ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

ZINC 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).

Zinc (Zn, CAS number 7440-66-6)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Zinc, the 25th most abundant element, is widely distributed in nature, making up between 0.0005% and 0.02% of the Earth's crust [253]. Zinc is found in the air, soil, and water, and is present in all foods. In its pure form, zinc is a bluish-white shiny metal. Metallic zinc has uses in industry. Metallic zinc is mixed with other metals to form alloys such as brass and bronze [954].

Zinc can combine with other chemicals to form salts. Most zinc ore found naturally in the environment is found as the salt, zinc sulfide. Zinc salts are widely used in industry [954]. Both of the zinc salts zinc sulfide and zinc oxide are used to make white paints, ceramics, and several other products. Zinc oxide is also used in producing rubber. Zinc salts, such as zinc acetate, zinc chloride, and zinc sulfate, are used in preserving wood and manufacturing and dyeing fabrics [954].

Zinc is an essential food element needed by the body in small amounts [954]. Zinc in low to moderate amounts is of very low toxicity in its ordinary compounds and in low concentrations is an essential element in plant and animal life [253].

Absorption of dietary zinc in higher animals is apparently regulated in part by metal thioneins, low molecular weight proteins containing high levels of cysteine [180]. Freshwater fish can regulate zinc over a wide range of ambient concentrations [180]. Increased zinc intake can afford some animals some protection against cadmium exposure [180].

Too little zinc in the diet can lead to poor health, reproductive problems, and lowered ability to resist disease [954] (see Br.Dev section below). Too much zinc can be harmful to health [954]. There have been cases of too much zinc causing poisoning in humans as well as fish and wildlife (see Br.Haz section below).

Zinc is listed by the Environmental Protection Agency as one of 129 priority pollutants [58].

Br.Haz: General Hazard/Toxicity Summary:

Potential Hazards to Fish, Wildlife, Invertebrates, Plants, or other non-human biota:

Zinc is a trace element which can be toxic in some cases but also has some useful physiological functions (see benefits section below for details).

Elevated concentrations of zinc in water are particularly toxic to many species of algae, crustaceans, and salmonids [180]. Elevated water concentrations of zinc have especially strong impacts on macroinvertebrates such as molluscs, crustaceans, odonates, and ephemeropterans [72].

In the aquatic environment, zinc toxicity is more often associated with direct toxicity of elevated concentrations of zinc in the water (through disruption of internal ion balance) rather than dietary or food chain toxicity [177]. (Note: The following reference further demonstrates the role of iono-regulatory upset in the acute toxicity of zinc: Spry, D.J. and C.M. Wood. 1985. Ion flux rates, acid-base status, and blood gases in rainbow trout, Salmo gairdneri, exposed to toxic zinc in natural soft water. Can.J.Fish. Aquat.Sci. 42:1332-1341.)

When sufficient acid volatile sulfide (AVS) was available to bind with the zinc, no toxicity was observed even at dry-weight metal concentrations in excess of 100 mg/kg. This is the first demonstration of the utility of the AVS:metal partitioning model using a chronic freshwater sediment test [756]. For additional discussion of SEM and AVS normalization of sediments vs bioconcentration, see Besser et al. [981] as summarized in the Sed.Misc. section above.

In western watersheds affected by metals, fish kills are often associated with runoff and rainstorm events. Metals responsible for toxicity are often copper and zinc, whose toxicity and/or mobility are enhanced by the depressions of pH, hardness/alkalinity, and dissolved organic carbon that typically accompany these events (David Mount, National Biological Survey, Columbia, MO, personal communication, 1994). For many metals, alkalinity is sometimes a more important co-factor for toxicity than hardness (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

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

In mammals excess zinc can cause copper deficiencies, affect iron metabolism, and interact with the chemical dynamics of lead and drugs [39,180].

Pertinent pathological findings in four goldeneyes which had ingested one or two pennies and were diagnosed with zinc poisoning included necrotizing ventriculitis. Pennies in various stages of dissolution were present in the ventriculus. The pancreas had degenerative lesions that resulted in acinar atrophy and ductular proliferation [959].

Poisoning has been observed/ in ferrets & mink from chewing corroded cages or in cattle & horses, as well as from food stuffs containing particles of metal, & in pigs & hens from use of zinc plated funnels. Zinc oxide fumes from welding of galvanized materials are thought to be responsible for poisoning of cattle in vicinity of welding operations. It is evident that young animals are much more susceptible to poisoning by zinc than mature animals (Clarke, M. L., D. G. Harvey and D. J. Humphreys. Veterinary Toxicology. 2nd ed. London: Bailliere Tindall, 1981. 76) [940].

Eisler reviewed zinc hazards to fish, wildlife, and invertebrates in 1993 [550]. Included in the review were: Ecological and toxicological aspects of zinc in the environment; sources and uses; chemical and biochemical properties; carcinogenicity, mutagenicity, teratogenicity; background concentrations in biological and nonbiological compartments; effects of zinc deficiency; toxic and sublethal effects on terrestrial plants and invertebrates, aquatic organisms, birds, and mammals; and recommendations for the protection of sensitive resources [550].

Potential Hazards to Humans:

In humans, prolonged excessive dietary intake of zinc can lead to deficiencies in iron and copper, nausea, vomiting, fever, headache, tiredness, and abdominal pain [173].

Various literature sources seem to indicate that some zinc intake in humans is good for immune and other beneficial functions but that too much is harmful. Like selenium, the demarcation between too much and too little is not precisely documented and may vary between individuals and species (Roy Irwin, National Park Service, Personal Commuicaiton, 1997).

Individuals were made acutely ill with dizziness, nausea, tightness in throat & in some cases diarrhea, from eating apples, stewed in galvanized iron vessels, which contained 7 g of zinc to 1 lb. (Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 352) [940].

Zinc is a human skin irritant (Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New York, NY: Van Nostrand Reinhold, 1984. 2751) [940].

It was concluded that an abnormal amount of zinc may enter & leave the body for years without causing symptoms or evidence which can be detected clinically or by laboratory examinations of gastrointestinal, kidney, or other damage (Hamilton, A., and H. L. Hardy. Industrial Toxicology. 3rd ed. Acton, Mass.: Publishing Sciences Group, Inc., 1974. 187) [940].

Zinc taken by mouth is relatively non-toxic, though the soluble salts in large doses may cause vomiting & diarrhea (Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 351) [940].

A comprehensive toxicological profile for zinc, especially as it relates to human health, is available from ATSDR [954]. Due to lack of time, important highlights from this ATSDR document have not yet been completely incorporated into this entry.

Symptoms of zinc toxicity are lassitude, slower tendon reflexes, bloody enteritis, diarrhea, lowered leukocyte count and depression of CNS, and paralysis of extremities (Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 72) [940].

Zinc is an essential metal, but over the past 10 years, cases of zinc toxicity (including hemolytic anemia have apparently been on the increase in both animals and humans primarily as a result of ingestion of pennies minted since 1983, which contain 98% zinc [959].

Benefits from Zinc:

In humans, some zinc in the diet is essential for normal growth and maturation, cell metabolism, development of reproductive organs, prevention of anemia, functioning of the prostate gland, healing of wounds, enzyme activity, regulating zinc dependent enzymes, manufacture of proteins, and manufacture of nucleic acids [173,180,253].

Zinc is an essential constituent of DNA and RNA polymerases and a number of metalloenzymes [180,951].

Zinc deficiency decreases production of DNA & RNA, which leads to reduced protein synthesis. Typical signs of severe deficiency including dermatitis, emaciation, testicular atrophy, retarded growth & anorexia. Endemic zinc deficiency syndrome among young men & women has been reported from Iran & Egypt. Prominent features included anemia, hepatosplenomegaly & hyperpigmentation (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 668) [366].

Zinc is ubiquitous & is considered an essential trace element. Its necessary roles involve enzymes & enzymatic functions, protein synthesis, & carbohydrate metabolism. It is necessary for normal growth & development in mammals & birds. Human dwarfism & lack of sexual development have been related to zinc deficiency. Zinc is present in metalloenzymes incl carbonic anhydrase, carboxypeptidase, alcohol dehydrogenase, glutamic dehydrogenase, lactic dehydrogenase & alkaline phosphatase (Doull, J., C.D. Klaassen, and M. D. Amdur (eds.). Casarett and Doull's Toxicology. 2nd ed. New York: Macmillan Publishing Co., 1980. 460) [American Medical Association, Department of Drugs. Drug Evaluations. 6th ed. Chicago, Ill: American Medical Association, 1986. 859) [366].

Resistance/Development of Tolerance:

Some plants and animals living in zinc-polluted environments have evidently become more tolerant of zinc than populations of the same species from cleaner areas [180].

Populations of organisms chronically exposed to chemical pollutants may develop increased tolerance to those pollutants [177,493]. Some of the aquatic issues related to tolerance, interactions with other metals, and/or indirect impacts related to zinc were summarized by Rand and Petrocelli [177]. Even metals such as cobalt, lead, manganese, and nickel, which do not directly induce synthesis of metallothionein may indirectly induce it by increasing the hepatic zinc pool [177].

Some plants and animals living in zinc-polluted environments have evidently become more tolerant of this metal than populations of the same species from cleaner areas [180].

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

EPA 1996 IRIS database information [893]:

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

Classification: D; not classifiable as to human carcinogenicity

BASIS: Based on inadequate evidence in humans and animals.

HUMAN CARCINOGENICITY DATA: Inadequate. There are no reports on the possible carcinogenicity of zinc and compounds per se in humans. Case studies have been used to evaluate the effects of zinc administered for therapeutic reasons. There are reports which compare zinc levels in normal and cancerous tissue. Studies of occupational exposure to zinc compounds have also been conducted, but have limited value because they do not correlate exposure with cancer risk.

ANIMAL CARCINOGENICITY DATA: Inadequate.

Not considered a carcinogen for certain EPA modeling purposes [868,903].

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

The risk associated with maternal ingestion of large amounts of zinc in human pregnancy is unknown [370].

When there was more zinc present in sediments than AVS, survival, growth, and fecundity were affected [756]. See also: Sed.Misc. Section below.

Zinc deficiency in humans is associated with pregnancy complication, particularly growth retardation. There is only one report of developmental effects occurring in humans exposed to high levels of zinc compounds [954].

No studies were located regarding reproductive toxicity in humans after inhalation, oral, or dermal exposure to high levels of zinc [954].

Genotoxicity studies conducted in a variety of test systems have failed to provide evidence for mutagenicity of zinc. However, there are indications of weak clastogenic effects following zinc exposure [954].

Zinc deficient diets showed that growth arrest occurred among rats fed with food containing slightly less than 12 mg/kg of zinc. Endemic zinc deficiency syndrome among young men & women has been reported from Iran & Egypt. Prominent features included retarded growth, infantile testis, and delayed sexual maturation (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 668) [940].

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

Zinc enters the air, water, and soil as a result of both natural processes and human activities. Waste streams from zinc and other metal manufacturing and zinc chemical industries, domestic waste water, and run-off from soil can discharge zinc into waterways [954].

Most of the zinc in bodies of water settles on the bottom. However, a small amount may remain either dissolved in water or as fine suspended particles. The level of dissolved zinc in water may increase as the acidity of water increases (that is, as pH decreases) [954].

Fish that live in water containing zinc collect it in their bodies. Most of the zinc in soil is bound to the soil and does not dissolve in water. However, depending on the characteristics of the soil, some zinc may reach groundwater. Contamination of groundwater from hazardous waste sites has been noticed [954].

Zinc removals by wetlands and detention ponds receiving highway runoff was high [220]. Zinc water concentrations exceeding state standards occurred in 78 % of wetland inlet samples but in only 34 % of outlet samples [220].

Zinc sediment samples were higher in a detention pond than in a downstream wetland [220].

Zinc dissolves in aqueous acids or bases, forming hydrogen gas and zinc ion or zincate ion, respectively [253]. Zinc forms compounds only in the +2 oxidation state [253]. More research needs to be done on the potential of increased toxicity of zinc in low alkalinity or low pH habitats [383].

Arsenic +5 can form relatively insoluble metallic salts with a number of cations, including zinc (e.g., arsenates of zinc) [445]. The sorption of arsenate ions in the soil by zinc greatly restricts the availability of arsenic to plants [445].

Zinc poisoning is mostly accidental from the intake of pesticides, inadvertent therapeutic use of heavy doses of zinc salts, or drinking of acidic juices or brews made in galvanized iron utensils (Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 69) [940].

Synonyms/Substance Identification:

Zinc Dust [617,940]
Zinc Powder [617,940]
Pasco [617]
Merrillite [617,940]
ASARCO L 15 [940]
BLUE POWDER [940]
EMANAY ZINC DUST [940]
GRANULAR ZINC [940]
JASAD [940]

Molecular Formula [940]:
Zn

Associated Chemicals or Topics (Includes Transformation Products):

Relationships between this metal versus indicator plants, other metals, and various rock types was summarized by Brooks in 1972 [951].

Impurities [940]:

The effect of small amount of common impurities is to incr corrosion resistance to solutions, but not in the atmosphere. Ordinary zinc is too brittle to roll at ordinary temperatures, but becomes ductile at elevated temperatures; brittleness is thought to be assoc with impurities such as tin. [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. 2035].

Lead contaminates special high grade zinc at 0.003%; high grade zinc at 0.07%; intermediate grade at 0.2%; brass special at 0.6%; prime western at 1.6% [Considine. Chemical and Process Technol Encyc 1974 p.1179].

Iron contaminants special high grade zinc at 0.003%; high grade at 0.02%; intermediate at 0.03%; brass special at 0.03%; prime western at 0.08% [Considine. Chemical and Process Technol Encyc 1974 p.1179].

Cadmium contaminates special high grade at 0.003%; high grade at 0.03%; intermediate grade at 0.4%; brass special at 0.5% [Considine. Chemical and Process Technol Encyc 1974 p.1179].

Flammability of some commercial zinc dusts or powders is attributed to presence of zinc chloride. [Bretherick, L. Handbook of Reactive Chemical Hazards. 3rd ed. Boston, MA: Butterworths, 1985. 1412].

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

W.Low (Water Concentrations Considered Low):

Leland and Kuwabara, 1985: In non-polluted areas, baseline concentrations as low as 0.0001 mg/l have been recorded [177].

W.High (Water Concentrations Considered High):

Streams affected by mine drainage can have 100 ug/L or more zinc [190].

W.Typical (Water Concentrations Considered Typical):

1971: 726 sites from U.S. steams had a median value of 20 ug/L [190].

USGS 1974-1981: the 50th percentile of 288 (not especially clean) NASQWAN and NWQSS river sites in the U.S. was 15 ug/l; the 25th percentile was 12 ug/l, and the 75th percentile was 21 ug/l, with concentrations trending downward more often than upward [219]. These riverine sites in the USGS study were mostly in (or downstream of) agricultural and urban areas [219].

In an Arizona intermittent stream, zinc was less than 0.05 mg/l above an open-pit copper mine outfall and 0.14 mg/l below the outfall [221].

California, 1986: Ambient background level for water was 2 ug/l [222].

Information from ATSDR (see ATSDR for information on ebedded references) [954]:

> In general, zinc is more concentrated in the sediments of streams and rivers than in the water column [954]. It is reported by NAS (1977) that zinc will probably be detected in 75% of all water samples examined for zinc from various locations [954].
>
> The zinc background concentrations in surface waters are usually less than 50 ug/L (EPA 1980d), but concentrations in different surface waters and groundwater can range from 0.002 to 50 mg/L (NAS 1977) [954].
>
> In many locations (e.g., New England, the southeast, the Missouri River basin, the Rio Grande River basin, and the Upper Colorado River basin), higher-than-background concentrations of zinc are common and appear to be correlated with mining activities in these areas and/or geological areas rich in zinc (EPA 1980d) [954]. However, in all river basins there are some locations with zinc concentrations of 0.1-1.0 mg/L (EPA 1980d) [954].
>
> The concentrations of zinc in water samples from Whitewood Creek, South Dakota, were measured by Hale (1977) [954]. The samples were collected upstream from the discharge of a local mining company [954]. In 42 analyses, zinc concentrations ranged from less than 0.004 to 0.048 mg/L with a mean concentration of 0.018 mg/L [954]. The level of dissolved zinc in water from Lakes Erie and Ontario ranged from 3x10-6 to 1.1x10-4 mg/L (Coale and Flegal 1989) [954]. Concentrations of zinc in surface water often correlate with the introduction of urban and industrial runoff [954].
>
> The Nationwide Urban Runoff Program (NURP), initiated to evaluate the significance of priority pollutants in urban storm water runoff, reports a frequency of detection for zinc of 95% with a concentration range of 0.01-2.4 mg/L (Cole et al. 1984) [954].
>
> The concentrations of zinc in drinking water can be higher than concentrations in surface waters [954]. Concentrations of 0.002-1.2 mg/L were detected in 77% of 1,577 surface water samples; levels of 0.003-2.0 mg/L were found in 380 drinking water

samples (NAS 1977) [954]. The higher concentrations in drinking waters are due to water treatment and to the distribution systems used for the water [954]. Zinc in drinking water at levels as great as several mg/L was due to galvanized pipes and tanks in alkaline-water distribution systems [954]. For example, drinking water samples from galvanized pipe plumbing systems in Seattle, Washington, contained zinc concentrations of 0.128-1.279 mg/L; these levels were greater than 10 times higher than those in homes with copper pipe plumbing systems (Sharrett et al. 1982a) [954]. The results of analyzing 43 tap-water samples, collected in homes in Dallas, Texas, for trace metals reported maximum, minimum, median, and average concentrations of 0.049, 0.005, 0.011, and 0.0124 mg zinc/L, respectively (NAS 1977) [954]. The high zinc concentrations in these water samples were believed to be due to the household plumbing [954]. In a study investigating associations between inorganic constituents of drinking water and cardiovascular diseases, Greathouse and Osborne (1980) collected and analyzed tap water samples in 35 geographic areas in the United States [954]. From 100 to 110 tap-water samples were collected from each area [954]. The maximum, minimum, and mean concentrations were 1.447, 0.025, and 0.144 mg zinc/L, respectively [954]. Seventy-five percent of the zinc values were below 0.236 mg/L [954]. Other investigators have also attributed the higher concentrations of zinc in household tap waters, compared to the raw originating water, to distribution and transmission lines (Maessen et al. 1985: Ohanian 1986; Schock and Neff 1988) [954]. The available data suggest that zinc concentrations in drinking water are far less than the levels required to meet a daily intake level of 15 mg/day (assuming an adult water consumption of 2 L/day) (NAS 1977) [954].

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):

NOTE: Zinc is an example of a metal which has relatively little difference between acute and chronic concentrations for water toxicity:

IRIS information EPA 1996 [893]:

Ambient Water Quality Criteria for Aquatic Organisms [893]:

Acute Freshwater: 1.2E+2 ug/L 1-hour average [893].

Note from Roy Irwin: This was rounded to two significant digits; the actual calculated value being 117, based on the equation below. The 120 ug/L criteria 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 to the power of (0.8473[ln]hardness)]+0.8604) where "e" = exponential [550]. The one hour concentration of acid-soluble zinc is not to exceed this once every three years on average [550].
Further clarification:

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

Older References:

Freshwater Acute Criteria: 120 ug/L at 100 mg/L CaCO3 [449,689].

Chronic Freshwater: 1.1E+2 ug/L 4-hour avg. [893].

Note from Roy Irwin: This was rounded to two significant digits, the actual calculated value being 106, based on the equation an equation. The 110 ug/L 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:

> Chronic = e to the power of (0.8473[ln}hardness) + 0.7614) where "e" = exponential [550]. The four day average of acid-soluble zinc is not to exceed this concentration more than once every three years on average [550]. Further clarification:
>
> > e is the base for the natural logarithm and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Older References:

> Freshwater Chronic Criteria: 110 ug/L at 100 mg/L CaCO3 [449,689].

Marine Acute: 9.5E+1 ug/L 1-hour average [893].

Older References:

> Marine Acute Criteria: 95 ug/L [449,689].

Marine Chronic: 8.6E+1 ug/L 4-hour avg. [893].

Older References:

> Marine Chronic Criteria: 86 ug/L [449,689]/

Reference: 52 FR 6213 (03/02/87) [893].

Contact: Criteria and Standards Division / OWRS / (202)260-1315 [893].

Discussion: The freshwater criteria are hardness dependent. Values given here are calculated at a hardness of 100 mg/L CaCO3. A complete discussion can be found in the referenced Federal Register notice. [893].

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

Oak Ridge National Lab, 1994: Ecological Risk Assessment Freshwater Screening Benchmarks for concentrations of contaminants in water [649]. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following ug/L benchmarks for zinc, CAS 7440-66-6 [649]:

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 120

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(0.8473[ln]hardness)]+0.8604) where "e" = exponential [550]. The one hour concentration of acid-soluble zinc is not to exceed this once every three years on average [550]. Note: Same as IRIS 1996 EPA equation given above [893]. Further clarification:

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

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: 110

> 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:
>
> > Chronic = e(0.8473[ln}hardness) + 0.7614) where "e" = exponential [550]. The four day average of acid-soluble zinc is not to exceed this concentration more than once every three years on average [550]. Note: same as EPA 1996 IRIS equation given above [893]. Further clarification:
> >
> > > e is the base for the natural logarithm and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

SECONDARY ACUTE VALUE: No information found.

SECONDARY CHRONIC VALUE: No information found.

LOWEST CHRONIC VALUE - FISH: 36.41

LOWEST CHRONIC VALUE - DAPHNIDS: 46.73

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: >5243

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 30

LOWEST TEST EC20 - FISH: 47

LOWEST TEST EC20 - DAPHNIDS: No information found.

SENSITIVE SPECIES TEST EC20: 21

POPULATION EC20: 80

Other Concern Levels for Water Concentrations:

Florida's water quality standard applied to some wetland sites was 0.025 mg/l [220].

A State of California recommendation based on direct toxicity was that 8.6 ug/L be the water quality criteria since 37 ug/l was an adverse effects level [222].

Colorado specified a zinc water quality standard (5000 ug/L) for drinking water supplies in 1991 [659].

Colorado specified an agricultural water quality standard of 2000 ug/L in 1991 [659].

Colorado specified a hardness dependent equation as the acute general aquatic life water quality standard for zinc in 1991; at a hardness of 100 mg/L, the standard is 218 (rounded to 220) ug/L [659].

> NOTE: The above is a hardness-dependent criteria (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(0.809[ln(hardness)]+2.351) where "e" = exponential [659]. Further clarification:
> >
> > > e is the base for the natural logarithm and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Colorado specified a 1991 chronic standard for waters with hardness values less than or equal to 200 mg/L of 45 ug/L [659].

Colorado specified a separate hardness dependent equation as the chronic water quality standard 1991 for waters harder than 200 mg/L [659]. The equation for hardness values greater than 200 mg/L: chronic = e to the power of (1.924[ln(hardness)]-6.393) [659]. So at 250 mg/L hardness the standard would be 68.7 (rounded to 69) ug/L [659].

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 7440-66-6, ZINC, the benchmark is 0.4 mg/L (groundwater or porewater).

W.Invertebrates (Water Concentrations vs. Invertebrates):

LC50s for Acartia clausi and A. tonsa (both Calanoid copepod) were 0.950 and 0.290 mg/L (ppm), respectively, for 96-hr exposures [998].

LC50s for Amnicola sp. (Spire snail) were 20.2 and 14.0 mg/L for 96-hr exposures [998].

LC50s for Ceriodaphnia reticulata (water flea) ranged from 0.076 to 0.264 mg/L for 48-hr exposures. Lowest-observed-effect-concentrations (LOEC) for death ranged from 0.198 to 0.618 mg/L for 7-day exposures. No-observed-effect-concentrations (NOEC) for death ranged from 0.101 to 0.140 mg/L for a 7-day exposure [998].

LC50s for Chironomus sp. (midge) were 21.5 and 18.2 mg/L for 24- and 96-hr exposures, respectively [998].

LC50s for Crangon crangon (common shrimp) ranged from 100 to 330 mg/L for 48-hr exposures [998].

LC50s for Daphnia lumholzi, D. magna and D. pulex (all water fleas) were 2.29, 0.068 and 0.107 mg/L, respectively, for 48-hr exposures [998].

LC50s for Nereis diversicolor (polychaete) ranged from 6.0 to 42.0 mg/L for 96-hr exposures, with most values above 30.0 mg/L [998].

LC50s for Perna viridis (green mussel) were 3.1 and 7.0 mg/L for 24- and 48-hr exposures, respectively [998].

LC50s for Trichoptera (Caddisfly order) were 62.6 and 58.1 mg/L for 24- and 96-hr exposures, respectively [998].

W.Fish (Water Concentrations vs. Fish):

Summary of Effects on Fish of Elevated Concentrations of Zinc in Water, Quoted from Sorensen [488], with permission of CRC Press Inc.:

> From 0.87 to 40.90 ppm zinc is reported as the 96-h LC50 level for several species. Variability is caused by differences in salinity tolerance, water hardness, temperature, pH, the presence of other elements, species and additional factors. Moreover, use of various behavioral paradigms yields behavioral changes in the 5.6 ppb to 6.7 ppm zinc concentration range. Avoidance behavior is altered at 5.6 ppb zinc. Fish are unable to compensate for torque alterations at 60.00 ppb zinc. Movement patterns change at 2.94-3.64 ppb zinc, and feeding rate changes at 6.70 ppm [488].

Colorado specified a hardness dependent equation as the acute trout water quality standard 1991; at a hardness of 100 mg/L, the calculated standard is 108 (rounded to 110) ug/L (half of the above general acute value) [659].

Zinc has found to be more acutely toxic to fish at higher temperatures than at lower temperatures [98].

LC50s for Osteichthyes (bony fish class) were 1.97, 2.63, 27.38, 79.98, 154.38 and 175.0 mg/L (ppm) for 48-hr exposures, and 1.36, 1.86, 21.60, 51.77, 57.59 and 128.43 mg/L for 96-hr exposures [998].

LC50s for Pimephales promelas (fathead minnow) ranged from 0.238 to 2.66 mg/L for 96-hr exposures, with most values above 2.0 mg/L [998].

LC50s for Chrysophrys major (Red sea bream) were

3.70, 2.22, 0.92 and 0.444 mg/L (ppm) for 24-, 48-, 72- and 96-hr exposures, respectively [998].

LC50s for Cirrhinus mrigala (carp, hawk fish) were 1.826, 1.787, 1.673 and 1.633 mg/L (ppm) for 24-, 48-, 72- and 96-hr exposures, respectively [998].

LC50s for Cyprinus carpio (common, mirror, colored, carp) were 14.4, 9.2 and 7.8 mg/L (ppm) for 24-, 48- and 96-hr exposures, respectively [998].

LC50s for Morone saxatilis (striped bass) were 11.3, 10.0 and 6.8 mg/L (ppm) for 24-, 48- and 96-hr exposures, respectively [998].

LC50s for Oncorhynchus mykiss (rainbow trout, donaldson trout) ranged from 2.60 to 3.50 mg/L for 48-hr exposures [998].

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

LC50s for Rana catesbeiana (bullfrog) were 130, 110 and 70 mg/L (ppm) for 24-, 48- and 96-hr exposures, respectively [998].

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

CAS 007440-66-6, ZINC (AS ZINC OXIDE)

SPECIES	WATER CONCENTRATION (ppm)
Rat (test species)	0.0000
Short-tailed Shrew	2056.5020
Little Brown Bat	3554.4500
White-footed Mouse	1329.0510
Meadow Vole	2326.0750
Cottontail Rabbit	1102.1960
Mink	1142.9490
Red Fox	815.7030
Whitetail Deer	456.3980

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

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

EPA 1996 Water Health Based Limit: 10 mg/L, based on RfD of 0.3 mg/kg-day [952].

EPA 1996 IRIS Database Information [893]:

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

RfD: 3E-1 mg/kg-day Confidence: Medium

Secondary Maximum Contaminant Level (SMCL)

Value: 5,000 ug/L [893].

Same as older published value (USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93) [940].

Reference: 54 FR 22062 (05/22/89) [893].

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

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. [893].

Older Human Health Criteria [689]:

Published Criteria for Water and Organisms: 5,000 ug/L [689].

IRIS Recalculated (7/93) Criteria for Water and Organisms: 9,100 ug/L (5,000 is the organoleptic based value) [689].

IRIS Recalculated (7/93) Criteria for Organisms Only: 69,000 ug/L [689].

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].

Federal Drinking Water Guidelines:

EPA 2000 ug/l /Lifetime health advisory/ (USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines, 11/93) [940].

Older MCL: 10,000 ug/L [446].

Colorado had a zinc water quality standard (5000 ug/L) for drinking water supplies in 1991 [659].

Other State Drinking Water Standards [940]:

(AZ) ARIZONA 5000 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

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

(MN) MINNESOTA 1000 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk

Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

There has been zinc poisoning associated with prolonged consumption of water from galvanized pipes. Irritability, muscular stiffness & pain, loss of appetite & nausea were reported when water contained 40 Mg/l, which was above the Secondary drinking-water std of 5 mg/l (National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 301)[940]

EPA 1995 Region 9 Tap Water Preliminary Remediation Goal: 11000 ug/L [868]. Same value 11000 ug/L given as EPA Region III RBC value for tap water [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 indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

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

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

Camp host: 92909 ug/L
Child Camper: 85325 ug/L
Boater: 331818 ug/L
Swimmer: 143677 ug/L

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

Child resident (living on properties adjacent to BLM lands): 142 ug/L

Camp host: 1106 ug/L
Child Camper: 3047 ug/L
Worker: 2323 ug/L
Surveyor: 23227 ug/L

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

Elevated concentrations of zinc in water are particularly toxic to many species of algae, crustaceans, and salmonids [180]. Elevated water concentrations of zinc have especially strong impacts on macroinvertebrates such as molluscs, crustaceans, odonates, and ephemeropterans [72].

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

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

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

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

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

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

> 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):

Leland and Kuwabara, 1985: In non-polluted areas, baseline concentrations as low as <10 mg/kg have been recorded [177].

In the upper Columbia River in B.C., sediment concentrations were 45 to 52 mg/kg [954].

Sed.High (Sediment Concentrations Considered High):

Texas: The statewide 90th percentile value was 120 mg/kg dry weight [7].

Sediment concentrations in Texas: The following text is quoted from the Trinity River Report [201] for reference comparison with values from other areas:

> Gradient Monitoring Levels: Sediment concentrations of zinc from our sites 9 through 12 exceeded the statewide 90th percentile level in 100% of the historical records from 1974 to 1985 [7]. These highly elevated levels were still present at our

site 12 as late as October of 1985, after the collections for this report were made [91].

Great Lakes Harbors, EPA 1977: Sediments having concentrations higher than 200 mg/kg dry weight were classified as "heavily polluted" [145,347]. If the zinc concentration is between 90 and 200 mg/kg dry weight, the sediment is considered to be moderately polluted [347].

Illinois EPA, 1984: Sediments having concentrations higher than 100.0 mg/kg dry weight were classified as "elevated" [145].

Leland and Kuwabara, 1985: In polluted areas, concentrations as high as 10,000 mg/kg have been recorded [177].

Highway Runoff, 1989: Detention pond sediments receiving runoff from highways averaged 250 mg/kg dry weight of zinc. The cypress wetlands the detention pond effluent was routed to, by contrast, had a median value of 14 mg/kg zinc, indicating most was removed by the detention pond [220].

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of zinc is 1,409.2 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The mean for zinc was 1,200 ppm (dry weight), the range was 170-13,000 ppm (dry weight) [347].

Playa Lake Study Sediment Concentrations of Zinc: Dry weight concentrations of zinc in four cattle feedlot-impacted playa lakes (in the Texas Panhandle) the author has studied ranged from 75.3-226 mg/kg (Roy Irwin, Personal Communication, 1992). By contrast, four ephemeral row-crop agriculture playas had zinc concentrations of 47.3 to 69.8 mg/kg. A Mann-Whitney statistical test showed zinc concentrations from the four row-crop agriculture samples to be significantly lower than the concentrations in the four samples known to be impacted by feedlot wastes (significant at 0.0304).

Zinc concentrations in three sediment samples from the upstream Tierra Blanca Creek site and three sediment samples from the playa lake off-stream site were at or below 29 mg/kg dry weight (Roy Irwin, Personal Communication, 1992). By contrast, three samples from a Tierra Blanca Creek site suspected of being polluted by a large feedlot had higher zinc concentrations (from 128-139 mg/kg dry weight) and the waste water pond in the feedlot had highly elevated zinc concentrations (491-538 mg/kg). Zinc occurs in many feed additives, one potential source in cattle feedlot impacted areas. A Mann-Whitney statistical test showed zinc concentrations from the six upstream samples to be significantly lower than the concentrations in the six samples known or suspected of being influenced by feedlot wastes (significance level 0.005).

NOAA National Status and Trends Program (1984-1990) [698]: High concentration for zinc in fine-grained sediment (n=233) = 270 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 zinc than course-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more zinc than sediments which are similar except for being lower in TOC, which is why NOAA and many others are now normalizing sediment values for grain size, and reporting TOC.

Sed.Typical (Sediment Concentrations Considered Typical):

Great Lakes Harbors, EPA 1977: Sediments having sediment concentrations lower than 90.0 mg/kg were classified as "non polluted" [145,347].

International Joint Commission, 1988: The International Joint Commission considered <120 mg/kg as a background sediment level [145]. The control site in one Great Lakes study had a sediment concentration of 45 mg/kg [145].

Averages and ranges of concentrations of elements in soils and other surficial materials in the United States (1971): The mean concentration of zinc was 54 ppm, the range was <25-2,000 ppm [347].

NOAA National Status and Trends Program (1984-1990) [698]: Geometric mean for zinc in fine-grained sediment (n=233) = 140 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 zinc than course-grained sediment, and

sediments higher in total organic carbon (TOC) would typically have more zinc 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 410 ppm dry weight Effects Range-Median (ERM) concentration and was lowest in sediments where its concentration was less than the 150 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	6.1
ERL-ERM	47.0
>ERM	69.8

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 7440-66-6 ZINC:

EFFECTS RANGE - LOW (NOAA): 150 mg/kg dry wt.
EFFECTS RANGE - MEDIAN (NOAA): 410 mg/kg dry wt.

St. Lawrence River Interim Freshwater Sediment Criteria, 1992. No effect: 100 mg/kg dry weight. Minimal effect level: 150 mg/kg dry weight. Toxic effect level: 540 mg/kg dry weight [761].

Environment Canada Interim Sediment Quality Assessment Values, 1994. Threshold effect level: 123.1 mg/kg dry weight. Probable effect level: 314.8 mg/kg dry weight [761].

Ontario Ministry of the Environment Freshwater Sediment Guidelines, 1993. Lowest effect level: 120 mg/kg dry weight. Severe effect level: 820 mg/kg dry weight [761]. Older references:

> Ontario, 1978, 1986: The concentration proposed by the Ontario Ministry of the Environment as a threshold for evaluations of dredging projects was 100 mg/kg dry weight [145]. Ontario Ministry of the Environment guidelines for open lake disposal of sediments (1986): Zinc should not exceed 100 ppm dry weight [347].

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

International Joint Commission, 1988: The IJC suggested sediment concentrations not exceed background levels of 120 mg/kg dry weight [145].

Guidelines for the pollutional classification of Great Lakes harbor sediments (1977): If the zinc concentration is less than 90 ppm the sediment is considered to be nonpolluted. If the zinc concentration is between 90 and 200 the sediment is considered to be moderately polluted. If the zinc concentration is above 200 the sediment is considered to be heavily polluted [347,951].

EPA Region 6, 1973: The concentration proposed by EPA Region 6 as a guideline for determining acceptability of dredged sediment disposal was 75 mg/kg dry weight [143].

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

When sufficient acid volatile sulfide (AVS) was available to bind with the zinc, no toxicity was observed even at dry-weight metal concentrations in excess of 100 mg/kg. When there was more zinc present than AVS, survival, growth, and fecundity were affected. This is the first demonstration of the utility of the AVS:metal partitioning model using a chronic freshwater sediment test [756]. The Environmental Protection Agency (ORD-Duluth) developed this fresh-water chronic life-cycle test using Chironomus tentans; the 56-day test was used to evaluate the validity of AVS (acid volatile sulfide) partitioning to predict the toxicity of zinc-spiked sediment.

For additional discussion of AVS issues: see Sed.Misc. section below.

Sed.Fish (Sediment Concentrations vs. Fish):

See Sed.Misc section below.

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

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

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

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

Deer/Mouse: 10 mg/kg
Rabbit: 64 mg/kg
Bighorn Sheep: 63 mg/kg
Whitetailed Deer: 32 mg/kg
Mule Deer: 39 mg/kg
Elk: 32 mg/kg

Mallard: 117 mg/kg
Canada Goose: 125 mg/kg
Trumpeter Swan: 134 mg/kg

Sed.Human (Sediment Concentrations vs. Human):

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

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

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

Camp host: 46455 mg/kg
Child Camper: 21331 mg/kg
Boater: 165909 mg/kg
Swimmer: 71839 mg/kg

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

Fish, especially those living or foraging in sediments contaminated by zinc, may accumulate zinc directly from the sediments [95].

A 1996 paper suggested that Simultaneously Extracted Metals (SEM) to AVS ratios (SEM:AVS), and the spatial and temporal variability of AVS, should be considered in sediment toxicology and may be important in bioavailability dynamics [981]. The AVS normalization hypothesis, which predicts greater bioavailability of metals (such as copper and zinc) at SEM:AVS ratios of greater than 1.0 seems generally useful in some cases but has several important limitations [981].

In early 1995, proposals were circulating in EPA suggesting that lower bound metals sediment criteria be developed along the following line: if sufficient AVS is present [that is, the total simultaneously extracted metal (SEM) is equal or less than the concentration of AVS, then no effects are expected [700]. If SEM exceeds AVS, then other binding phases become important; the next most important phase is organic carbon (TOC) [700]. EPA now suggests that AVS be conducted in combination with interstitial water, particularly if effects are seen when AVS criteria are not exceeded [700].

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

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

Other Information on acid volatile sulfides, summarized from Suter 1993 [577]

> DiToro et al. have proposed a model that used acid volatile sulfide (AVS) concentrations to normalize sediment concentrations of metals to pore water concentrations. It is believed to be applicable to metals whose sulfides are less soluble than FeS. Where only one metal competes for the AVS, the molar equivalent of the AVS would not be bioavailable, so the concentration in sediment (C(st), umol/g) that is equitoxic to a concentration in water (C(wt), umol/L) is: C(st) = AVS + K(p) C(wt) [577]. This model is not applicable to fully oxidized sediments and to sediments with extremely low AVS (< 1 umol/g). This model is fairly difficult to use because there is no ready means to estimate K(p), because of the need to account for competition among metals for AVS, because AVS is not routinely measured like f(oc), and because AVS can be seasonably variable

[577].

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):

Zinc in German Gulch (Upper Clark Fork Superfund Site Area, Montana) samples ranged from 78.4 to 196.3 ppm and averaged 135.9 ppm. Baseline mean zinc concentrations in U.S. soils average 50 ppm (range 17-125 ppm) [699].

About 50 times higher zinc concentration (5000 mg/kg) /was found/ in soil close to smelter compared with control area (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 667)[940].

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Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of zinc is 1,409.2 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The mean for zinc was 1,200 ppm (dry weight), the range was 170-13,000 ppm (dry weight) [347].

Soil.Typical (Soil Concentrations Considered Typical):

Western U.S. Soil Median Concentrations [715]: 65 mg/kg

The national average concentration for zinc in U.S. soils is 300 mg/kg [98].

Concentration in soils: 50 ppm [951].

Concentration in soils is 50 ppm [951]. Where the concentration of zinc in rocks was 80 ppm, the concentration in plants was 70 ppm, a much higher ratio than for many other metals [951].

Zinc, the 25th most abundant element, is widely distributed in nature, making up between 0.0005% and 0.02% of the Earth's crust [253].

Mean zinc content in surface soils ranges from 17 to 125 ppm (Kabata-Pendias and Pendias, 1992). The mean calculated for worldwide soils is 64 ppm. Kiekens (1990) cites an average content of 50 ppm. Highest naturally occurring mean values are found in alluvial soils; the lowest occurring mean values are in light mineral and organic soils [699].

Averages and ranges of concentrations of elements in soils and other surficial materials in the United States (1971): The mean concentration of zinc was 54 ppm, the range was <25-2,000 ppm [347].

The average concentration in the earth's crust is estimated to be 40 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 666)[366].

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):

The 1987 soil (clean up) criteria given by the New Jersey Department of Environmental Protection for zinc is 350 mg/kg dry weight [347,386].

The Dutch soil (clean up) criteria for zinc is 3,000 mg/kg dry weight; 500 mg/kg would be considered a moderate level that required additional study, and 200 mg/kg would be considered a background level [347,386].

Other maximum allowable concentration (MAC) levels (ppm dry weight): 300 (Stuttgart), 130 (London-Value given for the soluble pool of the element), 280 (London-Value given for the soluble pool of the element) [719].

Proposal of European Economic Commission for MAC in soils treated with sewage sludge: 150 (300) ppm dry weight (London). The value in parentheses is for mandatory concentrations [719].

Proposal of Ontario Ministry of Agriculture and Food for MAC in soils treated with sewage sludge: 220 ppm dry weight (published in Tokyo; work done for Ontario) [719].

In 1981 the U.S. Environmental Protection Agency proposed 2500 ppm as an upper limit for zinc for sewage sludges suitable for land application [391].

Soil cleanup criteria for decommissioning sites in Ontario (1987): For agricultural land zinc should not exceed 220 ppm, for residential/parkland zinc should not exceed 800 ppm, and for commercial/industrial land zinc should not exceed 800 ppm [347].

Suggested cleanup guidelines for inorganic contaminants in acidic soils in Alberta (1987): For sheep diets the acceptable level for zinc is 100 ppm, and for others the acceptable level for zinc is 700 ppm [347].

Quebec soil contamination indicators for zinc (1987): 200 ppm of zinc refers to background concentrations of zinc, 500 ppm refers to moderate soil contamination, and 1,500 ppm refers to threshold values that require immediate cleanup [347].

The maximum allowable concentration of zinc in the soil in the Soviet Union (1984): 23 ppm [347].

Maximum cumulative addition of metals from sewage sludge to Maryland agricultural soil (1986): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100 g zinc should not be added at greater than 280 kg/ha. For a soil with a CEC of greater to, or equal to, 5 zinc should not be added at greater than 560 kg/ha (these values are the same for addition to Massachusetts soil) [347].

Maximum cumulative addition of metals from sewage sludge that may be added to Minnesota soils used for growing crops (1987): For a soil with a cation exchange capacity (CEC) of less than 5 zinc should not be added at greater than 280 kg/ha. For a soil with a CEC between 5 and 15 zinc should not be added at greater than 560 kg/ha. For a soil with a CEC greater than 15 zinc should not be added at greater than 1,120 kg/ha (these values are the same for addition of zinc to privately owned Missouri farmland) [347].

Cumulative amounts of zinc per hectare that may be added to New York State soils with sewage sludge (1988): For productive agricultural soils zinc should not be added at greater than 168 kg/ha, for less productive agricultural soils zinc should not be added at greater than 250 kg/ha, and for forests zinc should not be added at greater than 560 kg/ha [347].

Maximum heavy metal loading recommended for sludge applications to privately owned Oregon farmland (1984): For a soil with a cation exchange capacity (CEC) of less than 5 zinc should not be added at greater than 250 kg/ha. For a soil with a CEC between 5 and 15 zinc should not be added at greater than 500 kg/ha, for a soil with a CEC of greater than 15 zinc should not be added at greater than 1,000 kg/ha [347].

Maximum cumulative additions of metals from sewage sludge that may be added to Vermont soils, by soil texture (1984): For loamy sand zinc should not be added at greater than 280 kg/ha, for fine sandy loam zinc should not be added at greater than 560 kg/ha, for a clay loam zinc should not be added at greater than 1,120 kg/ha [347].

Maximum cumulative applications of zinc from sewage sludge that may be added to Wisconsin soils (1985): For a soil with a cation exchange capacity (CEC) of less than 5 zinc should not be added at greater than 250 kg/ha. For a soil with a CEC between 5 and 10 zinc should not be added at greater than 500 kg/ha. For a soil with a CEC between 11 and 15 zinc should not be added at greater than 750 kg/ha. For a soil with a CEC above 15 zinc should not be added at greater than 1,000 kg/ha [347].

Soil limit values determined by the Council of European Communities for the addition of heavy metals from sewage sludge to soil with a pH of 6.0-7.0 (1986): The limit value for zinc is 150-300 ppm [347].

Soil.Plants (Soil Concentrations vs. Plants):

Levels of zinc (ppm dry weight) considered phytotoxic: 300 (Vienna), 300 (Warsaw), 250 (Tokyo), 300 (Warsaw), 70 (Missouri), 400 (Ontario) [719]

Minimum soil concentration causing phytotoxicity: 70-400 [699].

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

For CAS 007440-66-6, ZINC, the benchmark is 50 mg/kg in soil (WILL and SUTER, 1994).

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

See Soil.Misc section below.

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

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

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

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

Deer/Mouse: 10 mg/kg
Rabbit: 64 mg/kg
Bighorn Sheep: 63 mg/kg
Whitetailed Deer: 32 mg/kg
Mule Deer: 39 mg/kg
Elk: 32 mg/kg
Mallard: 117 mg/kg
Canada Goose: 125 mg/kg
Trumpeter Swan: 134 mg/kg

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 = 23,000 mg/kg for ingestion pathway [952].

SSL = None given for inhalation pathway [952].

SSL = 620 to 12,000 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: 23000 mg/kg wet wt.
Industrial Soil: 100000 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:

4.2E+02 mg/Kg dry weight [903].

Acceptable level of zinc for production of healthy food: 110 ppm dry weight (Moscow) [719]

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

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

>100 times the criteria: extremely high risk

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

Child resident (living on properties adjacent to BLM lands): 597 mg/kg
Camp host: 15485 mg/kg
Child Camper: 10666 mg/kg
ATV Driver: 217756 mg/kg
Worker: 23227 mg/kg
Surveyor: 232273 mg/kg

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

Earthworms concentrate this metallic element relative to soil concentrations, which is one potential hazard of birds feeding on sewage sludge amended soils [179]. Although earthworms regulate the concentrations of zinc in their tissues, earthworms nevertheless concentrate this metallic element relative to soil concentrations, typically more so than any other element other than cadmium [179,347].

There is not much concentration from rock to plants, the ratio of concentrations being 0.90 [951].

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:

Where the concentration of zinc in rocks was 80 ppm, the concentration in plants was 70 ppm, a much higher ratio than for many other metals [951].

Zinc concentrations in plant tissue across the (highly polluted) Smelter Hill (Upper Clark Fork Superfund Site Area, Montana) site averaged 208 ppm. Most agricultural crops exhibit toxicity when zinc tissue levels reach 200-300 ppm (MacNichol and Beckett, 1985), but the range for reported toxicity is much greater. Toxicity has been reported for tissue levels as low as 60 ppm [699].

The normal levels of zinc range from 10-100 mg/kg in most crops and pastures (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 666) [940].

See also Tis.Human, A) section below.

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:

Zinc 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 zinc in oysters (n=107), the Geometric Mean was 2400 ug/g dry and the "high" concentration was 5200 ug/g dry weight [697]. For zinc in mussels (n=107), the Geometric Mean was 130 ug/g dry and the "high" concentration was 190 ug/g dry weight [697]. NOAA "high" concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].

Tis.Fish:

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

EPA 1995 Region 3 Risk based concentration (RBC) to protect health of human consumers: 410 mg/kg zinc in fish tissue [903].

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 indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

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

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

Child resident (living on properties adjacent to BLM lands): 23505 ug/kg
Camp host: 48390 ug/kg
Child Camper: 133320 ug/kg

Legal Limits for Concentrations in Fish and Fishery Products: The lowest legal limit was 30-50 mg/kg (Poland) [216,418]. Seven countries have limits less than or equal to 100 mg/kg, but the U.S. apparently has no limit [216,418].

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:

Zinc whole-body levels above 40.1 mg/kg are higher than 85% of all fish in a national survey [23]. A more recent (1976-1984) NCBP survey report gave the national geometric mean level for zinc in whole-body fish as 21.7 mg/kg, the maximum level as 118.4 mg/kg, and the 85th percentile level as 34.2 mg/kg wet weight [384].

Zinc concentrations in mosquitofish samples from 24 Trinity River sites ranged from 7.2 to 44.7 mg/kg, with 20 of 28 samples exceeding 28 mg/kg. For comparison, we found concentrations of 27 to 34 mg/kg zinc in mosquitofish from the rural Rio Grande River at Big Bend National Park [65].

Residues of Zinc in Fish/Seafood (Concentrations): Fish: 32.0 ppm (avg concentration in prepared food composites) (Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23, 83, 333) [940].

Zinc Residues in Freshwater Fish Tissues Versus Residues in the Environment, Use of Tissues for Gradient Monitoring of Zinc Contamination:

> Zinc an example of a contaminant which is not consistently higher in freshwater fish tissues in polluted areas than at reference/control sites [201]. In other words, biological tissue concentrations are not always particularly reliable indicators for measuring gradients of zinc in the environment. Although excess zinc in water can cause direct toxicity to aquatic organisms, zinc in low concentrations is an essential dietary element for animal (and plant) life [253]. Freshwater fish can regulate zinc over a wide range of ambient concentrations [180].
>
> Although zinc at low levels is an essential to many animals and humans, zinc is toxic to fish at levels exceeding the minimum amount needed [57]. Water is not a significant dietary source of zinc [190], but fish, especially those living or foraging in sediments contaminated by zinc, may accumulate it directly from the sediments [95].
>
> Absorption of dietary zinc in higher animals is apparently regulated in part by metal thioneins, low molecular weight proteins containing high levels of cysteine [180]. Also, the bioavailability of zinc is related to sediment type [95]. A nationwide study of zinc in bivalves showed less variation in zinc concentrations from various locations than from various species [62].
>
> Zinc tends to be present in significant amounts (up to 25 mg/kg wet weight normally) in fish and animal meat products [366]. However, zinc does not tend to bioaccumulate in fish as much as some other contaminants.

In a study of contaminants in the Trinity River, zinc was one of the 3 of 67 contaminants which was not consistently higher in fish, turtles, and other aquatic organisms in highly polluted areas downstream of Dallas than at the reference/control site upstream of Fort Worth [201].

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

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

No information found.

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

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

CAS 7440-66-6 ZINC (AS ZINC OXIDE)

SPECIES	NOAEL (mg/kg/day)	FOOD CONCENTRATION (ppm)
Rat (test species)	160.0000	0.0000
Short-tailed Shrew	452.4300	754.0510
Little Brown Bat	568.7120	1706.1360
White-footed Mouse	398.7150	2579.9220
Meadow Vole	317.1920	2791.2900
Cottontail Rabbit	106.5460	539.4710
Mink	113.1520	825.9270
Red Fox	68.8820	688.8160
Whitetail Deer	29.8880	970.5010

Comment: Actually, the number of significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be rounded; otherwise the impression is given of a level of accuracy that is

> simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

A presumptive diagnosis of zinc toxicosis was made in one Bahama pintail (Anas bahamensis bahamensis) and two redhead ducks (Aythya americana) that had ingested metal fence clips, which contained 96% zinc [959].

Poisoning has been observed in ferrets & mink from chewing corroded cages or in cattle & horses, as well as from food stuffs containing particles of metal, & in pigs & hens from use of zinc plated funnels. It is evident that young animals are much more susceptible to poisoning by zinc than mature animals [366].

Abnormal fur and immunosuppression occurred among the offspring of pregnant mink fed a diet containing about 50 times the usual amount of zinc [370].

Birge and Roberts (1976) examined the effects of arsenic and other metals (selenium, cadmium, lead, mercury, methyl mercury, and zinc) on the chick embryo. Defects included brain deficiencies, absent eyes, skeletal anomalies, unabd yolk sacs, and severe motor impairment, which was the most common affliction. The author remarked that the types of defects did not vary substantially for the different metals [445].

Growth arrest occurred among rats fed with food containing slightly less than 12 mg/kg of zinc. Typical signs of severe deficiency incl dermatitis, emaciation, testicular atrophy, retarded growth & anorexia (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 668) [366].

The frequency of congenital anomalies was no greater than expected among the offspring of pregnant rats fed a diet containing 2.5 - 31 times the usual amount of zinc [370].

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

An American merganser from which a penny was removed endoscopically from the gizzard had an elevated serum zinc concentration of 16.6 ug/ml [959].

Zinc tends to be present in significant amounts (up to 25 mg/kg wet weight normally) in fish and animal meat products [366].

Assays for zinc and other minerals were performed on birds that had ingested pennies: four Barrow's goldeneyes (Bucephala islandica) that died and one American merganser (Mergus merganser americanus) survivor [959]. Two of four goldeneyes, from which serum was available, had elevated zinc concentrations of 12.6 and 13.1 ug/ml (normal range, 1.84-4.65 ug/ml, n=8); all four goldeneyes had liver zinc concentrations ranging from 242 to 548 ug/g (normal 35.9 ug/g, wet weight basis, n=1) [959].

Residues of Zinc in Animals (Concentrations) [940]:

> Average normal levels of zinc in cattle are: liver, 135 ppm; kidneys, 80 ppm; feces, 200 ppm, (all dry matter) and serum 0.14 Ppm. In animals suffering from zinc poisoning corresponding values are: liver, 2000 ppm; kidneys, 670 ppm; feces, 3740 ppm; and serum, 0.515 Ppm. /ZINC ION/ [Clarke, M. L., D. G. Harvey and D. J. Humphreys. Veterinary Toxicology. 2nd ed. London: Bailliere Tindall, 1981. 77].

Residues of Zinc, Results of Food Survey [940]:

> Dairy products: 4.9 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].
>
> Meat & poultry: 32.0 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].
>
> Meat, fish, and poultry on an average contained 24.5 mg/kg of zinc.

Tissue Concentrations in Texas: The following text is quoted from the Trinity River Report [201] for reference comparison with values from other areas:

> The highest zinc concentrations were from

composite samples of unionid clam flesh from site 14 (87.5 mg/kg) and from turtle shells from sites 11, 15, and 18 (71.6 to 78.8 mg/kg). In a previous study by the Texas Water Quality Board, zinc levels in sediments from Beltline Road (6.5 miles downstream of our site 11) were the highest recorded in the State at that time [74]. Zinc was one of the few contaminants which was not consistently higher in fish and wildlife tissues downstream of Dallas than at our reference/control site (site 1) upstream of Fort Worth. It is possible that the fish and wildlife samples we collected were not particularly good indicators for measuring gradients of zinc. Zinc's role as a dietary requirement may be a factor. Some aquatic organisms can apparently regulate the uptake of zinc, and the bioavailability of zinc is related to sediment type [95]. A nationwide study of zinc in bivalves showed less variation in zinc concentrations from various locations than from various species [62].

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

Food Survey Results [940]:

Dairy products: 4.9 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Meat & poultry: 32.0 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Grain & cereal products: 9.0 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Potatoes: 5.2 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and

Sons, 1978-1984.,p. 23(83) 333].

Leafy vegetables: 2.7 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Legume vegetables: 7.6 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Root vegetables: 2.3 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Garden fruits: 2.1 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Fruits: 2.4 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Oils, fats, shortening: 4.1 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Sugar & adjuncts: 3.0 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Beverages: 0.5 ppm (avg concentration in prepared food composites) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 333].

Meat, fish, and poultry on an average contained 24.5 mg/kg of zinc, whereas grains (and cereal products) and potatoes only provided 8 and 6 mg/kg, respectively. /Total zinc/ [Mahaffey et al; Environ Health Perspec 12: 63, 1975, as cited in USEPA; Ambient Water Quality Criteria Doc: Zinc p.C-3 (1980) EPA 400/5-80-079].

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):

EPA 1995 Region 3 Risk based concentration (RBC) to protect health of human consumers: 410 mg/kg zinc in fish tissue [903].

EPA 1996 IRIS Database Information [893]:

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

RfD: 3E-1 mg/kg-day Confidence: Medium

The average daily intake of zinc in different areas was summarized and arrived at a value in the order of 5-22 mg/day (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 666) [940].

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 indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

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

Child resident (living on properties adjacent to BLM lands): 23505 ug/kg
Camp host: 48390 ug/kg

Child Camper: 133320 ug/kg

A 16 yr old boy suffered ill effects after swallowing 12 g metallic zinc: high values for serum amylase & lipase levels indicated pancreatic derangement, & lightheadedness & a staggering gait suggested mild derangement in cerebellar function; the boy recovered fully after chelation therapy (Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 74) [366].

Individuals were made acutely ill with dizziness, nausea, tightness in throat & in some cases diarrhea, from eating apples, stewed in galvanized iron vessels, which contained 7 g of zinc to 1 LB (Browning, E. Toxicity of Industrial Metals. New York: Appleton-Century-Crofts, 1969. 352) [366].

Chronic anemia unresponsive to iron in 3 children was attributed to zinc poisoning. The urine contained 1.8-3.65 mg of zinc/l. Each of the children chewed metal toys made of zinc containing alloy. When the toys were withdrawn the anemia responded to continued treatment with iron (Reynolds, J.E.F., Prasad, A.B. (eds.) Martindale-The Extra Pharmacopoeia. 28th ed. London: The Pharmaceutical Press, 1982. 943) [366].

A 32 year old woman developed severe nausea, vomiting and fever on 6 occasions after home dialysis using water which had been stored in a galvanized tank. The plasma zinc concentration 36 hr after the sixth home dialysis was 7 mg/l and fell slowly after six week hospital dialysis to 1.58 mg/l. The red cell zinc concentration were respectively 35 and 12.3 mg/l (normal 10-14 mg/l). No further episodes occurred when the home water was deionized before use (Reynolds, J.E.F., Prasad, A.B. (eds.) Martindale-The Extra Pharmacopoeia. 28th ed. London: The Pharmaceutical Press, 1982. 943) [366].

Oral ingestion of 12 g of elemental zinc (800 times the RDA) resulted only in pronounced lethargy. Doses required to treat zinc deficiency (ie, elemental zinc 1 mg/kg/day) cause essentially no adverse reactions. However, ingestion of excessive doses for prolonged periods is not recommended. High concentration alter the immune response. Excessive intake also may induce copper and iron deficiency and may cause nausea, vomiting, headache, chills, fever, malaise, and abdominal pain (American Medical Association, Department of

Drugs. Drug Evaluations. 6th ed. Chicago, Ill: American Medical Association, 1986. 859) [366].

Toxicity of zinc cmpd by mouth is low. It was concluded from review of literature on metal fume fever & injury from powders & dusts of zinc/ that severe exposure to zinc might give rise to gastritis, with vomiting, due to swallowing of dusts of zinc compounds (American Conference of Governmental Industrial Hygienists. Documentation of the Threshold Limit Values and Biological Exposure Indices. 5th ed. Cincinnati, OH:American Conference of Governmental Industrial Hygienists, 1986. 645) [366].

Acid food prepd or stored in galvanized zinc cans or utensils may dissolve sufficient zinc metal, which is converted to zinc salts & subsequently ingested with food & liquids in sufficient amout to cause severe vomiting with or without nausea (Arena, J.M. and Drew, R.H. (eds.) Poisoning-Toxicology, Symptoms, Treatments. 5th ed. Springfield, IL: Charles C. Thomas Publisher, 1986. 349) [366].

It was concluded that abnormal amount of zinc may enter & leave the body for years without causing symptoms or evidence which can be detected clinically or by laboratory examinations of gastrointestinal, kidney, or other damage (Hamilton, A., and H. L. Hardy. Industrial Toxicology. 3rd ed. Acton, Mass.: Publishing Sciences Group, Inc., 1974. 187) [366]

Taken by mouth are relatively non-toxic, though the soluble salts in large doses may cause vomiting & diarrhea (Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 351) [366].

In a cross-sectional study of 20 gun-metal foundry workers (mean age 47yr) the subclinical neurophysiological effects of exposure to lead, zinc, copper, and tin were evaluated by "short-latency" somatosensory evoked potential. Controls were age and height-matched males without occupational exposure to lead. Range of employment was 1-16 yr (mean 10 yr). In exposed workers mean blood lead was 42 ug/dl, mean zinc plasma 95 ug/dl, mean copper plasma 105 ug/dl, and mean urinary tin 28 ug/l. In workers, the interpeak latency in the cervico-spino-bulbar region was significantly prolonged ($p<0.05$), and the motor conduction velocity and sensory conduction velocity in the forearm were significantly slowed ($0.01<p<0.05$) when compared with controls. The yield of urinary lead following challenge with Ca-EDTA was positively related to latency in the cervico-spino-bulbar region and inversely related to hematocrit ($p<0.05$). The interpeak latency in the upper central nervous system was inversely related to zinc concentration in erythrocytes. Latency up to the Erbs point was inversely related to urinary zinc. Motor conduction velocity in the in the palm was positively related to erythrocyte zinc concentration (Araki S et al; Am J Ind Med 10:163-75, 1986) [366]

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

See also Absorption, Distribution and Excretion information in Fate.Detail section below.

Human milk contains about 3 mg/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 666) [940].

Human therapeutic or normal blood level: 0.068-0.136 mg%, 0.68-1.36 ug/ml (Winek, C.L. Drug and Chemical Blood-Level Data 1985. Pittsburgh, PA: Allied Fischer Scientific, 1985.) [940].

The highest human concentration of zinc appears in the choroid of the eye, spermatozoa, hair, nails. In plasma, most zinc is protein bound, predominantly to albumin alpha 2-macroglobulin, and transferrin (American Medical Association, Department of Drugs. Drug Evaluations. 6th ed. Chicago, Ill: American Medical Association, 1986. 859) [940].

Zinc concentrations in tissues of 10 human males (mean age 43 yr) who suffered sudden death. Zinc was detected in all 10 tissues (brain, heart, kidney cortex, liver, lung, muscle, pancreas, small intestine, spleen, and stomach). Highest levels were in the liver, muscle, and kidney. Results were presented graphically and no values were given. In human liver there was a positive relationship between the concentration of zinc and the amount of metallothionein in the tissue (Heilmaier HE et al; Toxicol Lett 38 (3) 205-11, 1987) [940].

Tis.Misc. (Other Tissue Information):

A study in an Arkansas river system showed that macroinvertebrate concentrations were negatively correlated with zinc concentrations but not with concentrations of iron or copper [72].

Several plants are considered zinc indicators, part of a zinc flora [951]. Bryophytes and lichens tend to have an especially high ability to absorb trace elements from their substrates and to tolerate adverse ecological conditions [951]. There is not much concentration from rock to plants, the ratio of concentrations being 0.90 [951]. The toxicity of zinc to plants is typically moderate [951].

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

For a discussion of SEM and AVS normalization of sediments vs bioconcentration, see Besser et al [981] as summarized in the Sed.Misc. section above.

Earthworms concentrate this metallic element relative to soil concentrations, which is one potential hazard of birds feeding on sewage sludge amended soils [179]. Although earthworms regulate the concentrations of zinc in their tissues, earthworms nevertheless concentrate this metallic element relative to soil concentrations, typically more so than any other element other than cadmium [179,347]. However, zinc is more notorious as a direct aqueous poison to aquatic life than it is as an oral (food chain) poison to wildlife or fish consuming earthworms. High zinc levels in soil substantially reduce the concentration of cadmium in earthworms [179]. The concentration factors for zinc contaminated soils versus earthworms vary with soil concentrations [347].

Fish, especially those living or foraging in sediments contaminated by zinc, may accumulate zinc directly from the sediments [95].

There is not much concentration from rock to plants, the ratio of concentrations being 0.90 [951].

Zinc tends to be present in significant amounts (up to 25 mg/kg wet weight normally) in fish and animal meat products [366]. However, zinc does not tend to bioaccumulate in fish as much as some other contaminants. In our recent study of contaminants in the Trinity River zinc was one of the 3 of 67 contaminants which was not consistently higher in fish and wildlife tissues downstream of Dallas than at our reference/control site (site 1) upstream of Fort Worth [201].

Where the concentration of zinc in rocks was 80 ppm, the concentration in plants was 70 ppm, a much higher ratio than for many other metals [951].

Bioconcentration [940]:

The bioconcentration factor in edible portions of Crassostrea Virginia (adult oyster) is 16,700. /Total zinc/ [Shuster CN, Pringlo BH; Proc Nat Shellfish Assoc 59: 91 (1969) as cited in USEPA; Ambient Water Quality Criteria Doc: Zinc p.C-5 (1980) EPA 400/5-80-079].

The bioconcentration factor in edible portions of Mya arenaria (soft-shell clam) is 85. /Total zinc/ [Pringle BH et al; J Sanitary Engineer Div 94 (SA3): 455 (1968) as cited in USEPA; Ambient Water Quality Criteria Doc: Zinc p.C-5 (1980) EPA 400/5-80-079].

Bioconcentration factors in edible portions of Mytilus edulis (mussel) is 500. /Total zinc/ [Pentreath RJ; J Exp Mar Biol Ecol 12: 1 (1973)].

Biological Half-Life [940]:

In normal humans, for example, those without excessive intake of zinc, the body burden half-time of absorbed radio zinc has been observed to range from 162-500 days. After parenteral administration of zinc, half-times ranging from about 100-500 days have been reported. [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 670].

Interactions:

When sufficient acid volatile sulfide (AVS) was available to bind with the zinc, no toxicity was observed even at dry-weight metal concentrations in excess of 100 mg/kg. When there was more zinc present than AVS, survival, growth, and fecundity were affected. This is the first demonstration of the utility of the AVS:metal partitioning model using a chronic freshwater sediment test [756]. For additional discussion of SEM and AVS normalization of sediments vs bioconcentration, see Besser et al. [981] and other discussions in the Sed.Misc. section above.

In attempts to reproduce in animals zinc metal fume fever, preliminary exposure to acetic acid vapors tended to prepare the host for development of zinc metal fume fever by permitting contact between leukocytes & zinc oxide particles, resulting in release of endogenous pyrogens to metal fume fever (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. 2039 [940].

Although hardness is widely recognized to affect aquatic toxicity of metals (for example, hardness seems somewhat protective of rainbow trout related to copper and zinc toxicity), pH often has the largest effect on metals toxicity [25,39] (Confirmed by David Mount, NBS, Columbia, MO, personal communication). (NOTE: For pH data, see also: Schubauer-Berigan, M.K., J.R. Dierkes, P.D. Monson, and G.T. Ankley, 1993. pH dependent toxicity of Cd, Cu, Ni, Pb, and Zn to Ceriodaphnia dubia, Pimephales promelas, Hyalella azteca, and

Lumbriculus variegatus. Environmental Toxicology and Chemistry 12:1261-1267.)

Under some circumstances, selenium may interact in an antagonistic or protective manner with zinc [445]. Zinc in water acts synergistically with copper and ammonia to produce an increased toxic effect on fish [26,47]. The levels of dietary zinc at which toxic effects occur evidently depend on the ratio of zinc to copper [180]. In mammals excess zinc can cause copper deficiencies, affect iron metabolism, and interact with the chemical dynamics of lead and drugs [39,180].

> Information on interactions vs. fish from Sorensen [488] quoted word for word with written copyright permission of CRC Press Inc.:
>
>> The ratio of the concentration or molecular weight of one element to the other is of primary importance. In catfish, a 1:1 ratio of toxic units for Zn:Cu produces additive effects at lower concentrations, but synergistic effects at higher concentrations (Birge and Black, 1979). In trout, a 6:1 ratio of a mixture of soluble Zn:soluble Cu produce additive toxicity in hard water, but synergistic toxicity in soft water (Lloyd, 1961). Also in trout, a 1:5:40 ratio of the concentration of Cu:Zn:Ni and a Cu level of 0.14—0.48 ppm Cu, produces additive effects (Brown and Dalton, 1970).
>>
>> With increasing levels of intracellular Hg, metallothionein is eventually saturated by the mercurial, during a time in which hepatic levels of CU and zinc decrease. Upon saturation of the metal-binding protein, Hg is though to spill over to the enzyme pool (that of high molecular weight proteins). At this time, pathological effects first appear. Possibly, some of the effects (e.g., 50% reductions in growth of chum salmon) are a consequence to the decrease in intracellular levels of essential elements CU and zinc, rather than a direct toxic effect of Hg."
>>
>> Intermediate concentrations of CU and zinc (0.07 ppm Cu and 0.69 zinc) elicit greater responses in ventilation amplitude, ventilation rate, and coughing frequency than higher concentrations. Higher CU or zinc levels cause more variation in ventilation pressure changes than lower zinc levels. Singly or in combination, zinc causes increased coughing frequency; whereas, Cu does not. Therefore, combined exposure to zinc-Cu results in synergism at intermediate levels of the elements. In fact, coughing frequency at 0.04 ppm Cu and 0.66 ppm zinc combined is about one and one-half times greater than the sum of the responses to the single toxicants.
>>
>> Interactions between Cu and Hg at the epidermis of fish hint of the role of mucus in metal poisoning of fish.

Epithelial mucus from plaice (Pleuronectes platessa) binds Cu and zinc at levels 100-fold and 20-fold greater respectively, than levels in water during exposures of fish to low aqueous concentrations (Coombs et al., 1972). Dialysis of mucus against deionized water results in only a small decrease in the concentrations of Cu and zinc bound to mucus. Glycoproteins low in sialic acid, aromatic and sulfur-containing amino acids, phosphate, and sulphate appear to be involved in binding of the two divalent cations. Moreover, CU+2, Zn+2, and Hg+2 precipitate fresh plaice mucus in the order CU > Zn > Hg (Jones, 1938). Mucus serves a protective function by binding excess aqueous metals as a precipitate.

Accumulation of Elements from Mixtures: Copper, Zinc, Mercury, Iron, Manganese: A few environmental studies address accumulation levels for mixtures of metals. Cross and workers (1973) catch fish at 2500 m deep near Cape Hatteras for analysis of levels of Hg in white muscle. Mercury levels increase with body weight ($p<0.001$) for bluefish (Pomatomus saltatrix) and morid (Antimora rostrata). Bluefish are epipelagic (living in the part of the ocean into which light penetrates) and morids are bathyl-demersal (living near the sea bottom in a biogeographic realm about 180-1800 m deep). Mercury accumulation is probably increased as a result of high lipid solubility, high electronegativity, and/or high affinity for sulfhydryl groups. Decreasing levels of all metals except Hg are noted for morids—an effect possibly due to growth dilution effects, compositional changes in muscle, and/or dietary changes in metal levels. In contrast to Hg levels, the concentrations of Mn, Fe, Cu, and Zn decrease or remain unchanged. In white muscle, the concentration factors (CF) of Hg, Mn, Cu, Zn, and FE are 3700, 100, 200, 2100, and 2300, respectively. Obviously, metal accumulation patterns vary as a function of species, fish size, and metal analyzed.

Koeman et al. (1973) conduct multi-elemental analyses of livers from the common seal (Phoca vitulina), dolphins (Delphinus delphis, Tursiops truncatus, lagenorhynchus obscurus, and Sotalia guianensis). Levels of Hg and Se are strongly correlated, but no similar relationship exists between Se and Cd, As, Sb, Zn, or other elements.

Selenium, Mercury, Zinc, and Iron: In some areas in which environmental Se and Hg are elevated, however, Hg is not accumulated and other elements interact with Se. One such site is Martin Lake in east Texas site at the Texas Utilities Generating Company (TUGCO) electric generating station. Because of the manner in which Se-contaminated fly ash, scrubber sludge, and bottom ash are dispersed from ash ponds, fish kills result.

Uses/Sources:

Zineb, zinc phosphide, ziram, and many other pesticides (mostly fungicides) starting with the letters "zi" contain zinc. Maneb and zinc (0.05 million ha) was one of the three most common fungicides used on major crops in North Dakota 1984 [447, McMULLEN, M.P., A.G. Dexter, J.D. Natewaja, W. Hamlin, and K. Davison. 1985. Pesticide uses on major crops in North Dakota 1984. NDSU and North Dakota Crop and Livestock Rep Serv Agron Rep 3. North Dakota State University, Fargo. 31 pp.].

Summary from Eisler [550]:

> The estimated world production of zinc is 7.1 million metric tons; the United States produces about 4% of the total and consumes 14%. Zinc is used primarily in the production of brass, noncorrosive alloys, and white pigments; in galvanization of iron and steel products; in agriculture as a fungicide and as a protective agent against soil zinc deficiency; and therapeutically in human medicine. Major sources of anthropogenic zinc in the environment include electroplaters, smelting and ore processors, mine drainage, domestic and industrial sewage, combustion of solid wastes and fossil fuels, road surface runoff, corrosion of zinc alloys and galvanized surfaces, and erosion of agricultural soils [550].

Additonal paragraph summarizing zinc uses [253]:

> Zinc is widely used as a coating to protect iron and steel from corrosion and as a component of useful alloys. The two major uses of zinc metal are (1) to coat iron and steel--a process called galvanizing--to prevent corrosion and (2) as a component of several alloys. An additional 5% to 10% of total zinc production goes into dry-cell battery cans and sheet zinc for photoengraving. Zinc protects iron from rusting because it is the stronger reducing agent of the two metals. The best-known zinc alloy is brass, which is made of copper with 3% to 45% zinc. The most widely used zinc compounds are the oxide, the sulfide, and the chloride. The oxide is used as a reinforcer in rubber tires, a white paint pigment, a ceramic glaze, and an opaque base in cosmetics, salves, and lotions. The sulfide is used as a phosphor in fluorescent lamps and cathode ray tubes and as a white pigment. The chloride is useful as a soldering flux, a dry-cell battery electrolyte, and a wood preservative. Zinc is a good reducing agent and is used as such in many laboratory applications [253].

Major Uses [940]:

> Zinc base alloys used for die casting; galvanizing agent;

component in brass, bronze alloys, rolled zinc products, light metal alloy & in wet batteries; chem int for zinc oxide; desilverizing agent for lead [SRI].

Protective coating for metals to prevent corrosion; for electrical apparatus, esp household utensils, castings, printing plates, building materials, railroad car linings, automotive equipment; reducing agent in org chem; deoxidizing bronze; extracting gold by cyanide process, purifying fats for soaps; bleaching bone glue; mfr sodium hydrosulfite, insulin zinc salts; reagent in anal chem [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

As negative electrode in alkaline cell electrode [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 3(78) 592].

In bearings [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 3(78) 678].

In electroplating [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 8(79) 832].

In gold dental alloys [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 7(79) 491].

In magnesium alloys [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 14(81) 592].

In metallic driers [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 8(79) 43].

In mixed-metal stabilizers [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 12(80) 240].

In paper defoxing [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. S(84) 433].

Use in cadmium recovery [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 4(78) 391].

Use in cooling towers as anodic inhibitors [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p.

21(83) 73].

Zinc oxide: zinc is the most commonly used phosphor powder in vacuum fluorescence displays [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 7(79) 748].

Finely divided zinc incorporated in grease can be coated on the interior surfaces of an aluminum connector to provide lower initial contact resistance and better long term resistance stability [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 8(79) 656].

As galvanizing coating on steel wires and tapes for buried and submarine cables [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 13(81) 584].

Zinc is one of the most common contaminants associated with urban runoff. Other zinc sources include soil erosion, industrial discharges, pharmaceuticals, and pesticides [39]. In some areas up to 50% of the zinc comes from highway runoff [43]. Zinc is also present in the leachate of some municipal landfills [80] and is a common contaminant in sludges generated by sewage treatment plants [94].

Natural Occurring Sources [940]:

Occurs in smithsonite or zinc spar, sphalterite or zinc blende, zincite, willemite, franklinite ... Or gahnite ... [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

Occurs naturally as calamine, smithsonite & wurtzite [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1250].

The average concentration in the earth's crust is estimated to be 40 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 666].

Artificial Sources [940]:

During blasting & crushing of ore moderate losses of zinc to the atmosphere occur. Treatment of the crush by means of wet flotation may result in emissions into water. During smelting there are often large emissions into air, which will result in cadmium emissions. The total emission of zinc into the atmosphere during smelting in

USA during 1969 has been estimated at 50000 tons. Significant zinc contamination of soil is only seen in vicinity of point sources. [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 667].

Forms/Preparations/Formulations:

Radionuclide:

The symbol for Zinc-65 is 65Zn, the atomic number is 30, the half-life is 244 days, and positron emission and X-ray emission are the major forms of decay [674].

Information from HSDB [940]:

Forms available: Slab, rolled (strip, sheet, rod, tubing), wire, mossy zinc, zinc dust powder (99% pure); single crystals; zinc anodes [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1250].

Commercial forms include ingots, lumps, shots, sticks, granules. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

GRADES: Special high-grade (99.990%); high-grade (99.95%); intermediate (99.5%); brass special (99%); prime western (98%) [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1250].

Ten grades from 3 mm shot to 5 microns, 99.5 to 99.9999% purity grades [Kuney, J.H. and J.N. Nullican (eds.) Chemcyclopedia. Washington, DC: American Chemical Society, 1988. 218].

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

Solubilities [940]:

INSOL (sic, actually "relatively insoluble") in cold & hot water; sol in acid, alkalies, acetic acid [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-143].

Density/Specific Gravity [940]:

7.14 AT 25 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

Vapor Pressure [940]:

1 MM HG AT 487 DEG C [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. D-195].

Boiling Point [940]:

908 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

Melting Point [940]:

419.5 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

Molecular Weight [940]:

65.38 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

Color/Form [940]:

Bluish-white, lustrous metal, distorted hexagonal closepacked structure [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

Other Chemical/Physical Properties [940]:

Mohs hardness 2.5; When heated to 100-150 deg c becomes malleable, at 210 deg c brittle & pulverizable; burns in air with bluish-green flame; slowly attacked by sulfuric acid or hydrochloric acid, oxidizing agents or metal ions; forms zincates with alkali hydroxides; natural isotopes are 64 (48.89%), 66 (27.81%), 68 (18.57%), 67 (4.11%), & 70 (0.62%) [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1455].

Fair conductor of electricity [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-43

Zinc has standard electrode potential of +0.761 & is electropositive to most structural metals except aluminum & manganese [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. 2035].

Electrical conductivity: 28.3% IACS; Electrical resistivity: 5.9 uohm-cm; thermal conductivity: 122.958 W/m-deg K; tensile strength: 283-324 MPa at room temp [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 19(82) 57].

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

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

Absorption, Distribution and Excretion [940]:

In humans, the major part of total body zinc is found in muscle and bone, 60% and 30%, respectively. The highest concentration of zinc is found in prostate, followed by bone and muscle. Shortly after an intravenous injection of zinc to volunteers the highest activity was measured in the liver. [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 670].

In mice injected SC with finely dispersed zinc (Zn) powder (particle size 0.05-0.1 mu) increased amounts of Zn were found in the liver. [Fatullina LD et al; Izve Akade Nauk SSSR, Ser Biol (1): 130-3 (1984)].

Absorption by GI tract is variable in animals & Poor in human/ Excretion is chiefly by feces, in amounts roughly equal to that admin. Urinary excretion is small. Does not vary with intake & is independent of urine volume [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 349].

Some regulation of intake & output of zinc probably takes place in intestine. Studies on rats and mice suggest that metallothionein, a low molecular wt cytoplasmic metalloprotein, has a role in this homeostasis. [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. 669].

Zinc concentration in gastric content, blood, liver, kidney, & muscles of suicidal victim were 22.8, 2.4, 5.3, 5.3, & 5.7 Mg/100 g, respectively, versus corresponding normal levels of 1.9, 1.5, 8.0, 4.0, & 5.0 MG/100 G. [Giebelmann r et al; deut gesundheitsw 29 (29): 1378-9 (1974)].

In the tissues, the highest concentration of zinc are found in the male reproductive system where the prostate has the highest content. High concentration of zinc also occur in the muscle, bone, liver, kidney, pancreas, and some endocrine glands, especially the thyroid. The largest amounts of zinc are found in the muscles and the bone. Within tissues there may be variation; in the human prostate gland the highest zinc concentration are found in the lateral prostate and the lowest in the interior and inner prostate. Also significant is the finding that semen has a high zinc content. In most organs there are relatively small variations in zinc levels during a lifetime except that in the newborn, zinc concentration generally are higher than later in life. Zinc is generally an essential component of many enzymes. Zinc is also found in metallothionein. [USEPA; Ambient Water Quality Criteria Doc: Zinc p.C-13 (1980) EPA 400/5-80-079].

Zinc is mainly excreted via the gastrointestinal tract but part of that zinc is reabsorbed. Urinary excretion of zinc is relatively small but with certain conditions, ie, extreme heat or exercise, much larger quantities may be excreted in sweat. Zinc is also excreted via hair and milk, and in the female there is a placental transfer to the fetus. [USEPA; Ambient Water Quality Criteria Doc: Zinc p.C-14 (1980) EPA 400/5-80-079].

Only very small amount of zinc are absorbed & stored in tissues of laboratory animals, dogs, cats & rats fed zinc cmpd for long periods; chief sites of storage were liver & pancreas. [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. 2043].

The gastrointestinal absorption of soluble zinc salts in mammals is highly variable; it averages about 50% of the dietary intake and is dependent upon the zinc level in the diet. When small amounts of zinc are fed to experimental animals and ruminants, the absorption of zinc may increase to 80%. [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 70].

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

Baseline data on Zn accumulation in organs and tissues, and their variations with age, sex, and habitat in Japanese serows (Capricornus crispus) were determined. The animals were killed during the winter 1981-82 in the Gifu and Nagano Prefectures, Japan. The Zn concentrations were measured by flame absorption spectrometry. On a wet wt basis, the mean Zn concentration in muscle, liver, kidney, and whole body of fetuses (gestation age 0.3-0.7 yr, n= 13) were 11.5, 169, 25.0, and 44.2 ug/g, respectively; in fawns (age 0.0-0.5 yr, n= 12), 34.4, 38.0, 30.0, and 38.1 ug/g, respectively; in yearlings (age 0.5-2.5 yr, n= 6), 35.9, 37.1, 30.6, and 42.5 ug/g, respectively; in adults (age 2.5 to 10 yr, n= 42), 39.4, 36.7, 31.5, and 41.3 ug/g, respectively; and in adults (age 10 to 17.5 yr, n= 17), 41.2, 37.2, 29.0, and 42.3 ug/g, respectively. The mean Zn concentration in fleece of fawns, yearlings, and adults (age 2.5 to 10 yr) was 115, 119, and 98.8 ug/g. the Zn content of bone samples of two adult serows ranged from 68.4 to 88.9 ug/g wet wt. The data indicate that higher accumulation of Zn occurred in hard tissues such as fleece and bone than in soft tissues. The body burden of fetuses was low (<1%) compared with those of their mothers. There was no significant difference in Zn concentration between collection locations. The Zn uptake agreed well with the concentration on Zn in food plants. [Honda K et al; Arch Environ Contam Toxicol 16: 551-61 (1987)].

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)].

For information on persistence of zinc in a body, see Bio.Detail section.

Laboratory and/or Field Analyses:

Many methods have been used to monitor for zinc. [861, 954,1001,1003,1004,1005,1006,1013]. 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 [861,1005,1006,1013], 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 1639 and 1669 (see details below) should apply.

Often inductively coupled argon plasma (ICP) or atomic absorption methods are sufficient, with detection limits of 1.0 ppm dry weight in tissues, 5.0 ppm in sediments and soils; and 0.01 ppm (mg/L) in water (Roy Irwin, National Park Service, personal communication, 1996). However, EPA Water Quality Criteria are as low as 28 ug/L, and sometimes background levels of zinc in water are low enough to require lower water detection limits:

> If needed for comparison with lower benchmarks, detection limits can be as low as 50 ng/L (ppt) in water using AAS [954]. Using EPA ICP/MS method 200.8, an instrument detection limit of 0.07 ug/L zinc can be achieved in water samples [1006]. Water detection limits as low as 0.14 ug/L can be achieved using EPA methods 1638 or 1639 [1001,1003]. Low limits may be needed since EPA Water Quality Criteria are as low as 28 ug/L [1001,1003]. Ideally, the detection limit should be at least 10 times higher than the comparison benchmark or criteria [676].

Sometimes, higher environmental levels of zinc sometimes mean the lowest detection limits are not needed (Roy Irwin, National Park Service, 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].

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). In 1980 EPA recommended water criteria be expressed as total recoverable zinc [39]. As of January 1995, the U.S. EPA was recommending that states use dissolved measurements in water quality standards for metals, in concert with recommendations EPA previously made for the Great Lakes [672]. The conversion factors recommended by EPA for converting total recoverable metals criteria to dissolved metal criteria were given as follows [672]:

> Zinc conversion for acute criteria: 0.981; nickel conversion for chronic criteria: 0.992 (for example, total recoverable chronic zinc criteria x 0.992 = dissolved chronic zinc criteria).
>
> > Note: This conversion factor is not really universal and 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).

The conversion factors recommended by EPA for converting total recoverable zinc to dissolved concentrations in the January 1997 draft EPA Guidelines for 5 year 305(B) assessments were:

> For the Criterion Maximum Concentration (CMC): 0.978.
>
> For the Criterion Continuous Concentration (CCC): 0.986.
>
> > Note: None of these "generic" conversion factors may work well for all areas. Both total and dissolved concentrations should be checked at new locations before relying on generic conversion factors (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Filtration and Acidification of Water Samples:

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

> 1) For samples of "total or total recoverable elements," samples should be acidified to a pH of two or less at the time of collection or as soon as possible thereafter.
>
> > Note: In more recent (1996) guidance related to the more rigorous method 1669, EPA clarified (some would say confused or added data variability) the issue of when to acidify by stating:
> >
> > > "Preservation recommendations for Antimony, Arsenic, Cadmium, Copper, Lead, Nickel, Selenium, Silver, Thallium, and Zinc: Add 5 mL of 10% HN03 to 1-L sample; preserve on-site or immediately upon laboratory receipt" [1003].
> > >
> > > > Note: the nitric acid (triple distilled or not?) and dilution water (contaminated or not?) and containers (proper type, cleaned correctly or not?) used are all potential sources of contamination (see more detailed note below related to data variation factors).
>
> 2) For determination of dissolved elements, the samples must be filtered through a 0.45 micron membrane filter as soon as soon as practical after collection, using the first 50-100 ml to rinse the filter flask. Acidify the filtrate with nitric acid to a pH of 2 or less. Normally 3 mL of (1+1) of nitric acid per liter should be sufficient to preserve the sample.
>
> 3) For determination of suspended elements, the samples must be filtered through a 0.45 micron membrane filter as soon as soon as practical after collection. The filter is then transferred to a suitable container for storage and shipment, with no preservation required.

It is important to understand that 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.

More detailed discussion on 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].

> In a study at Yellowstone Park, Soda Butte Creek, filtering and then acidifying of water samples was done in two ways: The first way was in the field, per original standard EPA suggestions in 40 CFR. The second way was in the in the lab after 6 to 8 days. See copper entry for details. Information related to Zinc:
>
> > On two dates, lab filtered and acidified water was always higher in dissolved copper, a somewhat counter-intuitive result (Al, Fe, Mn, Zn, and Ni showed the opposite trend, tending to be higher in field filtered and acidified samples). On a third date 6 lab filtered and acidified samples were higher in copper and 3 field filtered and acidified samples were higher (Del Nimmo, USGS, personal communication, 1997).

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

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

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

1984 to 1985 Ambient Water Quality Criteria Documents for individual metals.

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

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

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

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

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

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

> "Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to

> > completely dissolve the metal(s) adsorbed on the container walls. The sample pH should be verified as <2 immediately before withdrawing an aliquot for processing or direct analysis. If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2" [1003].

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

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

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

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

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

I) If one field filters and acidifies, one often changes metal concentrations and colloidal content compared to samples not treated in this manner. Acidifying effects microbial changes. If one holds the samples a while before filtering and acidifying, the situation changes. In collection bottles, there are potential aging effects:

temperature changes, changes in basic water chemistry as oxygen and other dissolved gasses move from the water into the headspace of air at the top, potential aggregation of colloidal materials, precipitation of greater sizes over time, development of bigger and more colloids, and more sorption (Roy Irwin, National Park Service, personal communication, 1997).

4) The guidance of exactly where to take water samples varies between various state and federal protocols. Taking water samples at the surface microlayer tends to increase concentrations of various contaminants including metals. Other areas of the water column tend to produce different concentrations. Large quantities of anthropogenic substances frequently occur in the surface microlayer at concentrations ranging from 100 to 10,000 times greater than those in the water column [593]. These anthropogenic substances can include plastics, tar lumps, PAHs, chlorinated hydrocarbons, as well as lead, copper, zinc, and nickel [593]. Sometimes a perceived trend can be more the result of the details of the sample micro-location rather than real changes in environmental concentrations (Roy Irwin, National Park Service, personal communication, 1997). The new EPA method 1669 (see details below) mentions the microlayer, and states that one can use a fluoropolymer closing mechanism, threaded onto the bottle, to open and close a certain type of bottle under water, thereby avoiding surface microlayer contamination [1003]. However, even this relatively new EPA method 1669 also gives recommendations for ways to sample directly at the surface, and does not discourage the use of surface samples.

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

6) Just as there are numerous ways to contaminate, store, ship, and handle water samples, so are there different agency protocols and many different ways to handle samples from other media. One investigator may use dry ice in the field, another may bury the samples in a large

amount of regular ice immediately after collection in the field, while a third might place samples on top of a small amount of ice in a large ice chest. The speed with which samples are chilled can result in different results not only for concentrations of organics, but also for the different chemical species (forms) of metals (Roy Irwin, National Park Service, personal communication, 1997).

7) In comparing contaminants metals data, soil and sediment contaminant concentrations should usually be (but seldom has been) normalized for grain size, total organic carbon, and/or acid volatile sulfides before biologically-meaningful or trend-meaningful comparisons are possible (Roy Irwin, National Park Service, Personal Communication, 1997).

8) There has been tremendous variability in the precautions various investigators have utilized to avoid sample contamination. Contamination from collecting gear, clothes, collecting vehicles, skin, hair, collector's breath, improper or inadequately cleaned sample containers, and countless other sources must carefully be avoided when using methods with very low detection limits [1003]. Contamination of samples was one of the reasons that EPA has developed the 1600 series methods for water:

Highlights from EPA Method 1639: Determination of trace elements in ambient waters by stabilized temperature graphite furnace atomic absorption:

This 1996 proposed EPA method provides procedures to determine dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using stabilized temperature graphite furnace atomic absorption (GFAA) [1003]. It may also be used to determine total recoverable element concentrations in these waters [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.

This method was developed by integrating the analytical procedures contained in EPA Method 200.9 with the stringent 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 ensure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (the "Sampling Method") [1003]. The Sampling Method is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process [1003].

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

This method may be used with the following metals [1003]:

Antimony (Sb), CAS 7440-36-0
Cadmium (Cd), CAS 7440-43-9
Trivalent Chromium, CAS 16065-83-1
Nickel (Ni), CAS 7440-02-0
Selenium (Se), CAS 7782-49-2
Zinc (Zn), CAS 7440-66-6

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 the Sampling Method [1003]. Except for trivalent chromium, the filtered samples may be preserved in the field or transported to the laboratory for preservation [1003]. Procedures for field preservation are detailed in the Sampling Method; procedures for laboratory preservation are provided in this method [1003]. To determine trivalent chromium, a field preparation step, which is described in the Sampling Method, is used to isolate the trivalent chromium [1003].

To determine total recoverable analytes in ambient water samples, a digestion/extraction is required before analysis when the elements are not in solution (e.g., aqueous samples that may contain particulate and suspended solids) [1003].

Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polypropylene, polysulfone, or ultrapure quartz [1003]. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminates and is susceptible to serious memory contamination [1003]. Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of the other materials resulting either in contamination or low-biased results [1003]. All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using EPA procedures and must be known to be clean and metal free before proceeding [1003].

The following materials have been found to contain trace metals and must not be used to hold liquids that come in contact with the sample or must not contact the sample itself, unless these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor [1003]. In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided [1003].

Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the labware to injection into the instrument [1003]. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents [1003]. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all labware can be detected [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 should then verified to be pH < 2 just 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 16 h until verified to be pH < 2 [1003].

One of the requirements for the alternate total recoverable digestion procedure is to tightly recap the container and shake thoroughly [1003].

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

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

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

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

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

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

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

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

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

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

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

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

An alternate grab sampler design is available [1003].

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

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

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

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

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

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

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

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

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

Highlights from EPA 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 0.14 ug/L may be necessary for zinc, using EPA methods 1638 or 1639, since EPA Water Quality Criteria are as low as 28 ug/L [1001] [1003].

Methods in EPA 200 series:

Standard water methods used in the past have included EPA 289.1, 289.2, and ICP method 200.7 (40 CFR, Part 136.3, Table 1B, page 386, 1994).

Other Laboratory Method [940]:

Method 7950. Direct Aspiration Atomic Absorption Spectroscopy for Zinc. This method is applicable to drinking, surface, and saline waters and domestic and industrial wastes. Ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis. The optimum concentration range is 0.05-1 mg/l with a wavelength of 213.9 nm, sensitivity is 0.02 mg/l, and a detection limit of 0.005 mg/l. /Total zinc/ [USEPA; Test Methods for Evaluating Solid Waste. Physical/Chemical Methods 3rd Ed (1986) EPA 955-001-00000-1].

Sampling Procedures [940]: Sample volumes required depend upon the number of different digestion procedures necessary for analysis. Samples are collected in either polyethylene or glass containers. Preservation of the sample is maintained by adjusting the pH<2 with nitric acid. Maximum holding time is 6 months. Solid samples must be at least 200 g and usually require no preservation other than storing at 4 deg C until analyzed. /Total metals (except hexavalent chromium and mercury)/ [USEPA; Test Methods for Evaluating Solid Waste. Physical/Chemical Methods 3rd Ed (1986) EPA 955-001-00000-1].

For other details on methods for zinc, see ATSDR [954].