, although several lab studies had suggested that food and particulates are much more important sources of zinc than water (Patrick and Loutit 1976, Dallinger and Kautzky 1985, as cited in Miller et al. 1992). For both zinc and

Table 8.—Summary of comprehensive biotic effects of copper

["—" indicates that no data are available]

Medium	No effect	Level of concern	Toxicity threshold	Explanation
Water (µg/L)	0.23	0.23–12	12	Hardness-dependent criteria: 0.23 µg/L is lowest chronic value for aquatic organisms; 12 µg/L is NAWQ chronic criterion at hardness of 100 mg/L (as $CaCO_3$). (See Suter and Mabrey 1994.) Sensitive species may be affected in the "level of concern" range (depending partly on effects of pH, temperature, and dissolved oxygen).
Sediment (mg/kg, dw)	34	34–270	270	"ERL" and "ERM" values of Long et al. (1995). However, sulfides in the sediment may reduce copper toxicity (see text).
Plants (mg/kg dw)	3–30	—	>20	Kabata-Pendias and Pendias (1992). Toxicity threshold varies depending on species of Cu present.
Invertebrates	—	—	—	Diagnostic levels not established because Cu generally is homeostatically regulated. Some invertebrates (e.g., crustaceans and mollusks) require Cu for hemocyanin and may normally have higher levels than other species (Furness and Rainbow 1990).
Fish, whole body (mg/kg, dw)	9.8	9.8–13.3	13.3	Diagnostic levels not established because Cu generally is homeostatically regulated. After 9-week dietary exposure, rainbow trout showed decreased weight gain at 13.3 mg/kg but no significant effects at 9.8 (Julshamn et al. 1988).
Birds, liver (mg/kg dw)	<60	25–300	>540	Data for ducks from Puls (1988); toxic concentrations in waterfowl diets are >200 mg/kg dw.
Eggs (mg/kg dw)	5.5	—	—	Egg data from J.P. Skorupa (unpub. data, 1996).
Amphibians/reptiles	—	—	—	Diagnostic levels not established; even at uncontaminated sites, some amphibian tissues have 800–2,000 mg/kg dw (Hall and Mulhern 1984).
Mammals	—	—	—	Diagnostic levels for wild mammals not established; for sheep, liver concentrations >250 mg/kg dw may be toxic (Puls 1988).

copper, the water concentration was a better indicator of metal concentration in fish tissue than the sediment or invertebrate concentrations in this field study. Miller et al. (1992) also reported reduced growth in females of white sucker after sexual maturation, decreased egg size and fecundity, no sig-nificant increase in fecundity with age, and an increased incidence of spawning failure at a water-borne zinc concentration of 156 mg/L and a sediment concentration of 6,397 mg/kg. In addition, they found kidney and liver concentrations to be better indicators of chronic zinc and copper exposure than muscle concentrations.

Many more recent field studies have investigated the toxicity of copper and copper-zinc mixtures in effluents. Finlayson and Verrue (1980) and Finlayson and Ashuckian (1979) conducted long-term and short-term toxicity studies on Chinook salmon and steelhead trout, respectively, in order to estimate "safe" levels of copper and zinc for those species. Harrison and Klaverkamp (1990) also studied the bioaccumulation of copper, zinc, and other metals in northern pike and white suckers from lakes near a smelter.

Abiotic Factors Affecting Bioavailability

Water

In natural waters, dissolved copper occurs in several different chemical forms and in various inorganic and organic complexes. Copper is present as Cu^{+2} in acidic waters and $CuOH^+$ in soft waters, and a dissolved fraction of copper is believed to be toxic in fish (Davies et al. 1979). Factors that affect the speciation of copper in water are pH, temperature, hardness, and dissolved organic carbon (Bodek et al. 1988). Low pH, soft water, and higher temperature are known to increase the copper toxicity.

Bottom Sediment

Harrison and Klaverkamp (1990) found no consistent relationship between copper concentrations in bottom sediment and those in tissues of white sucker and northern pike (table 9). Long and Morgan (1990) concluded that copper in bottom sediment at concentrations of about 20 mg/kg dw may induce sublethal behavioral effects in clams if it is not tightly chelated or bound to sediments. However, Long et al. (1995) found that copper concentrations of 34 mg/kg rarely impair the survival or reproduction of benthic invertebrates but that concentrations of 270 mg/kg or higher usually do. Although many of the data that were evaluated were for estuarine and marine sediments, Hull and Suter (1994) concluded that those screening levels also were appropriate for freshwater sediments until more specific guidelines become available. However, they also recommend that these concentrations be compared to local background levels when possible, and that concentrations within the background range should not be considered a problem.

Acid-volatile sulfide (AVS) in the sediment may bind a certain portion of some metals (Cd, Cu, Ni, Pb, and Zn) and render that portion unavailable and nontoxic to biota (Di Toro et al. 1992). In order to assess the effects of acid-volatile sulfide on metal toxicity, the AVS is extracted from sediment with hydrochloric acid, and the metal concentration that comes with it is called the simultaneously extracted metal (SEM). All SEMs that would contribute appreciably to the total SEM are measured and totaled (Di Toro et al. 1992). *If* the sediments are not fully oxidized (Adams et al. 1992), then an SEM:AVS ratio <1 indicates that acute toxicity is unlikely. The method has not yet been adapted for chronic toxicity.

Soil

Copper is able to form complexes with various soil constituents. Copper in soils can precipitate with hydroxide, phosphate, carbonate, and silicate to become a component of the amorphous fraction of soil. It can be adsorbed on the negatively charged sorption sites of silicate clay and it can form both soluble and insoluble complexes with components of soil organic matter (Baker and Amacher 1982).

Table 9.—Biological effects of copper concentrations in sediment

Species	Cu in sediment (mg/kg)	Cu in biomass (mg/kg ww, except as noted) and other effects	Location/Comments	Reference
Food chain				
Invertebrates	102	Complete absence of Plecoptera, Ephemeroptera, Odonata, Trichoptera, Amphipoda, and Unionidae	Manitouwadge Lake, Ontario, Canada (Zn = 1,149 mg/L)	Munkittrick et al. 1991
Fish				
White sucker (*Catostomus commersoni*)	11.4	Liver 50 (dw), muscle 7 (dw), stomach contents 7 (dw)	Loken Lake, Ontario, Canada (Zn = 43 mg/L)	Munkittrick et al. 1991
	102	Liver 83 (dw), muscle 6 (dw), stomach contents 155 (dw). Lowered growth rate.	Manitouwadge Lake, Ontario, Canada (Zn = 1,149 mg/L)	
	34	Liver 0.21, muscle 0.25	Top soil of Lake Nekik, Manitoba, Canada	Harrison and Klaverkamp 1990
	49	Liver 0.01, muscle 0.28	Top soil of Lake Naosap Mud, Manitoba, Canada	
	76	Liver 0.01, muscle 0.28	Top soil of Lake Kotyk, Manitoba, Canada	
	2,775	Liver 13.4, muscle 0.16	Top soil of Lake Hamell, Flin Flon, Canada	
	2,858	Liver 24.3, muscle 0.25	Top soil of Lake Meridian, Flin Flon, Canada	
	5,950	Liver 19.8, muscle 0.24	Top soil of Lake Cliff, Flin Flon, Canada	
	6,988	Liver 14.3, muscle 0.26	Top soil of Lake Phantom, Flin Flon, Canada	
	12,625	Liver 29.2, muscle 0.18	Top soil of Lake Douglas, Flin Flon, Canada	
Northern pike (*Esox lucius*)	34	Liver 15.2, muscle 0.11	Top soil of Lake Nekik, Manitoba, Canada	Harrison and Klaverkamp 1990
	49	Liver 11.2, muscle 0.12	Top soil of Lake Naosap Mud, Manitoba, Canada	
	76	Liver 16.8, muscle 0.11	Top soil of Lake Kotyk, Manitoba, Canada	
	198	Liver 11.2, muscle 0.2	Top soil of Lake Cleaver, Manitoba, Canada	
	2,775	Liver 19.5, muscle 0.17	Top soil of Lake Hamell, Flin Flon, Canada	
	2,858	Liver 17.1, muscle 0.16	Top soil of Lake Meridian, Flin Flon, Canada	
	5,950	Liver 11.9, muscle 0.18	Top soil of Lake Cliff, Flin Flon, Canada	
	6,988	Liver 7.6, muscle 0.13	Top soil of Lake Phantom, Flin Flon, Canada	
	12,625	Liver 28.5, muscle 0.14	Top soil of Lake Douglas, Flin Flon, Canada	

The strength of copper sorption by soil constituents occurs in the following relative order: manganese oxides < organic matter < iron oxides < clay minerals. Other soil components that may play a less significant role in copper sorption include free phosphates, iron salts, and clay-size aluminosilicate minerals. Copper retention in soils increases with increasing soil pH. The lack of adsorption of copper at low pH may be due to competition for sorption sites from other soil cations (Mn^{+2}, Fe^{+2}, H^{+}, and Al^{+3}) (Brown et al. 1983).

Biotic Effects

Plants

Copper sulfate has been used for more than 80 years as an algicide, typically at a concentration of 1 mg/L for the upper 0.5 meter of water (Mackenthun and Ingram 1967). In the soil, copper is toxic to sensitive plants at concentra-tions of 25 to 50 mg/kg (Demayo et al. 1982). Cereals, legumes, spinach, citrus seedlings, and gladiolus are known to be most sensitive to copper. The general symptoms of copper toxicity to plants are dark green leaves fol-lowed by induced iron chlorosis (yellowing); thick, short, or barbed-wire roots; and depressed tillering (Kabata-Pendias and Pendias 1992).

Macroinvertebrates

Most aquatic organisms are relatively sensitive to copper, even at low concentra-tions. The effects of low concentrations of copper on various invertebrates are noted in table 10. In a field study, Munkittrick et al. (1991) observed concentrations of 9.7 µg Cu/L and 232 µg Zn/L in Manitouwadge Lake, Ontario, Canada. Under these conditions, they noted the complete absence of Unionidae and several families of arthropods (table 10). Miller et al. (1992) found a correlation between copper concentrations in invertebrates and water concentrations but observed no such relationship with sediment concentrations.

Sediments in the Upper Clark Fork River and Milltown Reservoir in Montana have been contaminated with mine-related wastes (As, Cd, Cu, Pb, Mn, and Zn). In soft sediment depositional areas, taxa of Oligochaeta and Chironomidae generally accounted for more than 90 percent of the benthic invertebrate communities. Canfield et al. (1994) observed higher numbers of Chironomidae genera in areas where sediments had been identified as toxic using 28-day laboratory tests with the amphipod *Hyalella azteca*. Frequency of Chironomidae mouthpart deformities and total abundance of organisms did not correspond to concentrations of metals in sediment. In areas where benthic communi-ties were affected, sediment and surface water Cu concentrations ranged from 364 to 7,820 micrograms per gram and 274 to 11,080 µg/L, respectively.

Some aquatic organisms can tolerate rela-tively high levels of copper in their diets. Hatakeyama (1989) compared the toxicity of copper through water and diets in mayfly larvae and concluded that the high mortality at 100 µg/L (table 10) was principally attributable to copper in the water because, at this level, algae bioaccumulated only 450 mg/kg (dw), and that much copper in the diet was not enough to kill mayfly larvae (table 11).

Fish

Miller et al. (1992) extensively studied the relationship between concentrations of copper and zinc in water, sediment, invertebrates, and fish. For both copper and zinc, the water concentration was a better indicator of metal concentration in fish tissue than the sediment or invertebrate concentrations. In addition, they found kidney and liver concentrations to be better indicators of chronic copper and zinc

Table 10.—Biological effects of copper on aquatic species

Species	Cu concen-tration in water (µg/L)	Effect	Comments	Reference
Invertebrates				
Cladoceran (*Daphnia magna*) egg	10,000	Significant effect in development	46-h exposure; eggs more tolerant than adult	Bodar et al. 1989
	22	16% reproduction impairment	Chronic exposure	Nriagu 1979
	44	3 week LC50		
Cladocerans (*Daphnia ambigua, D. parvula, D. pulex*)	60	Significant drop in instantaneous rate of population growth	Chronic exposure	Nriagu 1979
Amphipod (*Gammarus pseudolimnaeus*)	4.6	No effect	Chronic exposure	Nriagu 1979
	8	Second-generation growth affected, but no effect in first generation		
Crayfish (*Orconectes rusticus*)	15	15% growth retarded	Chronic exposure	Nriagu 1979
Mayfly larvae (*Epeorus latifolium*)	5–10	No significant effect in growth rate	Temp. 12.5°C	Hatakeyama 1989
	15	Growth rate decreased during first 3 weeks but restored gradually after 4 weeks		
	20–25	Growth rate <7% of the control. 100% mortality by 10 weeks		
	100	83% mortality in 1 week	Temp. 11.5°C	
Midge larvae (*Chironomus tentans*)	327	48-h EC50; immobilization	Temp. 14°C; pH 6.3	Khangarot and Ray 1989
Invertebrates, general	9.7	Complete absence of Plecoptera, Ephemeroptera, Odonata, Trichoptera, Amphipoda, and Unionidae	Manitouwadge Lake, Ontario, Canada. Zn concentration 232 µg/L	Munkittrick et al. 1991
Fish				
Brown bullhead (*Ameiurus nebulosus*)	19	Increased mortality, reduced growth	Water hardness 187 and 38 mg/L	Nriagu 1979
	27	Cu in biomass (mg/kg dw): gill 6.9, liver 11, kidney 10	20-month exposure	
		Cu in biomass (ppm dw): gill 9.4, liver 33, kidney 10	30-d exposure; pH 7.2–8.2,	
Brook trout (*Salvelinus fontinalis*)	5	Reduced growth	Water hardness 38 mg/L	Nriagu 1979
	8	Reduced growth	Water hardness 187 mg/L	

Table 10.—Biological effects of copper on aquatic species—Continued

Species	Cu concentration in water (µg/L)	Effect	Comments	Reference
Fish—Continued				
Bluegill (*Lepomis macrochirus*)	400	96-h LC50 (if Zn present)	pH 6.8–7.5; temp. 22°± 1°C; Zn = 1400 µg/L	Thompson et al. 1980
	1,000	96-h LC50 (if Zn absent)	pH 6.8–7.5; temp. 16.5°–23°C; Zn = 0	
Chinook salmon fry (*Oncorhynchus tshawytscha*)	54	96-h LC50	In fresh water. Mean weight 0.87 g	Hamilton and Buhl 1990
	58	96-h LC50	In fresh water. Mean weight 0.66 g	
	60	96-h LC50	In brackish water. Mean weight 1.6 g	
	78	24-h LC50	In fresh water. Mean weight 1.60 g	
	81	24-h LC50	In brackish water. Mean weight 0.87 g	
	145	24-h LC50	In brackish water. Mean weight 0.66 g	
Chinook salmon (*Oncorhynchus tshawytscha*) eggs (to hatching)	26	28-d LC10s, based on various mixed solutions of Cu and Zn	Zn = dissolved Cu	Finlayson and Verrue 1980
	29		Zn = 6× dissolved Cu	
	40		Zn = 3× dissolved Cu	
	49		Zn = 11× total Cu	
	50		Zn = 6× total Cu	
	70		Zn = 3× total Cu	
Chinook salmon (*Oncorhynchus tshawytscha*) hatchlings to swim-up fry	14	28-d LC50s, based on various mixed solutions of Cu and Zn	Zn = 11× dissolved Cu	Finlayson and Verrue 1980
	20		Zn = 6× dissolved Cu	
	27		Zn = 11× total Cu	
	32		Zn = 3× dissolved Cu	
	37		Zn = 6× total Cu	
	56		Zn = 3× total Cu	
Coho salmon (*Oncorhynchus kisutch*)	60	96-h LC50	Smolts in May; temp. 10–12°C; hardness 68–78 *or* 89–99 mg/L (as $CaCO_3$)	Lorz and McPherson 1976
	74	96-h LC50	Yearlings in November; other conditions as above	
Fathead minnow (*Pimephales promelas*)	18	Reduced spawning and egg production, increased mortality	Water hardness 31 mg/L	Nriagu 1979
	33	Reduced egg production	Water hardness 198 mg/L	
	37	Reduced egg production	Water hardness 200 mg/L	

Table 10.—Biological effects of copper on aquatic species—Continued

Species	Cu concentration in water (µg/L)	Effect	Comments	Reference
Fish—Continued				
Neomacheilus barbatulus	760	Cu in biomass (mg/kg dw): gill 164, liver 115, muscle 8.5	64-d exposure; pH 8.6	Nriagu 1979
Rainbow trout (*Oncorhynchus mykiss*)	19	Reduced percent hatch and increased mortality	Water hardness: 100 mg/L	Nriagu 1979
Steelhead trout (*Oncorhynchus mykiss*) eggs (to hatching)	<10	60-d LC10s, based on various mixed solutions of Cu, Zn, and Al	Cu:Zn:Al = 1:12:18, dissolved copper	Finlayson and Ashuckian 1979
	19		Cu:Zn:Al = 1:12:18, total copper	
	19		Cu:Zn:Al = 1:4:6, dissolved copper	
	43		Cu:Zn:Al = 1:4:6, total copper	
Steelhead trout (*Oncorhynchus mykiss*) hatchlings to swim-up fry	<10	60-d LC10s, based on various mixed solutions of Cu, Zn, and Al	Cu:Zn:Al = 1:12:18, for both total and dissolved copper	Finlayson and Ashuckian 1979
	14		Cu:Zn:Al = 1:4:6, dissolved copper	
	36		Cu:Zn:Al = 1:4:6, total copper	
White sucker (*Catostomus commersoni*)	2.1	Control group; Cu in biomass (mg/kg dw): liver 50, muscle 7, stomach contents 7	Loken Lake, Ontario, Canada; Zn conc. 10 µg/L	Munkittrick et al. 1991
	9.7	Lowered growth rate; Cu in biomass (mg/kg dw): liver 83, muscle 6, stomach contents 155	Manitouwadge Lake, Ontario, Canada; Zn conc. 232 µg/L	
Amphibians				
Narrow-mouthed toad (*Gastrophryne carolinensis*)	40	17-d LC50	Adult	Birge and Black 1979
	50	3-d LC50	Tadpole	
Southern gray tree frog (*Hyla chrysoscelis*)	40	9-d LC50	Adult	Birge and Black 1979
	60	3-d LC50	Tadpole	
Leopard frog *(Rana pipiens*)	40	8-d LC50	Adult	Birge and Black 1979
	60	4-d LC50	Tadpole	
Marbled salamander (*Ambystoma opacum*)	70	8-d LC50	Adult	Birge and Black 1979
	359	4-d LC50	Tadpole	
Birds				
Mallard (*Anas platyrhynchos*)	10,000	No adverse effect	Juveniles	Foster and Ramsdell 1997

Table 11.—Summary of exposure-response or exposure-bioaccumulation of copper

Species	Cu concentration in diet (mg/kg dw)	Exposure duration	Cu concentration in biomass (mg/kg ww)	Effects	Reference
Food chain					
Woodlouse (*Porcellio scaber*)	200,000			No effect on survival	Beyer et al. 1984
Mayfly (*Epeorus latifolium*) adult	<590 (in algae)	8 weeks		No change in mortality or growth rate	Hatakeyama 1989
Mayfly larvae	1,140 (in algae)	1 week		50% decrease in growth rate. Slight increase in mortality.	
Fish					
Rainbow trout (*Oncorhynchus mykiss*)	3.5	9 weeks	Whole fish 1.8; liver 7.9		Julshamn et al. 1988
	102		Whole fish 3.0; liver 18		
	194		Whole fish 4.7; liver 35		
	405		Whole fish 6.2; liver 35		
	603		Whole fish 7.8; liver 91		
	810		Whole fish 9.8; liver 112	Slight increase in mortality rate	
	990		Whole fish 13.3; liver 149	Significant decrease in weight gain; significant increase in mortality	
	178	20 weeks	Liver 159	No effect. (Diet also had 683 mg Zn/kg dw)	Knox et al. 1982
Birds					
Chicken	>500			Growth retardation	Melring et al. 1959
Turkey	>50			Purified diet; reduced growth and survival	Waibel et al. 1963
	>800			Natural diet; no effects	
Mammals					
Rat	500	4 weeks		Reduced growth	Boyden et al. 1937
Domestic sheep (*Ovis aries*)	30–60	10 weeks		Decreased food consumption, weight loss, hemolytic crisis, increased mortality	Zervas et al. 1990

exposure than muscle. Nriagu (1979) reported that brook trout are especially sensitive to copper concentrations in water (table 10), and yet Knox et al. (1982) found that rainbow trout can tolerate relatively high dietary concentrations of copper (table 11). The different tolerance levels are likely due in part to varying toxicities of the copper species used in the two studies.

As shown in table 10, Nriagu (1979) reported reduced egg production in fathead minnows at relatively low copper concentra-tions in water. In addition, Miller et al. (1992) reported reduced growth in white sucker (*Catostomus commersoni*) females after sexual maturation, decreased egg size and fecundity, no significant increase in fecundity with age, and an increased incidence of spawning failure at waterborne copper concentrations of 15 µg/L and sediment concentrations of 93 mg/kg.

Amphibians

Amphibians are relatively sensitive to water-borne copper concentrations during the developmental stages (table 10) but are relatively tolerant to high copper burdens as adults and accumulate large amounts of copper in their livers (Hall and Mulhern 1984).

Birds

There are few studies available on the toxicity of copper to birds, but it appears that they tolerate copper better than most aquatic organisms do. NAS (1980) reported that 300 mg Cu/kg in the diet is the maximum tolerable level for poultry. This value may be used to estimate the safety levels for avian wildlife with the use of safety factors. Puls (1988) considered the toxic dietary level for ducks to be >200 mg/kg and noted that ducks accumulate more copper in the liver than do chickens or turkeys fed the same dietary levels. The maximum safe dietary levels of copper for growing chicks and turkeys were estimated to be 250 and 500 mg/kg, respectively, in the diet (Neathery and Miller 1977). Juvenile mallards could tolerate a copper concentration up to 10 mg/L in drinking water with pH greater than 4.0 without adverse health effects (Foster and Ramsdell 1997).

Mammals

Mammals, too, are relatively tolerant to copper compared to aquatic organisms. For most domestic mammals, the maximum recommended tolerable level of copper in the diet ranges from 100 to 800 mg/kg (NAS 1980). The level for sheep, however, was only 25 mg/kg. Zervas et al. (1990) found that 30 mg Cu/kg in the diet was toxic to sheep (table 11). General signs of copper toxicity in mammals are inhibition of growth, muscular dystrophy, anemia, impaired reproduction, and decreased longevity. Symptoms of copper poisoning are especially apparent when molybdenum content is low (Demayo et al. 1982). Small mammals such as shrews, mice, and voles may be useful biomonitors for copper, as shown in table 12 (Talmage and Walton 1991). In shrews, copper concen-trated in individual tissues in the order hair > liver > kidney > whole body (Hunter and Johnson 1982).

Bioaccumulation

In order to evaluate the cumulative toxicity of copper and other metals (As, Cd, Hg, Pb) along the food chain, Yannai et al. (1979) raised a large quantity of algae (*Micractinium* and *Chlorella*) on metal-rich waste water, fed the algae to chickens and carp, and then fed the meat of these chickens and carp to rats. They found that bioaccumulation did not increase the levels of any of these metals in chickens or carp except for chickens' livers (which contained higher copper than the livers of control chickens), and they observed no change in the general appearance, behavior, and survival of the rats that ate the chicken and carp meat. They concluded that such meat would pose no hazard to consumers.

Table 12.—Accumulation of copper in small mammals compared to copper concentrations in soils
[Data from Hunter and Johnson (1982)]

	Copper concentration (mg/kg, dry weight)	
Medium	**Uncontaminated site**	**Copper refinery site**
Soil	9.3	2,480
Wood mouse *(Apodemus sylvaticus*)	10.8	11.9
Kidney	13.4	23.7
Liver	6.5	14.7
Hair	8.5	6.9
Muscle		
Field Vole *(Microtus agrestis*)		
Kidney	10.8	22.6
Liver	13.4	13.5
Hair	6.5	24.2
Muscle	8.5	9.3
Shrew (*Sorex araneus*)		
Kidney	22.8	38.5
Liver	31.1	56.1
Muscle	10.9	17.4

Interactions

Mixtures of copper and zinc are known to be additive or synergistic in toxicity to many aquatic organisms. Finlayson and Verrue (1980) conducted long-term and short-term toxicity studies on Chinook salmon (*Oncorhynchus tshawytscha*) using various water concentrations of copper and zinc mixture. They estimated that safe levels of copper and zinc for Chinook salmon would be below 11 and 83 µg/L, respectively. For most animals, the severity of copper toxicity changes greatly depending on the copper: molybdenum ratios in their diet. Many studies have reported that when animals consume low levels of molybdenum in their diet, copper accumulates much faster and causes copper poisoning at lower concentrations. High concentrations of molybdenum, on the other hand, are known to induce copper deficiencies. A low-molecular-weight protein, metallothionein, also plays an important role in the transport, storage, and detoxification of copper (Hamilton and Mehrle 1986). Metallothionein synthesis is induced in most vertebrates and some plants when they are chronically or acutely exposed to copper and other heavy metals. It provides protection against copper by sequestering copper more efficiently.

Regulatory Standards

Standards and criteria established by the U.S. Environmental Protection agency are listed in table 13. For standards and criteria set by State agencies, contact those agencies directly. See Appendix I for a listing of water quality officials in the 17 Western States.

Table 13.—U.S. Environmental Protection Agency standards and criteria for copper

(See Appendix II for explanation of terms. Source: EPA, 1985, 1995)

Status	EPA priority pollutant; carcinogencity unknown
Drinking water MCL	1,300 µg/L (may vary with treatment technique)
Freshwater criteria (hardness dependent)[1]	
At hardness of 50 mg/L $CaCO_3$	9.2 µg/L for acute exposure 6.5 µg/L for chronic exposure
At hardness of 100 mg/L $CaCO_3$	18 µg/L for acute exposure 12 µg/L for chronic exposure
At hardness of 200 mg/L $CaCO_3$	34 µg/L for acute exposure 21 µg/L for chronic exposure

[1] Official criteria are given as hardness-dependent equations; values listed here are examples that result from these equations at the stated hardness levels. The criterion for acute exposure is equal to $e^{[0.9422\{\ln(\text{hardness})\}-1.464]}$; that for chronic exposure equals $e^{[0.8545\{\ln(\text{hardness})\}-1.465]}$.

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