ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

SILVER ENTRY

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Like a library or many 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.

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 without 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 or summaries 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).

Silver (Ag, CAS number 7440-22-4)

NOTE: With the permission of Ron Eisler, Eisler's 1996 comprehensive summary on hazards of selected contaminants to plants and animals is used extensively in this document in word-for-word quotes. Each of these quotes is attributed to Eisler [947].

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Silver is a white, ductile metal occurring naturally in the pure form and in ores. Silver has the highest electrical and thermal conductivity of all metals. Some silver compounds are extremely photosensitive and are stable in air and water except for tarnishing readily when exposed to sulfur compounds. Silver is a normal trace constituent of many organisms [947].

In natural environments, silver occurs primarily in the form of the sulfide or is intimately associated with other metal sulfides, especially those of lead, copper, iron, and gold. Silver readily forms compounds with antimony, arsenic, selenium, and tellurium. Silver has two stable isotopes (107-Ag and 109-Ag) and 20 radioisotopes; none of the radioisotopes of silver occurs naturally, and the radioisotope with the longest physical half-life (253 days) is 110 m Ag. Several compounds of silver are potential explosion hazards: silver oxalate decomposes explosively when heated; silver acetylide (Ag2C2) is sensitive to detonation on contact; and silver azide (AgN3) detonates spontaneously under certain conditions [947].

Br.Haz: General Hazard/Toxicity Summary:

Hazards to fish, wildlife, and other non-human biota:

In fish and amphibian toxicity tests with 22 metals and metalloids, silver was the most toxic tested element as judged by acute LC50 values. In solution, ionic silver is extremely toxic to aquatic plants and animals. Among all tested species, the most sensitive individuals to silver were the poorly nourished and young and those exposed to low water hardness or salinity. It is emphasized that silver-induced stress syndromes vary widely among animal classes. Among marine organisms, for example, silver was associated with respiratory depression in marine gastropods and

cunners (Tautagolabrus adspersus), a teleost; however, silver increased oxygen consumption in 6 species of bivalve molluscs [947].

Although hardness is widely recognized as important in potential bioavailability and toxicity of various metals, alkalinity and availability of chloride ions are sometimes more important co-factors (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Silver occurs naturally in several oxidation states, the most common being elemental silver (Ag) and the monovalent ion (Ag+). Soluble silver salts are in general more toxic than insoluble salts; in natural waters, the soluble monovalent species is the form of environmental concern [947].

Silver (Ag) found in the body of mammals (including humans) has no known biological purpose and is suspected of being a contaminant [947]. Silver, as ionic Ag+, is one of the most toxic metals known to aquatic organisms in laboratory testing, although large industrial losses to the aquatic environment are probably infrequent because of its value as a recoverable resource. Silver, however, is of concern in various aquatic ecosystems because of the severity of silver contamination in the water column, sediments, and biota. San Francisco Bay, for example, is impacted from discharges of silver in wastewater outfalls and from the diagenic remobilization of silver from contaminated sediments in the estuary [947].

Silver element exhibits bactericidal properties [257,947]. These are not fully understood, although they are thought to be a result of its ability to absorb oxygen [257].

A simple, rapid assay, based on the lysosomal incorporation of neutral red by cells, conveniently carried out in 96 well microtiter plates, was used to evaluate the cytotoxic effect of cationic and anionic metal salts on BALB/c mouse 3T3 fibroblasts. Ranking of the metals according to their decreasing potency was revealed the rand order of cadmium > mercury > silver > zinc > manganese > copper > cobalt > nickel > chromium (III) for the cationic metals (Borenfreud E, Puerner JA; Toxicol 39 (2): 121-34, 1986) [940].

Signs of chronic silver intoxication in tested birds and mammals included cardiac enlargement, vascular hypertension, hepatic necrosis, anemia,

lowered immunological activity, altered membrane permeability, kidney pathology, enzyme inhibition, growth retardation, and a shortened life span [947].

Repeated exposure of animals to silver may produce anemia, cardiac enlargement, growth retardation, and degenerative changes in the liver. (Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 622) [940].

Elevated silver concentrations in biota occur in the vicinities of sewage outfalls, electroplating plants, mine wastes, and silver-iodide seeded areas; in the United States, the photography industry is the major source of anthropogenic silver discharges into the biosphere [947].

In studies of subsurface agricultural irrigation drainage waters of the San Joaquin Valley of California, silver was determined to be a "substance of concern, additional data needed" [445].

Ecological and toxicological aspects of silver have been reviewed by Smith and Carson (1977), the U.S. Environmental Protection Agency (1980, 1987), Lockhart (1983), the U.S. Public Health Service (1990), Andren et al. (1993, 1994), and Andren and Bober (1995) (see [947] for full references). Eisler's report (used extensively in this document) on silver is another in a series on hazards of selected contaminants to plants and animals, with an emphasis on fishery and wildlife resources [947]. It was prepared in response to requests for information on silver from environmental specialists of the U.S. Fish and Wildlife Service [947].

Hazards to humans:

In humans, prolonged ingestion of even small quantities may cause silver poisoning, called argyria; symptoms include a blue coloration of lips and gums as silver is deposited there [257].

Long-term industrial or medical exposure to silver and its compounds may increase blood concentrations of silver to levels which can have toxic effects, such as induction of sarcomas, anemia, and enlargement of the heart [947]. Repeated occupational handling of silver objects, especially after repeated minor injuries, may result in

localized argyria--a bluish-gray discoloration of the skin at the exposed site. In humans, the most common noticeable effects of chronic exposure to silver and its compounds are generalized argyria, localized argyria, and argyrosis. Generalized argyria consists of a slate-gray pigmentation of the skin and hair caused by deposition of silver in the tissues, a silver coloration of the hair and fingernails, and a blue halo around the cornea and in the conjunctiva [947].

Acute toxic effects of silver on humans have resulted only from accidental or suicidal overdoses of medical forms of silver. Symptoms of acute silver poisoning in patients dying after intravenous administration of Collargo (silver plus silver oxide) included gastrointestinal disturbances, pulmonary edema, tissue necrosis, and hemorrhages in bone marrow, liver, and kidney. High sublethal doses of silver nitrate taken orally cause some patients to experience violent abdominal pain, abdominal rigidity, vomiting, and severe shock; systemic effects among recovering patients are unlikely, although degenerative liver changes may occur. In humans, skin contact with silver compounds may cause mild allergic reactions such as rash, swelling, and inflammation; industrial and medicinal exposures to silver may cause lesions of the kidneys and lungs, and arteriosclerosis; colloidal silver compounds may interfere with nasal ciliary activity; and exposure to dust containing high levels of silver compounds, such as silver nitrate or silver oxide, may cause breathing problems, lung and throat irritation, and stomach pain [947].

The organs which are affected by exposure to silver and soluble silver compounds (as Ag) are nasal septum, skin, eyes (NIOSH. Pocket Guide to Chemical Hazards. 5th Printing/Revision. DHHS Publ. No. 85-114. Washington, D.C.: U.S. Dept. of Health and Human Services,NIOSH/Supt. of Documents, GPO, Sept. 1985. 209) [940].

The main sources of silver water pollution are mining and geological sources; silver can cause blue skin discoloration (argyria) in humans which drink tainted drinking water [658]. Silver's proposed use as a water disinfectant is unlikely to become a wide practice due to worries about the possibility of residual silver in the treated water [190].

Repeated exposure to silver salts or colloidal

silver by inhalation or ingestion brings about effects classically described as generalized argyria (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 527) [940].

A striking feature of argyria is the regular deposition of silver in blood vessels and connective tissue, especially around the face, conjunctiva, hands, and fingernails. (Hill WR Pillsbury DM; Argyia, the Pharmacology of Silver (1939) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-42, 1980, EPA 440/5-80-071) [940].

Silver may be a cause of metal fume fever. (Haddad, L.M. and Winchester, J.F. Clinical Management of Poisoning and Drug Overdosage. Philadelphia, PA: W.B. Saunders Co., 1983. 662) [940].

A comprehensive human toxicological profile for silver and silver compounds is available from ATSDR [956]. Due to lack of time, not all of the important highlights from this ATSDR document have yet been completely incorporated into this entry.

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

Information from 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: In animals, local sarcomas have been induced after implantation of foils and discs of silver. However, the interpretation of these findings has been questioned due to the phenomenon of solid-state carcinogenesis in which even insoluble solids such as plastic have been shown to result in local fibrosarcomas.

HUMAN CARCINOGENICITY DATA: No evidence of cancer in humans has been reported despite frequent therapeutic use of the compound over the years.

ANIMAL CARCINOGENICITY DATA: Inadequate. Local

sarcomas have been induced after subcutaneous (s.c.) implantation of foils and discs of silver and other noble metals.

Silver and its compounds are not known to be carcinogenic [940,947]. In fact, the connections between human cancers and silver as a causal agent are tenuous. All available evidence is negative or inconclusive on silver's ability to induce cancer, mutagenicity, or birth defects in animals by normal routes of exposure. Silver pellets, however, implanted under the skin of rodents, have caused sarcomas, malignant fibrosarcomas, fibromas, fibroadenomas, and invasions of muscle with connective tissue; in these cases, silver seems to act as a nonspecific irritant rather than as a specific carcinogen. Intratumoral injections of colloidal silver promotes cancer growth in rats, possibly by producing an area of lowered tissue resistance that allows resistant cancer cells to grow freely; however, silver nitrate seems to be a tumor inhibitor in mice [947].

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

Silver and its compounds are not known to be mutagenic or teratogenic [947].

Based on the existing information, it is not known whether silver causes developmental toxicity in humans [956].

Silver concentrations in human tissues apparently increase with age. It has been detected in fetal livers and placentae (Robkin MA et al; Trans Am Nucl Soc 17: 97 (1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-1, 1980, EPA 440/5-80-071) [940].

Additional animal studies are needed to elucidate the effects of silver and silver compounds on reproduction, development, immunotoxicity, neurotoxicity, absorption, distribution, metabolism, and excretion; and on oral, dermal, and inhalation routes of exposure. In animals, there is also the need to establish a target organ for intermediate exposures to silver; to establish suitable biomarkers of silver exposures and effects; and to measure effects of chronic silver exposures on carcinogenicity. These studies should be implemented with suitable sentinel organisms including waterfowl, aquatic mammals, and other species of wildlife [947].

The existing evidence does not point to a strong effect of silver on reproduction. However, no multigeneration reproductive studies were located, and therefore a firm

conclusion regarding reproductive toxicity in humans cannot be made [956].

Existing data on mutagenicity are inconsistent, but data on genotoxicity suggest that the silver ion is genotoxic [956]. No studies were located that examined the mutagenicity or genotoxicity of silver in human cells [956].

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

About 2.47 million kg of silver are lost each year to the domestic biosphere, mostly (82%) as a result of human activities. The photography industry accounts for about 47% of all silver discharged into the environment from anthropogenic sources [947]. See also the Uses/Sources section below.

Most of the silver lost to the environment each year enters terrestrial ecosystems where it is immobilized in the form of minerals, metal, or alloys; agricultural lands may receive as much as 80,000 kg of silver from photoprocessing wastes in sewage sludge [947].

An estimated 150,000 kg of silver enter the aquatic environment every year from the photography industry, mine tailings, and electroplaters [947]. During processing of photographic paper and film, silver is generally solubilized as the tightly bound thiosulfate complex. Silver thiosulfate in secondary biological waste treatment plants is converted to insoluble (sic, actually "relatively insoluble") silver sulfide, which is removed in the sludge; only trace amounts of complexed and adsorbed silver are discharged into the aquatic environment. The silver incorporated into the sludge is immobile and should not restrict the use of sludge for the enrichment of soils [947].

Silver is usually found in extremely low concentrations in natural waters because of its low crustal abundance and low mobility in water. Metallic silver is insoluble (sic, actually relatively insoluble) in water but many silver salts, such as silver nitrate, are soluble in water to more than 1,220 g/L [947].

Sorption is the dominant process that controls silver partitioning in water and its movements in soils and sediments. As discussed later, silver enters the animal body through inhalation, ingestion, mucous membranes, and broken skin. The interspecies differences in the ability of animals to accumulate, retain, and eliminate silver

are large. Almost all of the total silver intake is usually excreted rapidly in feces; less than 1% of the total silver intake is absorbed and retained in tissues, primarily liver, through precipitation of insoluble silver salts [940].

In oysters and other bivalve molluscs, the major pathway of silver accumulation was from dissolved silver; uptake was negligible from silver adsorbed onto suspended sediments or algal cells, and oysters eliminated adsorbed silver in the feces. Sometimes, benthic bivalve molluscs accumulated silver from certain sediments [947].

At concentrations normally encountered in the environment, food chain biomagnification of silver in aquatic systems is unlikely, although regular ingestion of fish from contaminated waters may significantly affect dietary silver intake [947].

Factors governing the environmental fate of silver are not well characterized, including silver transformations in water and soil and the role of microorganisms. Food chain transfer of silver requires more current information on sources and forms of silver and data on concentrations in field collections of flora and fauna, especially near hazardous waste sites. Although silver in sewage sludge is mostly immobilized, data are limited on uptake by vegetation of silver from soils amended with silver-contaminated sewage sludge and on silver concentrations in flesh and milk of livestock pastured or fed grains raised on soils amended with sewage sludge. Data are needed on partition coefficients and vapor pressures of silver compounds and on silver concentrations in emissions from cement producers and smelters and refineries of copper, lead, zinc, silver, iron, and steel. Also, technology to recapture silver from waste media before it reaches the environment must be improved [947].

Environmental Fate [940]:

> Aquatic Fate: Sorption and precipitation processes are effective in reducing the concentration of dissolved silver and result in higher concentrations in the bed sediments than in the overlying waters. Sorption by manganese dioxide and precipitation with halides are probably the dominant controls on the mobility of silver in the aquatic environment. [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. 17-1].

Soil Adsorption/Mobility [940]:

Sorbtion appears to be the dominant process leading to partitioning into sediments. It appears that magnesium dioxide, ferric compounds, and clay minerals all have some degree of adsorptive affinity for silver and are involved in its deposition into sediments. [USEPA; Ambient Water Quality Criteria Doc: Silver p.B-1 (1980) EPA 440/5-80-071].

Synonyms/Substance Identification:

ARGENTUM [940]
SILBER (GERMAN) [940]
SILVER ATOM [940]
SILVER METAL [940]
L 3 [940]
SILFLAKE 135 [940]
SR 999 [940]
TCG 7R [940]
V 9 [940]
Algaedyn [940]
Silpowder 130 [940]
CI 77820 [940]
C I 77820 [940]
Caswell No 735 [940]
EPA pesticide chemical code 072501 [940]
Germany: C-Pigment 2 [940]
Silver, colloidal [940]
Shell silver [940]
Amalgum [940]

Molecular Formula:
Ag [940]

Associated Chemicals or Topics (Includes Transformation Products):

Found native or associated with copper, gold & lead [940].

Site Assessment-Related Information Provided by Shineldecker (Potential Site-Specific Contaminants that May be Associated with a Property Based on Current or Historical Use of the Property) [490]:

Raw Materials, Intermediate Products, Final Products, and Waste Products Generated During Manufacture and Use:

- Arsenic
- Chlorine
- Hydrogen cyanide
- Mercury

Other Associated Materials:

- Fluorides

Impurities [940]:

Silver (99.99 wt%) may include the following: 0.01 wt% copper; 0.001 wt% lead, iron, or palladium; and 0.0005 wt% bismuth, selenium, and/or tellurium [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 21(83) 11 [940].

Metabolism/Metabolites [940]:

Colloidal silver compounds have been widely used to treat upper respiratory infections, but the amount of silver absorbed and permanently retained by the respiratory tract has not been determined. The total safe period for nasal instillation of colloidal silver is believed to be 3 to 6 months. Colloidal silver compounds in the nose interfere with normal ciliary activity. [Hill WR, Pillsbury DM; Argyria, the Pharmacology of Silver (1939) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-73 (1980) EPA 440/5-80-071.

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

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

Maximum concentrations of total silver recorded in selected nonbiological media were 0.1 ug/L in oil well brines; 6 ug/L in groundwater near a hazardous waste site; 8.9 ug/L in seawater from Galveston Bay, Texas; 260 ug/L in the Genesee River, New York--the recipient of photoprocessing wastes; 300 ug/L in steam wells; 300 ug/L in treated photoprocessing wastewaters; 4,500 ug/L in precipitation from clouds seeded with silver iodide; and 43 mg/L in water from certain hot springs [947]. It is emphasized that only a small portion of the total silver in each of these compartments is biologically available. For example, typical publicly owned treatment works receiving photoprocessing effluents show silver removal efficiencies greater than 90 percent; the mean concentration of free silver ion present in the effluents from these plants ranged from 0.001 to 0.07 ug/L [947].

One of the highest silver concentrations recorded in

freshwater of 38 ug/L occurred in the Colorado River at Loma, Colorado, downstream of an abandoned gold-copper-silver mine, an oil shale extraction plant, a gasoline and coke refinery, and a uranium processing facility. The maximum recorded value of silver in tapwater in the United States was 26 ug/L--significantly higher than finished water from the treatment plant (maximum of 5.0 ug/L)--because of the use of tin-silver solders for joining copper pipes in the home, office, or factory [947].

The Genesee River in New York has received photoprocessing effluents for approximately 70 years. In 1973, on most sampling dates from May 31 to October 17, it contained 20 ug/l silver. However, levels of 90 to 260 ug/l were detected in June. Sediments contained up to 150 mg/kg silver dry weight. Raw Lake Ontario water at the Eastman Kodak intake pipe contained 1 ug/l silver. (Bard CC et al; J Water Pollut Control Fed 48: 389, 1976, as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-9 (1980) EPA 440/5-80-071) [940].

The Susquehanna River in Pennsylvania, which contained the highest concentrations of silver, was estimated to be transporting 4.5 tons of silver per year to the ocean. (Turekian KK, Scott MR; Environ Sci Technol 1: 940, 1967, as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-10 (1980) EPA 440/5-80-071) [940].

W.Typical (Water Concentrations Considered Typical):

In Lake Michigan, storms contribute a large fraction of the annual load of tributary-derived silver; concentrations of particle-bound Ag in many rivers during storms were more than 0.1 ug/L [947].

USGS 1985: Levels of 10 ug/L appear to be the limit in natural water due to physical/chemical factors [190]. For river waters, 0.3 ug/l has been suggested as average [190].

Fresh water: avg 0.2 ug/l; sea water: avg 0.24 ug/l (USEPA; Ambient Water Quality Criteria Doc: Silver p.C-1, 1980, EPA 440/5-80-071) [940].

Public drinking water supplies and river waters have a median concn of silver between 0.09-0.23 ug/l. (Hem JD; USGS Paper 1473 Washington D.C., 1970, as cited in USEPA; Amient Water Quality Criteria Doc: Silver p.A-2, 1980, EPA 440/5-80-071) [940].

A range of nondetected to 5 ug/l was reported for 380 finished drinking waters from the USA. (Seiler, H.G., H.

Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 620) [940].

Seawater has been reported to contain silver concn of 0.055-1.5 ug/l. (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 523) [940].

Silver was found in 6.6% of 1,577 surface water samples collected in the United States. Concentrations in samples containing silver varied from 0.1 to 38 ug/l with a mean of 2.6 ug/l. The highest silver concentration was in the Colorado River at Loma, Colorado. (Kopp JF, Kroner RC; Water Pollut Cont Fed 39: 1660, 1967, as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-8, 1980, EPA 440/5-80-071) [940].

In general, silver concentrations in surface waters of the United States decreased between 1970-74 and 1975-79, although concentrations increased in the north Atlantic, Southeast, and lower Mississippi basins. About 30 to 70% of the silver in surface waters may be ascribed to suspended particles, depending on water hardness or salinity. For example, sediments added to solutions containing 2 ug Ag/L had 74.9 mg Ag/kg DW sediment after 24 h in freshwater, 14.2 mg/kg DW at 1.5% salinity and 6.9 mg/kg DW at 2.3% salinity. Riverine transport of silver to the ocean is considerable: suspended materials in the Susquehanna River, Pennsylvania--that contained as much as 25 mg silver/kg--resulted in an estimated transport of 4.5 metric tons of silver to the ocean each year [947].

Information from ATSDR (see ATSDR for details on embedded references) [956].

> Boyle (1968) reported average (background) ambient concentrations of silver in fresh waters of 0.2 ug/L and in sea water of 0.25 ug/L [956]. Waters that leach silver-bearing deposits (e.g., in mining areas) may carry up to 100 times more silver than other fresh waters (Scow et al. 1981) [956]. Leaching is enhanced by low pH (Smith and Carson 1977) [956].
>
> In samples of 170 lakes in California, silver concentrations averaged 0.1 ug/L with a maximum of 6.0 ug/L (Bradford et al. 1968) [956]. Kharkar et al. (1968) reported that the average silver concentration of 10 U.S. rivers was 0.30 ug/L (range: 0.092-0.55 ug/L) [956].

In another survey, Kopp (1969) found silver in 6.6% of 1,577 surface waters sampled with a mean detected concentration of 2.6 ug/L (range: 0.1-38 ug/L) [956]. For 1970-1979, according to U.S. surface water sampling data from EPA's STORET database, the annual mean levels ranged from 1 ug/L to 9 ug/L and annual maximum concentrations were 94 ug/L to 790 ug/L (Scow et al. 1981) [956].

In 10 out of 13 major U.S. river basins, silver concentrations decreased from 1975-1979 as compared with 1970-1974 [956]. Concentrations increased in the North Atlantic, Southeast, and Lower Mississippi basins. In the U.S. Geological Survey, Water Resources Division portion of the database (from the early 1960s to mid- 1988), silver was detected in 2,195 of over 10,000 surface water samples; the mean and median concentrations in these samples were 1.9 ug/L and 2.0 ug/L, respectively (Eckel and Jacob 1988) [956].

Hem (1970) reported a median silver concentration of 0.23 ug/L in U.S. drinking water [956]. Letkiewicz et al [956]. (1984) analyzed the results of three surveys of U.S [956]. groundwater and surface water used as drinking water supplies. These surveys were the 1969 U.S Public Health Service Community Water Supply Survey (CWSS 1969), the 1978 EPA Community Water Supply Survey (CWSS 1978), and the 1978 through 1980 EPA Rural Water Survey (RWS) [956]. In CWSS 1969, silver was detected (minimum positive value was 0.1 ug/L) in 309 of 677 groundwater supplies, (mean 1.7 ug/L, median 1.3 ug/L. and range 0.1 to 9 ug/L) [956]. Silver was detected in 59 of 109 surface water supplies with a mean and median of 1.3 ug/L and a range of 0.1 to 4 ug/L [956]. In CWSS 1978, silver was detected (minimum positive value was 30 ug/L) in 8 of 81 groundwater supplies (range 30-40 ug/L, mean 31.9 ug/L, and median 30 ug/L) [956]. In the RWS conducted between 1978 and 1980, silver was detected (minimum quantifiable concentration apparently was 20 ug/L) in 10 of 71 groundwater supplies (mean and median 40 ug/L and range 20-80 ug/L) [956]. Silver was detected in 8 of 21 surface water supplies [956]. The range, mean and median of these 8 supplies were 20-60 ug/L, 36.2 ug/L, and 35 ug/L, respectively [956].

Letkiewicz et al. (1984) also summarized information from EPA's Federal Reporting Data System as of 1984, which indicated that 14 public water supplies (13 from groundwater) in the United States reported silver levels above 50 ug/L [956].

Letkiewicz et al. (1984) stated that it is not possible to determine which of these surveys is representative of current levels of silver in the U.S. water supply [956]. The large range in apparent detection limits further limits the usefulness of these data in estimating silver levels in U.S. water supplies [956].

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):

EPA 1996 IRIS Information [893]:

Ambient Water Quality Criteria for Aquatic Organisms:

Acute Freshwater: 9.2E-1 ug/L [893].

NOTE: Equation to determine criteria using water hardness is: acute criteria = e(1.72[ln(hardness)]-6.52) where "e" = exponential [947].

Chronic Freshwater: 1.2E-1 ug/L [893].

Some older references seem to clarify that the criterion of 0.12 ug/L is a four day average not to be exceeded more than once every three years and that it refers to acid-soluble silver, silver that passes through a 0.45 um membrane after the sample has been acidified to a pH between 1.5 and 2.0 with nitric acid [947]. Other older references simply give the chronic exposure criterion as 0.12 ug/L total recoverable silver [947].

Other older sources also list a freshwater chronic criteria value of 0.12 ug/L [446,689].

Note: In 1995, Patrick Davies of the Colorado Division of Wildlife, Fort Collins Colorado, was doing work on the chronic freshwater standard for

silver. His information suggested certain scenarios in which the standard should be strengthened rather than weakened. In lab experiments, trout died at concentrations of 1 and 1.8 ppb, although industry complained that in the field more of the silver would be bound to particles (Roy Irwin, National Park Service, Personal Communication, 1995).

Marine Acute: 7.2E+0 ug/L [893].

Marine Chronic: 9.2E-1 ug/L [893].

Some older references seem to clarify that the criterion of 0.92 ug/L is an average not to be exceeded more than once every three years and that it refers to acid-soluble silver, silver that passes through a 0.45 um membrane after the sample has been acidified to a pH between 1.5 and 2.0 with nitric acid [947].

IRIS Reference: 55 FR 19986 (05/14/89) [893].

Contact: Criteria and Standards Division / OWRS / (202)260-1315

Discussion: Criteria were derived from a minimum data base consisting of acute and chronic tests on a variety of species. Requirements and methods are covered in the reference to the Federal Register [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].

NOTES from Eisler [947] on silver criteria:

1) Proposed silver criteria for the protection of freshwater aquatic life during acute exposure now range from 1.2 to 13.0 ug total recoverable silver per liter at water hardnesses of 50 and 200 mg CaCO3/L,

respectively. If all total recoverable silver were in the ionic form, these proposed criteria would overlap the 1.2 to 4.9 ug/L range found lethal to sensitive species of aquatic plants and animals and indicates that some downward modification is needed in the proposed freshwater acute silver criteria. For freshwater aquatic life protection during chronic exposure, the proposed criterion of less than 0.13 ug total recoverable silver per liter is probably protective. But the proposed silver criterion of 2.3 ug (sic, this is an older criteria [446](total silver/L to protect marine life is unsatisfactory because phytoplankton species composition and succession are significantly altered at 0.3-0.6 ug total silver/L and because some species of marine algae and molluscs show extensive accumulations at 1.0-2.0 ug total silver/L. Limited but insufficient data were available on correlations between tissue residues of silver with health of aquatic organisms; additional research seems needed on the significance of silver residues in tissues [947].

2) In aquatic environments, more research is needed on the chemical speciation of silver to evaluate risk to the organism and its consumers. Most silver criteria formulated for the protection of aquatic life are now expressed as total recoverable silver per liter. But total silver measurements do not provide an accurate assessment of potential hazard. Silver ion (Ag+), for example, is probably the most toxic of all silver chemical species and must be accurately measured in the assessment of silver risks in aquatic environments, perhaps as acid-soluble silver. Little is known of the biocidal properties of Ag2+ and Ag3+ that are the active ingredients in disinfectants and used increasingly in water purification systems of drinking water and swimming pools. The effects of these silver species on organism health clearly must be researched [947].

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 Silver, CAS 7440-22-4 (ug/L):

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 4.1

NOTE: The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration). For sites with different water hardness, site-specific criteria should be calculated with the following formula:

Acute = e(1.72[ln(hardness)]-6.52) where "e" = exponential [947].

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: No information found.

NOTE: Other sources list an older freshwater chronic criteria value of 0.12 ug/L [446,689,947].

SECONDARY ACUTE VALUE: No information found.

SECONDARY CHRONIC VALUE: 0.36

LOWEST CHRONIC VALUE - FISH: 0.12

LOWEST CHRONIC VALUE - DAPHNIDS: 2.6

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: No information found.

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 30

LOWEST TEST EC20 - FISH: 0.20

LOWEST TEST EC20 - DAPHNIDS: <0.56

SENSITIVE SPECIES TEST EC20: 0.14

POPULATION EC2O: 0.32

Note: 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).

Other Water Concentration Concern Levels, Criteria, and Standards:

Colorado had a water quality standard (50 ug/L) for drinking water in 1991 [659].

Colorado specified a hardness dependent equation as the acute aquatic life water quality standard 1991; at a hardness of 100 mg/L, the standard rounded to two significant digits is 2.0 ug/L [659]. The equation is acute = 0.5 e(1.72[ln(hardness)]-6.52) where "e" = exponential [659].

Colorado specified a hardness dependent equation as the chronic aquatic life water quality standard 1991; at a hardness of 100 mg/L, the standard is 0.32 ug/L [659]. The equation: chronic = e(1.72[ln(hardness)]-9.06) where "e" = exponential [659].

Water concentrations of 1.2 to 4.9 ug free silver ion/L killed sensitive species of aquatic organisms, including representative species of insects, daphnids, amphipods, trout, flounders, sticklebacks, guppies, and dace. At nominal water concentrations of 0.5 to 4.5 ug/L, accumulations in most species of exposed organisms were high and had adverse effects on growth in algae, clams, oysters, snails, daphnids, amphipods, and trout; molting in mayflies; and tissue histology in mussels. At sublethal concentrations, adverse effects were significant between 0.17 and 0.6 ug/L [947].

W.Plants (Water Concentrations vs. Plants):

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 7440-22-4, SILVER, the benchmark is 0.1 mg/L (groundwater or porewater).

Adverse effects occur on phytoplankton species composition and succession at 0.3 to 0.6 ug/L [947].

Smith and Carson (1977) report that sprays containing 9.8 mg dissolved Ag/L kill corn (Zea mays), and sprays containing 100-1,000 mg dissolved Ag/L kill young tomato (Lycopersicon esculentum) and bean (Phaseolus spp.) plants [947].

Sensitive aquatic plants accumulated silver from water containing as little as 2 ug Ag/L to whole cell burdens as high as 58 mg Ag/kg DW; grew poorly at 3.3-8.2 ug Ag/L during exposure for 5 days; and died at concentrations greater than 130 ug Ag/L [947].

Some metals seem to protect aquatic plants against adverse effects of silver. Algae in small lakes that contained elevated concentrations of metals, especially copper and nickel, had higher tolerances to silver than conspecifics reared in the laboratory under conditions of depressed concentrations of heavy metals. Species composition and species succession in Chesapeake Bay phytoplankton communities were significantly altered in experimental ecosystems continuously stressed by low concentrations (0.3-0.6 ug/L) of silver. At higher concentrations of 2 to 7 ug/L for 3 to 4 weeks, silver inputs caused disappearance of Anacystis marina, a mat-forming blue-green alga; increased dominance by Skeletonema costatum, a chain-forming centric diatom; and cell burdens of 8.6-43.7 Ag mg/kg DW. Dissolved silver speciation and bioavailablity were important in determining silver uptake and retention by aquatic plants. Silver availability was controlled by the concentration of free silver ion (Ag+) and the concentrations of other silver complexes, such as AgCl. Silver uptake by phytoplankton was rapid, in proportion to silver concentration, and inversely proportional to water salinity. Silver incorporated by phytoplankton was not lost as the salinity increased, and silver associated with cellular material was largely retained in the

estuary. Diatoms (Thalassiosira sp.), for example, readily accumulated silver from the medium. Once incorporated, silver was tightly bound to the cell membrane, even after the cells were mechanically disrupted [947].

W.Invertebrates (Water Concentrations vs. Invertebrates):

Marine gastropods exposed to concentrations as low as 1.0 ug Ag/L for as long as 24 months showed histopathology and accumulations as high as 34 mg Ag/kg FW soft parts; higher exposure concentrations of 5 and 10 ug Ag/L were associated with inhibited reproduction and whole body burdens as high as 87 mg Ag/kg FW. Histopathological findings in silver-exposed mussels (Mytilus edulis) were typical of argyria in humans and other mammals that have absorbed organic or inorganic silver compounds [947].

Juvenile Pacific oysters (Crassostrea gigas) exposed for 2 weeks to solutions containing 20 ug Ag/L had high silver accumulations in tissues and a reduced capacity to store glycogen; however, after 30 days of depuration, glycogen storage capacity was restored and 80% of the soluble silver and 27% of the insoluble forms were eliminated, suggesting recovery to a normal physiological state [947].

LC50 for Brachionus calyciflorus and B. plicatilis (both rotifers) were 7.5 and 120 ug/L (ppb) (0.0075 and 0.120 mg/L, ppm), respectively, for 24-hr exposures [998].

LC50 for Ceriodaphnia reticulata (water flea) was 11 ug/L (ppb) for a 48-hr exposure [998].

LC50 for Daphnia pulex (water flea) was 14 ug/L (ppb) for a 48-hr exposure [998].

LC50 for Simocephalus vetulus (water flea) was 15 ug/L (ppb) for a 48-hr exposure [998].

LC50 for Mysidopsis bahia (Opossum shrimp) was 0.249 mg/L (ppm) for a 96-hr exposure [998].

W.Fish (Water Concentrations vs. Fish):

Colorado specified a hardness dependent equation as the chronic trout water quality standard 1991; at a hardness of 100 mg/L, the standard is 0.08 ug/L [659]. The equation: chronic (trout) = e(1.72[ln(hardness)]-10.51) where "e" = exponential

[659].

Previous USGS concentrations of 10 ppb (a concentration which wold kill fish) from many locations in Colorado were found to have been wrong and possibly caused by field contamination, possibly contamination of filters which were carried with silver-bearing electrodes (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Complexed and sorbed silver species in natural waters are at least one order of magnitude less toxic to aquatic organisms than the free silver ion. Thus, silver nitrate--which is strongly dissociated--is extremely toxic to rainbow trout (Oncorhynchus mykiss); the 7-day LC50 value is 9.1 ug/L. Silver thiosulfate, silver chloride, and silver sulfide were relatively benign (7-day LC50 values >100,000 ug/L), presumably due to the abilities of the anions to remove ionic silver from solution [947].

Silver ion (Ag+) was the most toxic chemical species of silver to fishes. Silver ion was 300 times more toxic than silver chloride to fathead minnows (Pimephales promelas), 15,000 times more toxic than silver sulfide, and more than 17,500 times more toxic than silver thiosulfate complex; in all cases, toxicity reflected the free silver ion content of tested compounds; a similar pattern was noted in rainbow trout [947].

Silver was less toxic to fathead minnows under conditions of increasing water hardness between 50 and 250 mg CaCO3/L, increasing pH between 7.2 and 8.6, and increasing concentrations of humic acid and copper; starved minnows were more sensitive to ionic silver than minnows fed regularly. Eggs of rainbow trout (Oncorhynchus mykiss) exposed continuously to silver concentrations as low as 0.17 ug/L had increased embryotoxicity and hatched prematurely; resultant fry had a reduced growth rate. Removal of the egg capsule of eyed embryos of steelhead trout (O. mykiss) significantly lowered the resistance of the embryos to salts of silver, copper, and mercury but not zinc and lead. Silver accumulation in gills of juvenile rainbow trout exposed to 11 ug Ag/L for 2 to 3 h was significantly inhibited by various cations (Ca2+, Na+, H+) and complexing agents (dissolved organic carbon, thiosulphate, chloride); these variables must be considered when contructing predictive models of silver binding to gills [947].

No-observed-effect-concentration (NOEC) for Cyprinodon variegatus (sheepshead minnow) for death was 6.40 mg/L (ppm) for a 96-hr exposure [998].

LC50 for Cyprinodon variegatus (sheepshead minnow) was 58.0 mg/L (ppm) for a 96-hr exposure [998].

LC50 for Lepomis macrochirus (bluegill) was 64.0 ug/L (ppb) (0.064 mg/L, ppm) for a 96-hr exposure [998].

LC50 for Oncorhynchus mykiss (rainbow trout, donaldson trout) was 51.4 ug/L (ppb) for a 96-hr exposure [998].

LC50 for Pimephales promelas (fathead minnow) was 36.25 ug/L (ppb) for a 96-hr exposure [998].

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

Silver was harmful to poultry at concentrations as low as 100 mg total Ag/L in drinking water; sensitive mammals were adversely affected at total silver concentrations as low as 250 ug/L in drinking water [947].

Studies with small laboratory mammals--which require verification--show that long-term exposure to high levels of silver nitrate in drinking water may result in sluggishness and enlarged hearts; however, these effects have not been observed in silver-exposed humans. Concentrations as high as 200 ug Ag/L in drinking water of test animals for 5 months had no significant effect on animal health or metabolism. But 400 ug Ag/L for 5 months caused kidney damage, and 500 ug/L for 11 months was associated with impaired conditioned-reflex activities, immunological resistance, and altered brain nucleic acid content [947].

Sublethal effects are reported in rabbits given 250 ug Ag/L drinking water (brain histopathology), in rats given 400 ug Ag/L drinking water for 100 days (kidney damage), and in mice given 95 mg Ag/L drinking water for 125 days (sluggishness) [947].

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

EPA 1995 Region 9 Tap Water Preliminary Remediation Goal and Region III Risk Based Concentration for tap water: both 180 ug/L [868,903].

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

Drinking Water MCL: None Published [893,952].

Secondary Maximum Contaminant Level (SMCL)

Value: 0.1 (sic, units not specified in IRIS, probably mg/L?) [893]. Status/Year: Final 1991 Reference: 56 FR 3526 (01/30/91)

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

Discussion: SMCLs are non-enforceable and establish limits for contaminants which may affect the aesthetic qualities (e.g. taste and odor) of drinking water. It is recommended that systems monitor for these contaminants every three years. More frequent monitoring for contaminants such as pH, color, odor or others may be appropriate under certain circumstances. The SMCL for silver is based on the skin cosmetic effect called argyria.

Clean Water Act (CWA) Ambient Water Quality Criteria for Human Health:

Water & Fish: 5E+1 ug/liter

Discussion: This value is the same as the drinking water standard and approximates a safe level assuming consumption of contaminated organisms and water.

Criterion for Fish Only: None [893].

Older Value: IRIS Recalculated (7/93) Criteria for Organisms Only:

110,000 ppb [689].

Reference: 45 FR 79318 (11/28/80)

Contact: Criteria and Standards Division / OWRS / (202)260-1315

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].

EPA 1996 Health Based Limit (HBL) based on RfD: 2E-01 mg/L [952].

Older references to Human Health for Carcinogens (risk of one additional case in 1 million, 1E-06):

Published Criteria for Water and Organisms: 50 ug/L [446]. IRIS Recalculated (7/93) Criteria for Water and Organisms: 170 ug/L [689].

NOTE from Eisler [947]: The human drinking water criterion of 50 ug total Ag/L does not seem to represent a hazard to human health, although much lower concentrations adversely affect freshwater and marine organisms. Proposed long-term exposure criteria is <90 ug total silver/L. Short-term exposure (1-10 days) criteria is <1,142 ug total silver/L [947].

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 needed [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 silver in surface waters. These categories of humans not exposed to surface waters with concentrations of silver exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Camp host: 1548 ug/L
Child Camper: 1422 ug/L
Boater: 5530 ug/L
Swimmer: 2395 ug/L

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

Child resident (living on properties adjacent to BLM lands): 2 ug/L
Camp host: 18 ug/L
Child Camper: 51 ug/L
Worker: 39 ug/L
Surveyor: 387 ug/L

Under normal routes of exposure, silver does not pose serious environmental health problems to humans at less than 50 ug total Ag/L drinking water [947].

Note: EPA's Primary Drinking water Standard was listed in one publication as 0.05 mg/L [658]. Colorado had this same water quality standard (50 ug/L) for drinking water in 1991 [659].

The proposed short-term (10-day) allowable limit of 1,142 ug Ag/L in drinking water for human health protection should be reconsidered because it is 4.6 times higher than the value that produced adverse effects in sensitive laboratory mammals [947].

Older Federal Drinking Water Guidelines [940]:

EPA 100 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).

State Drinking Water Standards [940]:

(AL) ALABAMA 50 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).

(AZ) ARIZONA 50 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).

State Drinking Water Guidelines [940]:

(AZ) ARIZONA 50 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).

(ME) MAINE 50 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 20 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).

Drinking water criteria in California state, Germany, and Switzerland are <10, <100, and <200 ug total silver/L, respectively [947].

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

Most measurements of silver concentrations in natural waters prior to the use of clean techniques are considered inaccurate. Until analytical capabilities that exceed the dissolved-particulate classification are developed, it will be necessary to rely on laboratory and theoretical modeling studies to fully understand chemical speciation of silver in natural waters [947].

Sometimes, liquid effluents from the nuclear industry contained significant quantities of radiosilver-110m [947].

Silver concentrations in nonbiological materials tend to be naturally elevated in crude oil and in water from hot springs and steamwells. Anthropogenic sources associated with the elevated concentrations of silver in nonliving materials include smelting, hazardous waste sites, cloud seeding with silver iodide, metals mining, sewage outfalls, and especially the photoprocessing industry. Silver concentrations in biota were greater in organisms near sewage outfalls, electroplating plants, mine wastes, and silver-iodide seeded areas than in conspecifics from more distant sites [947].

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 metals, 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).

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).

Misc. Notes on colloids (Briant Kimball, USGS, Salt Lake City Office, Personal Communication, 1995):

> There is no question that dissolved metals are critical to fish and invertebrates, but less well recognized is the potential impact and movement of metals in colloids. 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 mobilized. In river banks, reducing environments form just under the surface quickly. Toxic metals of concern would include zinc, lead, copper, and cadmium.
>
> Colloids do move in surface water (for example, transport of metal in colloids 140 miles downstream of Leadville, CO), but also in groundwater, especially related to radionuclides.
>
> 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 cast which are ingested, once part of acid 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 annual flushing of the

colloids, loads are much greater during runoff.

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

Sed.Low (Sediment Concentrations Considered Low):

No information found.

Sed.High (Sediment Concentrations Considered High):

Maximum concentrations of total silver recorded in selected nonbiological media were 150 mg/kg in some Genesee River sediments; and 27,000 mg/kg in some solid wastes from photoprocessing effluents. It is emphasized that only a small portion of the total silver in each of these compartments is biologically available [947].

Freshwater sediment levels considered to be highly elevated: Texas: The statewide 90th percentile value for this compound was 3.0 mg/kg dry weight [7].

NOAA National Status and Trends Program (1984-1990) [698]: High concentration for silver in fine-grained sediment (n=233) = 1.2 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 silver than course-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more silver 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):

In California, anthropogenic sources contributed 50% more silver to sediments of coastal basins than natural sources, as judged by sedimentary basin fluxes of 0.09 ug/cm2 in anthropogenic sources of silver and 0.06 ug/cm2 in natural sources [947].

Silver has also been reported at concentrations of 14-20 mg/kg in bottom sediments in California coastal basins. (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 523) [940].

In general, silver concentrations in surface waters of the United States decreased between 1970-74 and 1975-79, although concentrations increased in the north Atlantic, Southeast, and lower Mississippi basins. About 30 to 70% of the silver in surface waters may be ascribed to suspended particles, depending on water hardness or salinity. For example, sediments added to solutions containing 2 ug Ag/L had 74.9 mg Ag/kg DW sediment after 24 h in freshwater, 14.2 mg/kg DW at 1.5% salinity and 6.9 mg/kg DW at 2.3% salinity. Riverine transport of silver to the ocean is considerable: suspended materials in the Susquehanna River, Pennsylvania--that contained as much as 25 mg silver/kg--resulted in an estimated transport of 4.5 metric tons of silver to the ocean each year [947].

NOAA National Status and Trends Program (1984-1990) [698]: Geometric mean for silver in fine-grained sediment (n=233) = 0.48 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 silver than course-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more silver 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.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):

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 3.7 ppm dry weight Effects Range-Median (ERM) concentration and was lowest in sediments where its concentration was less than the 1.0 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	2.6
ERL-ERM	32.3
>ERM	92.8

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]:

CAS 7440-22-4, SILVER:

EFFECTS RANGE - LOW (NOAA): 1 mg/kg dry weight
EFFECTS RANGE - MEDIAN (NOAA): 3.7 mg/kg dry weight

Ontario Ministry of the Environment Freshwater Sediment Guidelines, 1993. Lowest effect level: 0.5 mg/kg dry weight (this is not a sediment quality guideline but is for management decisions from the Open Water Disposal Guidelines.) [761].

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

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

No information found.

Sed.Human (Sediment Concentrations vs. Human):

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]. For more details, see: Risk Management Criteria (RMC). 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 silver in sediments. These categories of humans not exposed to sediments with concentrations of silver exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Camp host: 774 mg/kg
Child Camper: 356 mg/kg
Boater: 2765 mg/kg
Swimmer: 1197 mg/kg

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

Silver can remain attached to oceanic sediments for about 100 years under conditions of high pH, high salinity, and high sediment concentrations of iron, manganese oxide, and organics. Estuarine sediments that receive metals, mining wastes, or sewage usually have higher silver concentrations (>0.1 mg/kg DW) than noncontaminated sediments. Silver is tightly bound by sewage sludge, and elevated silver concentrations in sediments are often characteristic of areas near sewage outfalls. In the absence of sewage, silver in oxidized sediments is associated with oxides of iron and with humic substances [947].

Sediments in the Puget Sound, Washington, were significantly enriched in silver, in part, from human activities; concentrations were higher in fine-grained particles. Marine annelids and clams accumulate dissolved and sediment-bound forms of silver. Uptake of silver from sediments by marine polychaete annelids

decreased in sediments with high concentrations of humic substances or copper but increased in sediments with elevated concentrations of manganese or iron [947].

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

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

Maximum concentrations of total silver recorded in selected nonbiological media were 31 mg/kg in some Idaho soils; 50 mg/kg in granite; and 27,000 mg/kg in some solid wastes from photoprocessing effluents. It is emphasized that only a small portion of the total silver in each of these compartments is biologically available [947].

Soil.Typical (Soil Concentrations Considered Typical):

Silver is comparatively rare in the earth's crust--67th in order of natural abundance of elements; the crustal abundance is an estimated 0.07 mg/kg and predominantly concentrated in basalt (0.1 mg/kg) and igneous rocks (0.07 mg/kg) [947].

Granite igneous rock in Nevada contains up to 50 mg/kg silver. (Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 620) [940].

Concentration in soils: 1 ppm [951].

Average soil concentration in Canada (except for mineralized zones) estimated to be 0.3 ppm [956].

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):

Soil cleanup criteria for decommissioning industrial sites in Ontario (1987): For residential/parklands silver should not exceed 25 ppm. For commercial/industrial silver should not exceed 50 ppm [347].

Quebec soil contamination indicators that differ from those of the Netherlands (1987): 5 ppm of silver indicates a background concentration. 10 ppm indicates a moderate soil contamination. 40 ppm indicates a threshold value that requires immediate cleanup [347].

Soil.Plants (Soil Concentrations vs. Plants):

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 7440-22-4, SILVER, the benchmark is 2 mg/kg in soil [651].

Hirsch et al (1993) planted seeds of corn, lettuce (Lactuca sativa), oat (Avena sativa), turnip (Brassica rapa), soybean (Glycine max), spinach (Spinacia oleracea), and Chinese cabbage (Brassica spp.) in soils amended with silver sulfide and sewage sludge to contain 10, 50, or 100 mg Ag/kg DW soil. All plants germinated and most grew normally at the highest soil concentration of silver tested. But growth of Chinese cabbage and lettuce was adversely affected at 10 mg Ag/kg DW soil and higher. Silver concentrations in edible portions from all plants at all soil levels of silver tested, except lettuce, were less than 80 ug/kg DW. Lettuce grown in soil containing 100 mg Ag/kg DW had about 1.2 mg Ag/kg DW [947].

Criteria for agricultural crops:

<100 mg total silver/kg dry weight soil for most species; <10 mg/kg for sensitive species [947].

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found.

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

No information found.

Soil.Human (Soil Concentrations vs. Human):

EPA 1996 National Generic Soil Screening Level (SSL) designed to be conservative and protective at the majority of sites in the U.S. but not necessarily protective of all known human exposure pathways, land uses, or ecological threats [952]:

SSL = 390 mg/kg for ingestion pathway [952].

SSL = none given for inhalation pathway [952].

SSL = 2 to 34 mg/kg for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

EPA 1995 Region 9 Preliminary remediation goals (PRGs), 1995 [868]:

Residential Soil: 380 mg/kg wet wt.
Industrial Soil: 8500 mg/kg wet wt.

NOTE:
1) PRGs focus on the human exposure pathways of ingestion, inhalation of particulates and volatiles, and dermal absorption. Values do not consider impact to groundwater or ecological receptors.
2) Values are based on a non-carcinogenic hazard quotient of one.
3) PRGs for residential and industrial landuses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects [903].

EPA 1995 Region 3 Risk based concentration (RBC) to protect from transfers to groundwater:

None given [903].

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 needed [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 silver in soil. These categories of humans not exposed to soil with concentrations of silver exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 10 mg/kg
Camp host: 258 mg/kg
Child Camper: 178 mg/kg
ATV Driver: 3629 mg/kg
Worker: 387 mg/kg
Surveyor: 3871 mg/kg

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

Sewage sludge amended soils may have 10 times or more silver than normal. (Cooper CF, Jolly WC; Ambient Water Quality Criteria Doc: Silver p.C-18, 1980, EPA 440/5-80-071) [940].

Emissions of silver from coal-fired power plants may lead to accumulations in nearby soils. Silver in soils is largely immobilized by precipitation to insoluble (sic, actually "relatively insoluble") salts and by complexation or adsorption by organic matter, clays, and manganese and iron oxides [947].

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:

No information found.

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

Maximum concentrations of total silver recorded in field collections of living organisms, in mg Ag/kg DW, were 14 in marine algae and macrophytes, and 110 in whole mushrooms. Silver concentrations in conspecifics from areas remote from anthropogenic contamination were usually lower by 1 or more orders of magnitude [947].

Erigononum ovalifolium (Montana) and Lonicera confusa (Queensland) are considered plant indicators of the presence of silver [951].

Silver is a normal trace constituent of many organisms. In terrestrial plants, silver concentrations are usually less than 1.0 mg/kg ash weight (equivalent to less than 0.1 mg/kg DW) and are higher in trees, shrubs, and other plants near regions of silver mining; seeds, nuts, and fruits usually contain higher silver concentrations than other plant parts. Silver accumulations in marine algae (max. 14.1 mg/kg DW) are due mainly to adsorption rather than uptake; bioconcentration factors of 13,000 to 66,000 are not uncommon [947].

In background (clean) areas, trees and lesser plants growing over areas containing no known silver mineralization contained 0.1 to 1.4 ppm of silver [951].

Tis.Invertebrates:

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

No information found.

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:

Tissue residues in marine clams:

Normal Residues: <1 mg total silver/kg dry weight [947].

Under stressful or fatal conditions: >100 mg total silver/kg dry weight [947].

Criteria related to adverse effects on growth of the Asiatic clam, Corbicula fluminea:

The criterion is >1.65 mg total silver/kg soft tissues, wet weight basis [947].

See also Tis.Misc section below.

Maximum concentrations of total silver recorded in field collections of living organisms, in mg Ag/kg DW, were 30 in whole annelid worms from San Francisco Bay, 133 to 185 in soft parts of clams

and mussels near sewage and mining waste outfalls, and 320 in whole gastropods from South San Francisco Bay. Silver concentrations in conspecifics from areas remote from anthropogenic contamination were usually lower by 1 or more orders of magnitude [947].

Silver concentrations in molluscs vary widely between closely related species and among conspecifics from different areas. The inherent differences in ability to accumulate silver among bivalve molluscs are well documented (oysters >> scallops >> mussels). The highest silver concentrations in all examined species of molluscs were in the internal organs, especially in the digestive gland and kidneys. Elevated concentrations of silver (5.3 mg/kg DW) in shells of limpets from uncontaminated sites suggest that silver may actively participate in carbonate mineral formation, but this needs verification [947].

Mollusks collected from coastal areas of the North Sea have been reported to contain silver concentrations of up to 2.0 mg/kg. (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 523) [940].

Silver 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 silver in oysters (n=107), the Geometric Mean was 1.9 ug/g dry and the "high" concentration was 3.7 ug/g dry weight [697]. For silver in mussels (n=107), the Geometric Mean was 0.17 ug/g dry and the "high" concentration was 0.58 ug/g dry weight [697]. NOAA "high" concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].

In general, silver concentrations were elevated in molluscs collected near port cities and in the vicinities of river discharges, electroplating plant outfalls, ocean dumpsites, and urban point sources including sewage outfalls and from calcareous sediments rather than detrital organic or iron oxide sediments. Season of collection and latitude also influenced silver accumulations.

Seasonal variations in silver concentrations of Baltic clams (Macoma balthica) were associated with seasonal variations in soft tissue weight and frequently reflected the silver content in the sediments. Oysters from the Gulf of Mexico vary considerably in whole body concentrations of silver and other trace metals. Variables that modify silver concentrations in oyster tissues include the age, size, sex, reproductive stage, general health, and metabolism of the animal; water temperature, salinity, dissolved oxygen, and turbidity; natural and anthropogenic inputs to the biosphere; and chemical species and interactions with other compounds. Silver concentrations in whole American oysters (Crassostrea virginica) from the Chesapeake Bay were reduced in summer; reduced at increasing water salinities, and elevated near sites of human activity; chemical forms of silver taken up by oysters included the free ion (Ag+) and the uncharged AgCl. Declines in tissue silver concentrations of the California mussel (Mytilus californianus) were significant between 1977 and 1990; body burdens decreased from 10-70 mg/kg DW to less than 2 mg/kg DW and seem to be related to the termination of metal plating facilities in 1974 and decreased mass emission rates by wastewater treatment facilities [947].

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):

Bureau of Land Management RMC Benchmarks for fish tissue, 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 needed [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 silver in fish consumed by humans. These categories of humans not exposed to fish with concentrations of silver

exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 392 ug/kg
Camp host: 807 ug/kg
Child Camper: 2222 ug/kg

EPA Region III 1995 Risk Based Concentration (RBC) for fish tissues consumed by humans: 6.8 mg/kg based on non cancer risk [903].

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:

Maximum concentrations of total silver recorded in field collections of living organisms, in mg Ag/kg DW, were 2 in liver and 6 in bone of trout from ecosystems receiving precipitation from silver-iodide seeded clouds. Silver concentrations in conspecifics from areas remote from anthropogenic contamination were usually lower by 1 or more orders of magnitude [947].

Silver concentrations in fish muscles rarely exceeded 0.2 mg/kg DW and usually were less than 0.1 mg/kg FW; livers contained as much as 0.8 mg/kg FW, although values greater than 0.3 mg/kg FW were unusual; and whole fish contained as much as 0.225 mg/kg FW. Livers of Atlantic cod (Gadus morhua) contained significantly more silver than muscles or ovaries; a similar pattern was evident in other species of marine teleosts. Accumulations of silver in offshore populations of teleosts is unusual, even among fishes collected near dump sites impacted by substantial quantities of silver and other metals. For example, of 7 species of marine fishes from a disposal site in the New York Bight and examined for silver content, concentrations were highest (0.15 mg/kg FW) in muscle of blue hake (Antimora rostrata). Similarly, the elevated silver concentration of 0.8 mg/kg FW in liver of winter flounder (Pseudopleuronectes americanus) was from a specimen from the same general area [947].

Silver concentrations ranged from 0.18 to 2.11 mg/kg wet weight in four fish muscle samples from the Pecos River near Pecos National Monument &

Historical Park, New Mexico (Milford Fletcher, National Park Service, University of New Mexico, personal communication). The Fish and Wildlife Service reported silver concentrations of less than 1.5 mg/kg dry weight in biological samples collected upstream in the Pecos drainage in the 1991 study of the Terrero Mine waste study area [479]. The Fish and Wildlife Service further reported silver concentrations of less than 2.0 mg/kg dry weight in biological samples collected upstream in the 1991 study of the Terrero Mine waste study area [479]. Trout from Lake Cayuga, NY, contained 0.48-0.68 mg/kg dry weight silver (Tong SSC et al; J Fish Res Board Canada 31: 238 (1974) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-19 (1980) EPA 440/5-80-0710 [366].

Fish/Seafood Concentrations [940]:

Mollusks 0.1-10.0 mg/kg dry weight silver; crustaceans 2.0 mg/kg dry weight. [Boyle RW; Geol Surv Canada Bul No. 160 (1968) as cited in USEPA; Ambient Water Quality Crieria Doc Silver p.C-19 (1980) EPA 440/5-80-071].

Trout (Lake Cayuga NY) contained 0.48-0.68 mg/kg dry weight silver. [Tong SSC et al; J Fish Res Board Canada 31: 238 (1974) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-19 (1980) EPA 440/5-80-071].

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):

Silver was harmful to poultry at concentrations as low as 1.8 mg total Ag/kg whole egg fresh weight by way of injection, or 200 mg total Ag/kg in diets; sensitive mammals were adversely affected at total silver concentrations as low as 6 mg/kg in diets, or 13.9 mg/kg whole body [947].

Diets deficient in Vitamin E or selenium caused rapidly fatal hepatocellular necrosis and muscular dystrophy to rats if they contained the dietary-intake equivalent of 130 mg Ag/kg BW daily, a comparatively high silver intake [947].

Sublethal effects are reported in rats given diets containing 6 mg Ag/kg for 3 months (high accumulations in kidneys and liver) or 130 to 1,110 mg/kg diet (liver necrosis) [947].

Silver affects turkeys (Meleagris gallopavo) and domestic chickens (Gallus spp.). Turkey poults on diets containing 900 mg Ag/kg feed for 4 weeks had reduced growth, hemoglobin, and hematocrit and an enlarged heart. Chicken eggs injected with silver nitrate at 0.1 mg Ag/egg (equivalent to about 1.8 mg Ag/kg egg FW) had a 50% reduction in survival but no developmental abnormalities. Adverse effects of silver were reported in normal chicks fed diets containing 200 mg Ag/kg ration (growth suppression) or given drinking water containing 100 mg Ag/L. Chicks on copper-deficient diets had adverse effects at 10 mg Ag/kg ration (reduced hemoglobin; reversible when fed copper-adequate diet) and at 50-100 mg Ag/kg ration (growth suppression and increased mortality). Chicks that were deficient in Vitamin E experienced reduced growth when given drinking water containing 1,500 mg Ag/L. Chickens infected with Salmonella pullorum-gallinarum and Escherichia coli were cured with aerosol treatments containing 10 ug Ag/L air [947].

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

Maximum concentrations of total silver recorded in field collections of living organisms, in mg Ag/kg DW, were 1.5 in liver of marine mammals, and 7 in kidneys and 44 in liver of birds from a metals-contaminated area. Silver concentrations in conspecifics from areas remote from anthropogenic contamination were usually lower by 1 or more orders of magnitude [947].

Silver concentrations in muscles of Antarctic birds were low (0.01 mg/kg DW) when compared to livers (0.02-0.46 mg/kg DW) or feces (0.18 mg/kg DW). Silver concentrations in avian tissues, especially in livers, were elevated in the vicinity of metals-contaminated areas and in diving ducks from the San Francisco Bay. Birds with elevated concentrations

of silver in tissues--as much as 44 mg/kg DW in liver in the common eider (Somateria mollissima)--seemed outwardly unaffected [947].

Silver in mammalian tissues is usually present at low or nondetectable concentrations. The concentration of silver in tissues of 3 species of seals collected in the Antarctic during 1989 was highest in liver (1.55 mg/kg DW) and lowest in muscle (0.01 mg/kg DW); intermediate in value were kidney (0.29 mg/kg DW) and stomach contents (0.24 mg/kg DW). The mean concentration of silver in livers from normal female California sea lions (Zalophus calfornianus), having normal pups, was 0.5 mg/kg DW. Mothers giving birth to premature pups had only 0.4 mg Ag/kg DW liver. In general, Zalophus mothers delivering premature pups had lower concentrations in liver of silver, cadmium, copper, manganese, mercury, and zinc than mothers delivering normal pups. Silver concentrations in tissues of Antaractic seals were related to, and possible governed by, concentrations of other metals. In muscle, silver inversely correlated with zinc; in liver, silver positively correlated with nickel, copper, and zinc; and in kidney, correlations between silver and zinc and between silver and cadmium were negative [947].

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

See also Tis.Fish, C) and Tis.Invertebrate, C) sections above.

Daily intake of total silver from all sources by humans in the United States ranged from 70 to 88 ug; diet accounted for 35-40 ug daily. Sources of elevated dietary silver include seafood from areas near sewage outfalls or industrial sources and crops grown in areas with high ambient levels of silver in the air or soil [947].

0.027-0.054 mg/kg of silver was detected in cow milk from market samples in various USA cities. (Murthy GK, Rhea U; J Dairy Sci 51: 610 (1968) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-18, 1980, EPA 440/5-80-071) [940].

Food Survey Results [940]:

Beef: 0.004-0.024 mg/kg; Mutton and lamb: 0.006-0.011 mg/kg. [Armour Research

Foundation; Spectrographic Study of Meats for Mineral Element Content (1952).

Beef liver 0.005-0.194 mg/kg. [USEPA; Ambient Water Quality Criteria Doc: Silver p.C-19 (1980) EPA 440/5-80-071].

Milk powder 0.010 + or - 0.04 mg/kg Ag; potato powder 0.015 + or - 0.005 mg/kg Ag. [Schelenz R; J Radioanal Chem 31: 539 (1977) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-19 (1980) EPA 440/5-80-071].

Brown sugar 0.3 mg/kg silver, demerara sugar 0.004 mg/kg Ag, granulated sugar 0.002 mg/kg. [Hamilton EI, Minski MJ; Sci Total Environ 1: 375 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-19 (1980) EPA 440/5-80-071].

Wheat 0.5 mg/kg dry weight silver, bran 1.0 mg/kg dry weight silver, flour 0.4 mg/kg dry weight silver. [Kent-Jones DW, Amos AJ; Modern Cereal Chemistry 5th ed (1957) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-19 (1980) EPA 440/5-80-071].

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):

See also Tis.Fish, C) above.

Crit. Dose: 0.014 mg/kg-day [Study 1 LOAEL(adj)] UF: 3 MF: 1 [893].

RfD: 5E-3 mg/kg-day Confidence: Low [893,952].

Bureau of Land Management RMC Benchmarks for fish tissue, 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 needed [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 silver in fish consumed by humans. These categories of humans not exposed to fish with concentrations of silver exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 392 ug/kg
Camp host: 807 ug/kg
Child Camper: 2222 ug/kg

EPA Region III 1995 Risk Based Concentration (RBC) for fish tissues consumed by humans: 6.8 mg/kg based on non cancer risk [903].

Average Daily Intake [940]:

Estimates of silver in human diets have varied widely from an avg of 0.4 ug/day for three Italian populations to 27 + or - 17 ug/day in the United Kingdom. [USEPA; Ambient Water Quality Criteria Doc: Silver p.C-119 (1980) EPA 440/5-80-071].

Two subjects had ingested between 10 and 20 ug/d from food during a 30-day period. /The investigator/, by NAA, found a daily intake from food of 1-16 ug. [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 523].

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

Humans afflicted with silver poisoning (argyria) contained 72 mg total Ag/kg dry weight skin and 1,300 mg total Ag/kg fresh weight whole body [947].

In humans, EPA (1980) states that silver is present in placentas and fetal livers, that silver concentrations in tissues increase with age, and that variations in tissue concentrations of silver are wide. Very little of the silver ingested from nontherapeutic sources is retained [947].

Body Burdens [940]:

Silver is one of the most physically & physiologically cumulative of the elements, leading to a disturbing, permanent cosmetic effect when body burden has accumulated Ag in excess of 1 g. [Clayton, G. D. and F. E.

Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 1888].

The highest concentrations of silver are usually found in the liver and spleen and to some extent in the muscle, skin, and brain. Normal values of silver in kidneys, liver, and spleen are reported to be about 0.4, 0.7, and 2.7 mg/kg dry wt, respectively, by emission spectrometry. ... By neutron activation analysis: up to 0.045 mg/kg wet wt (kidney); up to 0.032 mg/kg (liver); and up to 0.060 mg/kg (lung). [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 621].

Reported silver concentration(s) in the skin of persons with argyria are of the magnitude 50-70 mg/kg dry wt, ie, several thousand times higher than normal values (0.035 + or - 0.015 mg/kg dry wt). [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 622].

Normal concentration(s) in skin was reported as 0.035 + or - 0.015 mg/kg dry wt ... 0.006 + or - 0.002 mg/kg wet wt in liver, 0.001 + or - 0.002 in kidney and 0.002 + or - 0.0001 in lung. [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 526].

The silver concentration(s) in the skin of persons with argyria was 63 + or - 8 mg/kg dry wt. ... 72 mg/kg wet wt in one case. [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 528].

Silver content in 8 human kidney medulla in the United Kingdom= 0.002 + or - 0.0002 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 11 human livers in the

United Kingdom= 0.006 + or - 0.002 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 6 human lymph nodes in the United Kingdom= 0.001 + or - 0.0002 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 6 human muscles in the United Kingdom= 0.002 + or - 0.0005 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 5 human testes in the United Kingdom= 0.002 + or - 0.0004 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 6 human ovaries in the United Kingdom= 0.002 + or - 0.0005 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 22 bones (ribs) from patients who lived in a hard water area in the United Kingdom= 1.1 + or - 0.2 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 22 bones (ribs) from patients who lived in a soft water area in the United Kingdom= 1.1 + or - 0.2 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 10 samples of the human whole brain in the United Kingdom= 0.004 + or - 0.002 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in

USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 2 samples of the human frontal lobe in the United Kingdom= 0.003 + or - 0.001 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 2 samples of the human basal ganglia in the United Kingdom= 0.004 + or - 0.002 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 8 human kidneys in the United Kingdom= 0.002 + or - 0.0002 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Silver content in 8 human kidney cortex in the United Kingdom= 0.001 + or - 0.0002 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Urine samples collected from six males, aged 28 to 51 years, who had been employed in jewelry handicraft for 7 to 23 years, were analyzed for silver. Urinary silver ranged from 5 to 261 micrograms per 24 hours. A mean value of about 27 micrograms was found after shifts over 5 days in workers performing investment casting with oxyacetylene flame, while the mean urinary silver level in workers performing the electromagnetic induction process was about 5 micrograms after shifts. [Minoia C et al; Occupational and Environmental Chemical Hazards p.349-54 (1987)].

Silver content in 11 human lung in the United Kingdom= 0.002 + or - 0.0001 ug/g wet wt. [Hamilton EI et al; Sci Total Environ 1: 341 (1972/73) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-2 (1980) EPA 440/5-80-071].

Tis.Misc. (Other Tissue Information):

Among arthropods, pyrophosphate granules isolated from barnacles have the capability to bind and effectively detoxify silver and other metals under natural conditions.

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

Silver is a normal trace constituent of many organisms. Silver accumulations in marine algae (max. 14.1 mg/kg DW) are due mainly to adsorption rather than uptake; bioconcentration factors of 13,000 to 66,000 are not uncommon [947].

Dissolved silver speciation and bioavailablity were important in determining silver uptake and retention by aquatic plants. Silver availability was controlled by the concentration of free silver ion (Ag+) and the concentrations of other silver complexes, such as AgCl. Silver uptake by phytoplankton was rapid, in proportion to silver concentration, and inversely proportional to water salinity. Silver incorporated by phytoplankton was not lost as the salinity increased, and silver associated with cellular material was largely retained in the estuary. Diatoms (Thalassiosira sp.), for example, readily accumulated silver from the medium. Once incorporated, silver was tightly bound to the cell membrane, even after the cells were mechanically disrupted [947].

The ability to accumulate dissolved silver from the medium ranges widely between species. Some reported bioconcentration factors (mg Ag per kg FW organism/mg Ag per liter of medium) are 210 in diatoms, 240 in brown algae, 330 in mussels, 2,300 in scallops, and 18,700 in oysters. Silver is the most strongly accumulated of all trace metals by marine bivalve molluscs. Studies with radiosilver-110m suggest that the half-time persistence of silver is 27 days in mussels, 44-80 days in clams, and more than 180 days in oysters [947].

In oysters and other bivalve molluscs, the major pathway of silver accumulation was from dissolved silver; uptake was negligible from silver adsorbed onto suspended sediments or algal cells, and oysters eliminated adsorbed silver in the feces. Sometimes, benthic bivalve molluscs accumulated silver from certain sediments. Sediment-bound silver was taken up by the Baltic clam (Macoma balthica) at 3.6 to 6.1 times the concentration in calcite sediments but less than 0.85 times from manganous, ferrous, and biogenic CaCO3 sediments [947].

In oysters, silver associated with food was unavailable for incorporation which may be due to the ability of silver to adsorb rapidly to cell surfaces and to remain tightly bound despite changes in pH or enzymatic activity. Silver concentrations in American oysters (Crassostrea virginica) held in seawater solutions containing 1.0 mg Ag/L for 96 h rose from 6.1 mg/kg FW soft parts to 14.9 mg/kg FW; in gills, these values were 5.9 and 33.9 mg/kg FW. A similar pattern was evident in common mussels (Mytilus

edulis) and quahaug clams (Mercenaria). Adults of surf clams (Spisula solidissima) immersed for 96 h in seawater containing 10 ug Ag/L had 1.0 mg Ag/kg FW soft tissues vs. 0.08 mg/kg in controls. Oysters accumulated radiosilver-110m from the medium by factors of 500 to 32,000; uptake of dissolved silver by oysters was higher at elevated temperatures in the range of 15-25 C. American oysters maintained near a nuclear power plant in Maryland that discharged radionuclides on a daily basis into the Chesapeake Bay accumulated radiosilver-110m; accumulations were higher in summer and fall than in winter and spring [947].

About 70% of the insoluble (sic, actually "relatively insoluble") silver in Pacific oysters was sequestered as Ag2S, a stable mineral form that is not degradable, thereby limiting the risk of silver transfer through the food chain. Most (69-89%) of the silver accumulated from the medium in soft tissues of oysters and clams was sequestered in amoebocytes and basement membranes; in scallops and mussels, silver was stored in basement membranes and pericardial gland. In all species of bivalve molluscs, sequestered silver was in the form of silver sulfide. American oysters excreted about 60% of their accumulated silver in soft tissues within 30 days of transfer to silver-free seawater; soluble forms were preferentially eliminated and insoluble forms retained. Interspecies differences in ability to retain silver among bivalve molluscs are large, even among closely related species of crassostreid oysters. For example, the half-time persistence of silver was about 149 days in American oysters but only 26 days in Pacific oysters [947].

In a Colorado alpine lake, silver concentrations in caddisflies and chironomid larvae usually reflected silver concentrations in sediments; seston, however, showed a high correlation with lake water silver concentrations from 20 days earlier [947].

Among arthropods, grass shrimp (Palaemonetes pugio) rapidly incorporate silver dissolved in brackish water in proportion to its concentration but not from planktonic or detrital food sources containing elevated silver burdens. Variations in ability of decapod crustaceans to accumulate radiosilver-110m from seawater are large, as judged by concentration factors that ranged from 70 to 4,000. The reasons for this variability are unknown but may be associated with hepatopancreas morphology. It is generally acknowledged that hepatopancreas or digestive gland is the major repository of silver in decapods. Aquatic insects concentrate silver in relative proportion to environmental levels, and more efficiently than most fish species. Whole body bioconcentration factors (BCF) of silver in 3 species of aquatic insects ranged from 21 to 240 in water containing 30 to 65 mg CaCO3/L during exposure of 3-15 days; in bluegill sunfish (Lepomis macrochirus), this value was less than 1 after exposure for 28 days. Molt frequency of the stonefly (Isonychia bicolor) was a sensitive indicator of silver stress over time, and 1.6 ug total Ag/L over a 20-day period inhibited molting [947].

Largemouth bass (Micropterus salmoides) and bluegills accumulated silver from the medium; accumulations increased with increasing concentrations of ionic silver and increasing duration

of exposure. Bioconcentration factors of radiosilver-110m and various species of teleosts were as high as 40 after 98 days. However, flounders (Pleuronectes platessa) and rays (Raja clavata) fed nereid polychaete worms labeled with radiosilver-110m retained about 4.2% of the ingested dose after 3 days, which suggests that the high silver concentration factors reported by Pouvreau and Amiard (1974) may have been due to loosely bound adsorbed silver. Flounders (Pleuronectes sp.) held in seawater solutions containing 40 ug Ag/L for 2 months had elevated silver concentrations in the gut (0.49 mg Ag/kg FW) but less than 0.05 mg/kg in all other examined tissues. Similarly exposed rays (Raja sp.) contained 1.5 mg Ag/kg FW in liver, 0.6 in gut, 0.2 in heart, and 0.05-0.18 mg/kg FW in spleen, kidney, and gill filament; liver is usually considered the major repository of silver in teleosts [947].

At concentrations normally encountered in the environment, food chain biomagnification of silver in aquatic systems is unlikely, although regular ingestion of fish from contaminated waters may significantly affect dietary silver intake. Silver--as thiosulfate-complexed silver at nominal concentrations of 500 or 5,000 ug Ag/L--was concentrated and magnified over a 10-week period in freshwater food chains of algae, daphnids, mussels, and fathead minnows, although the mechanisms of accumulation in this study were imperfectly understood [947].

The extent of absorption of an administered dose of silver depends on silver speciation, the presence and extent of silver-binding proteins, and other variables. But absorption is dependent mainly on the transit time through the gastrointestinal tract; the faster the transit time is, the less silver is absorbed. Transit times ranged from about 8 h in mice and rats to about 24 h in monkeys, dogs, and humans. Route of administration affected the excretion rate of silver. Clearance of silver from mammals 2 days after silver was administered intravenously ranged from 15% in dogs to 82% in mice; clearance rates were intermediate in monkeys and rats. When silver was administered orally, clearance was more rapid, and extended from 90.4% in dogs to 99.6% in mice. The half-time persistence of silver administered orally to mice was 0.1 day for the short-lived component and 1.6 days for the long-lived component. Other species of tested laboratory animals had biphasic or triphasic whole-body silver-excretion profiles that differed significantly from mice. Monkeys, for example, had a biphasic excretion profile with peaks at 0.3 and 3.0 days; rats had a triphasic profile with peaks at 0.1, 0.7. and 5.9 days; and dogs had half-time persistence peaks at 0.1, 7.6, and 33.8 days [947].

Silver may enter the body of mammals through inhalation, ingestion, mucous membranes, or broken skin (Smith and Carson 1977; EPA 1980; Klaassen et al. 1986; PHS 1990). In most cases of occupational argyria, absorption occurs via the respiratory tract or at the eyes (Smith and Carson 1977; EPA 1980). Silver is retained by all body tissues; tissue concentrations are related to the dose, form of administered silver, and route of exposure. Silver also accumulates in mammalian tissues with increasing age of the individual, even if none is administered intentionally. Inside the body, silver is transported mainly in the protein fractions of plasma, presumably as silver albuminate or silver chloride (Smith

and Carson 1977; EPA 1980). In mammals, the highest concentrations of silver are usually found in the liver and spleen and to some extent in the muscles, skin, and brain (Fowler and Nordberg 1986). The primary sites of silver deposition in the human body are the liver, skin, adrenals, lungs, muscle, pancreas, kidney, heart, and spleen; silver is also deposited in blood vessel walls, the trachea, and bronchi (Smith and Carson 1977). Dogs exposed to silver by inhalation accumulated most of the administered dose in the liver; concentrations in the lung, brain, skin, and muscle were lower (EPA 1980; Fowler and Nordberg 1986). Intravenous injection of silver produces accumulations in the spleen, liver, bone marrow, lungs, muscle, and skin (Klaassen et al. 1986). Intestinal absorption of silver by rodents, canids, and primates has been recorded at 10% or less after ingestion of radioactive silver; a value of 18% was estimated in a single human given radiosilver acetate (EPA 1980; Klaassen et al. 1986) and about 3 to 10% of the absorbed silver is retained in the tissues (Smith and Carson 1977). In a human given radioactive silver, more than 50% of the whole body burden of silver was found in the liver after 16 days (Fowler and Nordberg 1986).

Deposition of silver in tissues of warm-blooded animals results from precipitation of relatively insoluble silver salts, such as silver chloride and silver phosphate (PHS 1990). These insoluble (sic, actually "relatively insoluble") salts may be transformed into soluble silver sulfide albuminates that bind or complex with amino and carboxyl groups in RNA, DNA, and proteins, or may be reduced to metallic silver by ascorbic acid or catecholamines. In humans with argyria, the blue or gray skin discoloration is caused by the photoreduction of silver chloride to metallic silver during exposure to ultraviolet light. Metallic silver, in turn, is oxidized and bound as black silver sulfide (PHS 1990). Silver sulfide (Ag2S) is localized in extracellular structures such as basement membranes and in macrophageous cells (Baudin et al. 1994). Before storage as a stable mineral combination, silver binds to proteins that contain a large proportion of sulfhydryl groups such as metallothioneins (Fowler and Nordberg 1986). The last stage in the catabolic pathway of these proteins leads to storage of silver after reaction with a sulfur ligand (Baudin et al. 1994). These mechanisms explain why liver, the most important organ for protein synthesis, shows the highest capacity for silver accumulation. High concentrations of silver in the digestive tract are linked to the numerous basement membranes contained in its tissues. Interspecies differences in the ability to accumulate, retain, and eliminate silver are large (Baudin et al. 1994).

Bioconcentration [940]:

> Algae, daphnia, fresh water mussels, and fathead minnows were all found capable of accumulating silver; but the food chain was not an important route of silver accumulation for animals at higher tropic levels, suggesting no food chain magnification. [Luoma SN, Jenne EA; The Availibility of Sediment Bound Cobalt, Silver,

and Zinc to a Deposit Feeding Clam (1977)].

Biological Half-Life [940]:

The biological half-life for silver is a few days for animals and up to 50 days for human liver. [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 621].

After rabbits had inhaled 4 um monodispersed silver coated Teflon particles, /it was/ found that an avg of 30% of the particles deposited were cleared from the lung in one day and another 30% during the rest of the first week of the exposure. After exposure by inhalation, dogs cleared 59% of an admin dose of radioactive silver from the lungs in 1.7 days. The liver had a somewhat slower clearance of 9 days. An apparent biological half-time of about 1 day was found by whole-body scintillation counting in mice, rats, monkeys, and dogs after oral ingestion. Somewhat longer half-times were observed for these species after iv injection of silver, with monkeys and dogs having half-times of 1.8 and 2.4 days, respectively. [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 525].

High local concentration(s) of silver from a prosthetic cement were associated with a slowly resolving focal neuropathy. The terminal elimination half-life in this 78 year old patient was long (approx 6 months). [Ellenhorn, M.J. and D.G. Barceloux. Medical Toxicology - Diagnosis and Treatment of Human Poisoning. New York, NY: Elsevier Science Publishing Co., Inc. 1988. 1060].

In rats, silver is eliminated from the lung in two or three phases. The fastest phase (0.3 to 1.7 days) removes most of the inhaled dose by mucociliary clearance. A second phase and third phase remove absorbed silver, mostly via the liver, with half-lives of about 8 to 15 and 40 to 50 days, respectively. [USEPA; Ambient Water Quality Criteria Doc: Silver p.C-58 (1980) EPA 440/5-80-071].

Interactions:

In mammals, silver usually interacts antagonistically with selenium, copper, and Vitamin E; in aquatic environments, silver interferes with calcium metabolism in frogs and marine annelids and with sodium and chloride uptake in gills of fishes [947].

Algae in small lakes that contained elevated concentrations of metals, especially copper and nickel, had higher tolerances to

silver than conspecifics reared in the laboratory under conditions of depressed concentrations of heavy metals [947]. (see W.Plants section above for details).

Silver interacts competitively with selenium, vitamin E, and copper and induces signs of deficiency in animals fed adequate diets or aggravates signs of deficiency when diets were lacking one or more of these nutrients; antagonistic effects of silver have been described in dogs, pigs, rats, sheep, chicks, turkey poults, and ducklings. Conversely, the addition of selenium, copper, or vitamin E to diets of turkey poults decreased the toxicity of diets containing 900 mg Ag/kg. Dietary administration of silver acetate antagonized selenium toxicity; silver prevented growth depression and death in chicks fed diets containing excess selenium. The addition of selenium to the diets of rats exposed to silver in drinking water prevented growth retardation but increased the concentration of silver in liver and kidneys. Silver deposits in rat liver, kidneys, and other internal organs were in the form of sulfides; under high selenium exposure, the sulfur can be replaced with selenium and formation of silver selenide deposits in the liver may be considered a silver detoxification process [947].

Silver interactions with other metals and compounds in solution are not well defined. For example, mixtures of salts of silver and copper markedly increased the survival of oyster embryos, but only when copper concentrations were less than 6 ug/L and total silver less than 11 ug/L [947].

In the Puget Sound, Washington, uptake of silver from sediments by marine polychaete annelids decreased in sediments with high concentrations of humic substances or copper but increased in sediments with elevated concentrations of manganese or iron [947].

Silver was less toxic to fathead minnows under conditions of increasing water hardness between 50 and 250 mg CaCO3/L, increasing pH between 7.2 and 8.6, and increasing concentrations of humic acid and copper [947].

Silver concentrations and metallothionein levels in gills and livers of rainbow trout increased with increasing exposure to Ag; internal toxicity associated with increased Ag accumulations may be lessened by the formation of silver-induced metallothioneins (Hogstrand 1995). In seawater, silver nitrate is less toxic to biota than in freshwater (Wood et al. 1995c). This difference is probably due to the low concentration of free Ag+ (the toxic moiety in freshwater) in seawater from the high levels of chloride and the predominance of negatively charged Ag-chloro complexes. However, high levels of silver nitrate are toxic to marine invertebrates despite the absence of Ag+, and this is attributed to the bioavailability of Ag-chloro complexes; mechanisms of silver toxcity in marine fishes are still unknown [947].

Ionic silver interferes with calcium metabolism of frogs and marine polychaete worms. Silver ions cause muscle fibers of frogs (Rana spp.) to deteriorate by allowing excess calcium to enter the cell. Studies with frog skeletal muscle fibers exposed to 1.08 mg/L showed that silver activated the calcium ion channel by acting on sulfhydryl groups in a calcium ion channel protein (Aoki et al. 1993). In marine polychaetes contaminated with silver, the calcium content of nephridial cells was reduced, although silver was not

detected in the calcium vesicles (Koechlin and Grasset 1988). Silver binds with protein sulfhydryl groups and this process protects the worm against silver poisoning (Koechlin and Grasset 1988). In marine molluscs, however, sulfide anion was the ligand of silver (Truchet et al. 1990). In marine gastropods (Littorina littorea), silver was stored in the basement membranes of the digestive system; in clams (Scrobicularia plana), it was stored in the basement membrane of the outer fold of the mantle edge and in the amoebocytes (Truchet et al. 1990). The availability of free silver in marine environments was strongly controlled by salinity because of the affinity of silver for the chloride ion (Sanders et al. 1991). Silver sorbs readily to phytoplankton and to suspended sediments. As salinity increases, the degree of sorption decreases. Nearly 80% of silver sorbed to suspended sediments at low salinities desorb at higher salinities, but desorption does not occur when silver is associated with phytoplankton. Thus, silver incorporation in or on cellular material increases the retention of silver in the estuary, reducing the rate of transport (Sanders and Abbe 1987).

The inhibiting action of silver ions may be due to the binding of sulfhydryl groups of some enzymes. Binding, in certain enzymes, is probably at a histidine imidazole group; in the case of glucose oxidase, silver ions compete with molecular oxygen as a hydrogen acceptor (Smith and Carson 1977). About 60% of the silver in liver and kidneys of silver-injected rats were in the cytosol fractions bound to the high molecular weight proteins and metallothionein fractions; however, in spleen and brain only 30% of the total tissue silver was found in the cytosol fractions (Fowler and Nordberg 1986). At moderate doses (0.4 mg Ag/kg BW) in rats, the liver handles most of the absorbed silver from the body in the bile; at higher doses, silver deposits are markedly increased in the skin (EPA 1980). In house sparrows (Passer domesticus), a silver binding protein was identified in liver after radiosilver-110m injection; the protein was heat-stable, resistant to low pH, and of low molecular weight (Kumar and Bawa 1979). The properties of the hepatic silver-binding protein in birds were similar to other studied metallothioneins, but more research is needed to distinguish differences from mammalian metallothioneins (Kumar and Bawa 1979).

Exposure of Nostoc muscorum to different concentrations of nickel and silver brought about reduction in growth, carbon fixation, heterocyst production, and nitrogenase activity and increase in the loss of ions (K+, Na+). In an attempt to ameliorate the toxicity of test metals by ascorbic acid, glutathione, and sulfur containing amino acids (L-cysteine and L-methionine), it was found that the level of protection by ascorbic acid and glutathione was more for Ag than nickel. However, metal induced inhibition of growth and carbon fixation was equally ameliorated by methionine. But the level of protection by cysteine was quite different, ie, 27% for nickel and 22% for Ag (Rai LC, Raizada M; Ecotox Environ Safety 14 (1): 12-21, 1987) [940].

Interactions [940]:

The binding of Ag+ to metallothionein was investigated, and a silver saturation assay was developed for the measurement of metallothionein in tissues. When samples of purified hepatic zinc metallothionein or cadmium metallothionein were titrated with Ag+ followed by RBC hemolysate-heat treatment (to remove non-MT bound Ag+), it was found that saturation of MT occurred at 17 to 18 g-atoms Ag+/mol protein. The rank order of potencies of metals to displace Ag+ from 110mAg-labelled Ag-metallothionein was Ag+ > Cu2+ > Cd(2+) > Hg(2+) > Zn(2+) at pH 8.5 in 0.5 M glycine buffer. [Scheuhammer AM, Cherian MG; Toxicol Appl Pharmacol 82 (3): 417-25 (1986)].

The antagonism between silver and selenium is mediated through the selenium containing enzyme glutathione perioxidase. To test the effect of selenium intake on silver toxicity, two levels of silver, 76 and 751 mg/l, and a control (no silver) were administered in drinking water for 52 days. All experimental groups consisted of ten, 21 day old Holtzman rats, fed a vitamin E deficient diet. A similar regimen was administered to vitamin E deficient rats which had selenium added to their diet. Silver, at 751 mg/l severely depressed the growth of rats on the low selenium diet. Selenium addition overcame this deficit completely in the 76 mg/l silver group but not in the 751 mg/l group. Activity of liver glutathione perioxidase in the selenium supplemented group was reduced to 30% of control at 76 mg/l silver in drinking water and to 4 % of control at 751 mg/l. This activity was not reduced at all in erythrocytes and was not detectable in the livers of rats fed the low selenium (0.02 ppm) basal diets. [Wagner PA et al; Proc Soc Exp Biol Med 148: 1106-10 (1975) USEPA, Office of Drinking Water; Criteria Document (Draft): Silver p.V-8 (1985)].

Experiments to clarify the relationship between ceruloplasmin synthesis and copper (Cu) status involving metallothionein induction as modified by cadmium (Cd), silver (Ag), and lead (Pb) were described. Specific pathogen free male mice, age 5 weeks, were fed /ad libitin/ a standard diet containing 11 ppm Cu. Metals were injected subcutaneously three times every 24 hours at doses of 1.5 mg/kg Ag, 20 mg/kg Pb, 1.5 mg/kg Cd, and 3.0 mg/kg Cu. Two groups were treated with combinations of Cd plus Ag and Cu plus Ag, the metals being injected at the same time but at different sites. Mice were sacrificed at 24 hours postinjection and serum was collected to determine ceruloplasmin activity and metal content. Liver homogenates and bile were also assessed. Cd injection significantly increased serum ceruloplasmin and serum Cu, accompanied by an increase in hepatic Cu. Pb injection slightly increased serum ceruloplasmin and serum Cu. Ag injection significantly reduced

ceruloplasmin activity and Cu levels in serum and slightly increased hepatic Cu. The Ag effect was evident in combination with Cd. Cu in combination with Ag negated the effect of Ag on ceruloplasmin with a concomitant loss of Ag from serum ceruloplasmin. [Sugawara N, Sugawara C; Arch Toxicol 59 (6): 432-6 (1987)].

Intraperitoneal pretreatment with a large dose of cadmium, zinc, mercury, manganese or silver remarkably depressed the lethal effects of X-ray. Metal binding protein may not play an important role in protective effects of metal pretreatment on the lethal effects of X-ray, but quantum mechanical characters of metals may do so. [Nomiyama K et al; Sangyo Ika Daigaku Zasshi 9: 95-110 (1987)].

Uses/Sources:

The principal industrial use of silver is as silver halide in the manufacture of photographic plates; other products include jewelry, coins, indelible inks, and eating utensils. In medicine, silver salts are used as caustics, germicides, antiseptics, and astringents; the use of silver nitrate for prophylaxis of ophthalmia neonatorum in the eyes of newborn infants is a legal requirement in some states [947].

Colloidal silver is used as an antiseptic, germicide, astringent, and caustic and for water sterilization [257].

In 1990, about 50% of the refined silver consumed domestically was used to manufacture photographic products; 25% in electrical and electronic products; 10% in electroplated ware, sterlingware, and jewelry; 5% in brazing alloys; and 10% in other products and processes [947].

Silver is the 68th most abundant element in the Earth's crust and 65th in cosmic abundance. Silver often occurs as a minor constituent in the ores of copper, lead, and zinc. Refinement of these metals yields large quantities of silver (and some gold). Silver is found in minute quantities in seawater. Historically, the principal use of silver has been for coinage, but its unique properties and the demand for more sophisticated manufacturing methods and product uses have relegated coinage to a minor application. By 1970, 28% of all silver used was for photographic processes, and only 8% for coinage. The remaining 64%, although largely used for industrial uses, was also used for art, jewelry, and miscellaneous purposes. Silver's exceedingly high electrical conductance and resistance to oxidation make it valuable in critical electrical contacts, switches, printed circuits, solders, long-lasting batteries, and many forms of electrical and electronic equipment. It is used in bearing alloys for airplanes and diesel engines and recently in some automobiles as well, for the production of mirrors and photochromic lenses, in colloidal form as a catalyst in the manufacture of certain alcohols, as an alloy with cesium in photocells, in the form of silver iodide (AgI) for weather modification. The photographic industry, the largest

single user of silver, depends on the chemical reactions of the element. Silver compounds are still occasionally used as disinfectants on mucous membranes, especially to prevent gonorrheal infection in the eyes of newborn babies [947].

Emissions from smelting operations, manufacture and disposal of certain photographic and electrical supplies, coal combustion, and cloud seeding are some of the anthropogenic sources of silver in the biosphere. Fallout from cloud seeding with silver iodide is not always confined to local precipitation; silver residuals have been detected several hundred kilometers downwind of seeding events. In 1978, the estimated loss of silver to the environment in the United States was 2.47 million kg, mostly to terrestrial and aquatic ecosystems; the photography industry alone accounted for about 47% of all silver discharged into the environment from anthropogenic sources [947].

Because of its bacteriostatic properties, silver compounds are used in filters and other equipment to purify water of swimming pools and drinking water and in the processing of foods, drugs, and beverages. Activated charcoal filters coated with metallic silver to yield water concentrations of 20-40 ug Ag/L are used in filtering systems of swimming pools to control bacteria. Silver may also function as an algicide in swimming pools if chlorine, bromine, and iodine are absent; it prevents growth of blue-green algae at 80-140 ug Ag/L. Aboard orbiting Russian space stations and spaceships, potable water is routinely treated with 100-200 ug Ag/L to eliminate microorganisms; sterilization is usually complete in 20 min. Silver-containing ceramic water filters are used to purify potable water in Swiss ski resorts, German breweries, British ships, oil tankers, drilling rigs, U.S. home consumption, and more than half the world's airlines. Monovalent and metallic silver compounds are considered excellent disinfectants; however, Ag2+ and Ag3+ are about 50 to 200 times more effective than Ag+ or Ag, possibly because of their higher oxidation states [947].

Major Uses [940]:

Manufacturing of ornaments; for electroplating; ingredient in dental alloys; for making vessels & apparatus used in production of medicinal chemicals, in processing foods & beverages, in handling org acids; as catalyst in hydrogenation & oxidn processes [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1221].

Electrical contacts; high capacity silver-zinc & silver-cadmium batteries [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 620].

Bearing linings in air-cooled aircraft engines [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 32].

Component of photographic materials, eg, camera films,

electric & electronic products, sterling ware, brazing alloys & solders, electroplated ware, commemorative medals, minted coinage, jewelry, medical & dental supplies, mirrors, & ceramic paints; catalyst, eg, in oxidation of ethylene to ethylene oxide [SRI].

Medication: Antiinfective agent. [Hall RE; J Oral Maxillotaf Surg 45 (9): 779-84 (1987)].

Therapeutic Uses [940]:

One promising alternative to antibiotics in the treatment of localized infections is the generation of antimicrobial silver ions by the use of low intensity direct current from a pure silver anode implanted at the site of an infection. [Hall RE; J Oral Maxillofac Surg 45 (9): 779-84 (1987)].

Percutaneous silver wire implants were looped through the dorsal skin of rats inoculated with Staphylococcus aureus to test the effect on bacteria. The silver was activated with four brief daily applications of anodic microcurrent. Contralateral 316L stainless steel implants, in rats indentically inoculated, served as controls. Cultures from the silver implants showed a marked reduction or elimination of bacteria. In rats with colonization established for 1 week, subsequent electrical activation of the silver also suppressed the bacteria. Inflammatory reactions at 3 weeks were mild at both the silver and stainless steel implants and no giant cells or toxicity were seen. [Spadaro JA et al; J Biomed Mater Res 20 (5): 565-77 (1986).

Natural Sources [940]:

Occurrence in earth's crust: 0.1 ppm; also present in seawater: 0.01 ppm. Found native or assoc with copper, gold & lead. Principal ores are argentite, cerargyrite or horn silver (mixture of halides), proustite ... /&/ Pyrargyrite [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1221].

Present in unpolluted freshwaters at concentration(s) up to 0.5 ug/l while sediments, soils, rocks, and minerals contain from 0.1 to 0.5 mg of silver/kg. /Silver ions/ [Boyle RW; Geochemistry of Silver and its Deposits with Notes on Geochemical Prospecting for the Element p.1 (1968)].

Artificial Sources [940]:

Sources of silver in the atmosphere include emissions from smelting operations, cloud seeding operation (silver iodide), coal combustion, steel and iron production,

cement manufacture, urban refuse incineration, and cigarette tobacco. [Freeman RA; ASTM Spec Tech Pub 667: 342 (1979)].

Urban refuse incineration contributes about 1.7 ng/cu m to the ambient air as silver. [Greenberg RR et al; Environ Sci Technol 12: 566 (1978) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-23 (1980) EPA 440/5-80-071

Other Environmental Concentrations [940]:

Measured 2.61 mg silver/kg in a reference cigarette tobacco by neutron activation analysis and 2.87 mg silver/kg in the paper. [USEPA; Ambient Water Quality Criteria Doc: Silver p.C-25 (1980) EPA 440/5-80-071

Forms/Preparations/Formulations:

The atomic weight of silver is 107.868, and natural silver consists of two stable isotopes: silver-107 (51.82%) and silver-109 (48.18%) [257]. Forms of silver in atmospheric emissions are probably silver sulfide, silver sulfate, silver carbonate, silver halides, and metallic silver [947]. About 50% of the silver released into the atmosphere from industrial operations is transported more than 100 km and is eventually deposited in precipitation [947]. Minute amounts of Ag 110 have been detected in natural waters and is attributed to atmospheric fallout from nuclear explosions [947].

Radionuclides:

The symbol for Silver-108m is 108mAg, the atomic number is 47, the half-life is 130 years, and X-ray emission and isometric transition from higher to lower energy states are the major form of decay [674].

The symbol for Silver-110m is 110mAg, the atomic number is 47, the half-life is 250 days, and beta emission and isometric transition from higher to lower energy states are the major forms of decay [674].

The symbol for Silver-110 is 110Ag, the atomic number is 47, the half-life is 24.6 seconds, and beta emission is the major form of decay [674].

The symbol for Silver-111 is 111Ag, the atomic number is 47, the half-life is 7.5 days, and beta emission is the major form of decay [674].

The symbol for Silver-113 is 113Ag, the atomic number is 47, the half-life is 5.3 hours, and beta emission is the major form of decay [674].

Information from HSDB [940]:

Forms avail: pure (fine), sterling (7.5% Copper), various alloys, plate; ingot, bullion, moss, sheet, wire, tubing, castings; powder; high purity (impurities less than 100 ppm); single crystals; whiskers. [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1042].

Available: 99.99 wt% Ag & 99.90 wt% Ag [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 21(83) 10].

Amalgum-70% silver, 26% tin, 3% copper, and 1% zinc is used in combination with mercury to fill cavities in teeth. [Considine. Chemical and Process Technol Encyc 1974 p.1038].

Alloys: Ag-Au; Ag-Cu; Ag-Pd; Ag-Pt; Ag-Cu-Ni; Ag-Mg-Ni; Ag-Au-Cd-Cu; & Ag-Cd-Cu-Ni [CONSIDINE. CHEMICAL AND PROCESS TECHNOL ENCYC 1974 p.1037].

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

Solubilities [940]:

Sol in fused alkali hydroxides in presence of air, fused peroxides, & alkali cyanides in presence of oxygen [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1221].

Insol (sic, actually "relatively insoluble") in hot or cold water, alkali; sol in nitric acid; hot sulfuric acid, potassium cyanide /Aqueous/ [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-127].

Molecular Weight [940]:

107.868 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1221].

Density/Specific Gravity [940]:

10.49 @ 15 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1221].

Boiling Point [940]:

Approx 2000 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1221].

Melting Point [940]:

960.5 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1221].

Color/Form [940]:

White metal, face-centered cubic structure [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1221].

Other Chemical/Physical Properties [940]:

Poor reflector of uv; pure silver has highest electrical & thermal conductivity & lowest contact resistance of all metals. [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-35].

Molten metal dissolves 20 times its vol of oxygen under 1 atm & gives it up on solidification. [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 296].

Soft, ductile, malleable, lustrous metal. [Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New York, NY: Van Nostrand Reinhold, 1984. 2401].

Silver has the oxidation states +1, and less frequently +2; higher ones are rare. [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 620

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

The global biogeochemical movements of silver are characterized by releases to the atmosphere, water, and land by natural and anthropogenic sources, long-range transport of fine particles in the atmosphere, wet and dry deposition, and sorption to soils and sediments. The chief source of silver contamination of water is silver thiosulfate complexes in photographic developing solutions that photofinishers discard directly to sewers. Secondary waste treatment converts most of the silver thiosulfate complex to insoluble (sic, actually "relatively insoluble") silver sulfide and forms some metallic silver [947].

Silver occurs naturally in several oxidation states, usually as Ag and Ag+; other possible oxidation states of silver are Ag2+ and Ag3+. In surface freshwater, silver may be found as the monovalent ion; in combination with sulfide, bicarbonate, or sulfate; as part of more complex ions with chlorides and sulfates; and adsorbed onto particulate matter. The argentous ion (Ag+) does not hydrolyze appreciably in solution and is considered to be a

mild oxidizing agent. Hypervalent silver species, such as Ag2+ and Ag3+, are significantly more effective as oxidizing agents than Ag and Ag+,but are unstable in aqueous environments, especially at water temperatures near 100 C [947].

In natural waters, silver may exist as metalloorganic complexes or adsorbed to organic materials. In freshwater and soils, the primary silver compounds under oxidizing conditions are bromides, chlorides, and iodides; under reducing conditions the free metal and silver sulfide predominates. In river water, one study showed silver present as the monovalent ion (Ag+) at 53-71% of the total silver, as silver chloride (AgCl) at 28-45%, and as silver chloride ion (AgCl2-) at 0.6-2.0%. Increasing salinity of brackish and marine waters increased concentrations of silver chloro complexes; these chloro complexes retain some silver in dissolved form, and relatively small anthropogenic quantities can substantially enrich the environment. In the open ocean, the principal dissolved form of silver is AgCl2-, but the most bioavailable form may be the neutral monochloro complex AgCl [947].

Sorption is the dominant process that controls silver partitioning in water and its movement in soils and sediments. Silver may leach from soils into groundwater; the leaching rate increases with decreasing pH and increasing drainage. Silver adsorbs to manganese dioxide, ferric compounds, and clay minerals, and these compounds are involved in silver deposition into sediments; sorption by manganese dioxide and precipitation with halides reduce the concentration of dissolved silver, resulting in higher concentrations in sediments than in the water column. Under reducing conditions, adsorbed silver in sediments may be released and subsequently reduced to metallic silver or combine with reduced sulfur to form the insoluble (sic, actually "relatively insoluble") silver sulfide [947].

Sediments may be a significant source of silver to the water column. In one study, anoxic sediments containing 1.0 to 27.0 grams of silver/kg DW and 10 mmoles of acid volatile sulfide/kg DW were resuspended in oxygenated seawater for several hours to days. The seawater in contact with sediment containing 10.8 g/kg had 20 ug Ag/L; seawater in contact with sediments containing 27 g Ag/kg had about 2,000 ug Ag/L, which seems to be the solubility of silver in seawater [947].

Metabolism information from Eisler [947]:

> The acute toxicity of silver to aquatic species varies drastically by the chemical form and correlates with the availability of free ionic silver. In natural aquatic systems, ionic silver is rapidly complexed and sorbed by dissolved and suspended materials that are usually present. Complexed and sorbed silver species in natural waters are at least one order of magnitude less toxic to aquatic organisms than the free silver ion. Thus, silver nitrate--which is strongly dissociated--is extremely toxic to rainbow trout (Oncorhynchus mykiss); the 7-day LC50 value is 9.1 ug/L. Silver thiosulfate, silver chloride, and silver sulfide were relatively benign (7-day LC50 values >100,000 ug/L), presumably due to the

abilities of the anions to remove ionic silver from solution. The probable cause of hyperventilation in rainbow trout exposed to silver nitrate was a severe metabolic acidosis manifested in decreased arterial plasma pH and HCO3- levels. Lethality of ionic silver to trout is probably due to surface effects at the gills--disrupting Na+, Cl-, and H+--causing secondary fluid volume disturbance, hemoconcentration, and eventual cardiovascular collapse. Morgan et al. (1995) suggest that the sites of action of silver toxicity in rainbow trout may be inside the cells of the gill epithelium rather than at the external surface and linked to carbonic anhydrase--a gill enzyme involved in Na+ and Cl- transport [947].

Most absorbed silver is excreted into the intestines by the liver in the bile and subsequently excreted in feces; urinary excretion of silver is generally very low (EPA 1980; Fowler and Nordberg 1986; Klaassen et al. 1986; PHS 1990). Rodents, monkeys, and dogs given radioactive silver salts by oral and other routes excreted more than 90% of the absorbed dose in the feces (Fowler and Nordberg 1986). Rats injected intravenously with radioactive silver nitrate excreted silver in bile mainly bound to a low molecular weight complex similar to glutathione (Fowler and Nordberg 1986). Excretion was faster and percentages excreted by mice, rats, monkeys, and dogs were larger when silver was administered orally than by intravenous or intraperitoneal injection (Smith and Carson 1977).

Among mammals, low doses of ingested silver were eliminated from the body within 1 week (PHS 1990). In rats, mice, and rabbits, about 99% of a single oral dose of silver was eliminated within 30 days (EPA 1980). Time for 50% clearance of silver in rats, mice, monkeys, and dogs after oral ingestion was about 1 day; this short half-time is due, in part, to fecal elimination of unabsorbed silver; the half-times were longer (1.8-2.4 days) after intravenous injection (Fowler and Nordberg 1986). Rodents dosed with silver accumulated high initial concentrations in the liver, which greatly decreased within 10 days; however, silver concentrations in spleen and brain were retained for longer periods. The biological half-time of radiosilver in rats given a single intraperitoneal injection was 40 h in whole blood, plasma, kidney, and liver; 70 h in spleen; and 84 h in brain. After exposure by inhalation, dogs cleared 59% of an administered dose of radiosilver-110m from the lungs in 1.7 days and from the liver in 9 days (Fowler and Nordberg 1986). The mean daily intake of silver in humans is about 88 ug; about 60 ug is excreted daily in the feces (Smith and Carson 1977). In humans, the whole body effective half-time of persistence was 43 days (EPA

1980). The biological half-time of silver in the lungs of an exposed person was about 1 day; in liver it was 52 days (Fowler and Nordberg 1986). In humans, 80% of the retained silver in lung was cleared in about 1 day; 50% of the remainder was usually cleared in 3 days (EPA 1980). In persons who had accidentally inhaled radiosilver-110m, most of the inhaled silver had a half-time persistence of about 1 day, probably because of rapid mucociliary clearance, swallowing, and fecal excretion; most of the absorbed radiosilver translocated to the liver (EPA 1980).

Absorption, Distribution and Excretion [940]:

Silver, once deposited in the body, is poorly excreted in the urine in amounts detectable by spectrochemical methods. /Silver metal and soluble silver compounds/ [Mackison, F. W., R. S. Stricoff, and L. J. Partridge, Jr. (eds.). NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) PublicationNo. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981. 2].

Regardless of route and chemical form administered, fecal excretions of silver always predominate over urinary excretion. Most absorbed silver is excreted into the intestine by the liver via the bile. [USEPA; Ambient Water Quality Criteria Doc: Silver p.C-56 (1980) EPA 440/5-80-071].

In argyria, aside from the blood vessels and connective tissues, the dermis of the skin, glomeruli of the kidney, chorioid plexus, mesenteric glands, and thyroid contain the greatest amounts of deposited silver. [Buckley WR et al; Arch Dermatol 92: 697 (1965)].

Fecal (0-4 days), urinary (0-4 days), and biliary (0-2h) excretion and tissue distribution of /silver was/ examined in rats after iv administration. Total (fecal plus urinary) excretion was relatively rapid (> 50% of dose in 4 days). ... 45% (Ag) salt was excreted into bile in 2 hr, and they exhibited high bile/plasma concentration ratios. ... Feces was the predominant route of excretion for Ag. ... Biliary excretion seems to be an important determinant for the fecal excretion for Ag. ... Most of the metals reached the highest concentration(s) in liver and kidney. However there was no direct relation between the distribution of metals to these excretory organs and their primary route of excretion. [Gregus Z, Klaassen CD; Toxicol Appl Pharmacol 85 (1): 24-38 (1986)].

The highest concentration(s) of silver are usually found in the liver and spleen and to some extent in the muscle,

skin, and brain. [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 621].

Excretion of silver from the body is mainly gastrointestinal. Urinary excretion (around 10 ug/day) and fecal elimination (30-80 ug/day) has been reported from two healthy subjects. ... These values might reflect a certain overestimation of true silver concn. ... Using neutron activation analysis ... 1 ug/day /was found/ in urine of normal persons. [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 621].

The deposition fraction of 0.5 um spherical silver particles in the lung of dogs has been found to be about 17%. ... The intestinal absorption of silver by mice, rats, monkeys, and dogs has been recorded at about 10% or less following ingestion of radioactive silver. [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 524].

Absorption upon exposure or the extent of exposure, itself, may vary considerably among normals as reflected in tissue levels. For example, the silver content of the hair of school children from 21 school districts in Selesia, Poland, ranged from 0.23 to 1.96 mg/kg (average 0.69 mg/kg; analyses by neutron activation). [Dutkuwicz T et al; Chem Anal 23: 261 (1978) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-1 (1980) EPA 440/5-80-071].

Silver is retained by all body tissues. The primary sites of deposition in persons who have never taken silver therapeutically are the skin, adrenals, lung, muscle, pancreas, kidney, heart, and spleen. Silver is also deposited in blood vessel walls, testes, pituitary, nasal mucous membrane, maxillary antra, trachea, and bronchi. [Sax NI; Dangerous Properties of Industrial Materials 2nd edition: 1174 (1963) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-40 (1980) EPA 440/5-80-071].

Although silver does not accumulate in the lungs with age, it was present in 39 percent of the lungs from Americans analyzed. [Tipton IH, Cook MJ; Health Phys 9: 103 (1963) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-40 (1980) EPA 440/5-80-071].

Examinations of accidental death victims indicated that the silver content of the myocardium, aorta, and pancreas tended to decrease with age. [Bala YU et al; Tr Voronczh-

GOS Med Inst 64: 37 (1969) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-40 (1980) EPA 440/5-80-071].

The adrenals, lungs, dura mater, bones, cartilage, muscles, and nervous tissue are minimally or never involved as deposition sites for silver. [Hill WR, Pillsbury DM; Argyria, the Pharmacology of Silver (1939) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-43 (1980) EPA 440/5-80-071].

Silver was found only as a lipoid-silver complex or in lipofuschin-like lysosomes and in residual bodies. The lysosomes were thought to be responsible for the intracellular transport and extrusion of silver. In the liver, there was incr activity of cytochrome oxidase, but marked decr in the activity of succinate dehydrogenase. [Putzke HP; Z Ges Inn Med 22: 48 (1967) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-49 (1980) EPA 440/5-80-071].

In rats, silver is eliminated from the lung in two or three phases. The fastest phase (0.3 to 1.7 days) removes most of the inhaled dose by mucociliary clearance. A second phase and third phase remove absorbed silver, mostly via the liver, with half-lives of about 8 to 15 and 40 to 50 days, respectively. [USEPA; Ambient Water Quality Criteria Doc: Silver p.C-58 (1980) EPA 440/5-80-071].

The skin is an excretory organ in generalized argyria with gradual translocation of silver from the general body pool through the dermis and finally into the epidermis as soluble silver. One worker with generalized agryria was studied. Silver appeared to be released from melanin-silver complex as a soluble ionic form near the surface of the epidermis. [Buckley WR, Terhaar CJ; Trans St Johns Hosp Dermatol Soc 59: 39 (1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-63 (1980) EPA 440/5-80-071].

The oral dose is absorbed into the portal circulation passing through the general circulation. Intravenous doses are carried to all internal organs. Dermal absorption occurs through mucous membranes and through broken skin. [USEPA, Office of Drinking Water; Criteria Document (Draft): Silver p.I-1 (1985)].

If dust of metal or its salts is absorbed, it is precipitated in tissues in metallic state & cannot be eliminated from body in this state. /SILVER & CMPD/ [International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 204].

Distribution of silver in the rat at day 6 following intramuscular injections of 1.0 mg dose of silver; 53.5 percent of the dose was absorbed (0.59 percent absorbed by the heart and lung; 2.69 percent absorbed by spleen; 3.03 percent absorbed by blood; 33.73 percent absorbed by liver; 0.63 percent absorbed by kidney; 8.21 percent absorbed by GI tract; 2.39 percent absorbed by muscle; 2.20 percent absorbed by bone; 7.39 percent absorbed by skin; 1.82 percent excreted by urine; 37.33 percent absorbed by feces) and 46.5 percent of absorbed by the heart and lung; 0.01 percent absorbed by spleen; 0.50 percent absorbed by blood; 0.36 percent absorbed by liver; 0.07 percent absorbed by kidney; 1.12 percent absorbed by GI tract; 0.27 percent absorbed by muscle; 0.18 percent absorbed by bone; 0.24 percent absorbed by skin; 0.64 percent excreted by urine; 96.56 percent excreted in feces) and 7.9 percent was unabsorbed. [Scott KG, Hamilton JG; J Clin Invest 27: 555 (1948) as cited in USEPA; Ambient Water Quality Criteria Doc: Silver p.C-47 (1980) EPA 440/5-80-071].

Extensive toxicokinetics of binary combinations of metals including silver are described in rats following their administration at small (0.004-0.1 LD50) and large doses (0.04-0.1 LD50). Absorption of these metals after their combined administration shows a definite pattern. Thus, in a majority of cases silver inhibited absorption. ... /Silver cation/ [Kazimov MA, Roshchin AV; Gig Tr Prof Zabol 3: 11-16 (1986)].

Nonradioactive and radioactive metal salts were administered intravenously to Sprague Dawley rats. The highest amount of each metal approached the maximum tolerated dose. Cobalt (Co), silver (Ag), and manganese (Mn) were eliminated rapidly. The elimination of 20 to 50 percent of the dosage was observed for copper (Cu), thalium (Tl), bismuth (Bi), lead (Pb), cesium (Cs), gold (Au), zinc (Zn), mercury (Hg), selenium (Se), and chromium (Cr). The slowest excretion rate was measured for arsenic (As), cadmium (Dc), iron (Fe), methyl mercury (MeHg), and tin (Sn). No substantial elimination rate decline was observed for MeHg and Fe, and the decline was small for Tl, Cs, Hg, Sn, Co, Ag, Zn, Cr, and As. Elimination of Ag and Mn via feces was fast, with more than 70 percent eliminated on the first day. Cu, Tl, Pb, and Zn 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. Co was removed rapidly via urine, while Pb, Sn, Zn, MeHg, Ag, Fe, Mn, and Cd were eliminated slowly. The biliary excretion of Ag, As, and Mn was fast, with 25.5, 30.2 and 16.2 percent eliminated in two hours. Cu, Se, Cd, Pb, Bi, and Co were eliminated at an intermediate rate via the biliary route. Ag, As, Mn, Cu, Se, Cd, Pb, Bi, and MeHg

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 Ag, Mn, Cu, Tl, Pb, Zn, Cd, Fe, and MeHg. Co, Cs, Au, Se, and Cr, were removed predominantly by urine. For Bi, Hg, As, and Sn the two routes were similar. [Gregus Z, Klaassen CO; Toxicol Appl Pharm 85 (1): 24-38 (1986)].

Laboratory and/or Field Analyses:

A variety of spectrographic, colorimetric, polarographic, and other analytical techniques have been used for routine measurement of silver in biological and abiotic samples, including neutron activation analysis, emission spectrochemical, and atomic absorption spectrometry methods [861,940,947,956, 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 1638 and 1669 (see details below) should apply.

Most measurements of silver concentrations in natural waters prior to the use of clean techniques are considered inaccurate. Until analytical capabilities that exceed the dissolved-particulate classification are developed, it will be necessary to rely on laboratory and theoretical modeling studies to fully understand chemical speciation of silver in natural waters [947].

Previous USGS concentrations of 10 ppb (a concentration which wold kill fish) from many locations in Colorado were found to have been caused by field contamination, possibly contamination of filter which were carried with silver-bearing electrodes (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

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].

Detection limits: for risk or hazard assessment purposes, low concentration criteria or benchmarks require rigorous methods. In some situations (as when background concentrations are low), water detection limits as low as 0.029 ug/L may be necessary, using EPA method 1638, since EPA Water Quality Criteria are as low as as 0.31 ug/L [1001]. In any case, the detection limits should be no higher than comparison benchmarks or criteria for various media (water,

sediments, soil, tissues, etc), some of which are low (see water and sediment media sections above).

The detection limit of silver in biological tissues with scanning electron microscopy and X-ray energy spectrometry is 0.02 ug/kg and sometimes as low as 0.005 ug/kg [947]. In air, water, and soil samples, the preferred analytical procedures include flame and furnace atomic absorption spectrometry, plasma emission spectroscopy, and neutron activation.

Contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see also, discussion in the disclaimer section at the top of this entry).

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 false negatives due to the use of detection limits that are too high, the loss of contaminants through inappropriate handling, or the use of inappropriate methods.

Additional more detailed notes on typical 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. 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 very 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.

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 copper and silver entries for examples 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. Colorado recommends very short holding times for silver concentrations in water since up 50% adsorption losses were seen in one day and up to 90% losses were seen in a week, even if samples were properly acidified

to a pH of 2 or less right away (Pat Davies, Colorado Division of Wildlife, personal communication, 1997). 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 Colorado infomatin above 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).

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]. The newer EPA 1600 series methods for water, some of which are described below, were designed to minimize collector and lab analyst contamination.

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]. However, Great Lakes and other generic conversion factors may not hold up for many areas. Both total and dissolved concentrations should be checked at new locations before relying on this conversion factor (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) [1010]:

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.

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

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].

In some situations (as when background concentrations are low), water detection limits as low as 0.029 ug/L may be necessary for silver, using EPA method 1638, since EPA Water Quality Criteria are as low as 0.31 ug/L [1001].

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

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].

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.

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].

EPA Method 7760:

EPA Method 7760 is an older atomic absorption procedure which was approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and ground water [940].

EPA Method 200.7:

EPA Method 200.7 is an older Inductively Coupled Plasma (ICP)- Atomic Emission Spectrophotmetric method for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters with a typical detection limit of 7 ug/l (40 CFR 136, 7/1/87) [940].