ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

COPPER ENTRY

July 1, 1997

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Like a library or most large databases (such as EPA's national STORET water quality database), this document contains information of variable quality from very diverse sources. In compiling this document, mistakes were found in peer reviewed journal articles, as well as in databases with relatively elaborate quality control mechanisms [366,649,940]. A few of these were caught and marked with a "[sic]" notation, but undoubtedly others slipped through. The [sic] notation was inserted by the editors to indicate information or spelling that seemed wrong or misleading, but which was nevertheless cited verbatim rather than arbitrarily changing what the author said.

Most likely additional transcription errors and typos have been added in some of our efforts. Furthermore, with such complex subject matter, it is not always easy to determine what is correct and what is incorrect, especially with the "experts" often disagreeing. It is not uncommon in scientific research for two different researchers to come up with different results which lead them to different conclusions. In compiling the Encyclopedia, the editors did not try to resolve such conflicts, but rather simply reported it all.

It should be kept in mind that data comparability is a major problem in environmental toxicology since laboratory and field methods are constantly changing and since there are so many different "standard methods" published by EPA, other federal agencies, state agencies, and various private groups. What some laboratory and field investigators actually do for standard operating practice is often a unique combination of various standard protocols and impromptu "improvements." In fact, the interagency task force on water methods concluded that [1014]:

> It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...
>
> No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

Differences in field and laboratory methods are also major issues related to (the lack of) data comparability from media other than water: soil, sediments, tissues, and air. For additional information on data variability, see Laboratory and/or Field Analyses section below.

In spite of numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of a broad universe of conflicting results or conflicting expert opinions rather than having a portion of this information arbitrarily censored by someone else. Frequently one wants to know of the existence of information, even if one later decides not to use it for a particular application. Many would like to see a high percentage of the information available and decide for themselves what to throw out, partly because they don't want to seem uniformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it simply means that during our efforts, the editors found none. For many topics, there is probably information "out there" that is not in the Encyclopedia. The more time that passes without encyclopedia updates (none are planned at the moment), the more true this statement will become. Still, the Encyclopedia is unique in that it contains broad ecotoxicology information from more sources than many other reference documents. No updates of this document are currently planned. However, it is hoped that most of the information in the encyclopedia will be useful for some time to come even with out updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

> The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

> **Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese**, and **W. Basham.** 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an

Electronic Document (Projected public availability
on the internet or NTIS: 1998).

Copper (Cu, CAS number 7440-50-8)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

The chemical element copper is a reddish metal [280]. Copper is widely distributed in nature in the elemental state, in sulfides, arsenites, chlorides, and carbonates; Copper is only superficially oxidized in air, sometimes giving a green coating of hydroxy carbonate and hydroxy sulfate [366].

Copper exhibits oxidation states of +2 (the most common, forming Cu(II) compounds), and +1 (Cu(I), stable only in aqueous solution if part of a stable complex ion) [280]. A few compounds of copper(III) are also known [280].

Copper is listed by the Environmental Protection Agency as one of 129 priority pollutants [58]. Copper is a toxic pollutant designated pursuant to section 307(a)(1) of the Clean Water Act and is subject to effluent limitations (40 CFR 401.15, 7/1/88) [609].

Copper sulfides have gotten quite a bit of attention in environmental toxicology related to their tendencies to bind copper in the sediments and the relationship of sulfides to acid mine drainage. The primary ores of copper are chalcopyrite ($CuFeS2$) and chalcocite ($Cu2S$) [495].

Br.Haz: General Hazard/Toxicity Summary:

Bionecessity:

Although copper in water is a hazard to many aquatic organisms, minute amounts of copper in the diet are needed for human, plant, and animal enzymes (serving as enzyme activators) [173,180,280,951]. Copper is an important trace element in plant metabolism [180].

Potential Hazards to Fish, Wildlife, Invertebrates, Plants,and other Non-Human biota:

Although an essential dietary element for some plants and animals, high concentrations of copper in water can be toxic to fish and other aquatic species [25,83,366]. Elevated concentrations of copper in water are particularly toxic to many species of algae, crustaceans, annelids, cyprinids, and salmonids [180].

Copper can be toxic in large quantities, especially to lower organisms such as bacilli, fungi, and algae [280]. Copper's aquatic toxicity of often due to disruption of internal ion balance [177] (Confirmed by David Mount, National Biological Service, Columbia, MO, personal communication, 1994).

Copper sensitivity demonstrated by phytoplankton and zooplankton can vary seasonally in ways not explained by concentrations of dissolved organic carbon or hardness. Ceriodaphnia dubia at times is less sensitive to copper toxicity than are other pond organisms and therefore should not be used to set copper standards (Robert Winner, University of Wyoming, personal communication).

In western watersheds affected by metals, fish kills are often associated with runoff and rainstorm events. Metals responsible for toxicity are often copper and zinc, whose toxicity and/or mobility are enhanced by the depressions of pH, hardness/alkalinity, and dissolved organic carbon that typically accompany these events (David Mount, National Biological Service, Columbia, MO, personal communication, 1994).

Large fish are often 2.5 to 3 times more resistant to copper than juveniles [25]. As most adult fish are able to tolerate relatively high concentration of copper for short periods of time, the critical effect of copper is its greater toxicity to younger fish [302].

Temperature produces complex effects, but elevated thermal levels increase fish sensitivity to Cu. Moreover, death of fish is not related to a specific Cu level accumulated by any one of several tissues normally examined, as may be the case of zinc and Cd. This may be due to differential accumulation of different species of Cu (that is, toxic and non-toxic Cu species). Alternatively, in whole body uptake studies, non-specific epidermal binding of Cu might mask the specific binding occurring in a target organ prior to death [488].

Increased salinity and increased hardness protect fish from copper (Cu) poisoning; however, pH, alkalinity, organic level, temperature, fish size, and other factors also play important roles in Cu poisoning of fish. Generally, the greater the hardness, alkalinity, salinity, organic level, pH, and fish size, the more resistant fish are to Cu [488].

Although hardness is widely recognized to affect aquatic toxicity of metals (for example, hardness seems somewhat protective of rainbow trout related to copper and zinc toxicity), pH often has the largest effect on metals toxicity [25,39] (Confirmed by David Mount, National Biological Service, Columbia, MO, personal communication, 1994).

For many metals, alkalinity is sometimes a more important co-factor for toxicity than hardness (Pat Davies, Colorado Division of Wildlife, personal communication, 1997). A water's alkalinity directly affects the toxicity of copper to aquatic life, which generally is augmented at lower alkalinities [375,383]. However, recent (1992) data suggests hardness may not be as important for toxicity of copper to aquatic life as is implied in the EPA Gold Book [302]; using currently available water chemistry data it is not possible to accurately predict copper toxicity in water, especially chronic toxicity (Robert Winner, University of Wyoming, personal communication).

As most adult fish are able to tolerate relatively high concentration of copper for short periods of time, the critical effect of copper is its greater toxicity to younger fish [302].

Some researchers believe that negative effects of copper on fish are more likely the result of toxicity of high concentrations in water than toxicity from intake of prey containing copper [25]. However, in all animals studied, continued ingestion of copper in excess of dietary requirements led to some accumulation in tissues, particularly the liver and kidneys [180]. Fish living or foraging in contaminated sediments may accumulate it directly from the sediments [95]. Excess copper accumulation can lead to copper toxicosis and cell damage [180].

In water, copper acts synergistically with other common urban contaminants such as ammonia, cadmium, mercury, and zinc to produce an increased toxic effect on fish [26,47]. Sublethal concentrations adversely affect minnow fry survival and growth [57].

Sorensen provided a chapter on copper in a 1991 book on metal poisoning in fish [488]. Generally, fresh-water species are more sensitive to metals than are marine species; however, this is not true in cases of Cu-poisoning in fish. Reasons for equal sensitivity of markedly different species has not been elucidated. Nor have explanations been given for the pronounced species-specific differences in Cu accumulation levels, which seem to involve capability for iso-metallothionein synthesis and hepatic storage of Cu [488].

Copper sulfate was one of the first weed killers, used as long ago as 1882 [492].

Resistance/Development of Tolerance:

Populations of organisms chronically exposed to chemical pollutants may develop increased tolerance to those pollutants [177,493]. Many of the aquatic issues related to tolerance, interactions with other metals, and/or indirect impacts related to copper were summarized by Rand and Petrocelli [177].

In some Colorado settings, net spinning caddisflies were shown to be more sensitive to predation when copper is present (Will Clements, Colorado State University, personal communication). Thus, direct toxicity is only one of the many types of impact which copper can have on aquatic life, and some of the indirect forms of impact relate to tolerance mechanisms.

Absorption of dietary copper in higher animals is apparently regulated in part by metallothioneins (low molecular weight proteins containing high levels of cysteine) [180]. Increased synthesis of metallothionein in response to copper exposure may help animals acquire a somewhat increased tolerance of this metal [180].

Some grasses around copper polluted areas are copper tolerant [366].

Potential Hazards to Humans:

Copper poisoning or deficiency problems are rare in humans [173].

It is generally agreed that copper itself is less toxic than its salts (Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 147) [609].

The fumes and dust cause irritation of the upper respiratory tract, and will also cause irritation of the eyes, nose and throat [609]. Fumes from the heating of metallic copper can cause nausea, gastric pain, & diarrhea in humans (International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 547) [609].

Copper sulfate was used as one of the first food colors, and copper gluconate is still used as a food additive [492].

The ATSDR Toxicological Profile for Copper (1990) (ATSDR/TP-90/08) summarizes human health effects of copper [979]. In humans, some oral intake of copper is necessary for good health, but massive doses can cause problems, especially for children [979]. Due to lack of time, not all of the important highlights of the ATSDR document [979] have been summarized herein.

Br.Car: Brief Summary of Carcinogenicity/Cancer Information:

Information from the Integrated Risk Information System (IRIS) OF EPA 1996 [893]:

Evidence for classification as to human carcinogenicity; weight-of-evidence classification:

Classification: D; not classifiable as to human carcinogenicity

BASIS: There are no human data, inadequate animal data from assays of copper compounds, and equivocal mutagenicity data.

HUMAN CARCINOGENICITY DATA: None.

ANIMAL CARCINOGENICITY DATA: Inadequate.

According to the ASTDR, in humans copper is not known to cause cancer [979].

Br.Dev: Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

The large number of Cu-containing enzymes and glycoproteins in fish probably accounts for the diversity of biological effects--effects spanning practically every system evaluated in the teleost (that is, group consisting of fishes with bony skeletons and rayed fins). Hematology is altered, as is respiratory and cardiac physiology. Copper-induced histological alterations are found in the gill, kidney, hematopoietic tissue, mechanoreceptors, chemoreceptors, and other tissues

[488].

Reproductive effects are noted at low levels of Cu and include blockage of spawning, reduced egg production per female, abnormalities in newly-hatched fry, reduced survival of young, and other effects. From most studies, growth and survival are affected at higher Cu levels than are reproductive changes. Copper poisoning of surface waters is considered hazardous to teleost life in those ecosystems; levels of ≥4 ppb can severely alter migratory and other behaviors. In view of the chronic bioaccumulation of Cu and the many effects observed in Cu-exposed fish, revision of existing water quality standards for Cu seems prudent [488].

Highly localized deposits of hepatic and renal copper have been observed in monkeys with copper IUDs and in control monkeys. Both copper and inert material IUDs have been observed to increase plasma copper levels. This may be explained by the observation that stress or inflammation alone can result in increased serum copper levels [25].

Incubation of human spermatozoa with metallic copper is found to bring about a significant fall in the percentage of motile sperm in humans (Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B., eds. Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 247) [609].

For fathead minnows, the percentage of embryos with abnormalities was greater at 338 and 621 ug/l total copper concentration than at 204 ug/l total copper and lower concentrations (Scudder BC et al; Aquat Toxicol, AMST, 12 (2): 107-24, 1988) [609] (see W.Fish section below for more information).

The data on the effects of cations such as copper, cadmium, and chromium on the biochemical parameters in a freshwater fish, Clarias batrachus, showed an increase of the protein content in the liver, kidney, stomach, intestine, testis, and ovary, and a decrease in the muscle after copper and cadmium treatment. The administration of copper and cadmium increased the concentration(s) of free amino acids in all the fish organs, whereas chromium did not change this concentration(s) in the muscle. A decrease in dry wt, and an increase in tissue permeability after these treatments were recorded in all the organs studied. In general, the above biochem parameters of the organs were affected by treatments of the above cations in the following order: cadmium > copper > chromium over control values of C batrachus, and their effects were markedly pronounced in the liver and kidney, followed by the intestine, stomach, muscle, testis, and ovary in this species (Jana S, Sahana SS; Physiol Bohemoslov 37, 1: 79-82., 1988) [609].

Br.Fate: Brief Summary of Key Bioconcentration, Fate, Transport, Persistence, Pathway, and Chemical/Physical Information:

Copper is tightly bound to ligand sites, containing oxygen, sulfur, or nitrogen atoms on the protein [280]. Many higher organisms can conserve copper when it is deficient and excrete it when an excess amount enters the body [180]. Freshwater fish can regulate copper over a wide range of ambient concentrations [180].

Highway runoff routed through a detention pond and then a cypress wetland resulted in much higher sediment levels of copper in the detention pond than in the wetland [220]. The same study indicated that copper deposits near the outlet of a freshwater wetland were lower than those in the middle [220].

More research needs to be done on the toxicity, mobilization, and bioavailability of copper in low alkalinity and/or low pH waters [383].

Plants take up copper from soil [83].

When sulfide is present, as it is in estuarine sediments rich in organic debris, it will combine with metals such as copper, cadmium, zinc, and lead. The metal sulfides that form are highly insoluble and will tend to be sequestered in the sediments (Bender M, 1989, Heavy metals in Narragansett Bay sediments. Maritimes, 33, 4: 5-7. Off. Mar. Programs, Mar. Resour. Build., URI Narragansett Bay Campus, Narragansett, RI 02882-1197, USA) [940].

In 1985, Hem updated a summary of many basic water quality issues related to this element, including its sources and species, solubility controls, and its occurrence in natural water [190].

Environmental Fate Summaries from HSDB [609]:

> AQUATIC FATE: Some copper complexes may be metabolized /however/ there is no evidence that biotransformation processes have a significant bearing on the aquatic fate of copper. /Copper salts and complexes/ [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 11-16].

TERRESTRIAL FATE: Factors affecting the balance between copper in the parent rock & in the derivative soil include the degree of weathering, the nature & intensity of the soil formation, drainage, pH, oxidation-reduction potential, & the amount of organic matter in the soil. Since copper in rocks is likely to be more mobile under acidic than alkaline conditions, the relation of pH to copper in the environ has been of great concern to agriculturalists & biologists. Alkaline conditions in the soil & the surface water favor precipitation of copper. Acid conditions promote solubility of copper, increase the concentration(s) of ionic copper, & thereby change the microorganism & other aquatic animal populations, depending on tolerance for various levels of copper in solution. The reports of acid rain in various parts of the world are of serious concern. Due to the variety of conditions which influence the metal's avail, the total copper content of the soils is not an accurate indication of deficiencies or excess of copper in soil rooted plants. /Copper salts/ [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 273].

Synonyms/Substance Identification:

1721 GOLD [609]
ALLBRI NATURAL COPPER [609]
ANAC 110 [609]
ARWOOD COPPER [609]
BRONZE POWDER [609]
CDA 101 [609]
CDA 102 [609]
CDA 110 [609]
CDA 122 [609]
CI 77400 [609]
CI PIGMENT METAL 2 [609]
COPPER BRONZE [609]
COPPER M 1 [609]
COPPER POWDER [609]
COPPER SLAG-AIRBORNE [609]
COPPER SLAG-MILLED [609]
COPPER-AIRBORNE [609]
COPPER-MILLED [609]
CU M3 [609]
GOLD BRONZE [609]
KAFAR COPPER [609]
M 1 [609]
M 3 [609]
M 4 [609]
M1 (COPPER) [609]

M2 (COPPER) [609]
M3 (COPPER) [609]
M3R [609]
M3S [609]
M4 (COPPER) [609]
OFHC CU [609]
RANEY COPPER [609]
Caswell No 227 [609]
CE 1110 [609]
Copper, Metallic Powder [609]
E 115 (metal) [609]
EPA Pesticide Chemical Code 022501 [609]
Cuprum (Latin) [609].

Molecular formula [609]:
Cu

Associated Chemicals or Topics (Includes Transformation Products):

See also individual metals entries which are important because of interactions with copper:

Cadmium
Mercury
Zinc

Copper usually occurs as part of the oxidizing enzymes such as ascorbic acid oxidase, tyrosinase, lactase, and monoamine oxidase [280]. These enzymes, which are high-molecular-weight proteins containing 0.05%-0.35% of Cu, play an important part in living oxidation and reduction reactions, in which the copper undergoes cyclic changes between Cu(I) and Cu(II) oxidation states [280].

Toxic compounds in distilled water, frequently copper, may result in low BOD [861].

Metabolism/Metabolites [940]:

Transition metals (such as copper) are known to catalyze lipid peroxidation, possibly forming free radicals. However, copper is usually incorporated into stable complexes within cells or vascular fluids. [USEPA; Drinking Water Criteria Document for Copper (Final Draft) p.VII-1 (1985) EPA-600/X-84-190-1].

Copper is incorporated into >12 specific copper proteins, such as cytochrome oxidase, tyrosinase, and erythrocyte superoxide dismutase. Copper is essential for hemoglobin formation, carbohydrate metabolism, catecholamine biosynthesis, and cross-linking of collagen, elastin, and hair keratin. Other metals such as zinc, iron, and molybdenum interact with copper to affect copper absorption, distribution, metabolism, and utilization. [USEPA; Health Issue Assessment: Copper p.3 (1987) EPA/600/8-87/001].

Impurities [609]:

In electrolytic copper, the highest level of impurities other than oxygen are found only to the extent of 15-30 ppm. Up to 0.05% oxygen is present in the form of copper(I) oxide. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 6(79) 859].

Impurity with corresponding range: Antimony, 1-20 ppm; arsenic, 1-10 ppm; bismuth, 0.1 to 5 ppm; lead, 3-50 ppm; iron, 5-25 ppm; nickel, 4-40 ppm; tellurium, 1-15 ppm; tin, 2-15 ppm [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 6(79) 862].

Water Data Interpretation, Concentrations and Toxicity (All Water Data Subsections Start with "W."):

W.Low (Water Concentrations Considered Low):

Leland and Kuwabara, 1985: In non-polluted areas, baseline concentrations as low as 0.0003 mg/l have been recorded [177].

Very low concentrations are usually the result of pH and other physical/chemical factors [190].

W.High (Water Concentrations Considered High):

In polluted areas, baseline concentrations as high as 100 ug/l have been recorded [190].

Leland and Kuwabara, 1985: In polluted areas, concentrations as high as 9 mg/l have been recorded [177].

While experiments show that copper does not leach significantly from soil, levels of copper as high as 2.8 ppm have been found in some groundwater [979].

Copper concentrations in wastewater from a selected open pit and underground copper mine were 1.05 ppm and 0.87 ppm, respectively [979]. Results of an EPA industrial effluent survey show that mean and maximum levels of copper in treated wastewater from six industries exceeded 1 and 10 ppm, respectively [979]. These industries and their mean and maximum discharges in ppm are: inorganic chemicals manufacturing (less than 1.6, 18); aluminum forming (less than 160, 2200); 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 (less than 1.0, 60.0) [979].

W.Typical (Water Concentrations Considered Typical):

USGS 1985: Levels near 10 ug/L can be commonly expected in river water [190]. Very low concentrations are usually the result of pH and other physical/chemical factors [190].

Median for Treated Drinking Water: 8.3 ug/L [190].
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 as a result of wet deposition [979]. For central and northern Ontario, the mean concentrations of copper in rain were 1.36 and 1.58 ppb, respectively [979].

The median concentration of copper in natural water is 4-10 ppb [979]. It is predominantly in the Cu(II) state [979]. Most of it is complexed or tightly bound to organic matter; little is present in the free (hydrated) or readily exchangeable form [979]. The combined processes of complexation, adsorption, and precipitation control the level of free Cu(II) [979]. 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 [979].

Copper in wastewater discharged into a river leading into Chesapeake Bay, MD, contained 53 ppb of copper, of which 36 ppb were in the form of settleable solids [979]. The concentration of copper rapidly decreased downstream of the outfall; 2-3 km from the outfall, the copper concentration had fallen to 7 ppb [979]. The concentration of copper in sediment downstream from the outfall was about a factor of 10 higher than in uncontaminated 6 [979].

Geometric mean from Storet Database, surface waters: 4.2 ppb [979].

Median concentration from Storet Database, surface waters: 4.0 ppb [979].

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 ug/L (ppb) [979]. Of the 71 priority pollutants analyzed for, copper, along with lead and zinc, was the most frequently detected [979]. The geometric mean copper concentration in runoff water was 18.7 ug/L [979].

Concentrations of copper in influents to 239 wastewater treatment plants (12,351 observations) were 0.0001-36.5 ppb [979]. and the median value was ~0.4 ppb [979].

Typical Ocean Concentrations:

> EPA 1981: 0.003 mg/l [83], sometimes lower or higher [177].
>
> Copper is present to the extent of 0.020-0.001 parts per million in seawater [280,366].

Typical Freshwater Concentrations:

> EPA 1981: 0.01 mg/l [83].
>
> In an Arizona intermittent stream, copper was less than 0.05 mg/l above an open-pit copper mine outfall and 0.09 mg/l below the outfall [221].
>
> California, 1986: Ambient background level for water was 0.001 mg/l [222].

The average concentration of copper in tap water ranges from 20 to 75 parts copper per billion parts water (ppb) [979]. However, many households have copper concentrations of over 1000 ppb [979]. That is more than 1 milligram per liter of water [979]. This is because copper is picked up from copper pipes and brass faucets when the water sits in the pipes overnight [979]. After the water is allowed to run for a while, the concentration of copper in the water decreases [979]. The average concentration of copper in lakes and rivers is 4 ppb [979]. The average copper concentration in groundwater is similar to that in lakes and rivers; however, monitoring data indicate that some groundwater contains higher levels of copper [979]. This copper is generally strongly attached to particles in the water [979].

Effluents from power plants that use copper alloys in the heat exchangers of their cooling systems discharge copper into the receiving waters [979]. The largest discharges occur after start-up and decrease rapidly thereafter [979]. At the Diablo Canyon Nuclear Power Station, a very high start-up discharge containing 7700 ppb of copper fell to 67 ppb after 24 hours [979]. During normal operation at two nuclear power stations, copper levels ranged between 0.6 and 3.3 ppb [979].

Information from HSDB [609]:

DRINKING WATER: Because the concentration of copper in drinking water is highly variable, means are of limited significance. Approx 55% of the 604 water samples analyzed by the USEPA (1975) contained measurable levels of copper. The mean of these samples was 60 ug/l. The mean of another study was 150 ug/l. /Copper salts and copper (II) oxides/ [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 313] [609].

DRINKING WATER: Very large variations may occur depending on type of water, eg, hardness & pH, & types of pipes & taps. Concentrations from a few micrograms to more than 1 mg/l have been reported ... . /Copper salts and copper (II) oxides/ [Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. (eds). Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 236] [609].

A combination of low pH and soft water passing through copper pipes and fittings may produce high copper levels in drinking water; however, only a little over 1% of USA drinking water exceeds the drinking water standard of 1 mg/l, with the avg copper concentration(s) in drinking water reported as approx 0.13 mg/l. ... Background concentration(s) of copper in USA surface waters is < 20 ug/l. /Copper salts and Copper(II) oxides/ [USEPA; Health Issue Assessment: Copper p.22 (1987) EPA/600/8-87/001] [609].

Water particularly water that is acidic, low in hardness and alkalinity, and consequently corrosive to piping, may leach copper from drinking water pipes. /Soluble copper salts and copper(II) oxides/ [USEPA; Drinking Water Criteria Document for Copper (Final Draft) p.II-12 (1985) EPA-600/X-84-190-1] [609].

A study was conducted on the distribution of manganese, iron, copper, lead, and zinc in the water and sediment of Kelang esturary in 1981. The mean total levels of manganese, iron, copper, lead, and zinc in the estuarine water were 27.1 ug/l, 106.5 g/l, 10.0 ug/l, 4.1 ug/l and 17.9 ug/l respectively. The results indicate that Kelang estuary is polluted with lead, manganese, and iron. However, levels of these heavy metals may still be considered safe for aquaculture, if the farm is located at least 10 km away from the river mouth.

[Law AT, Singh A; Pertanika 9 (2): 209-18 (1986)] [609]

W.Concern Levels, Water Quality Criteria, LC50 Values, Water Quality Standards, Screening Levels, Dose/Response Data, and Other Water Benchmarks:

W.General (General Water Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Water Concentrations Versus Mixed or General Aquatic Biota):

Notes on total vs. acid soluble vs. dissolved metals:

Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, some regulatory authorities nevertheless recommend comparing criteria with dissolved or acid soluble metals concentrations. EPA gave many reasons why water quality criteria should be compared to acid soluble values [25]. For detailed discussion, see the Laboratory and/or Field Analyses section (far below).

EPA 1996 IRIS database information [893]:

Clean Water Act (CWA) Ambient Water Quality Criteria for Aquatic Organisms [893]:

Acute Freshwater Criterion: 9.2E+0 ug/L hardness dependent [893].

The equation is acute = e to the power of (0.9422[ln(hardness)]-1.464) [649]. Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Older published freshwater acute criteria was 18 ug/L, hardness dependent criterion rounded to two integers (100 mg/L CaCO3 used)

[446,689].

Chronic Freshwater Criterion: 6.5E+0 ug/L hardness dependent [893].

Older Freshwater Chronic Criteria was 12 ug/L, a hardness dependent criterion rounded to two integers (100 mg/L CaCO3 used) [689]. The equation is chronic = e to the power of (0.8545[ln(hardness)]-1.465) [649].
Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Marine Acute Criterion: 2.9E+0 ug/L [446,893].

Marine Chronic Criterion: None Published [893].

NOTE: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest one. Work on the replacement for the Gold Book [302] was underway in March of 1996, and IRIS is updated monthly [893].

Oak Ridge National Lab, 1994: Ecological Risk Assessment Freshwater Screening Benchmarks for concentrations of contaminants in water [649]. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks [649]:

For CAS 7440-50-8 (Copper, the benchmarks in ug/L are [649]:

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 18

The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration).

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: 12

The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration).

SECONDARY ACUTE VALUE: No information found

SECONDARY CHRONIC VALUE: No information found

LOWEST CHRONIC VALUE - FISH: 3.8

LOWEST CHRONIC VALUE - DAPHNIDS: 0.23

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: 6.066

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 1

LOWEST TEST EC20 - FISH: 5

LOWEST TEST EC20 - DAPHNIDS: 0.205

SENSITIVE SPECIES TEST EC20: 0.26

Other Concern Levels for Water Concentrations:

EPA's original 1980s permissible concentration(s) of total recoverable copper in water to protect freshwater aquatic life was 5.6 ug/l as a 24 hr avg. The log of this concentrtion should not exceed the numerical value of log (0.94 In (sic) (hardness) -1.23). The corresponding value to protect saltwater aquatic life is 4.0 ug/l as a 24 hr avg, and should not exceed 23 ug/l at any time [25,609].

NOTE: Recent (1992) data suggests hardness may not be as important for toxicity of copper to aquatic life as is implied in the gold book; using currently available water chemistry data it is not possible to accurately predict copper toxicity in water, especially chronic toxicity (Robert Winner, University of Wyoming, personal communication).

Florida's water quality standard applied to some wetland sites was 30 ug/l [220].

A State of California recommendation based on direct toxicity was that 1.2 ug/L be the water quality criteria (1.4 ug/l was one adverse effects level) [222].

W.Plants (Water Concentrations vs. Plants):

LC50 for Enteromorpha sp. (green algae) is 9.9 ug/L (ppb) for a 5-day exposure [998].

LC50s for Scenedesmus dimorphus (green algae) were 76.9 ug/L for a 24-hr exposure, 61.7 ug/L for a 6-day exposure, and 91.8 ug/L for a 15-day exposure [998].

Copper (copper sulfate) is used in aquatic herbicides, and copper concentrations as low as 1 ug/L have been shown to inhibit growth of aquatic plants [25]. Some of the highest bioconcentration factors recorded for copper are for the freshwater alga Chlorella regularais [25].

Shallow Groundwater Ecological Risk Assessment Screening Benchmark for Terrestrial Plants Listed by Oak Ridge National Lab, 1994 [651]:

To be considered unlikely to represent an ecological risk, field concentrations in shallow groundwater or porewater should be below the following benchmark for any aqueous solution in contact with terrestrial plants. Toxicity of groundwater to plants may be affected by many variables (pH, Eh, cation exchange capacity, moisture content, organic content of soil, clay content of soil, differing sensitivities of various plants, and various other factors). Thus, the following solution benchmark is a rough screening benchmark only, and site specific tests would be necessary to develop a more rigorous benchmark for various combinations of specific soils and plant species [651]:

For CAS 7440-50-8, COPPER, the Benchmark is 0.03 mg/L (porewater or groundwater).

W.Invertebrates (Water Concentrations vs. Invertebrates):

LC50s for Acartia tonsa (Calanoid copepod) were 17, 17, 31, 55 and 64 ug/L (ppb) for 96-hr exposures [998].

LC50s for Amnicola sp. (Spire snail) were 1.50 and

4.50 mg/L (ppm) for 24-hr exposures and 9.30 and 0.90 mg/L (ppm) for 96-hr exposures [998].

LC50s for Artemia salina (brine shrimp) were 0.80 mg/L for a 24-hr exposure and 0.44 mg/L for a 48-hr exposure [998].

LC50s for Balanus improvisus (barnacle) were 0.14 mg/L for a 12-hr exposure, 0.11 mg/L for a 24-hr exposure, and 0.10 mg/L for 48-, 72-, and 96-hr exposures [998].

LC50s for Brachionus calyciflorus (rotifer) were about 30 ug/L (ppb) for 24-hr exposures [998].

LC50s for Calanoida (copepod order) were about 52 ug/L (ppb) for 96-hr exposures [998].

LC50s for Ceriodaphnia dubia (water flea) were: 649 ug/L (ppb) for a 24-hr exposure; 17 to 406 ug/L for a 48-hr exposure, with most between 20 and 80 ug/L; 302 ug/L for a 5-day exposure; and 192 ug/L for a 10-day exposure [998].

24-hr LC50s were 3.16 to 23.6 mg/L (ppm) for Chironomus plumosus (midge), 3.40 to 13.43 mg/L for Chironomus riparius (midge), and 2.70 to 10.10 mg/L for Chironomus tentans (midge) [998].

96-hr LC50s were 0.53 to 2.20 mg/L (ppm) for Chironomus plumosus (midge), 0.64 to 1.27 mg/L for Chironomus riparius (midge), and about 0.50 mg/L for Chironomus tentans (midge) [998].

LC50s for Crangon crangon (common shrimp) were 10.0 to 33.0 mg/L for 48-hr exposures [998].

LC50s for Crassostrea rhizophorae (mangrove oyster) were 40.0 mg/L for a 5-day exposure and 2.5 mg/L for a 7-day exposure [998].

LC50s for Daphnia magna (water flea) ranged from 24 to 96 ug/L (ppb) for 48-hr exposures, with most below 55 ug/L [998].

LC50s for Daphnia pulicaria (water flea) ranged from 7.24 to 627 ug/L (ppb) for 48-hr exposures, with most below 85 ug/L [998].

LC50 for Lamellidens marginalis (mussel) was 5.00 mg/L (ppm) for a 96-hr exposure [998].

LC50s for Tubifex tubifex (Tubificid worm) were 0.4 ug/L (ppb) for a 12-hr exposure, 0.21 ug/L for a

48-hr exposure, and 0.15 ug/L for a 5-day exposure [998].

Acute values are as low as 6.5 ug/L for Daphnia magna in hard waters [25].

Estuarine clams were exposed to copper or mercury at 300 or 600 ug/l for 96 hr and the toxic effects evaluated by determining tissue carotenoids, lactic acid and glycogen contents; with carotenoids increasing, lactic acid increasing, and glycogen levels decreasing in the metal exposed claims compared to the controls. During the 1st 48 hr of exposure, the metabolic rates of the clams were decreased by both metals; some adaptation of the clams occurred during the next 48 hr (Sathyanathan B et al; Bull Environ Contam Toxicol 40 (4): 510-16, 1988) [609].

See also the below W.Misc section.

W.Fish (Water Concentrations vs. Fish):

Water copper levels of ≥4 ppb can severely alter migratory and other behaviors of teleost fish [488]. In view of the chronic bioaccumulation of Cu and the many effects observed in Cu-exposed fish, revision of existing water quality standards for Cu seems prudent [488].

LC50s for Osteichthyes (bony fish class) were 14 to 3120 ug/L (ppb) for 48-hr exposures, and 8.7 to 1130 ug/L for 96-hr exposures [998].

LC50s for Pimephales promelas (fathead minnow) ranged from 0.0885 to 21.0 mg/L (ppm) for 96-hr exposures, and was 0.070 mg/L for a 7-day exposure [998].

LC50s for Atherinops affinis (topsmelt) were about 0.235 mg/L (ppm) for 96-hr exposures, and ranged from 0.134 to 0.365 mg/L for 7-day exposures [998].

The no-observed-effect-concentrations (NOEC) for death of topsmelt were 90 to 160 ug/L (ppb) for 96-hr exposures, and 100 and 180 ug/L for 7-day exposures [998].

LC50 for Channa striata (snake-head catfish) was 12.4 mg/L (ppm) for a 72-hr exposure [998].

LC50s for Oncorhynchus mykiss (rainbow trout, donaldson trout) were 130 ug/L for a 24-hr exposure and 250 ug/L for a 96-h exposure [998].

Information from HSDB [366]:

> Embryos of the fathead minnow, Pimephales promelas Rafinesque, were exposed to total copper concentrations of 0.6, 61, 113, 204, 338, and 621 ug/l from 5 to 10 hr post fertilization through 2 days post hatch. A decrease in hatching time was observed with increasing total copper concentration but there was no decrease in embryonic developmental rate. Therefore, embryos hatched at earlier stages of development. Significant (p= 0.05) declines in percent survival and percent total hatch were observed at 621 ug/l total copper concentration(s) but not at 338 ug/l total copper concentration(s) or lower concentrations. The percentage of embryos with abnormalities was greater at 338 and 621 ug/l total copper concentration(s) than at 204 ug/l total copper concentration(s) and lower concentrations. Individuals exposed to copper during early development were then exposed to the same test concentrations for 28 days post hatch. Survivors at 113 through 338 ug/l total copper concentration(s) were at earlier stages of development than were control fish. The percentage of fish surviving decreased with increasing copper concentration over the range 61 through 204 ug/l total copper concn. The percentage of fish surviving at 204 ug/l total copper concentration(s) was not significantly different from that at 338 ug/l total copper concn. Surviving larvae at all copper concentrations from 61 through 621 ug/l total copper concentration(s) showed decreased length, weight, and coefficient of condition compared to controls. The percentage of larvae with abnormalities increased significantly with increasing copper concentration. The calculated 96 hr LC50 (larval stage) was 250 ug/l total copper concentration(s) and the 28 day LC50 (larval stage) was approximately 123 ug/l total copper concn. [Scudder BC et al; Aquat Toxicol (AMST) 12 (2): 107-24 (1988)]

W.Wildlife (Water Concentrations vs. Wildlife or Domestic Animals):

To protect livestock/cattle use, general irrigation water should not exceed 0.2 ppm copper in coarse soils or 5 ppm in firm soils [671].

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (see Tis.Wildlife, B) section below for these). To be considered unlikely to represent an ecological risk, water concentrations should be below the following benchmarks for each species present at the site [650]:

For CAS 7440-50-8, COPPER AS COPPER SULFATE, the benchmarks are:

SPECIES	WATER CONCENTRATION (ppm)
Mink (test species)	0.00000
Short-tailed Shrew	212.82600
Little Brown Bat	367.84600
White-footed Mouse	137.54200
Meadow Vole	240.72400
Cottontail Rabbit	114.06500
Mink	118.28300
Red Fox	84.41600
Whitetail Deer	47.23000

Comment: Actually, the number of significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be rounded; otherwise the impression is given of a level of accuracy that is simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

Lifetime exposure to 42.5 mg Cu/kg/d as copper gluconate in drinking water resulted in a 12.8% reduction of the maximal lifespan (from 986 to 874 days) in mice [979].

W.Human (Drinking Water and Other Human Concern Levels):

EPA 1996 IRIS database information [893]:

Maximum Contaminant Level Goal: 1.3 mg/L [893].

Status/Year: Final 1991 Reference: 53 FR 31516 (08/18/88); 56 FR 26460 (06/07/91); 56 FR 32112 (07/15/91) [893].

Contact: Health and Ecological Criteria

Division / (202)260-7571 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: The MCLG of 1.3 mg/L for copper is based on potential adverse effects (gastrointestinal) reported in human studies [893].

Maximum Contaminant Level (MCL): None given in IRIS [893]..

Status/Year: Final 1991 Econ/Tech?: Yes, does consider economic or technical feasibility Reference: 53 FR 31516 (08/18/88); 56 FR (06/07/91); 56 FR 32112 (07/15/91) [893].

Contact: Drinking Water Standards Division / OGWDW / (202)260-7575 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: EPA concluded that setting an MCL for copper is not feasible and believes that the treatment approach contained in the final rule (corrosion control, source water reduction, public education and copper service line replacement) will achieve the public health goals of the SDWA without the problems associated with establishing MCL's [893]. [893].

Note: The older proposed Drinking Water MCL was 1300 ug/L [446].

Older Federal Drinking Water Standards [609]:

EPA 1300 ug/l (Action Level) [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

Plain language summary: EPA says drinking water should not contain more than 1.3 ppm copper [979].

Older Federal Drinking Water Guidelines [609]:

EPA 1000 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines

(11/93)].

Plain language summary: EPA says surface waters should not contain more than 1.0 ppm copper to protect humans from copper ingested in water and aquatic organisms [979].

The national secondary drinking water contaminant level for copper and compounds for public water systems is 1 mg/l (40 CFR 143.3, 7/1/88) [609].

Older Water Quality Criteria in ug/L [446]:

Human Health Risk Level for Carcinogens (risk of one additional case in 1 million, 1E-06):

Older Published Criteria for Water and Organisms: 1000 ug/L [689]. The Environmental Protection Agency (EPA) has determined that the level of copper in water (lakes, streams) should be limited to 1 ppm to protect human health from the toxic properties of copper ingested through water and contaminated aquatic organisms [979]. Older IRIS Recalculated (9/90) Criteria for Water and Organisms: 1300 ug/L [446,689].

IRIS Recalculated (9/90) Criteria for Organisms Only: None

Bureau of Land Management RMC Benchmarks, 1995: Risk Management Criteria (RMC) developed for the mostly dry BLM lands in the western U.S. These risk management criteria should be used by the land manager as a cautionary signal that potential health hazards are present and that natural resource management or remedial actions are indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

Less than criteria: low risk
1-10 times the criteria: moderate risk
10-100 times the criteria: high risk
>100 times the criteria: extremely high risk

Human RMC (BLM) criteria for copper in surface waters. These categories of humans not exposed to surface waters with concentrations of copper exceeding the below RMCs are not expected to experience adverse toxic effects

[715]:

Camp host: 11,490 ug/L
Child Camper: 10,522 ug/L
Boater: 41,035 ug/L
Swimmer: 17,768 ug/L

Human RMC (BLM) criteria for copper in ground water. These categories of humans not exposed to ground waters with concentrations of copper exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 18 ug/L
Camp host: 137 ug/L
Child Camper: 377 ug/L
Worker: 287 ug/L
Surveyor: 2872 ug/L

State drinking water standards: the lowest listed are Kansas and Rhode Island (1000 ug/L) and Minnesota (1300 ug/L) [979].

Other Listing of State Drinking Water Standards [609]:

(AZ) ARIZONA 1000 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

(IL) ILLINOIS 5000 ug/l /Standard applies only to source water sample/ [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

State Drinking Water Guidelines [609]:

(AZ) ARIZONA 1300 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

(MA) MASSACHUSETTS 1300 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

(MN) MINNESOTA 1000 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

W.Misc. (Other Non-concentration Water Information):

Domestic wastewater is the major anthropogenic source of copper in waterways. Louis showed discharges of copper into sewer systems from residential areas to be significant, with an average loading of 42 mg/day/person [979].

In some Colorado settings, net-spinning caddisflies were shown to be more sensitive to predation when copper is present (Will Clements, Colorado State University, personal communication, 1994). Thus, direct toxicity is only one of the many types of impact which copper can have on aquatic life, and some of the indirect forms of impact relate to tolerance mechanisms.

Lakes and reservoirs recently treated with copper compounds to control algae or receive cooling water from a power plant may have high concentrations of dissolved copper [979]. Once in natural water, much of this copper soon attaches to particles or converts to forms that cannot easily enter the body [979].

As most adult fish are able to tolerate relatively high concentration of copper for short periods of time, the critical effect of copper is its greater toxicity to younger fish [302].

Increased synthesis of metallothionein in response to copper exposure may help animals (including fish) acquire a somewhat increased tolerance of this metal [180].

Colloids can potentially play a role in copper toxicity, at least from the standpoint of colloidal iron hydroxide in the water column and on the bottom attracting toxic compounds such as copper and zinc, then moving those toxic compounds to bottom habitats or far downstream (in either case this provides movement of toxics into proximity of new biota and they can be mobilized later by changes in pH, after exposure to air and chemical changes. Perhaps the spring toxicity seen at Soda Butte Creek in Yellowstone related partly to colloidal and other changes going on the bioassay cups? In the field, we might expect spring toxicity to relate to rapid mobilization of metals from formerly dry stream banks and other spring flushing aspects (Roy Irwin, National Park Service, personal communication, 1997].

In metals avoidance experiments, fish can detect and avoid metals even if the metals are attached to colloidal particles. Colloidal transport into the food chain can be very important. Bio-film: the slime layer on rock increases in metals due to colloids and presence of bacteria. Scraper and grazer invertebrates are eating the whole thing; the periphyton, bio-film, and colloidal metals. Metals are typically highest in sediments and bio-film. Herbivores are high in metals after feeding feed on slime layers. Small filter feeders get more metals; so fish that feed on small invertebrates get more metals too, and this is often the smallest (first 100 mm of growth) immature fish which are at a vulnerable stage. (Don Woodward, USGS, personal communication, 1996).

Algae filter out colloids and the colloids settle on rocks. Iron fixing bacteria are important. The orange bottom is the collection of colloidal material. Colloids become part of the food chain, can serve as toxic metal storage medium. Metals can coat benthic invertebrates eaten by fish. Seasonal variation: high flows flush out colloids first; zinc and copper can double in concentration in a storm. New areas are inundated by high water, colloids and metals in general (some now in more bioactive form) are now mobilized and can cause spikes in toxicity. There are good reasons to think that the colloids can affect chronic toxicity. Annual and seasonal flushes may relate to spring toxicity. Colloids can interact with sewage discharges (Briant Kimball, USGS, personal communication, 1996).

Dissolved metals are critical to fish and invertebrates, but the possibility of having colloidal material present means there is a readily available supply of metals in a state in which the metals can quickly be reduced and/or mobilized. In river banks, reducing environments form just under the surface quickly. Toxic metals of concern would include zinc, lead, copper, and cadmium. Colloidal metals may effect biota more than is widely recognized. Brown trout are effected by colloids which travel kind of like dissolved fractions, don't settle out. There may be little understood colloidal pathways of metals to fish, for example. Colloidal metals become part of the caddis fly cast. Once the cast is in the acidic fish stomach or gut, metals can be released. On the Arkansas River of Colorado below Leadville, the dissolved metals have gone down with treatment, but Will Clements of CSU has discovered the toxicity has not been reduced to the same extent as have the dissolved metals. Treatment has not eliminated colloidal fractions loaded with cadmium and copper, and this is possibly impacting the fish. In rivers, there is often annual flushing of the colloids, loads are much greater during runoff. Colloids do move in surface water, 140 miles downstream of Leadville, CO for example, but also in groundwater (Briant Kimball, USGS, personal communication, 1996).

Copper is not entirely removed in POTWs, and releases from these facilities contribute ~8% of all copper released to water [979]. Inputs into the Narraganset Bay, Rhode Island, in decreasing order of importance, are: sewage effluent, rivers, urban runoff, and atmospheric fallout [979]. Ninety percent of both dissolved and particulate copper was from effluent of sewage treatment plants that discharged into the Providence River [979]. While copper is removed from the waste stream by sewage treatment facilities, considerable copper remains in the effluent and is released into receiving waters [979]. The range of removal efficiencies reported for pilot and full scale plants suggests that removal depends strongly on plant operation or influent characteristics [979]. The best data on typical POTWs using secondary treatment are that 55-90% of copper is removed in these plants with a median and mean removal of 82% [979]. 1980) [979]. By contrast, those plants using only primary treatment had a 37% median removal efficiency [979]. A more recent study focused on heavy metal removal in three POTWs that received primarily municipal sewage and which used activated sludge as a secondary treatment [979]. The study looked at removals in both the primary and secondary treatment stage [979]. The average removal of soluble copper and total copper after secondary treatment was 49- 82% and 83-90%, respectively [979]. The average copper concentration in the final effluent was 17-102 ppb [979]. Discharges to water from active mining and milling are small, and most of the western operations do not release any water; water is a scarce resource and is recycled [979]. Discharges from electroplating operations are either directly to water or indirectly via POTWs [979]. Runoff from abandoned mines is estimated to contribute 314 million tons annually [979]. These discharges are primarily insoluble silicates and sulfides and readily settle out [979]. Releases from copper-containing products may be substantial but difficult to predict [979]. Corrosion of copper in plumbing or construction may result in direct discharges or runoff into waterways [979]. Copper and brass production releases relatively little copper to water [979]. Wastewater generated from mining operations comes from seepage, runoff from tailing piles, or from utility water used for mine operation [979].

Hazardous amounts of copper should not leach into groundwater from sludge, even from sandy soils [979] (see Soil.general section for details).

A potential complication in comparing contaminants data is that different investigators have sometimes meant different things when they put the words "dissolved" or "total" in front of a reported measurement. In the case of nutrients, the "dissolved" portion is usually simply that portion which has passed through a 0.45-micrometer membrane filter and the "total" measurements implies that it was not filtered and includes both dissolved and other forms of the nutrient [141]. However, usage of the words dissolved and total has not been uniform in the past and there is still considerable debate about which methods should truly be considered "dissolved" or "total" (Merle Schlockey, USGS, personal communication).

Water bodies are often marked by heterogeneity of the distribution of undissolved materials [691]. The size of any effects depends on the difference in density of the undissolved materials and the water, the size of the particles or bubbles of the materials, and various hydrodynamic factors such as the degree of turbulence in the water. Thus, undissolved inorganic materials in rivers and other natural water-bodies tend to increase in concentration with increasing depth because the particles tend to settle [691]. On the other hand, certain biological detritus may tend to rise towards the surface of the water because its density is less than that of water; oils also commonly demonstrate this effect markedly [691]. The surface microlayer is usually higher in concentration of many metallic and organic contaminants than the water column further down.

If the only change one makes is to use the prefix "dissolved" rather than the prefix "total" in an otherwise identical water quality standard, the effect can be a weakening of the standard related to total loading of a system. Many contaminants which are not currently dissolved can become dissolved at a later time, when encountering different conditions (perhaps downstream), such as changes in pH, additions of surfactants or humic substances, bioturbation, methylating organisms, and various other physical, chemical, or biological changes.

One problem with relying too heavily on dissolved fractions of metals is that the dissolved fraction misses the metals carried by colloids. Colloids were found to carry toxic metals 140 miles downstream of mining sources in Leadville, Colorado, to be repeatedly washed from flood deposited lowlands back into the river year after year in spring runoff (Briant Kimball, USGS Salt Lake City, as quoted in U.S. Water News, April 5th, 1995).

See Laboratory section below for EPA generic (guesstimate) conversion factors to convert total to dissolved concentrations.

Some environmental toxicologists make the argument that dissolved metals in surface water and porewaters represent most of what is bioavailable and thus "total" metals parameters are not good as a measure of potential biological effects. This is mostly true in many situations, but it should be kept in mind that fish and other aquatic organisms do not typically live in filtered water and that many fish and other aquatic organisms live in the sediments and in other situations in which they come in contact with toxic or otherwise harmful compounds (as certain colloids, precipitates, oxides, adsorbed metals), etc. Sometimes the effect of total metals is partially related to physical or chemical aspects, such as when ferric oxide coats or covers benthic organisms. Another factor to consider: contaminants carried downstream by erosion of bottom sediments or colloids can be mobilized when they come in contact with different physical/chemical environments downstream (for example, a tributary bringing low pH into the system).

Sediment Data Interpretation, Concentrations and Toxicity (All Sediment Data Subsections Start with "Sed."):

Sed.Low (Sediment Concentrations Considered Low):

Leland and Kuwabara, 1985: In non-polluted areas, baseline concentrations as low as 5 mg/kg dry weight have been recorded [177].

In relatively clean sediment, the copper concentration is 50 ppm [979].

Sed.High (Sediment Concentrations Considered High):

Texas: The statewide 90th percentile value was 40 mg/kg dry weight [7].

Cu can reach several thousand ppm in polluted areas [979].

Texas Playa Lake Study Sediment Concentrations: Two feedlot playa lakes had copper concentrations which were somewhat elevated (42.3 and 35.1 mg/kg dry weight) (Roy Irwin, National Park Service, personal communication 1992).

Great Lakes Harbors, EPA 1977: Sediments having concentrations of copper higher than 50 mg/kg dry weight were classified as "heavily polluted" [145,347]. Also, 25 to 50 mg/kg dry weight is considered "moderately polluted" [347,386].

Illinois EPA, 1984: Sediments having concentrations higher than 60.0 mg/kg dry weight were classified as "elevated" [145].

Leland and Kuwabara, 1985: In polluted areas, concentrations as high as 2000 mg/kg have been recorded

[177].

Highway runoff routed through a detention pond and then a cypress wetland resulted in much higher sediment levels of copper in the detention pond (49 ppm) than in the wetland (3 ppm) [220].

Buffalo Lake National Wildlife Refuge, Texas, Sediment Concentrations: Copper concentrations in three sediment samples from the upstream Tierra Blanca Creek site (NRB) and three sediment samples from the playa lake (PL) off-stream site were quite low, all samples being at or below 10 mg/kg dry weight [401]. By contrast, three samples from the Tierra Blanca Creek site (TRIS) suspected of being polluted by a large feedlot had higher copper concentrations (from 25-29 mg/kg dry weight) and the waste water pond in the feedlot had highly elevated copper concentrations (81-90 mg/kg). A Mann-Whitney statistical test showed copper concentrations from the six samples to be significantly lower than the six samples known or suspected of being influenced by feedlot wastes (significant at 0.0051). Copper compounds are used as a feed additives at some feedlots [401].

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of copper was 562.4 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The median for copper was 390 ppm and the range was 45-5,200 [347].

Estuarine and Marine Information:

> NOAA National Status and Trends Program (1984-1990) [698]: High concentration for copper in fine-grained sediment (n=233) = 84 ug/g dry weight at 4.6% TOC dry weight. The above concentration was adjusted for sediment grain-size in the following way: the raw concentrations were divided by the fraction of particles less than or equal to 64 um. "High" NOAA concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].
>
> > NOTE: Fine-grained sediment would typically contain more copper than course-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more copper than sediments which are similar except for being lower in TOC, which is why NOAA and many others are now normalizing sediment values for grain size, and reporting TOC.

Sed.Typical (Sediment Concentrations Considered Typical):

Great Lakes Harbors, EPA 1977: Sediments having sediment concentrations lower than 26.0 mg/kg dry weight were classified as "non polluted [145]." Guidelines for the pollution classification of Great Lakes harbor sediments (1977): A copper value of less than 25 ppm (dry weight) indicates nonpolluted sediment [347].

International Joint Commission, 1988: The International Joint Commission considered <21.1 mg/kg dry weight as a background sediment level [145]. The control site in one Great Lakes study had a sediment concentration of 10.4 mg/kg dry weight [145].

NOAA National Status and Trends Program (1984-1990) [698]: Geometric mean for copper in fine-grained sediment (n=233) = 35 ug/g dry weight at 1.4% TOC dry weight. The above concentration was adjusted for sediment grain-size in the following way: the raw concentrations were divided by the fraction of particles less than or equal to 64 um.

> NOTE: Fine-grained sediment would typically contain more copper than course-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more copper than sediments which are similar except for being lower in TOC, which is why NOAA and many others are now normalizing sediment values for grain size, and reporting TOC.

The range of copper in sediments of eddy drop zones in (metals-impacted) Soda Butte Creek, Montana, was 15-57 ppm (Andrew Marcus, Montana State University, personal communication, 1995).

Playa Lake Study Sediment Concentrations: Dry weight concentrations of copper in two of the four cattle feedlot-impacted playa lakes (in the Texas Panhandle) Roy Irwin has studied were not especially elevated (14.6 and 18.6 mg/kg). However, the other two feedlot playa lakes had copper concentrations which were somewhat elevated (42.3 and 35.1 mg/kg). By contrast, ephemeral row-crop agriculture playas had sediment copper concentrations of 11.9, 15.9, 19.1 and 15.9 mg/kg [401].

Sed.Concern Levels, Sediment Quality Criteria, LC50 Values, Sediment Quality Standards, Screening Levels, Dose/Response Data and Other Sediment Benchmarks:

Sed.General (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic

Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Sediment Concentrations. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks in mg/kg (ppm) dry weight [652]:

For CAS 7440-50-8 (Copper, the benchmarks are:

EFFECTS RANGE - MEDIAN (NOAA): 270
EFFECTS RANGE - LOW (NOAA): 34

Other Concern Levels for Sediment Concentrations (Dry Weight):

EPA Region 6, 1973: The concentration proposed by EPA Region 6 as a guideline for determining acceptability of dredged sediment disposal was 50 mg/kg [143].

Ontario Ministry of the Environment Freshwater Sediment Guidelines, 1993: Lowest effect level: 16 mg/kg dry weight. Severe Effect Level: 110 mg/kg dry weight [761].

Older benchmarks: Ontario, 1978,1986: The concentration proposed by the Ontario Ministry of the Environment as a threshold for evaluations of dredging projects was 25.0 mg/kg [145]. Ontario Ministry of the Environment guidelines for open lake disposal of sediments (1986): The guideline for copper is 25 ppm [347].

International Joint Commission, 1988: The IJC suggested sediment concentrations not exceed background levels of 21.0 mg/kg [145].

AET 1988: The apparent effects threshold concentrations for copper in sediments proposed for Puget Sound ranged from 390 mg/kg dry weight (microtox) to 1300 mg/kg dry weight (amphipods) [416].

NOTE: Although the authors of the Puget Sound AETs have cautioned that Puget Sound AETs may not be appropriate for comparison with data from other geographic areas, so few concern levels for this chemical have been published that the proposed Puget Sound concern level is included in this text as an item of interest.

NOAA 1995 Concern Levels for Coastal and Estuarine Environments: After studying its own data from the National Status and Trends Program as well as many literature references concerning different approaches to determining sediment criteria, NOAA suggested that the potential for biological effects of this contaminant sorbed to sediments was highest in sediments where its concentration exceeded the 270 ppm dry weight Effects Range-Median (ERM) concentration and was lowest in sediments where its concentration was less than the 34 ppm dry weight Effects Range-Low (ERL) concentration [664]. To improve the original 1990 guidelines [233], the 1995 report included percent (ratios) incidence of effects for ranges below, above, and between the ERL and ERM values. These numbers represent the number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range [664]:

<ERL	9.4
ERL-ERM	29.1
>ERM	83.7

Wisconsin interim criteria for sediments from Great Lakes harbors for disposal in water (1985): Copper should not exceed 100 ppm (dry weight) [347].

St. Lawrence River Interim Fresh Water Sediment Criteria, 1992: No effect: 28 mg/kg dry weight. Minimal effect: 28 mg/kg dry weight. Toxic effect 86 mg/kg dry weight [761].

Environment Canada Interim Sediment Quality Assessment Values, 1994. Threshold effect level: 35.7 mg/kg dry weight. Probable effect level: 196.6 mg/kg dry weight [761].

Guidelines for the pollutional classification of Great Lakes harbor sediments (1977): A copper value of less than 25 ppm (dry weight) indicates nonpolluted sediment, a copper value between 25-50 ppm (dry weight) indicates moderately polluted sediment, copper values above 50 ppm (dry weight) indicate heavily polluted sediment [347,761].

Guideance for New York Freshwater Dredging, 1994: A copper value of less than 16 ppm (dry weight) indicates nonpolluted sediment, a copper value between 16-110 ppm (dry weight) indicates moderately contaminated sediment, and copper values above 110 ppm (dry weight) indicate heavily contaminatged sediment [761].

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

In a study of the Trinity River, crayfish, turtles, and clams tended to be higher in copper than fish at identical sites [201]. A nationwide study of copper in bivalves showed less variation in levels from various locations than from various species [62]. The number of insect and macroinvertebrate species is very sensitive to the degree of exposure to elevated levels of copper [110,111]. Sediment concentrations of copper from Trinity River sites 9 through 12 downstream of Dallas exceeded the statewide 90th percentile level, 40.0 mg/kg, in at least 50% of the historical records from 1974 to 1985 [7].

Sed.Fish (Sediment Concentrations vs. Fish):

Fish living or foraging in contaminated sediments may accumulate it directly from the sediments [95]. In a study of the Trinity River, crayfish, turtles, and clams tended to be higher in copper than fish at identical sites [201].

Sed.Wildlife (Sediment Concentrations vs. Wildlife or Domestic Animals):

Bureau of Land Management RMC Benchmarks, 1995: Risk Management Criteria (RMC) were developed for the mostly dry BLM lands in the western U.S. These risk management criteria should be used by the land manager as a cautionary signal that potential health hazards are present and that natural resource management or remedial actions are indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

Less than criteria: low risk

1-10 times the criteria: moderate risk
10-100 times the criteria: high risk
>100 times the criteria: extremely high risk

Wildlife criteria for copper in soils and sediments. Wildlife not exposed to soils/sediments with concentrations of copper exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Rabbit: 77 mg/kg
Bighorn Sheep: 16 mg/kg
Whitetailed Deer: 38 mg/kg
Mule Deer: 47 mg/kg
Elk: 39 mg/kg
Mallard: 119 mg/kg
Canada Goose: 111 mg/kg
Trumpeter Swan: 120 mg/kg

Sed.Human (Sediment Concentrations vs. Human):

No information found.

Sed.Misc. (Other Non-concentration Sediment Information):

Sediment is an important sink and reservoir for copper [979]. The form of copper in the sediment will be site-specific [979]. Organics (humic substances) and iron oxides are the most important contributor to binding of copper by aerobic sediments [979]. However, in some cases, copper is predominantly associated with carbonates [979]. In anaerobic sediment, Cu(II) will be reduced to Cu(I) and insoluble cuprous salts will be formed [979].

In sediments of (metals-impacted) Soda Butte Creek, Montana (NE corner of Yellowstone Park) copper concentrations were highest in attached bars and lowest in low gradient riffles. Copper concentrations were found in the following habitats in order of highest sediment concentrations to lowest sediment concentrations: attached bars, backwater pools, high gradient riffles, lateral scour pools, detached bars, glides, and low gradient riffles. There was no significant difference up and downstream within each micro-habitat sub-unit (attached bars, glides, low gradient riffles, etc.). There was no significant difference in lateral variation (right side of stream, middle, left side) within each micro-habitat sub-unit (Andrew Marcus, Montana State University, personal communication, 1995).

In sediments of (metals-impacted) Soda Butte Creek, Montana (NE corner of Yellowstone Park) copper concentrations were higher in the fall than in the spring; more metals seemed to be carried on the down-side of flood events than during the event (Del Nimmo, NBS, personal communication, 1995).

A cycle of bio-mobilization of sedimentary copper by algae, followed by movement of the algae downstream and return of the copper to the sediments when the algae dies, may play a role in moving copper downstream [95].

Highway runoff routed through a detention pond and then a cypress wetland resulted in much higher sediment levels of copper in the detention pond than in the wetland [220]. The same study indicated that copper deposits near the outlet of a freshwater wetland were lower than those in the middle [220].

General notes related to interpretation of copper sediment data vs. AVS and SEM:

> Copper sulfides have gotten quite a bit of attention in environmental toxicology related to their tendencies to bind copper in the sediments and the relationship of sulfides to acid mine drainage. The primary ores of copper are chalcopyrite (CuFeS2) and chalcocite (Cu2S) [495].
>
> For some metals, copper for example, acid volatile sulfides are not consistently predictive of bioavailability in freshwater sediments and may not be as good for such predictions of toxicity as are pore water concentrations (Bill Brumbaugh, Columbia National Fisheries Contaminant Research Center, Fish and Wildlife Service, personal communication, 1992).
>
> A 1993 paper confirmed that Acid Volatile Sulfides alone is not an appropriate partitioning phase for predicting copper bioavailability in freshwater sediments [496]. A more recent paper suggests that Simultaneously Extracted Metals (SEM) to AVS ratios (SEM:AVS), and the spatial and temporal variability of AVS, should be considered in sediment toxicology and may be important in bioavailability dynamics [981]. The AVS normalization hypothesis, which predicts greater bioavailability of metals (such as copper and zinc) at SEM:AVS ratios of greater than 1.0 seems generally useful in some cases but has several important limitations [981].
>
> In early 1995, proposals were circulating in EPA suggesting that lower bound metals sediment criteria be developed along the following line: if

sufficient AVS is present [that is, the total simultaneously extracted metal (SEM) is equal or less than the concentration of AVS, then no effects are expected [700]. If SEM exceeds AVS, then other binding phases become important; the next most important phase is organic carbon (TOC) [700]. EPA now suggests that AVS be conducted in combination with interstitial water, particularly if effects are seen when AVS criteria are not exceeded [700].

Some have argued that AVS is not necessary for biological assessment work because significant AVS presence reflects anoxic conditions and AVS tends to go to zero when exposed to oxygen. Great care must be taken when collecting sediment samples for AVS not to expose them to air. Since most living things require oxygen, if there is no oxygen there are few if no living things so why use AVS to look at toxicity aspects (Tom O'Connor, NOAA, personal communication, 1995)?

Others would respond that it seems to work as a toxicity normalization parameter anyway, and point out that certain invertebrates, bacteria, etc. do live in low oxygen conditions in sediments. For mid to high range levels of AVS, exposure to air while sampling does not seem to critical, though head space in the jar should be minimized. As of October, 1995, the EPA method for AVS (method 376.3, similar but different from older reactive sulfide methods) was still a draft. AVS detection limits should be down in the 3 ppm range (~0.1 micro mole); any lower than that and the problems of lack of buffering and field contamination of samples by air or redox changes become more critical (Bill Brumbaugh, Columbia Lab, NBS, personal communication, 1995).

When sulfide is present, as it is in estuarine sediments rich in organic debris, it will combine with metals such as copper, cadmium, zinc, and lead. The metal sulfides that form are highly insoluble and will tend to be sequestered in the sediments (Bender M, 1989, Heavy metals in Narragansett Bay sediments. MARITIMES, 33 (4): 5-7. Off. Mar. Programs, Mar. Resour. Build., URI Narragansett Bay Campus, Narragansett, RI 02882-1197, USA) [940].

Soil Data Interpretation, Concentrations and Toxicity (All Soil Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

The low for copper in U.S. soils was 1 ppm [347].

Soil.High (Soil Concentrations Considered High):

Copper in German Gulch (highly polluted Upper Clark Fork Superfund Site Area, Montana) samples ranged from 58.6 to 236.5 ppm and averaged 148.4 ppm [699].

Copper concentrations close to 7000 ppm have been found near copper production facilities [979]. High concentrations of copper may be found in soil because dust from these industries settles out of the air, or waste from mining and other copper industries are disposed of on the soil [979]. Another common source of copper in soil results from spreading sludge from sewage treatment plants [979]. This copper generally stays strongly attached to the surface layer of soil [979]

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of copper was 562.4 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The median for copper was 390 ppm and the range was 45-5,200 [347].

Soil.Typical (Soil Concentrations Considered Typical):

The national average concentration for copper in U.S. soils is 30 mg/kg [98].

A 1984 survey: average copper concentrations in soil [979]:

25 ppm agriculural land
50 ppm suburban/residential land
100 ppm industrial land mixed with residential
175 ppm inner city and industrial

Western U.S. Soil Median Concentrations [715]: 27 mg/kg.

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of copper was 562.4 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The median for copper was 390 ppm and the range was 45-5,200 [347].

Soil generally contains between 2 and 250 ppm copper [979].

Based on recent compilations of estimates, the average natural copper concentration in soil ranges from 20 to 30 ppm (Baker, 1990) [699]. Generally, copper concentrations reported for various soil types (sandy soil and podzols, silty soils, loamy and clay soils, rendzinas, chernozems, histosols, and other organic soils) range from 1 to 100 ppm (Kabata-Pendias and Pendias, 1992) [699]. Copper concentrations typically are lowest in soils formed by granitic, igneous, or carbonate parent materials. Kabata-Pendias and Pendias (1992) cite 13-24 ppm as the average copper concentration in soils of the United States, and Adriano (1986) cites 25 ppm as an average value for naturally occurring copper in the U.S. soils [699].

Typical Soil Concentrations according to EPA 1981: 20 mg/kg dry weight [83].

Averages and ranges of concentrations of elements in soils and other surficial materials in the United States (1971): The mean for copper was 25 ppm and the range was between 1 and 300 ppm [347].

Typical Igneous Rocks (Earth's Crust) Concentrations:

Average concentration in the earth's crust is about 50 parts copper per million parts soil (ppm) [979].

55 mg/kg dry weight [83].
70 parts per million of the Earth's [280,366].

Copper is present in concentration(s) averaging about 4 ppm in limestones, 55 ppm in igneous rocks, 50 ppm in sandstones, and 45 ppm in shales [366].

The copper content of ore deposits ranges from 0.5-5% by weight, whereas igneous rock contains 0.010% (Duby 1980) and crystalline rock, 0.0055% by weight (55 ppm) [979].

Soil.Concern Levels, Soil Quality Criteria, LC50 Values, Soil Quality Standards, Screening Levels, Dose/Response Data and Other Soil Benchmarks:

Soil.General (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

Other Maximum Acceptable Concentration (MAC) levels in ppm dry weight: 100 (Stuttgart, Germany), 50 (London-value given for soluble pool of the element), 140 (London-value given for soluble pool of the element) [719].

Proposal of European Economic Commission for MAC in soils treated with sewage sludge: 50 (100) ppm dry weight (London). Value in parentheses are mandatory concentration [719].

Proposal of Ontario Ministry of Agriculture and Food for MAC in soils treated with sewage sludge: 100 ppm dry weight (published in Tokyo; work done for Ontario) [719].

The 1987 soil (clean up) criteria given by the New Jersey Department of Environmental Protection for copper is 170 mg/kg (ppm) dry weight [347,386].

In 1981 the U.S. Environmental Protection Agency proposed 1000 ppm as an upper limit for copper for sewage sludges suitable for land application [391].

Soil criteria for evaluating the severity of copper contamination under the Dutch Soil Cleanup (Interim) Act (1982): The background concentration of copper is 50 ppm, moderate soil contamination is 100 ppm, and threshold value is 500 ppm [347].

Soil cleanup criteria for decommissioning industrial sites in Ontario (1987): For agricultural land copper should not exceed 100 ppm, for residential or parklands copper should not exceed 300 ppm, for commercial or industrial land copper should not exceed 300 ppm [347].

Suggested cleanup guidelines for inorganic contaminants in acidic soils in Alberta (1987): The acceptable level of copper for acidic soils (pH <6.5) is 200 ppm [347].

Maximum cumulative addition of metals (kg/ha) from sewage sludge to Maryland agricultural soil (1986): For a soil with a cation exchange capacity of less than 5 meq/100 g copper addition should not exceed 140, for a soil with a cation exchange capacity of greater than 5 copper addition should not exceed 280 [347]. The numbers are the same for addition of metals from sewage sludge to Massachusetts agricultural soil (1983) [347].

Maximum cumulative addition of metals from sewage sludge that may be added to Minnesota soils used for growing food crops (1987): For a soil with a soil cation exchange capacity (CEC) of less than 5 meq/100 g copper should not be added at greater than 140 kg/ha, for a soil with a soil CEC between 5 and 15 meq/100 g copper should not be added at greater than 280 kg/ha, and for a soil with a CEC greater than 15 copper should not be added at greater than 560 kg/ha [347]. These values are the same for addition of metals to privately owned Missouri farmland (1988).

Cumulative amounts of metals per hectare that may be added to New York State soils with sewage sludge (1988): For productive agricultural soils copper should not be added at greater than 84 kg/ha, for less productive agricultural soils copper should not be added at greater than 125 kg/ha, and for forests copper should not be added at greater than 280 ppm [347].

Maximum heavy metal loading (kg/ha) recommended for sludge applications to privately owned Oregon farmland (1984): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100 g copper should not be added at greater than 125 kg/ha, for a soil with a CEC between 5 and 15 copper should not be added at greater than 250 kg/ha, for a soil with a CEC greater than 15 copper should not be added at greater than 500 kg/ha [347].

Maximum cumulative additions (kg/ha) of metals from sewage sludge that may be added to Vermont soils, by soil texture (1984): For loamy sand copper should not be added at greater than 140 kg/ha, for fine sandy loam copper should not be added at greater than 280 kg/ha, and for clay loam copper should not be added at greater than 560 kg/ha [347].

Maximum cumulative applications (kg/ha) of copper from sewage sludge that may be added to Wisconsin soils (1985): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100 g copper should not be added at more than 125 kg/ha, for a soil with a CEC between 5 and 10 copper should not be added at greater than 250 kg/ha, for a soil with a CEC between 11 and 15 copper should not be added at greater than 375 kg/ha, and for a soil with a CEC greater than 15 copper should not be added at greater than 500 kg/ha [347].

Soil limit values determined by the Council of European Communities for the addition of heavy metals from sewage sludge to soil with a pH of 6.0 to 7.0 (1986): The limit value for copper is 50-140 ppm [347].

Concern or Regulatory Levels for Soil Concentrations of Copper Extractable with Ammonium Acetate Buffer (mg/kg dry weight):

Soviet Union Maximum Allowable Concentration in Soils, 1984: 3.0 mg/kg [347].

In laboratory experiments, three sludges containing 51, 66, and 951 ppm (dry weight) of copper were applied to soil columns containing four coastal plain soils [979]. The columns were subsequently leached with distilled water at a rate of 2.5 cm/day for a total column application of 25.4 cm of water [979]. Only small amounts (less than 0.01-0.87 ppm) of copper were found in the leachate (Ritter and Eastburn 1978) [979]. This indicates that hazardous amounts of copper should not leach into groundwater from sludge, even from sandy soils [979]. In another study, soil cores taken after sewage sludge was 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 [979]. Similarly, copper remains in the surface layer when it is applied to soil as a liquid [979].

Soil.Plants (Soil Concentrations vs. Plants):

Some grasses around copper polluted areas are copper tolerant [366].

Levels of copper (ppm dry weight) considered phytotoxic: 100 (Vienna), 100 (Warsaw), 125 (Tokyo), 100 (Warsaw), 60 (Missouri), 100 (Ontario) [719]

Minimum soil concentration causing phytotoxicity: 60-125 [699].

At 400 ppm copper in the soil, several crops have symptoms; at 15-30 ppm, citrus crops had effects; spinach and gladiolus affected at 98-130 ppm, and clover and alfalfa most sensitive of crops tested [670].

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Terrestrial Plants. To be considered unlikely to represent an ecological risk to terrestrial plants, field concentrations in soil should be below the following dry weight benchmark for soil [651]:

For CAS 007440-50-8 (COPPER), the benchmark is 100 mg/kg dry weight in soil.

Density and biomass of certain grasses in meadows of Soda Butte Creek (NE Yellowstone Park) seemed to be reduced at copper soil concentrations (dry weight) above 250 ppm (Julie Stoughton, Montana State University, personal communication, 1995).

Some plants accumulate copper at high levels, with low growing grasses generally having the highest concentrations and tree foliage the lowest. The major route of uptake appears to be from soil rather than direct atmospheric deposition, since copper is unlikely to be transported across leaf cuticles. Radishes grown in controlled environments in soils taken from areas of atmospheric deposition exhibited elevated copper levels. Plants grown on soils from areas closest to smelters exhibited decreased growth but growth was improved by addition of lime, presumably because higher soil pH decreased metal solubility and uptake [366].

See also Soil.Misc section.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

The concentration of copper in earthworms is correlated with soil concentrations, which may be a consideration relative to birds feeding on sewage sludge amended soils [179]. However, although earthworms can usually live in metals contaminated soils, copper is somewhat more toxic to them than most metals and earthworms have been eliminated from soils due to copper contamination [347].

Soil.Wildlife (Soil Concentrations vs. Wildlife or Domestic Animals):

See also the Bureau of Land Management (BLM) Risk Management Criteria (RMC) Benchmarks from [715] in the Sed.Wildlife section above.

The concentration of copper in earthworms is correlated with soil concentrations, which may be a consideration relative to birds feeding on sewage sludge amended soils [179].

Soil.Human (Soil Concentrations vs. Human):

Acceptable level of copper for production of healthy food: 23 (value given for soluble pool of the element) ppm dry weight (Moscow) [719].

Bureau of Land Management RMC Benchmarks, 1995: Risk Management Criteria (RMC) were developed for the mostly dry BLM lands in the western U.S. These risk management criteria should be used by the land manager as a cautionary signal that potential health hazards are present and that natural resource management or remedial actions are indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

Less than criteria: low risk
1-10 times the criteria: moderate risk
10-100 times the criteria: high risk
>100 times the criteria: extremely high risk

Human RMC criteria for copper in soil. These categories of humans not exposed to soil with concentrations of copper exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 74 mg/kg
Camp host: 1915 mg/kg
Child Camper: 1319 mg/kg
ATV Driver: 26929 mg/kg
Worker: 2872 mg/kg
Surveyor: 28724 mg/kg

Soil.Misc. (Other Non-concentration Soil Information):

Hazardous amounts of copper should not leach into groundwater from sludge, even from sandy soils [979] (see Soil.general section for details).

Secondary sewage effluent spiked with 0.83 ppm of copper was applied weekly to four different soils [979]. After 1 year of treatment, the concentration of copper in the surface horizons increased greatly; 50-76X of applied copper was found in the upper 2.5 cm and 91-138X was found in the upper 12.7 cm [979].

Soil fertilization with copper has been used in Australia & New Zealand but was ineffective in a high molybdenum area in Nevada in reducing molybdenum or increasing copper content of feeds. Treatment of pasture or crops with copper has not been extensively used in the USA [366].

Editor's note: According to an article in the Bozeman (Montana) Daily Chronicle Newspaper of December 30, 1996, increasing soil pH by adding lime, a remediation sometimes used to reduce soil acidity and reduce the mobility of metals such as copper, can result in the (unintended) consequence of increasing the mobility of arsenic and its transport to groundwater. The article stated that Bill Inskeep, soil scientist at Montana State University had seen an increase of arsenic percolation of 10 to 100 times after lime was added to arsenic contaminated soils (News Media Report, not yet independently confirmed, but included since lime is such a common treatment for acidic metals contaminated soils).

Tissue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

Tis.Plants:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Plants:

A level of copper in alfalfa possibly toxic to cattle is 115 ppm dry weight [739]. Alfalfa grown in contaminated water downstream of Summitville Mine, Colorado was slightly elevated above the 10 ppm dry weight copper dietary requirement for cattle, but was still far below the 115 ppm concern level for cattle [739].

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Copper plant tissue concentrations at the (highly polluted) Smelter Hill (Upper Clark Fork Superfund Site Area, Montana) site averaged 91.87 (ranging as high as 467 ppm in horsebrush). Levels in un-impacted plants generally range between 1.5 and 30 ppm (CH2M Hill, 1987b, as cited in PTI, 1991a) [699].

The following ranges of concentrations of copper in plants (dry weight) were found in samples collected along metals-impacted Soda Butte Creek in Yellowstone Park in 1992 (Daniel Norton, USGS, personal communication, 1995):

Grasses: 2.9 to 10 ppm
Lichen: 26.9 ppm (one sample)
Moss: 21.1 to 62 ppm
Willow: 4 to 11 ppm

The contents of copper, molybdenum, sulphur, zinc, selenium, iron, manganese, and the copper/molybdenum ratio were determined in different native plant species from a mountain area of central southern Norway. The overall mean values and ranges (mg/kg DM) were copper: 6.0, 0.9-27.2; molybdenum: 0.25, 0.01-3.57; zinc: 77, 8-320; selenium: 0.05, less than 0.01-0.32; iron:

208, 15-2245; manganese: 338, 31-3784; sulfur: (g/100 g DM) 0.20, 0.03-0.56; copper/molybdenum: 79, 1-7955. Levels of the individual elements showed considerable variability, both between and within plant groups. Mineral contents were compared with the established requirements for sheep and cattle, the following conclusion being drawn. The levels of zinc, sulphur, iron, and manganese were found to be adequate for ruminants (Garmo TH et al; Acta Agric Scand 36 (2): 147-161, 1986) [609].

Willows and grasses downstream of Montana mining areas tended to uptake some heavy metals (copper, lead) in polluted areas to a greater degree than farther downstream: results for zinc were inconclusive, and levels of various metals in moss and lichens tended to be much higher than willow and grass (Daniel Norton, USGS, personal communication, 1995).

Both tree lichens and mosses are capable of absorbing large quantities of metals and have been used to map zones of impact from air pollution, so the USGS has been developing baseline levels for these plants [739].

Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

Note: In humans, some oral intake of copper is necessary for good health, but massive doses can cause problems, especially for children [979].

Legal Limits for Concentrations in Fish and Fishery Products (these levels relate mostly but not totally to fish, since fishery products includes some general seafood and/or invertebrates in some countries): The lowest legal limit is 10 mg/kg (Venezuela, India, Ecuador, Chile) [216,418]. Nine countries have limits less than or equal to 70 mg/kg, but the U.S. apparently has no limit [216,418]. The Australian National Health and Medical Research Council recommends 30 mg/kg copper as a maximum content for seafood products [84].

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

No information found.

C) Body Burden Residues in Invertebrates: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Accumulation of copper in a population of the grasshopper, Chorthippus brunneus, from grasslands around a copper refinery complex (0.75 sq km divided into four sites) was monitored, and compared with a control site distant from sources of metal contamination. A sub-control site in an unpolluted stabilized sand dune system where the soil copper concentration was deficient was also studied. Each site contained similar mixed grass swards of copper-tolerant Agrostis stolonifera and Festuca rubra which were the major components of fecal pellets of refinery site grasshoppers. Monthly samples of grasses and the insects, adult and nymphal specimens were obtained for analysis from June to November (n= >100/species/site). Monthly mean copper concentrations in A stolonifera were; (a) refinery sites, 39.4 ug/g to 152 ug/g, respectively); (b) 1 km site, 16.8 ug/g; and (c) control respectively); (b) 1 km site, 16.8 ug/g; and (c) control site, 8.2 ug/g. For F rubra, copper concentrations were: (a) refinery sites, 26.4 ug/g to 86.3 ug/g; (b) 1 km site, 20.1 ug/g, and (c) control site, 7.4 ug/g. For C brunneus concentrations were: (a) refinery sites, 300 to 380 ug/g respectively); (b) 1 km site, 66.4 ug/g; and (c) control site 37.5 ug/g. Total body concentration of Cu in grasshoppers increased with mean dietary contamination levels; the relationship was not linear and reached a peak at 50 ug/g of dietary Cu. Accumulation of Cu in the insects closely followed the seasonal increase in contamination levels of the grasses. Copper accumulated progressively through the instars of the insects. Nymphs from the refinery sites had significantly increased copper concentration above control values for all instars, and the accumulation seemed to begin soon after hatching. Concentrations are reduced in newly emerged adults which suggests some copper is excluded at the final molt. Both body and integumental concentrations were significantly elevated in refinery samples compared to controls, and refinery insects had a significant elevation of integument over body copper (Hunter BA et al; Arch Environ Contam Toxicol 16 (6): 711-6, 1987) [366].

Copper does not accumulate to the same extent in both oysters and mussels. Therefore, the following information summarizes data gathered on both oysters and mussels from the NOAA National Status and Trends (NS&T) Program for the year 1990 [697]:

> For copper in oysters (n=107), the Geometric Mean was 150 ug/g dry and the "high" concentration was 360 ug/g dry weight [697]. For copper in mussels (n=107), the Geometric Mean was 8.9 ug/g dry and the "high" concentration was 11 ug/g dry weight [697]. NOAA "high" concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].

Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

> Note: In humans, some oral intake of copper is necessary for good health, but massive doses can cause problems, especially for children [979].

Legal Limits for Concentrations in Fish and Fishery Products: The lowest legal limit is 10 mg/kg (Venezuela, India, Ecuador, Chile) [216,418]. Nine countries have limits less than or equal to 70 mg/kg, but the U.S. apparently has no limit [216,418]. The Australian National Health and Medical Research Council recommends 30 mg/kg copper as a maximum content for seafood products [84].

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Bureau of Land Management RMC Benchmarks, 1995: Risk Management Criteria (RMC) were developed for the mostly dry BLM lands in the western U.S. These risk management criteria should be used by the land manager as a cautionary signal that potential health hazards are present and that natural resource management or remedial actions are indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

Less than criteria: low risk
1-10 times the criteria: moderate risk
10-100 times the criteria: high risk
>100 times the criteria: extremely high risk

Human RMC criteria for copper in fish consumed by humans: These categories of humans not exposed to fish with concentrations of copper exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 2907 ug/kg
Camp host: 5984 ug/kg
Child Camper: 16487 ug/kg

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

No information found.

C) Body Burden Residues in Fish: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Mean NCBP Levels (Tissue Concentrations): Copper whole-body levels above 0.9 mg/kg wet weight were higher than the concentrations of 85% of all fish samples in a (NCBP) national survey [23]. A more recent (1976-1984) NCBP survey report gave the nationwide geometric mean concentration of copper in composite samples of whole fish as 0.65 mg/kg wet weight [384].

Edible Tissues (Mostly Fillet) Concentrations for Copper:

Copper concentrations (1.21 to 7.76 mg/kg) in muscle samples from the Pecos River near Pecos National Monument & Historical Park were consistently higher than copper concentrations (<0.13 to 0.60) reported for trout collected upstream in the Fish and Wildlife Service 1991 study of the Terrero Mine waste study area. For additional comparison, highest concentrations of copper in 5 studies of edible fish tissues in several states ranged from 0.88 to 14.97 mg/kg wwt [57].

Copper whole-body levels above 0.9 mg/kg are higher than 85% of all fish in a NCBP national survey [23]. This level was exceeded in 9 of 14 Big Bend National Park tissue samples 65]. Four of the 5 highest Big Bend NP (Rio Grande River) copper concentrations were from mosquitofish [65]. The highest fish concentrations in Big Bend collections were 2.6, 1.6, 1.5 mg/kg, respectively [65]. The highest concentration (2.6 mg/kg) of copper from Rio Grande river mosquitofish was higher than was found in any of 24 mosquitofish samples from the urbanized upper Trinity River [201]. This finding is of interest because copper is one of the most common urban runoff contaminants and therefore might be expected to be more elevated in the highly urbanized parts of the upper Trinity than in rural areas. Gut-contents were not separated from the above samples [65,201].

The highest concentration of copper found in 32 fish samples from the heavily agricultural areas of the lower Rio Grande river, far downstream of Big Bend National Park, was 5.09 mg/kg [202].

In a study of the Trinity River, mosquitofish data showed no uniform upstream/downstream distribution trends for copper (unlike other contaminants) [201]. If they had been more uniformly present, clams might be a better choice for gradient monitoring of copper since they have an affinity for heavy metals and tend to be good indicators of metal pollution in general [95]. A nationwide study of copper in bivalves showed less variation in levels from various locations than from various species [62]. Crayfish, turtles, and clams tended to be higher in copper than fish at identical sites [201]. The seven highest Trinity River concentrations were from crayfish, turtles, and clams rather than fish [201]. Nevertheless, copper concentrations in the lean tissues of mosquitofish, bullhead minnows, and red-eared slider turtles were at least slightly higher at the site impacted by urban runoff and urban point sources than those from our reference/control site [201].

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (mg contaminant per kg body weight per day). To be considered unlikely to represent an ecological risk, wet-weight field concentrations should be below the following (right column) benchmarks for each species present at the site [650]:

For CAS 7440-50-8, COPPER AS COPPER SULFATE, the benchmarks are:

SPECIES	NOAEL (mg/kg/day)	FOOD CONCENTRATION (ppm)
Mink (test species)	11.71000	0.00000
Short-tailed Shrew	46.82200	78.03600
Little Brown Bat	58.85500	176.56600
White-footed Mouse	41.26300	266.99400
Meadow Vole	32.82600	288.86800
Cottontail Rabbit	11.02600	55.82900
Mink	11.71000	85.47400
Red Fox	7.12800	71.28500
Whitetail Deer	3.09300	100.43200

Comment: Actually, the number of significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be rounded; otherwise the impression is given of a level of accuracy that is simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

A level of copper in alfalfa possibly toxic to cattle is 115 ppm dry weight [739]. Alfalfa grown in contaminated water downstream of Summitville Mine, Colorado was slightly elevated above the 10 ppm dry weight copper dietary requirement for cattle, but was still far below the 115 ppm concern level for cattle [739].

There appear to be few predator protection levels suggested in the literature. However the concentration of copper in earthworms is correlated with soil concentrations, which may be a consideration relative to birds feeding on sewage sludge amended soils [179]. However, although earthworms can usually live in metals contaminated soils, copper is somewhat more toxic to them than most metals and earthworms have been eliminated from soils due to copper contamination [347].

Increased mortality was observed in rats fed a diet containing 4000 ppm of copper (≈133 mg Cu./kg/d) for 1 week [979]. Anorexia, possibly the result of taste aversion, contributed to the deaths [979]. Weanling rats exposed to 300 mg Cu/kg/d as Cu(II) in the diet (6000 ppm) died after 2 weeks [979]. The deaths were attributed to extensive centrilobular necrosis [979].

C) Body Burden Residues in Wildlife, Birds, or Domestic Animals: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Upper Trinity River: (The following text is quoted from the Trinity River Report [201] for reference comparison with values from other areas): Copper concentrations above the detection limit (0.01 mg/kg) were found in 74 of 77 Trinity River samples. The three samples containing less than the detection level were from red-eared turtle shells. Maximum Levels: The highest copper concentrations were in whole-body samples of spiny softshell turtles from sites 18 (12.8 mg/kg) and 11 (18.5 mg/kg) and from crayfish from site 5 (25.4 mg/kg) [201].

The Japanese serow, a bovine ruminant, is long-lived and free-ranging. The animals were killed during the winter 1981-82 in the Gifu and Nagano Prefectures, Japan. The Cu concentrations were measured by flame absorption spectrometry. On a wet wt basis, the mean Cu concentration in muscle, liver, kidney, and whole body of fetuses (gestation age 0.3-0.7 yr, N= 13) were 0.59, 66.4, 3.76, and 2.56 ug/g, respectively; in fawns (age 0.0-0.5 yr, N= 12), 2.02, 12.0, 2.90, and 1.52 ug/g, respectively; in yearlings (age 0.5-2.5 yr, N= 6), 1.96, 32.8, 2.80, and 1.75 ug/g, respectively; in adults (age 2.5 to 10 yr, N= 42), 1.84, 34.1, 2.81, and 2.15 ug/g, respectively; and in adults (age 10 to 17.5 yr, N= 17), 1.79, 40.5, 2.63, and 2.25 ug/g, respectively. Sex differences were observed in liver, with significantly higher concentrations ($p < 0.05$) in males than in females. The mean Cu concentration in fleece of fawns, yearlings, and adults (age 2.5 to 10 yr) was 13.3, 14.8, and 10.6 ug/g, respectively. Bone samples of two adult serows contained 0.35 to 0.83 ug/g. The body burden of fetuses was low (<1%) compared with that of their mothers. The Cu levels were high during gestation and decreased after birth until about 2.5 yr of age as a result of hepatic accumulation. There was no significant difference in Cu concentration between collection locations. The Cu uptake agreed well with the concentration found in food plants (Honda K et al; Arch Environ Contam Toxicol 16: 551-61, 1987) [366].

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

Copper content in human food was summarized by ATSDR; unless massive doses are ingested, copper by this route is usually not a problem [979].

Humans eat and drink about 1 milligram (l/1000 of a gram) of copper every day [979]. The 1980 Recommended Dietary Allowances estimate that a daily dietary intake of 2-3 mg Cu/d (0.03-0.04 mg/kg/d) by adults is safe and adequate [979]. The dietary requirements for copper in rats and pigs is 3-6 mg/kg diet (0.15- 0.30 mg/kg bw/day) and 3-5 mg/kg diet, respectively [979].

B) Concentrations or Doses of Concern in Food Items Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

Note: In humans, some oral intake of copper is necessary for good health, but massive doses can cause problems, especially for children [979].

See also Tis.Fish, A) section above.

Legal Limits for Concentrations in Fish and Fishery Products: The lowest legal limit is 10 mg/kg (Venezuela, India, Ecuador, Chile) [216,418]. Nine countries have limits less than or equal to 70 mg/kg, but the U.S. apparently has no limit [216,418]. The Australian National Health and Medical Research Council recommends 30 mg/kg copper as a maximum content for seafood products [84].

Thirteen of 53 patients died after ingesting 6-637 mg/kg copper [979]. Patients provided information on intakes; thus, the reported doses may be inaccurate [979]. The deaths were attributed to shock and hepatic and/or renal complications [979].

The normal diet of humans includes between 2 and 5 mg of copper per day, exceeding the body maintenance requirements of about 2 mg per day [280]. Many forms of copper are not very toxic to humans, with most problems related to human health reported from individuals who have copper metabolism disorders or who distill alcohol with copper tubing [173]. Except for inhalation of copper dusts, in humans copper itself probably has little or no toxicity, although there are conflicting reports in literature [366].

There are numerous reports of acute gastrointestinal effects in humans after ingestion of large amounts of copper, in the form of Cu (II) [979]. Exposure levels that produced these gastrointestinal effects were 0.07-1421 mg Cu/kg as Cu (II) [979].

Oral RfD: none given [893].

The average daily dietary intake of copper by an individual in the United States may range from < 2 to approx 4 mg. For ingestion, the dietary intake is, in general, an order of magnitude higher than intake from drinking water, except in rare cases of consumption of soft water which has been supplied by copper pipes. In the latter case, intake from drinking water may be as high as >2 mg/day. /Copper cmpd/ (USEPA; Health Issue Assessment: Copper p.23, 1987) EPA/600/8-87/001) [609].

The eastern oyster can concentrate copper by a factor of 28200 and can accumulate so much copper that they turn bluish green, but even high amounts consumed by man orally may not be harmful [25].

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

No information found.

Tis.Misc. (Other Tissue Information):

Copper occurs naturally in plants and animals [979].

A number of plants have been described as indicators of higher-than-normal concentrations of this element in the soil [951]. A typical ratio of copper concentration from plants to rock is 0.13 [951]. Bryophytes and lichens tend to have an especially high ability to absorb trace elements from their substrates and to tolerate adverse ecological conditions [951].

Bio.Detail: Detailed Information on Bioconcentration, Biomagnification, or Bioavailability:

For a discussion of SEM and AVS issues vs bioconcentration, see the Sed.Misc. section above.

Some plants accumulate copper at high levels, with low growing grasses generally having the highest concentrations and tree foliage the lowest. The major route of uptake appears to be from soil rather than direct atmospheric deposition, since copper is unlikely to be transported across leaf cuticles. Radishes grown in controlled environments in soils taken from areas of atmospheric deposition exhibited elevated copper levels. Plants grown on soils from areas closest to smelters exhibited decreased growth but growth was improved by addition of lime, presumably because higher soil pH decreased metal solubility and uptake [366].

Some of the highest bioconcentration factors recorded for copper are for the marine invertebrate polychaete worm Neanthes (BCF = 2550), the eastern oyster (BCF =28200), and the freshwater alga Chlorella regularais (BCF =2000) [25]. The oysters contained so much copper that they turned bluish green, but even high amounts consumed by man orally may not be harmful [25].

Preliminary data suggests the potential for bioaccumulation or bioconcentration of copper is high to very high for the following biota: mammals, birds, fish, mosses, lichens, algae, mollusks, crustacea, lower animals, and higher plants [83]. The best potential mediums for biological monitoring (including gradient monitoring) appear to include clams, lichens, mosses, algae, and higher plants [83]. As mentioned above, continued ingestion of copper by animals in excess of dietary requirements led to some accumulation in tissues, particularly the liver and kidneys [180]. The concentration of this metallic element in earthworms is correlated with soil concentrations, which is a consideration relative to birds feeding on sewage sludge amended soils [179].

In a study of the Trinity River, mosquitofish data showed no uniform upstream/downstream distribution trends for copper (unlike other contaminants) [201]. If they had been more uniformly present, clams might be a better choice for gradient monitoring of copper since they have an affinity for heavy metals and tend to be good indicators of metal pollution in general [95]. A nationwide study of copper in bivalves showed less variation in levels from various locations than from various species [62]. Crayfish, turtles, and clams tended to be higher in copper than fish at identical sites [201]. The seven highest Trinity River concentrations were from crayfish, turtles, and clams rather than fish [201]. Nevertheless, copper concentrations in the lean tissues of mosquitofish, bullhead minnows, and red-eared slider turtles were at least slightly higher at the site impacted by urban runoff and urban point sources than those from our reference/control site [201].

From Sorensen's book [488], quoted with written permission of CRC Press Inc.:

> "Accumulation of Elements from Mixtures: Copper, Zinc, Mercury, Iron, Manganese: A few environmental studies address accumulation levels for mixtures of metals. Cross and workers (1973) catch fish at 2500 m deep near Cape Hatteras for analysis of levels of Hg in white muscle. Mercury levels increase with body weight ($p<0.001$) for bluefish (Pomatomus saltatrix) and morid (Antimora rostrata). Bluefish are epipelagic (living in the part of the ocean into which light penetrates) and morids are bathyl-demersal (living near the sea bottom in a biogeographic realm about 180-1800 m deep). Mercury accumulation is probably increased as a result of high

> lipid solubility, high electronegativity, and/or high affinity for sulfhydryl groups. Decreasing levels of all metals except Hg are noted for morids—an effect possibly due to growth dilution effects, compositional changes in muscle, and/or dietary changes in metal levels. In contrast to Hg levels, the concentrations of Mn, Fe, Cu, and Zn decrease or remain unchanged. In white muscle, the concentration factors (CF) of Hg, Mn, Cu, Zn, and Fe are 3700, 100, 200, 2100, and 2300, respectively. Obviously, metal accumulation patterns vary as a function of species, fish size, and metal analyzed."

Interactions:

When sulfide is present, as it is in estuarine sediments rich in organic debris, it will combine with metals such as copper, cadmium, zinc, and lead. The metal sulfides that form are highly insoluble and will tend to be sequestered in the sediments (Bender M, 1989, Heavy metals in Narragansett Bay sediments. MARITIMES, 33 (4): 5-7. Off. Mar. Programs, Mar. Resour. Build., URI Narragansett Bay Campus, Narragansett, RI 02882-1197, USA) [940].

For a discussion of SEM and AVS issues vs copper hazards and bioconcentration, see the Sed.Misc. section above.

Toxic compounds in distilled water, frequently copper, may result in low BOD [861].

Although hardness is widely recognized to affect aquatic toxicity of metals (for example, hardness seems somewhat protective of rainbow trout related to copper and zinc toxicity), pH often has the largest effect on metals toxicity [25,39] (Confirmed by David Mount, National Biological Service, Columbia, MO, personal communication, 1994).

> NOTE: For pH data, see also: Schubauer-Berigan, M.K., J.R. Dierkes, P.D. Monson, and G.T. Ankley, 1993. pH dependent toxicity of Cd, Cu, Ni, Pb, and Zn to Ceriodaphnia dubia, Pimephales promelas, Hyalella azteca, and Lumbriculus variegatus. Environmental Toxicology and Chemistry 12:1261-1267.

Mercury can attack copper and copper alloy materials (Mackison, F. W., R. S. Stricoff, and L. J. Partridge, Jr., eds., NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS-NIOSH Publication No. 81-123, 3 VOLS,. Washington, DC: U.S. Government Printing Office, Jan. 1981. 2) [940].

Copper and mercury are antagonistic at lower concentrations, additive at intermediate concentrations, and synergistic at higher concentrations [488]. Evaluation of hatchability of trout embryos shows synergistic, additive, and antagonistic relationships between Cu and Hg. As with Cu and zinc, synergistic interaction exists at high Cu and Hg concentrations in the water [488]. Additive effects are noted at an intermediate level of about 0.03 ppm of equal proportions of either element. Antagonism is noted at low levels (<or=0.01 ppm of equal proportions of each metal). Moreover, the complexity of elemental interactions is confirmed in such

comparisons, although Cu-Hg interactions seem less complicated for channel catfish Ictalurus punctatus) and goldfish (Carassius auratus) than for largemouth bass (Micropterus salmoides) and rainbow trout (Salmo gairdneri). The LC50 values show Hg to be twenty-five times more toxic than Cu to bass, trout, catfish, and goldfish under conditions of this series of studies [488].

Interactions between Cu and Hg at the epidermis of fish hint of the role of mucus in metal poisoning of fish [488]. Epithelial mucus from plaice (Pleuronectes platessa) binds Cu and zinc at levels 100-fold and 20-fold greater respectively, than levels in water during exposures of fish to low aqueous concentrations. Dialysis of mucus against deionized water results in only a small decrease in the concentrations of Cu and zinc bound to mucus. Glycoproteins low in sialic acid, aromatic and sulfur-containing amino acids, phosphate, and sulphate appear to be involved in binding of the two divalent cations. Moreover, Cu+2, Zn+2, and Hg+2 precipitate fresh plaice mucus in the order Cu > Zn > Hg. Mucus serves a protective function by binding excess aqueous metals as a precipitate [488].

Zinc in water acts synergistically with copper and ammonia to produce an increased toxic effect on fish [26,47]. A study in an Arkansas river system showed that macroinvertebrate concentrations were negatively correlated with zinc concentrations but not with concentrations of iron or copper [72].

In western watersheds affected by metals, fish kills are often associated with runoff and rainstorm events. Metals responsible for toxicity are often copper and zinc, whose toxicity and/or mobility are enhanced by the depressions of pH, hardness/alkalinity, and dissolved organic carbon that typically accompany these events (David Mount, National Biological Survey, Columbia, MO, personal communication, 1994).

Intermediate concentrations of copper (Cu) and zinc (0.07 ppm Cu and 0.69 zinc) elicit greater responses in fish ventilation amplitude, ventilation rate, and coughing frequency than higher concentrations [488]. Higher Cu or zinc levels cause more variation in ventilation pressure changes than lower zinc levels. Singly or in combination, zinc causes increased coughing frequency; whereas, Cu does not. Therefore, combined exposure to zinc-Cu results in synergism at intermediate levels of the elements. In fact, coughing frequency at 0.04 ppm Cu and 0.66 ppm zinc combined is about one and one-half times greater than the sum of the responses to the single toxicants. The marked individual variability in ventilatory activity is noteworthy and is generally considered a result of irritation of buccal (and possibly gill) membranes. Amplitude may be low and ventilation rate may be high for one subject (or for one concentration) but not for a second subject (or concentration). Unfortunately, the authors do not report total respiratory activity for individual fish using ventilation rate and amplitude date (e.g., volume of water breathed per unit time). Perhaps the individual variation would be reduced in such comparisons [488].

See also "Accumulation of elements from mixtures" information [488] in Bio.Detail section above.

Interactions [609]:

The antineoplastic drug BCNU, a known and potent inhibitor of erythrocyte glutathione reductase, may enhance the oxidant stress of known oxidizing agents (including copper) commonly found in the environment. A BCNU induced deficiency of erythrocyte glutathione reductase produced no enhanced formation of methemoglobin or decrease in glutathione, under exposure to the stressors. [Bott M, Calabrese EJ; J Environ Sci Health A23 (3): 219-30 (1988)].

Vanadium compounds (sodium trivanadium and vanadyl sulfate) in different oxidation states influenced metabolism in rats. The intoxication with sodium trivanadium and vanadyl sulfate significantly reduced the intestinal absorption of copper. The inhibitory effect was elicited both by acute (single oral dose) and subchronic (12 wk) administration. Furthermore, the levels of ceruloplasmin in serum and the concentration(s) of copper in liver were decreased in the rats exposed to continuous oral administration of vanadium cmpd. [Witkowska D et al; Bull Environ Contam Toxicol 40 (2): 309-16 (1988)].

Cysteine, via chelation reactions, ameliorates biochemical lesions caused by excessive ingestion of several trace elements. Because oral cysteine per se is considerably more protective than the in vivo metabolic cysteine precursors, methionine or cystine, chelation of cysteine with trace elements likely occurs primarily in the gut, thereby decreasing absorption of both cysteine and the trace element in question. Using copper as an example, orally administered cysteine markedly improves growth and reduces liver copper deposition in chicks or rats fed a high level of inorganic copper. Likewise, excessive copper ingestion impairs sulfur amino acid utilization and increases the dietary requirement for sulfur amino acid. [Baker DH, Czarnecki-Maulden GL; J Nutr 117 (6): 1003-10 (1987)].

Intestinal copper absorption and blood measures of copper status were studied in healthy young men receiving varying intakes of ascorbic acid over 14 wk. Copper absorption and retention were assessed during four ascorbic acid intake periods: 2 wk x 65 mg ascorbic acid, 4 wk x 5 mg/day, 3 wk x 605 mg/day and 4 wk x 5 mg/day. Measures of copper status were serum copper and serum ceruloplasmin. Copper absorption, copper retention, total serum copper and the serum level of ceruloplasmin protein were not affected significantly by the changes in ascorbic acid intake; however, the oxidase activity of serum ceruloplasmin was decreased an average of 21% during the high (605 mg/day) ascorbic acid intake period. The results suggest that in adult men moderate supplemental intakes of ascorbic acid reduce ceruloplasmin oxidase activity specifically but do not depress intestinal copper absorption or overall body copper status. [Jacob RA et al; J Nutr 117 (2): 2109-15 (1987)].

The effects of elevated dietary ascorbic acid and iron on copper utilization were examined. Male Sprague-Dawley rats were fed one of two levels of copper (deficient, 0.42 microgram copper/g, or adequate, 5.74 micrograms copper/g), iron (moderate, 38 micrograms iron/g or high, 191 micrograms iron/g), and ascorbic acid (low, 0% or high, 1% of the diet) for 20 days. High iron decreased copper absorption only in copper deficient rats. High ascorbic acid significantly decreased tissue copper levels in copper adequate rats. High iron with ascorbic acid caused severe anemia in copper deficient rats and decreased plasma ceruloplasmin by 44% in copper adequate rats. Copper, zinc superoxide dismutase activity in erythrocytes was decreased by 14% during copper deficiency but was not affected by iron or ascorbic acid. [Johnson MA, Murphy CL; Am J Clin Nutr 47 (1): 96-101 (1988)].

An experiment was conducted with female Cobb feather sexed chicks to study the influence of methionine and selected nutrient supplement on the performance of chicks fed high copper levels. Day old chicks were alloted randomly to pens for the 22 day experiment. Treatments included copper at 0, 400, and 800 mg/kg. Supplemental methionine reversed the growth depression observed in birds fed 400 but not 800 mg/kg copper. Additions of 400 and 800 mg/kg copper to the basal diet depressed feed consumption by 8.6 and 19.4%, respectively. Hepatic copper concentrations increased linearly with increasing dietary copper and were not influenced by supplemental methionine or selected nutrient. Serum glutamic-oxaloacetic transaminase activity was not influenced by dietary copper. [Ledoux DR et al; Poult Sci 66 (8): 1379-84 (1987)].

Sodium aurothiomalate was given to male Wistar rats (initial body weights: 150 g) by subcutaneous injection at doses of up to 7.5 mg/kg (corresponding to 4.27 mg gold/kg), twice a week, for 4-5 weeks. The concentrations of calcium, magnesium, iron, copper, and zinc were measured in serum, urine, feces and in the liver, kidney, spleen, heart, lung, testis, bone, and muscle. The concentration of copper was increased 5 fold in kidney while smaller increases of zinc in kidney, copper in muscle, iron in muscle and testis, and calcium in spleen were found. There was a significant reduction in the concentration of copper in serum. Kidney cytosol from gold treated but not from control animals contained a low molecular weight protein which was associated with copper, zinc, and gold. The rats developed proteinuria and microscopic changes to renal tubular cell structure were also observed. It is suggested that the gold induced accumulation of copper may follow from an increased rate of synthesis of metallothionein and could be responsible for the renal dysfunction which develops in a proportion of rheumatoid arthritis patients who are treated with gold. [Taylor A et al; Toxicol 47 (3): 339-50 (1987)].

Sea scallops Placopecten magellanicus in early gametogenesis from the southern shelf of Hudson Canyon, New Jersey, were exposed to sublethal levels of copper and cadmium in a flowing seawater system. Exposure was to copper (10 and 20 ug/l: low copper and high copper groups) or to a combination of copper and equimolar cadmium (10 ug copper + 17.7 ug cadmium/l: low copper/cadmium group) for 8 wk, with sampling at 2 wk intervals. Copper had a strongly inhibitory effect on gamete production and maturation, which was partially moderated in the presence of cadmium in the female gonad only. Total gamate wt/scallop doubled in control individuals but dropped 60% in both high metal exposure groups over the 8 wk exposure period, with a smaller, temporary decrease in the low copper group. Cadmium did not add to the inhibition by copper of gamate development in the low copper/cadmium group, but there was no partial recovery at 8 wk, as was seen in female scallops exposed to low copper alone. Gonadal RNA, higher in the females, decreased proportionately more in that sex than in the males of the metal exposure groups. Conversely, DNA levels were higher in the male than in the female gonad, and decreased sharply in all metal exposed males. Gonadal protein concentration(s) also dropped in all metal exposed scallops with time and degree of metal exposure. Copper uptake in the gonad increased with time and metal exposure concn, and cadmium increased in the low copper/cadmium group with time. [Gould E et al; Mar Biol (Berlin) 97 (2): 217-23 (1988)].

The therapy of copper poisoning and of Wilson's disease with 2,3-dimercaptopropane-1-sulfonate may increase the copper induced hemolysis. Incubation of 2,3-dimercaptopropane-1-sulfonate with copper ions (free or bound with erythrocyte membranes) is accompanied with generation of oxygen radicals. Activated oxygen species produced via oxygen gas are able to increase the hemolytic effects of cupric salts. Hence 2,3-dimercaptopropane-1-sulfonate treatment in cases of copper poisonings or Wilson's disease may involve risk of side effects on the basis of activated oxygen species generation. [Aaseth J et al; Pharmacol Toxicol 61 (4): 250-3 (1987)].

Five Bedlington Terriers with inherited copper (Cu) hepatotoxicosis and with hepatic Cu concentrations ranging from 3,000 to 11,000 micrograms/g of dry weight (normal, less than 350 micrograms/g of dry weight) were treated daily for up to 200 days with 2,3,2-tetramine tetrahydrochloride. During treatment, no change was made in the dietary Cu intake, which ranged from 12 to 16 micrograms/g of dry diet. Concentrations of hepatic and serum Cu, iron, and zinc were determined before and at the conclusion of the treatment period. In one dog, 24 hour urinary Cu concentration was measured before and during treatment. A liver biopsy specimen obtained after treatment had significantly ($p < 0.05$) reduced hepatic Cu concentration (3,282 micrograms/g of dry weight; a 54.9% reduction), compared with the pretreatment value (7,281 micrograms/g of dry weight). After treatment, there was an overall general lessening of the extent of hepatic morphologic damage.

Cytochemical examination for Cu in rhodanine stained biopsy specimens revealed decreased numbers of Cu laden hepatic lysosomes. The mean daily urinary Cu concentration increased as much as 25 fold during 2,3,2-tetramine treatment. Hepatic iron and zinc concentrations and serum Cu concentrations remained within normal ranges after treatment. Clinical or laboratory evidence of 2,3,2-tetramine tetrahydrochloride toxicosis was not detected during treatment. [Twedt DC et al; J Am Vet Med Assoc 192 (1): 52-6 (1988)].

Other metals such as zinc, iron, and molybdenum interact with copper to affect copper absorption, distribution, metabolism, and utilization. [USEPA; Health Issue Assessment: Copper p.3 (1987) EPA/600/8-87/001].

Uses/Sources:

Elemental copper supplied from a mixed copper ethanolamine complex (Cutrine-plus algicide liquid concentrate, made by Applied Biochemists Inc.) is a registered herbicide/algicide for use in controlling Chara, Nitella, and hydrilla [218]. Copper sulfate is also used to control Chara and pondweeds [218].

Plants take up copper from soil, groundwater, sewage sludge, biocides, fertilizers and air pollution [83]. A number of plants have been described as indicators of higher-than-normal concentrations of this element in the soil [951]. Animals take up copper from industrial sources, contaminated water, and contaminated food [83]. Copper is one of the most common contaminants associated with urban runoff, and specific sources include soil erosion, corrosion of pipes and tubes, industrial discharges, and sewage treatment plant discharges [25]. Copper is also present in the leachate of some municipal landfills [80] and in sludges generated by sewage treatment plants [94]. Water (particularly water that is acidic, low in hardness and alkalinity, and consequently corrosive to piping) may leach copper from drinking water pipes [366].

Additional Information on Uses [280]:

Copper was the first metal used by humans and is second only to iron in its utility through the ages. Copper mixes well with many elements, and more than 1,000 different alloys have been formed, several of which are technologically significant. The presence of the other element or elements can modify the hot or cold machining properties, tensile strength, corrosion fatigue, and wear resistance of the copper; it is also possible to create alloys of pleasing colors.

The electrical industry is a major consumer of copper. The metal is used for the windings of generators and for conveying electrical power. Its resistance to chemical attack and its high thermal conductivity make copper a useful metal for condensers in chemical plants and for car radiators. Copper tubing is widely employed in plumbing, and finely divided copper is used as an industrial catalyst in the oxidation of methanol to formaldehyde. Copper compounds, such as Fehling solution, are used in analytical tests for sugars. Copper(II) sulfate has many industrial applications, including the preparation of Bordeaux mixture (a fungicide) and the manufacture of other copper compounds. It is also used in electroplating solutions, in textile dyeing, and as a timber preservative. Probably the earliest use of copper as a fungicide was in the form of copper sulfate solution employed as a seed dressing to destroy cereal disease, such as bunt.

New materials are increasingly replacing copper: plastic for pipe and tubing, glass fiber for wire, lightweight aluminum for automobile parts.

Major Uses [609]:

Heating, chemical, and pharmaceutical machinery; alloys (monel metal, beryllium-copper); electroplated protective coatings and undercoats for nickel, chromium, zinc, etc; cooking utensils; corrosion-resistant piping; catalyst; flakes used as insulation for liquid fuels; whiskers used in thermal and electrical composites. [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 308].

In works of art. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 359].

Metal for electrical & electronic products (eg, wire) building construction (eg, plumbing pipes), industrial machinery & equipment, transportation industry (eg, automobiles), consumer & general products (eg, coins), & in inorganic pigments (eg, pigment metal 2); chem intermediate for copper chems (eg, cupric sulfate). [SRI].

Copper has a contraceptive effect when present in the uterus. It is added to some intrauterine contraceptive devices permitting reduction in their size with concomitant reduction in the associated side effects such as pain and bleeding. [Reynolds, J.E.F., Prasad, A.B. (eds.) Martindale-The Extra Pharmacopoeia. 28th ed. London: The Pharmaceutical Press, 1982. 930].

In agricultural products (insecticides, fungicides, herbicides), anti-fouling paints, catalysts, corrosion inhibitors, electrolysis and electroplating processes, electronics, fabric and textiles, flameproofing, fuel additives, glass, and ceramics. ... Used in cement, food and drugs, metallurgy, nylon, paper products, pigment and dyes, pollution control catalyst, printing and photo copying, pyrotechnics, and wood preservatives. /Copper and cmpd/ [USEPA; Health Issue Assessment: Copper p.15 (1987) EPA/600/8-

87/001].

Natural Sources [609]:

Occurrence /all forms/ in earth's crust: 70 ppm ... In seawater: 0.001-0.02 Ppm. ... Found in nature in its native state; also in combined form in several minerals incl chalcopyrite, chalcocite, bornite, tetrahedrite ... Enargite ... Antlerite. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 358].

Copper is present in concentration(s) averaging about 4 ppm in limestones, 55 ppm in igneous rocks, 50 ppm in sandstones, and 45 ppm in shales. The marked concentrations of copper in shales & sandstones suggest that copper in the lithosphere exists largely as adsorbed ions, fine grained particles or as one of many discrete sedimentary copper minerals. Generally, these minerals occur only as sparse tiny grains that are widely disseminated throughout the sedimentary rocks. [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 11-1].

Copper is widely distributed in nature in the elemental state, in sulfides, arsenites, chlorides, and carbonates. The element is only superficially oxidized in air, sometimes giving a green coating of hydroxy carbonate and hydroxy sulfate. The concentration of copper in the continental crust, generally estimated at 50 ppm, tends to be highest in the ferromagnesium minerals, such as the basalts pyropene and biotite, where it averages 140 ppm. Sandstones contain 10-40 ppm, shales 30-150 ppm, and marine black shales 20-300 ppm. Coal is relatively low in copper. /Copper and compounds/ [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 266].

In the sedimentary cycle copper is concentrated in the clay mineral fractions with a slight enrichment in those clays rich in organic carbon. /Copper and compounds/ [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 266].

Artificial Sources [609]:

In the vicinity of copper mines or smelting works, where the water and pasture have been shown to be contaminated with copper. [Clarke, M. L., D. G. Harvey and D. J. Humphreys. Veterinary Toxicology. 2nd ed. London: Bailliere Tindall, 1981. 45].

Smelting operations may produce elemental copper ... /and/ it is likely that municipal incineration will produce copper ...

. [USEPA; Health Issue Assessment: Copper p.1 (1987) EPA/600/8-87/001].

The principal source of elevated copper levels in air is copper dust generated by copper processing operations. ... Other possible sources of copper in air may be tobacco smoke and stack emissions of coal burning power plants. /Copper dust and copper oxides/ [USEPA; Ambient Water Quality Criteria Doc: Copper p.C-18 (1980) EPA 440/5-80-036].

The reaction of soft water with the copper pipes that are used in some household plumbing systems contributes to the copper levels in water at the tap. /Oxidized copper (Cu(II)) complex/ [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 312].

On a global basis, the atmospheric copper flux from anthropogenic sources are approximately three times higher than its flux from natural sources. Non-ferrous metal production is the largest contributor of atmospheric copper flux in the United States. /Copper dust, mist, and fume/ [USEPA; Health Issue Assessment: Copper p.1 (1987) EPA/600/8-87/001].

Windblown dust accounts for approximately 65% of the overall nonanthropogenic sources of copper emission to the atmosphere. Sources of copper emission are: iron and steel production, 7.4%; coal and oil combustion, 4.6%; zinc smelting, 3.3%; copper sulfate production, 2.7%; municipal incineration, 1.9%; others, 2.3%. /Copper dust, mist, and fume/ [USEPA; Health Issue Assessment: Copper p.13-14 (1987) EPA/600/8-87/001].

Forms/Preparations/Formulations:

Radionuclides:

The symbol for Copper-64 is 64Cu, the atomic number is 29, the half-life is 12.7 hours, and beta emission, positron emission, and X-ray emission are the major forms of decay [674].

Formulations/Preparations [609]:

Commercial copper (Cu) is available in six general types: Electrolytic tough-pitch, 99.90% Cu; Deoxidized, 99.90% Cu; Oxygen-free, 99.92% Cu; Silver-bearing, 99.90% Cu; Arsenical, 99.68%; Free-cutting, 99.4-99.5% [Considine. Chemical and Process Technol Encyc p.316 (1974)].

Forms available: ingots, sheet, rod, wire, tubing, shot, powder; high purity (impurities less than 10 ppm) as single crystals or whiskers. [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 308].

See also: Laboratory Section below for discussion of total vs. Acid Soluble Metals.

Chem.Detail: Detailed Information on Chemical/Physical Properties:

Solubilities [609]:

Insol (sic: note from Roy Irwin, editor: it is mostly the sulfides are "relatively insoluble" while some of the salts are more soluble) in hot & cold water; sol in nitric acid, hot sulfuric acid; very slightly sol in hydrochloric acid, ammonium hydroxide [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-88].

Vapor Pressure [609]:

1 MM HG AT 1628 DEG C [Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New York, NY: Van Nostrand Reinhold, 1984. 804].

Density/Specific Gravity [609]:

8.94 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 358].

Molecular Weight [609]:

63.546 [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-88].

Heat of Vaporization [609]:

1150 CAL/G [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 358].

Boiling Point [609]:

2595 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 358].

Melting Point [609]:

1083 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 358].

Color/Form [609]:

REDDISH METAL; FACE CENTERED CUBIC STRUCTURE [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 358].

Other Chemical/Physical Properties [609]:

Lustrous, ductile, malleable metal; mohs' hardness: 3.0; Specific resistance: 1.673 Microohm/cm; heat of fusion: 48.9 Cal/g; heat capacity (solid): 0.092 Cal/g/deg c at 20 deg c, (liq): 0.112 Cal/g/deg c; becomes dull when exposed to air; very slowly attacked by cold hydrochloric acid, dil sulfuric acid, readily by dil nitric acid, hot concentration(s) sulfuric acid and hydrobromic acid, attacked by acetic & org acids; two naturally occurring isotopes: 63 (69.09%), 65 (30.91%); 9 Artificial isotopes [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 358].

It conducts heat and electricity exceedingly well [International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 546].

Copper forms two series of salts, cu(1+) and cu(2+) both valence types form complex ions that are stable. [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 308].

Readily attacked by alkalies. [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 308].

Reactivities and Incompatibilities [609]:

Reacts violently with ... ammonium nitrate, bromates, chlorates, iodates, chloride, ... ethylene oxide, ... hydrazine mononitrate, hydrazoic acid, ... and potassium oxide ... . [Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New York, NY: Van Nostrand Reinhold, 1984. 804].

In the presence of wet acetylene and ammonia, copper and brasses down to 60% copper react readily to form explosive acetylides. ... A combination of finely divided copper with finely divided bromates (also chlorates or iodates) of barium, calcium, magnesium, potassium, sodium, or zinc will explode with heat, percussion and sometimes light friction. [National Fire Protection Association. Fire Protection Guide on Hazardous Materials. 9th ed. Boston, MA: National Fire Protection Association, 1986.,p. 491M-68].

Unstable acetylides form when acetylene is passed over copper that has been heated enough to form a tarnish of oxide coating. [National Fire Protection Association. Fire Protection Guide on Hazardous Materials. 9th ed. Boston, MA: National Fire Protection Association, 1986.,p. 491M-68].

Sodium azide ... Reacts violently with ... Copper ... . [National Research Council. Prudent Practices for Handling

Hazardous Chemicals in Laboratories. Washington, DC: National Academy Press, 1981. 146].

Fate.Detail: Detailed Information on Fate, Transport, Persistence, and/or Pathways:

For a discussion of SEM and AVS issues vs fate, see the Sed.Misc. section above.

A cycle of biomobilization of sedimentary copper by algae, followed by movement of the algae downstream and return of the copper to the sediments when the algae dies, may play a role in moving copper downstream [95].

It is not always possible to separate the environmental fate processes related to transport and partitioning from those related to transformation and degradation for a metal, its various compounds and complexes [979]. Part of this problem is that the form of copper is rarely identified [979]. It is also difficult to determine when a process such as adsorption should be treated as partitioning or transformation, since the formation of strong bonds to an adsorbent may be construed as a transformation to new molecular species [979]. Separating weak and strong adsorption is awkward and not always possible [979].

Copper is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter [979]. It is removed by gravitational settling (bulk deposition), dry deposition (inertial impaction characterized by a deposition velocity), washout by rain (attachment to droplets within clouds), and rainout (scrubbing action below clouds) [979].

In a groudwater study, copper showed a pronounced solubility only in the oxidizing environment; in the reducing environment, solubility was low, possibly due to the formation of sulfides [979]. The form of copper at polluted and unpolluted sites may affect its leachability, particularly by acid rain [979]. The leaching of heavy metals by simulated acid rain (pH 2.8-4.2) was measured by applying rainwater to columns containing humus layers from sites in a Swedish spruce forest both near to and far from a brass mill [979]. Leaching of copper increased considerably when water with a pH 3.4 was applied to soil from polluted sites [979]. Since 25 to 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 [979]. This does not appear to be the case [979]. Hazardous amounts of copper should not leach into groundwater from sludge, even from sandy soils [979].

Environmental Fate [609]:

AQUATIC FATE: ... some copper complexes may be metabolized /however/ there is no evidence that biotransformation processes have a significant bearing on the aquatic fate of copper. /Copper salts and complexes/ [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of

129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 11-16].

TERRESTRIAL FATE: Factors affecting the balance between copper in the parent rock & in the derivative soil include the degree of weathering, the nature & intensity of the soil formation, drainage, pH, oxidation-reduction potential, & the amount of organic matter in the soil. Since copper in rocks is likely to be more mobile under acidic than alkaline conditions, the relation of pH to copper in the environ has been of great concern to agriculturalists & biologists. Alkaline conditions in the soil & the surface water favor precipitation of copper. ... Acid conditions promote solubility of copper, increase the concentration(s) of ionic copper, & thereby change the microorganism & other aquatic animal populations, depending on tolerance for various levels of copper in solution. ... The reports of acid rain in various parts of the world are of serious concern. Due to the variety of conditions which influence the metal's avail, the total copper content of the soils is not an accurate indication of deficiencies or excess of copper in soil rooted plants. /Copper salts/ [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 273].

Terrestrial Fate: The fate of copper with respect to its leachability in purely organic spruce forest soils was studied. Appreciable mobilization of copper occurred only with prolonged leaching at pH 2.8. Therefore, it does not appear likely that acidic rainfall will result in significant mobilization of copper from organic soils unless the pH of rainfall decreases to < 3. ... Estimated that approx 50% of copper in the top few centimeters of these soils was organically bound, approx 18% was in the hydroxy carbonate form, approx 7% was in the adsorbed state, approx 11% was bound by other anions and 6% was irreversibly adsorbed. Only 3% of the copper was extractable with water at pH 4.5; hence only 3% was mobile at this pH. ... In urbanized areas the effects of land clearing, profile disruption and increased acid rainfall may increase copper mobilization in these soils. [Tyler G; Water, Air, Soil Pollut 9 (2): 137-48 (1978) as cited in USEPA; Health Issue Assessment: Copper p.18 (1987) EPA/600/8-87/001].

In soils exposed to atmospheric deposition, high levels of copper and other metals may occur that can be directly toxic to certain soil microorganisms and can disrupt important microbial processes in soil, such as nutrient cycling. Studies concerning heavy metal effects on microbial and fungal activity in soils, found that copper and other metals inhibited mineralization of nitrogen and phosphorus in contaminated forest soils. Regression analysis indicated that copper was more important than other metals in controlling these processes. Studies reported lower fungal species diversity in soils contaminated with heavy metals. Copper was found to be more toxic to these species than other metals. This evidence suggests that while other metals in contaminated soils contributed to the observed effects, copper may be the most important in terms of toxicity. /Copper(II) salts and other heavy metal salts/ [Hutchinson TC; Copper Environ p.451-502 (1979) as cited in USEPA; Health Issue Assessment: Copper p.25 (1987) EPA/600/8-87/001].

Absorption, Distribution and Excretion [940]:

1. Small fragments of copper ... in the anterior vitreous just behind the lens in a number of cases have been observed for years, gradually dissolving & disseminating copper to lens, cornea & iris, where copper has a predilection for the basement membranes. [Grant, W.M. Toxicology of the Eye. 3rd ed. Springfield, IL: Charles C. Thomas Publisher, 1986. 261]..

2. Copper dissolved from the wire used in certain intrauterine contraceptive devices has been shown to be absorbed systemically. [International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 547].

3. Intrauterine devices containing metallic copper ... raise the endometrial copper concentration 2 fold, & this copper excess might be transferred to the fetus. [Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. (eds). Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 247].

4. Nonradioactive and radioactive metal salts were administered intravenously to Sprague-Dawley rats. The highest amount of each metal approached the maximum tolerated dose. Cobalt, silver, and manganese were eliminated rapidly. The elimination of 20 to 50 percent of the dosage was observed for copper (Cu), thallium, bismuth, lead, cesium, gold, zinc, mercury, selenium, and chromium. Copper, thallium, lead, and zinc were excreted at a slower rate, with 30.6 to 38.3 percent excreted on the first day. The rest of the metals were eliminated slowly by the intestinal route. Copper was removed rapidly via urine, while lead, tin, methyl mercury, silver, iron, manganese, and cadmium were eliminated slowly. Copper, selenium, lead, bismuth, and cobalt were eliminated at an intermediate rate via the biliary route. Silver, arsenic, manganese, copper, selenium, cadmium, lead, bismuth, and methyl mercury were highly concentrated in bile relative to plasma. Liver and kidney contained the highest concentrations of most metals. The intestinal route was the major path of elimination for silver, manganese, copper, thallium, lead, zinc, cadmium, iron, and methyl mercury. Copper, cesium, gold, selenium, and chromium were removed predominantly by urine. [Gregus Z, Klaassen CO; Toxicol Appl Pharm 85 (1): 24-38

(1986)].

5. Circadian rhythms in the urinary excretion of eleven heavy metals and organic substances were examined under free, water restrictive and water loading conditions for 6 days (2 days for each of the three conditions) in twenty metal workers exposed to lead, zinc, and copper. Circadian rhythms were found for all heavy metals and organic substances as well as for urinary flow rate, creatinine and total urinary solutes. The rhythm in the copper excretion depends on the creatinine rhythm, ie the rhythm of glomerular filtration. [Aono H, Araki S; Int Arch Occup Environ Health 60 (1): 1-6 (1988)].

6. The relationship between tissue levels of metallothionein and metal concentrations was assessed for zinc, copper, and cadmium in ten different organs from human autopsies and rats. Human autopsy specimens were obtained from ten males between the ages of 20 and 50 years within 2 days of sudden death. Tissues assayed included pancreas, liver, kidney, brain, small intestine, stomach, muscle, heart, lung, and spleen. Human metallothionein levels were higher than rat levels for all tissues assayed except brain and small intestine. The highest metallothionein levels were found in human liver and kidney cortex and rat kidney and brain. Zinc levels were highest for human liver, kidney, and muscle; and copper levels were highest for human liver, brain, and heart and rat liver, kidney, and heart. Elevated cadmium levels were found in human liver and kidney. All cadmium levels were below detectable limits in rats. Significant correlations were established between metallothionein levels and zinc and copper in human liver and between metallothionein and cadmium in human kidney cortex. [Heilmauer HE et al; Toxicol Lett 38 (3): 205-11 (1987)].

7. Accumulation of copper in a population of the grasshopper, Chorthippus brunneus, from grasslands around a copper refinery complex (0.75 sq km divided into four sites) was monitored, and compared with a control site distant from sources of metal contamination. A sub-control site in an unpolluted stabilized sand dune system where the soil copper concentration was deficient was also studied. Each site contained similar mixed grass swards of copper-tolerant Agrostis stolonifera and Festuca rubra which were the major components of fecal pellets of refinery site grasshoppers. Monthly samples of grasses and the insects, adult and nymphal specimens were obtained for analysis from June to November (n= >100/species/site). Monthly mean copper concentrations in A stolonifera were; (a) refinery sites, 39.4 ug/g to 152 ug/g, respectively); (b) 1 km site, 16.8 ug/g; and (c) control respectively); (b) 1 km site, 16.8 ug/g; and (c) control site, 8.2 ug/g. For F rubra, copper concentrations were: (a) refinery sites, 26.4 ug/g to 86.3 ug/g; (b) 1 km site, 20.1 ug/g, and (c) control site, 7.4 ug/g. For C brunneus concentrations were: (a) refinery sites, 300 to 380 ug/g respectively); (b) 1 km site, 66.4 ug/g; and

(c) control site 37.5 ug/g. Total body concentration of Cu in grasshoppers increased with mean dietary contamination levels; the relationship was not linear and reached a peak at 50 ug/g of dietary Cu. Accumulation of Cu in the insects closely followed the seasonal increase in contamination levels of the grasses. Copper accumulated progressively through the instars of the insects. Nymphs from the refinery sites had significantly increased copper concentration above control values for all instars, and the accumulation seemed to begin soon after hatching. Concentrations are reduced in newly emerged adults which suggests some copper is excluded at the final molt. Both body and integumental concentrations were significantly elevated in refinery samples compared to controls, and refinery insects had a significant elevation of integument over body copper. The copper [Hunter BA et al; Arch Environ Contam Toxicol 16 (6): 711-6 (1987)].

8. Cultured C6 rat glioma cells were exposed to lead acetate (0, 1, 10, or 100 uM) for 3-4 days. Cells were analyzed for changes in viability and intracellular lead, iron, and copper concentrations after lead treatment was discontinued. Lead uptake did not affect intracellular iron or copper concentrations. Unlike C6 cells, however, astroglia showed elevations of intracellular iron or copper after lead treatment. C6 cells appear to be an adequate model for selected events in glial toxicosis, such as lead stimulated protein synthesis in oligodendroglia and lead uptake in astroglia, but not lead induced alterations of intracellular copper and iron in astroglia. [Bratton GR; J Toxicol Environ Health 23 (2): 267-80 (1988)].

9. The Japanese serow, a bovine ruminant, is long-lived and free-ranging. The animals were killed during the winter 1981-82 in the Gifu and Nagano Prefectures, Japan. The Cu concentrations were measured by flame absorption spectrometry. On a wet wt basis, the mean Cu concentration in muscle, liver, kidney, and whole body of fetuses (gestation age 0.3-0.7 yr, N= 13) were 0.59, 66.4, 3.76, and 2.56 ug/g, respectively; in fawns (age 0.0-0.5 yr, N= 12), 2.02, 12.0, 2.90, and 1.52 ug/g, respectively; in yearlings (age 0.5-2.5 yr, N= 6), 1.96, 32.8, 2.80, and 1.75 ug/g, respectively; in adults (age 2.5 to 10 yr, N= 42), 1.84, 34.1, 2.81, and 2.15 ug/g, respectively; and in adults (age 10 to 17.5 yr, N= 17), 1.79, 40.5, 2.63, and 2.25 ug/g, respectively. Sex differences were observed in liver, with significantly higher concentrations ($p< 0.05$) in males than in females. The mean Cu concentration in fleece of fawns, yearlings, and adults (age 2.5 to 10 yr) was 13.3, 14.8, and 10.6 ug/g, respectively. Bone samples of two adult serows contained 0.35 to 0.83 ug/g. The body burden of fetuses was low (<1%) compared with that of their mothers. The Cu levels were high during gestation and decreased after birth until about 2.5 yr of age as a result of hepatic accumulation. There was no significant difference in Cu concentration between collection locations. The Cu uptake agreed well with

the concentration found in food plants. [Honda K et al; Arch Environ Contam Toxicol 16: 551-61 (1987)].

10. Copper concentrations in tissues of 10 human males (mean age 43 yr) who suffered sudden death and six male Wistar rats were measured. Copper was detected in all 10 tissues (brain, heart, kidney cortex, liver, lung, muscle, pancreas, small intestine, spleen, and stomach) of both rat and man. Highest levels were in the liver of man and in the kidney of the rat. In most tissues the levels of copper were within a factor of two for the two species. Results were presented graphically and no values were given. In human liver there was a positive relationship between the concentration of copper and the amount of metallothionein in the tissue. [Heilmaier HE et al; Toxicol Lett 38 (3): 205-11 (1987)].

Laboratory and/or Field Analyses:

Many methods have been used to monitor for copper [861,979, 1001,1003,1004,1005,1006]. EPA methods recommended depend on the application: whether for drinking water [40 CFR Part 141 and 1005,1006,1008], NPDES discharge permits [40 CFR 136 and 1005,1006], CERCLA [861,1005,1006], RCRA [861,1005,1006], or low-detection-limit water-quality based permitting [1001,1003,1004]. Other agencies (USGS, APHA, ASTM, NOAA, etc. also publish different "standard methods." If one simply wants to know whether or not the concentration exceeds EPA criteria or various low concentration benchmarks for humans, fish, or wildlife, it is not always too clear which "standard method" is optimum, although some might argue that for water, the 1996 EPA methods 1640 and 1669 (see details below) should apply.

Standard water methods used in the past have included EPA 220.1, 220.2, and ICP method 200.7 (40 CFR, Part 136.3, Table 1B, page 381, 1994). Inductively-coupled plasma (ICP) methods often have sufficiently low detection limits for considering risks to fish and wildlife.

However, detection limits should be no higher than comparison benchmarks or criteria for various media (water, sediments, soil, tissues, etc, see sections above) being considered. In some situations (as when background concentrations and benchmark comparisons are low), water detection limits as low as 0.024 ug/L may be necessary, using EPA method 1640, since EPA Water Quality Criteria are as low as 2.5 ug/L [1001]. Detection limits can be as low as 0.2 ug/g in tissues and other solids [979].

In the case of copper, natural background levels are often higher and thus the following ICP detection limits (the default concentrations often recommended by the Fish and Wildlife Service and the National Park Service) are often sufficiently low: 0.50 ppm dry weight in tissues, 1.0 ppm in sediments and soils; 0.005 ppm (mg/L) in water (Roy Irwin, National Park Service, Personal Communication, 1996).

Acceptable containers (after proper cleaning per EPA protocols) for Antimony, Arsenic, Cadmium, Copper, Lead, Nickel, Selenium, Silver, Thallium, and Zinc: 500-mL or 1-L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid [1003].

Since most analytical methods for copper do not distinguish the form of copper present; it is known how much total copper is present, but not the nature of the copper compounds or complexes present or how labile or available they are [979].

Notes on total vs. acid soluble vs. dissolved metals:

Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, the lab settings were typically fairly clean and the numbers generated by the lab tests are therefore often even more comparable to field "dissolved" values than to field "total" values (Glen Suter, Oak Ridge National Lab, Personal Communication, 1995). As of January 1995, the U.S. EPA was recommending that states use dissolved measurements in water quality standards for metals, in concert with recommendations EPA previously made for the Great Lakes [672]. The conversion factors recommended by EPA for converting total recoverable metals criteria to dissolved metal criteria were given as follows [672]:

Cooper conversion for acute or chronic criteria: 0.958 (that is, total recoverable metals criteria x 0.958 = dissolved metals criteria).

The conversion factor recommended by EPA for converting total recoverable copper (both continuous and maximum concentrastions) to dissolved concentrations in the January 1997 draft EPA Guidelines for 5 year 305(B) assessments was 0.960.

Note: None of these "generic" conversion factors work well for all areas. Both total and dissolved concentrations should be checked at new locations before relying on generic conversion factors (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Filtration and Acidification of Water Samples:

For ICP water samples for metals, EPA recommends the following (40 CFR Part 136, Appendix C, pertaining to ICP analyses using method 200.7, 1994 edition of CFR Part 40):

1) For samples of "total or total recoverable elements," samples should be acidified to a pH of two or less at the time of collection or as soon as possible thereafter.

> Note: In more recent (1996) guidance related to the more rigorous method 1669, EPA clarified (some would say confused or added data variability) the issue of when to acidify by stating:
>
> > "Preservation recommendations for Antimony, Arsenic, Cadmium, Copper, Lead, Nickel, Selenium, Silver, Thallium, and Zinc: Add 5 mL of 10% HN03 to 1-L sample; preserve on-site or immediately upon laboratory receipt" [1003].
> >
> > > Note: the nitric acid (triple distilled or not?) and dilution water (contaminated or not?) and containers (proper type, cleaned correctly or not?) used are all potential sources of contamination (see more detailed note below related to data variation factors).

2) For determination of dissolved elements, the samples must be filtered through a 0.45 micron membrane filter as soon as soon as practical after collection, using the first 50-100 ml to rinse the filter flask. Acidify the filtrate with nitric acid to a pH of 2 or less. Normally 3 mL of (1+1) of nitric acid per liter should be sufficient to preserve the sample.

3) For determination of suspended elements, the samples must be filtered through a 0.45 micron membrane filter as soon as soon as practical after collection. The filter is then transferred to a suitable container for storage and shipment, with no preservation required.

Sources of potential variation in contaminants data:

Variation in concentrations of contaminants may sometimes be due to differences in how individual investigators treat samples in the field and lab rather than true differences in environmental concentrations. Contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable. In fact, as mentioned above in the disclaimer, the interagency task force on water methods concluded that [1014]:

> It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a

> scientifically sound basis, and that...
>
> No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather than better. The trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

At minimum, before using contaminants data from diverse sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate.

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to quality assurance problems due to the use of detection limits that are too high, the loss or addition of contaminants through inappropriate handling, or the use of inappropriate methods.

It was recognition that collectors and labs often contaminate samples that led EPA to develop the

1600 series of water protocols for low detection limit applications [1001,1002,1003,1004]. In comparing contaminants data from different labs, different states, and different agencies, one should keep in mind that they are often not comparable. They may be as different as apples and oranges since:

1) Different Agencies (EPA, USGS, NOAA, and various State Agencies) publish different lab and field protocols. Each of these protocols is different and has typically changed over time.

> Note: Even "Standard EPA Methods" which are supposedly widely used by consultants, industry, and academia, have been variable over time and between application category (Drinking Water vs. NPDES, vs. RCRA, vs. CERCLA, vs. Water-Quality Based permits, etc.).
>
> Preservation and other details of various EPA lab and field protocols have changed over the years, just as they have at USGS and various States and other agencies. USGS data from 30 years ago may be different than USGS data today due to differences (drift) in lab and field protocols rather than differences in environmental concentrations.

2) Independent labs and field investigators are not always using "the latest and greatest methods," and it is difficult for them to keep up with all the changes from various agencies in the midst of their "real world" busy lives. Updates are not always convenient to obtain. For example, EPA changes are scattered through various proposed Federal Register Notices, various updates of CFRs, and numerous publications originating in many different parts of EPA and their contractors. The wording is sometimes imprecise and is often inconsistent between EPA methods for different applications.

3) The details of the way one person collects, filters, and acidifies water samples in the field may be different than the way another does it. Sources of potential variation include the following:

> A) The protocol phrases "As soon as

practical or as soon as possible." Different situations can change the elapsed time considered by the field collector to be "as soon as practical." It may take different amounts of time to get to a safe or otherwise optimum place to filter and/or acidify and cool the samples. In one case precipitation and other changes could be going on in the collection bottle while the bottle is on the way to filtration and acidification. In other cases, the field collector filters and acidifies the samples within minutes. Weather, safety concerns, and many other factors could play a role.

> Further insight related specifically to copper:
>
> > In a study at Yellowstone Park, Soda Butte Creek, filtering and then acidifying of water samples was done in two ways: The first way was in the field, per original standard EPA suggestions in 40 CFR. The second way was in the in the lab after 6 to 8 days. On two dates, lab filtered and acidified water was always higher in dissolved copper, a somewhat counter-intuitive result (Al, Fe, Mn, Zn, and Ni showed the opposite trend, tending to be higher in field filtered and acidified samples). On a third date 6 lab filtered and acidified samples were higher in copper and 3 field filtered and acidified samples were higher (Del Nimmo, USGS, personal communication, 1997).
> >
> > In other Yellowstone investigations, grab samples of clear leachate water from mine tailings started precipitating all of sudden, fairly soon after collection. The water was toxic if tested fresh from the seep--it began the test as clear but turned red on oxidation. If the sample was

held overnight, shaken or aerated, or centrifuged, it became non-toxic to fish and daphnids. An attempt was made to analyze both the water and (reddish) sediment that forms after the water emerges and is oxidized. The sample was brought (unfiltered and non-acidified) back to Colorado State University. It was split into two portions. One water portion was analyzed using total analysis, the other as dissolved. The sediments were also analyzed. Upon shaking the sample, the red sediment on the bottom became re-suspended. There were many metals in the water but the sediment was made up of mainly Fe and Mn, both very difficult to dissolve. Results of the analysis of sediment that precipitated in the sample using ICP: Fe at 90.5 mg/l (not kg because he had to dissolve it with HNO3) and Mn at 3.8 mg/l. Another worker used the standard EPA recommended practice of used acidification with HNO3 then AA and reported Fe at below detection as dissolved but 86 mg/l as total. Mn was 2.7 mg/l as dissolved and 4.2 as total (Del Nimmo, USGS, personal communication, 1997).

B) Differences in numerous other details of the method used can drastically change the results. Some cold, wet, hurried, or fire ant-bitten collectors might decide that it is not "practical" to filter and acidify quite so immediately in the field, and may decide the shore, a vehicle, a motel room, or even a remote lab are more "practical" locations. Filtering and acidifying in the field immediately has been thought of as a better option for consistency (see silver entry fo an example of what can happen if there is a delay). However, in recent methodology designed to prevent some the contamination and variability listed above, EPA has recently suggested that waiting until the sample arrives at the lab before acidifying is OK [1003].

C) What kind of .45 micron filter was used? The flat plate filters that were used for years tended to filter .45 micron sizes at first and then smaller and smaller sizes as the filtering proceeded and the filter loaded up with particulate matter. As the filter clogged, the openings grew smaller and colloids and smaller diameter matter began to be trapped on the filter. For this reason, both the USGS and EPA 1600 series protocols have gone to tortuous-path capsule filters that tend to filter .45 micron sizes more reliably over time. Example of specifications from EPA method 1669:

> Filter—0.45-um, 15-mm diameter or larger, tortuous-path capsule filters, Gelman Supor 12175, or equivalent [1003].

D) "Normally 3 mL of (1+1) of nitric acid per liter should be sufficient to preserve the (water) sample" (40 CFR Part 136, Appendix C, pertaining to ICP analyses using method 200.7, 1994 edition of CFR Part 40). Sometimes it is not, depending on alkalinity and other factors. What field collectors sometimes (often?) do is just use pop tabs of 3 mL of nitric acid and hope for the best rather than checking to see that the acidity has been lowered to below a pH of two. EPA CFR guidelines just call for a pH of below two, whereas samples meant to be "acid soluble" metals call for a pH of 1.5 to 2.0 [25]. See also, various USEPA 1984 to 1985 Ambient Water Quality Criteria Documents for individual metals.

> Note: Some shippers will not accept samples with a pH of less than 1 for standard shipping (John Benham, National Parks Service Personal Communication, 1997).

E) One person might use triple distilled concentrated nitric acid rather than reagent grades of acid to avoid possible contamination in the acid, while another may not. When using very low detection limits, some types of acid may introduce contamination and influence the results. Using a 10% dilution of nitric acid as called for by EPA [1003] is another potential source of contamination, since the dilution water and/or containers may be contaminated. Sometimes people may be incorrectly determining that background concentrations are high due to contamination sources such as these (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

> Note: Just using triple distilled nitric acid may not be the total answer to potential contamination. The key issue to be sure that the acid used is free of the metals being analyzed. In guidance for EPA method 1669, the use of "ultrapure nitric acid; or Nitric acid, dilute, trace-metal grade" is specified [1003]. In guidance for EPA method 1638, the use of "Nitric acid—concentrated (sp gr 1.41), Seastar or equivalent" is specified [1003].

F) Holding times can strongly influence the results and there can be quite a bit of variation even within EPA recommended 6 month limits (see Silver entry for details). Holding times recommended for EPA for water samples of metals other than mercury or chromium VI have usually been listed as 6 months (Federal Register, Volume 49, No. 209, Friday, October 28, 1984, page 43260). In the 1994 version of the CFR, NPDES holding times for mercury and Chromium VI are the same ones listed in 1984, but no EPA holding times are given for other metals (40 CFR, Part 136.3, Table 2, page 397, 1994). EPA sources stated this was a typo, that no one else brought it to their attention in the last 3 years, that 6 months is still an operable holding time for "other metals" including this one, and that 6 months is actually an artifact from the days when 6 month composite samples were used for NPDES permits rather than having been originally scientifically derived.

Counterpoint: Although some information suggests that 6 months is probably too long for some contaminants in some scenarios (see silver and copper entries), not all of the information in the literature casts the 6 month metals holding time in such questionable light. In one study, two EPA research chemists found that preservation under certain conditions of drinking water (EPA Method 200.8) metals samples to a pH of less than 2 effectively stabilized the metal concentrations for 6 months. They found that trace metal standards in the 10 to 50 ug/L concentration could be held in 1% nitric acid if a 5% change of concentration was acceptable [1009]. Some metal concentrations changed more than 5% (Zinc up to 24%, Selenium up to 23%) [1009]. Vanadium, Manganese and Arsenic changed up to 5-7% [1009]. In some of the trials, metals were higher after 6 months due to leaching from containers, while in some they were lower [1009]. The changes were nevertheless considered not of great consequence related to drinking water MCLs and EPA method 200.8 [1009]. However, it is not clear that the careful measures utilized (like rechecking to make sure the pH was less than 2, the use of particular kinds of water samples, the use of particular acids, etc.) in this one study replicates what goes on in day to day ("real world") contaminants lab work around the country.

Some EPA sources state that 6 months should be OK if the sample bottle is vigorously shaken and re-acidified in the lab prior to lab analyses, a practice not universally or even particularly commonly done in labs today. The degree to which a water sample is re-acidified, re-checked for pH, shaken before analysis, and the length of time it sits before and after these steps, seems to vary a lot between laboratories, and EPA guidance for various methods is not consistent. Some labs recheck pH, some don't. Some shake, some don't, etc. For drinking water, preservation is considered complete after the sample is held in pH of less than 2 for at least 16 hours [1007]. New EPA Method 1638 specifies:

> "Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls. The sample pH should be verified as <2 immediately before withdrawing an aliquot for processing or direct analysis. If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2" [1003].

For many other methods, the minimum holding time in acid is not stated or is different (see various EPA and other Agency methods).

G) If present, air in head space can cause changes in water sample concentrations (Roy Irwin, National Park Service, Personal Communication, based on several discussions with EPA employees and various lab managers in February 1997).

Note: air from the atmosphere or in headspace can cause oxidation of anaerobic groundwater or anaerobic sediment samples. This oxidation can cause changes in chemical oxidation states of contaminants in the sample, so that the results are not typical of the anaerobic conditions which were present in the environment prior to sampling (John Benham, National Park Service, Personal Communication, 1997).

H) When is the sample shaken in the lab or the field? If the filter is acidified in the field, it will be shaken on the way back to the lab. If lab acidified, how much and when is the sample shaken and then allowed to sit again for various times periods before analyses? Many methods treat this differently, and what many field collectors and labs actually do before analyzing samples is different as well. For EPA method 1638, the word shake appears in the "Alternate total recoverable digestion procedure":

> "..Tightly recap the container and shake thoroughly" [1003].

I) If one field filters and acidifies, one often changes metal concentrations and colloidal content compared to samples not treated in this manner. Acidifying effects microbial changes. If one holds the samples a while before filtering and acidifying, the situation changes. In collection bottles, there are potential aging effects: temperature changes, changes in basic water chemistry as oxygen and other dissolved gasses move from the water into the headspace of air at the top, potential aggregation of colloidal materials, precipitation of greater sizes over time, development of bigger and more colloids, and more sorption (Roy Irwin, National Park Service, personal communication, 1997).

4) The guidance of exactly where to take water samples varies between various state and federal protocols. Taking water samples at the surface microlayer tends to increase concentrations of various contaminants including metals. Other areas of the water column tend to produce different concentrations. Large quantities of anthropogenic substances frequently occur in the surface microlayer at concentrations ranging from 100 to 10,000 times greater than those in the water column [593]. These anthropogenic substances can include plastics, tar lumps, PAHs, chlorinated hydrocarbons, as well as lead, copper, zinc, and nickel [593]. Sometimes a perceived trend can be more the result of the details of the sample micro-location rather than real changes in

environmental concentrations (Roy Irwin, National Park Service, personal communication, 1997). The new EPA method 1669 mentions the microlayer, and states that one can use a fluoropolymer closing mechanism, threaded onto the bottle, to open and close a certain type of bottle under water, thereby avoiding surface microlayer contamination [1003]. However, even this relatively new EPA method 1669 also gives recommendations for ways to sample directly at the surface, and does not discourage the use of surface samples.

5) Although the above examples are mostly related to water samples, variability in field and lab methods can also greatly impact contaminant concentrations in tissues, soil, and sediments. Sediment samples from different microhabitats in a river (backwater eddy pools vs. attached bars, vs. detached bars, vs. high gradient riffles vs. low gradient riffles, vs. glides, etc.) tend to have drastically different concentrations of metals as well as very different data variances (Andrew Marcus, Montana State University, personal communication, 1995). Thus, data is only optimally comparable if both data collectors were studying the same mix of microhabitats, a stratified sampling approach which would be unusual when comparing random data from different investigators.

6) Just as there are numerous ways to contaminate, store, ship, and handle water samples, so are there different agency protocols and many different ways to handle samples from other media. One investigator may use dry ice in the field, another may bury the samples in a large amount of regular ice immediately after collection in the field, while a third might place samples on top of a small amount of ice in a large ice chest. The speed with which samples are chilled can result in different results not only for concentrations of organics, but also for the different chemical species (forms) of metals (Roy Irwin, National Park Service, personal communication, 1997).

7) In comparing contaminants metals data, soil and sediment contaminant concentrations should usually be (but seldom has been) normalized for grain size, total organic carbon, and/or acid volatile sulfides before biologically-

meaningful or trend-meaningful comparisons are possible (Roy Irwin, National Park Service, Personal Communication, 1997).

8) There has been tremendous variability in the precautions various investigators have utilized to avoid sample contamination. Contamination from collecting gear, clothes, collecting vehicles, skin, hair, collector's breath, improper or inadequately cleaned sample containers, and countless other sources must carefully be avoided when using methods with very low detection limits [1003].

Highlights from EPA Method 1669 for Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels [1003]:

As of March 1997, the 1600 series methods had not yet been officially approved in 40 CFR for use in NPDES permits, but the improvements in these methods were suggested by EPA staff to be wise practice when attempting low detection limit analyses for metals.

This "field method details" protocol is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved Antimony, Arsenic, Cadmium, Copper, Chromium III, Chromium VI, Lead, Mercury, Nickel, Selenium, Silver, Thallium, and Zinc, at low (Water Quality Criteria Range) concentrations [1003]. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act [1003].

This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities [1003]. Existing regulations (40 CFR Parts 400–500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range [1003]. This guidance is therefore directed at the collection of samples to be measured at or near the water quality criteria levels [1003]. Often these methods will be necessary in a water quality criteria-based approach to EPA permitting [1001]. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions [1003].

The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized [1003]. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination [1003].

Clean and ultraclean—The terms "clean" and "ultraclean" have been used in other Agency guidance [1004] to describe the techniques needed to reduce or eliminate contamination in trace metals determinations [1003]. These terms are not used in this sampling method due to a lack of exact definitions [1003]. However, the information provided in this method is consistent with summary guidance on clean and ultraclean techniques [1004].

Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations [1003]. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels [1003]. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals [1003].

There are numerous routes by which samples may become contaminated [1003]. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles [1003]. Even human contact can be a source of trace metals contamination [1003]. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation [1003].

For dissolved metal determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The filtering procedures are described in this method [1003]. The filtered samples may be preserved in the field or transported to the laboratory for preservation [1003].

This document is intended as guidance only [1003]. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance [1003]. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures [1003]. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected [1003].

The method includes a great many details regarding prevention of field contamination of samples, including clothing needed, clean hands vs. dirty hands operations, and numerous other details [1003].

Surface sampling devices—Surface samples are collected using a grab sampling technique [1003]. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device [1003]. Grab samplers may be used at sites where depth profiling is neither practical nor necessary [1003].

An alternate grab sampler design is available [1003]. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap removed, sample collected, and bottle recapped at a selected depth [1003]. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination [1003]. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated [1003].

Subsurface sampling devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary [1003]. Subsurface samples are collected by pumping the sample into a sample bottle [1003]. Examples of subsurface collection systems include the jar system device or the continuous-flow apparatus [1003].

Advantages of the jar sampler for depth sampling are (1) all wetted surfaces are fluoropolymer and can be rigorously cleaned; (2) the sample is collected into a sample jar from which the sample is readily recovered, and the jar can be easily recleaned; (3) the suction device (a peristaltic or rotary vacuum pump, is located in the boat, isolated from the sampling jar; (4) the sampling jar can be continuously flushed with sample, at sampling depth, to equilibrate the system; and (5) the sample does not travel through long lengths of tubing that are more difficult to clean and keep clean [1003]. In addition, the device is designed to eliminate atmospheric contact with the sample during collection [1003].

Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.) [1003]. When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection [1003].

Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity [1003]. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified [1003]. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing [1003]. Horizontal mixing occurs in constrictions in the channel [1003]. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples) [1003].

To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles [1003]. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads [1003]. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow [1003].

The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations [1003]. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last [1003]. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location [1003].

One grab sampler consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point [1003]. The collar holds the sample bottle [1003]. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination [1003]. Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials unless mercury is a target analyte [1003]. Assembly of the cleaned sampling device is as follows:

Sample collection procedure—Before collecting ambient water samples, consideration should be given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers) [1003]. Sufficient sample volume should be collected to allow for necessary quality control analyses, such as matrix spike/ matrix spike duplicate analyses [1003].

Highlights from EPA Lab Method 1640: Determination of trace elements in ambient waters by on-line chelation preconcentration and inductively coupled plasma-mass spectrometry:

This method is for the determination of dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using on-line chelation preconcentration and inductively coupled plasma-mass spectrometry (ICP-MS) [1003]. It may also be used for determination of total recoverable element concentrations in these waters [1003]. This method was developed by integrating the analytical procedures contained in EPA Method 200.10 with the quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels [1003]. This method contains QC procedures that will assure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (the "Sampling Method") [1003]. The Sampling Method is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process [1003].

This method is applicable to the following elements:

Cadmium (Cd), Copper (Cu), Lead (Pb), and Nickel (Ni) [1003].

Many of the requirements for this method are similar to those for other EPA 1600 series methods [1003].

As of March 1997, the EPA 1600 series methods had not yet been officially approved in 40 CFR for use in NPDES permits, but the improvements in these methods were suggested by EPA staff to be wise practice when attempting low detection limit analyses for metals [1003].

For dissolved metal determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The Sampling Method describes the filtering procedures [1003]. The filtered samples may be preserved in the field or transported to the laboratory for preservation [1003]. Procedures for field preservation are detailed in the Sampling Method; provides procedures for laboratory preservation are provided in this method [1003].

Acid solubilization is required before the determination of total recoverable elements to aid breakdown of complexes or colloids that might influence trace element recoveries [1003].

This method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), including the interpretation of spectral and matrix interferences and procedures for their correction; and should be used only by personnel thoroughly trained in the handling and analysis of samples for determination of metals at EPA WQC levels [1003]. A minimum of six months' experience with commercial instrumentation is recommended [1003].

Sample preservation—Preservation of samples and field blanks for both dissolved and total recoverable elements may be performed in the field when the samples are collected or in the laboratory [1003]. However, to avoid the hazards of strong acids in the field and transport restrictions, to minimize the potential for sample contamination, and to expedite field operations, the sampling team may prefer to ship the samples to the laboratory within 2 weeks of collection [1003]. Samples and field blanks should be preserved at the laboratory immediately when they are received [1003]. For all metals, preservation involves the addition of 10% HNO3 to bring the sample to pH <2 [1003]. For samples received at neutral pH, approx 5 mL of 10% HNO3 per liter will be required [1003].

Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls [1003]. The sample pH should be verified as <2 immediately before an aliquot is withdrawn for processing or direct analysis [1003]. If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for 16 h until verified to be pH <2 [1003].

Highlights from EPA Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma — Mass Spectrometry:

This 1996 proposed EPA method is for the determination of dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using inductively coupled plasma-mass spectrometry (ICP-MS) [1003]. It may also be used for determination of total recoverable element concentrations in these waters [1003]. This method was developed by integrating the analytical procedures in EPA Method 200.8 with the quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels [1003]. This method contains QC procedures that will assure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels ("Sampling Method") [1003]. The Sampling Method is necessary to assure that trace metals determinations will not be compromised by contamination during the sampling process [1003].

This method may be used with the following metals:

Antimony (Sb), CAS 7440-36-0
Cadmium (Cd), CAS 7440-43-9
Copper (Cu), CAS 7440-50-8
Lead (Pb), CAS 7439-92-1
Nickel (Ni), CAS 7440-02-0
Selenium (Se), CAS 7782-49-2
Silver (Ag), CAS 7440-22-4
Thallium (Tl), CAS 7440-28-0
Zinc (Zn), CAS 7440-66-6

Lower detection levels for copper are available with EPA method 1640 (see description above).

As of March 1997, the EPA 1600 series methods had not yet been officially approved in 40 CFR for use in NPDES permits, but the improvements in these methods were suggested by EPA staff to be wise practice when attempting low detection limit analyses for metals [1003].

This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities [1003]. Existing regulations (40 CFR Parts 400–500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range [1003].

The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized [1003]. This method includes suggestions for improvements in facilities and analytical techniques that should maximize the ability of the laboratory to make reliable trace metals determinations and minimize contamination [1003]. These suggestions are ...based on findings of researchers performing trace metals analyses [1003]. Additional suggestions for improvement of existing facilities may be found in EPA's Guidance for Establishing Trace Metals Clean Rooms in Existing Facilities, which is available from the National Center for Environmental Publications and Information (NCEPI) at the address listed in the introduction to this document [1003].

Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations [1003]. These terms are not used in this method because of their lack of an exact definition [1003]. However, the information provided in this method is consistent with the summary guidance on clean and ultraclean techniques [1003].

The procedure given in this method for digestion of total recoverable metals is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L [1003]. For the analysis of samples containing higher concentrations of silver, succeedingly smaller volume, well-mixed sample aliquots must be prepared until the analysis solution contains <0.1 mg/L silver [1003].

Sample preservation—Preservation of samples and field blanks for both dissolved and total recoverable elements may be performed in the field at time of collection or in the laboratory [1003]. However, to avoid the hazards of strong acids in the field and transport restrictions, to minimize the potential for sample contamination, and to expedite field operations, the sampling team may prefer to ship the samples to the laboratory within two weeks of collection [1003]. Samples and field blanks should be preserved at the laboratory immediately upon receipt [1003]. For all metals, preservation involves the addition of 10% HNO3 to bring the sample to pH <2 [1003]. For samples received at neutral pH, approx 5 mL of 10%

HNO3 per liter will be required [1003].

Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipet and test the aliquot [1003]. When the nature of the sample is either unknown or known to be hazardous, acidification should be done in a fume hood [1003].

Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls [1003]. The sample pH should be verified as <2 immediately before withdrawing an aliquot for processing or direct analysis [1003]. If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2 [1003].

For drinking water methods, EPA lists the following older methods [893]:

Monitoring Requirements: Ground water systems monitored annually; surface water systems monitored quarterly; repeat monitoring dependent upon detection and compliance history with a minimum of 5 years between sampling; community and non-transient non-community water systems to have different monitoring requirements for determining compliance with corrosion control treatment techniques.

Analytical Methods: Atomic absorption/furnace technique (EPA 220.2;ASTM D1688-90C; SM 3113); atomic absorption/direct aspiration (EPA 220.1;ASTM D1688-90A; SM 3111-B); inductively-coupled plasma (EPA 200.7; SM 3120);inductively-coupled plasma/mass spectrometry (EPA 200.8); atomic absorption/platform furnace (EPA 200.9).

See also: note on colloids in W.Misc. section above.

Detailed Information from ATSDR [979]:

BIOLOGICAL MATERIALS:

Copper in other biological materials such as hair and nails can be determined by using suitable procedures for dissolving the sample matrix and employing the same analytical techniques as with blood and tissue [979]. These methods determine the total amount of copper in the sample [979]. The methodology for analyzing biological material is similar to that used for environmental samples [979]. The most commonly employed methods use atomic adsorption spectroscopy or inductively coupled plasma-atomic emission spectroscopy [979].

ENVIRONMENTAL SAMPLES:

Analytical methods determine the total copper content of the samples; determining specific copper compounds and complexes in samples is difficult [979]. The most common methods used for environmental samples are atomic absorption spectrometry, either flame or graphite furnace, and inductively coupled plasma-atomic emission spectroscopy [979]. Water and wastewater samples can be analyzed for copper by EPA Test Method 220.1 (atomic absorption, direct aspiration) or 220.2 (atomic absorption, furnace technique) [979]. These methods are suitable for groundwater and surface water and domestic and industrial effluents [979]. Both freshwater and saline water samples can be analyzed by these methods [979]. If the determination of dissolved and suspended copper is required, samples should be filtered using a 0.45 um membrane filter [979]. Suspended solids, as well as sludge and sediment, may be analyzed by EPA Methods 220.l and 220.2 after an initial acid digestion with HNO3 [979]. Interference by other elements is not a problem in the analysis; however, background correction may be required in using atomic absorption to correct for nonspecific absorption and scattering which may be significant at the analytical wavelength 324.7 nm [979]. In the determination of trace metals, major concerns are contamination and loss [979]. Contamination can be introduced from impurities in reagents and containers as well as from laboratory dust [979]. Losses may also occur due to adsorption onto containers [979].

AAS = atomic absorption spectrometry; ASV = anodic stripping voltammetry; ICP-AES = inductively coupled plasma-atomic emission spectroscopy [979].

Other analytical methods used for copper analysis include x-ray fluorescence, anodic stripping voltammetry, neutron activation analysis, photon-induced x-ray emission, as well as chemical derivation, followed by gas chromatographic or liquid chromatographic analysis [979].