ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

CADMIUM ENTRY

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This document was put together by human beings, mostly by compiling or summarizing what other human beings have written. Therefore, it most likely contains some mistakes and/or potential misinterpretations and should be used primarily as a way to search quickly for basic information and information sources. It should not be viewed as an exhaustive, "last-word" source for critical applications (such as those requiring legally defensible information). For critical applications (such as litigation applications), it is best to use this document to find sources, and then to obtain the original documents and/or talk to the authors before depending too heavily on a particular piece of information.

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

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

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

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

Differences in field and laboratory methods arre 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 with out updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

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

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

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

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

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

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

on the internet or NTIS: 1998).

Cadmium (Cd, CAS number 7440-43-9)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

The chemical element cadmium is a relatively rare, soft, silver-white, transition element metal closely related to zinc [333]. Its place in the periodic table is below zinc and above mercury, and it has many properties in common with these elements [333]. In nature, two oxidation states are possible (0 and +2), however, the zero or metallic state is rare [838]. Cadmium has no known essential biological function [379,383]. However, cadmium has been detected in more than 1000 species of aquatic and terrestrial flora and fauna [379].

Cadmium enters the environment via three main routes: refining and use of cadmium, copper and nickel smelting, and fuel combustion [838]. The principal natural sources of cadmium entering the atmosphere include windblown transport of soil particles, forest fires, and volcanic emissions. It is estimated that globally, anthropogenic activities add roughly 3 to 10 times more cadmium into the atmosphere than from natural sources; 56 to 85% of this originates from the smelting of base metal ores [907].

Cadmium acts as a cumulative poison [83] and is listed by the Environmental Protection Agency as one of 129 priority pollutants [58,446]. Cadmium is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [93].

Br.Haz: General Hazard/Toxicity Summary:

Potential Effects to Fish, Wildlife, Invertebrates, and other Non-Human Biota:

Cadmium is very toxic to a variety of species of fish and wildlife. Cadmium causes behavior, growth, and physiological problems in aquatic life at sublethal concentrations [57]. Cadmium is the only metal that clearly accumulates with increasing age of the animal, and the kidneys are the preferred site of cadmium accumulation [838].

Cadmium ions are extremely poisonous; their action is similar to those of mercury [333]. All cadmium compounds are potentially harmful or toxic [83].
It has been implicated in various deleterious

effects to fish and wildlife [379].

Immunosuppressive effects of cadmium have been shown in mice [366], fish [982], and oysters [982].

Summary from chapter on cadmium in Sorensen's book on metal poisoning in fish [488]:

> Roughly, the toxicity of Cd in fish is equivalent to that of Pb, but twenty-five times less than that of Hg. Species-specific variation is the rule. Cadmium-induced toxicity is a function of water quality (e.g., salinity, water hardness, pH, alkalinity, and temperature) and parasitism. Mucous production, asphyxiation, inhibition of acetylcholinesterase, depression of the respiratory center, hypocalcemia, and gill injury are causal factors in death, depending on the species.

Cadmium is sometimes less toxic to freshwater organisms in hard water than in softwater [838]. Humic acid or other complexing materials have a varying effect on cadmium toxicity [838]. The presence of complexing materials in water decreased cadmium uptake and toxicity in fish, but had mixed effects on toxicity to invertebrates. Monthly tests demonstrated that cadmium toxicity in river water varied by a factor of three or more over the year due to fluctuating levels of suspended solids [838].

The freshwater fish, Clarias batrachus, showed an increase of the protein content in the liver, kidney, stomach, intestine, testis, and ovary, and a decrease in the muscle after copper and cadmium treatment. The administration of copper and cadmium increased the concentration of free amino acids in all the fish organs (Jana S, Sahana SS; Physiol Bohemoslov 37 (1): 79-82, 1988) [366].

Several comprehensive reports on the hazards of cadmium are available. Cadmium hazards to fish and wildlife are summarized in Eisler's 1985 synoptic review [379]. The EPA published the Ambient Water Quality Criteria for Cadmium (includes supporting documentation) in 1984 [906]. A more recent chapter on cadmium was published in 1991 as part of Sorensen's book on metal poisoning in fish [488]. Environment Canada has prepared a priority substances list assessment report for cadmium [907]. Wren et al. provided a 1995 summary of biological effects of mercury and cadmium [838].

Resistance/Development of Tolerance:

Populations of organisms chronically exposed to chemical pollutants may develop increased tolerance to those pollutants [177,493]. Increased synthesis of metallothionein (metal-binding proteins) in response to exposures to various metals may help animals acquire a somewhat increased tolerance to the metals [180]. Cadmium exposure can induce metal-binding proteins (Denny Buckler, FWS Columbia, personal communication). In this way, cadmium is sequestered in metallothionein complexes [838].

The metallothionein compounds have a high proportion of sulfur-containing amino acids that bind with cadmium such that it becomes unavailable for interaction with intracellular receptor sites. Tissue accumulation and distribution of cadmium is dependent upon the route of exposure (food or water vector) [838]. Some of the aquatic issues related to tolerance, interactions with other metals, and/or indirect impacts related to cadmium were summarized by Rand and Petrocelli [177].

A mouse hepatoma cell line selected for resistance to cadmium (Cdr 80 hepa) was compared to the unselected parental hepatoma cell line (Cds hepa) in terms of its sensitivity to a variety of metal ions. The Cdr 80 hepa cells have double minute chromosomes which carry amplified copies of the MT-I and MT-II genes and can accumulate approximately 20 fold more MT mRNA than Cds hepa cells when stimulated with an optimal sode of cadmium. The metals zinc, copper, silver, cobalt, mercury, and bismuth also induce higher levels of MT mRNA in the resistant cells than in the unselected cells, yet the Cdr 80 hepa cella only show increased resistance to the toxic effects of zinc, copper, mercury, and bismuth [366].

Potential Effects of Cadmium Upon Humans:

All cadmium compounds are potentially harmful or toxic [83]. When cadmium is smelted, it vaporizes into the atmosphere, and heavy concentrations can cause kidney and bone-marrow diseases and emphysema [335]. It has been implicated as the cause of human deaths [379].

Cadmium is reported to block renal synth of 1,25-dihydroxycholecalciferol, the metabolically active form of vitamin D; this could be indirectly responsible for skeletal abnormalities found in cadmium embryotoxicity for lack of bone mineralization & osteomalacia (Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 82) [366].

Populations at special risk include [940]:

1) Individuals with renal disease of other etiology, which may add to or magnify the effect of cadmium on the kidney.

2) genetic differences in the induction of metallothionein in response to cadmium exposure;

3) dietary deficiencies in metal ions and/or protein, which may increase cadmium absorption from the gastrointestinal tract; and,

4) neonates or young children possibly having higher gastrointestinal absorption rates than adults. (DHHS/ATSDR; Toxicological Profile for Cadmium, Draft p.62, 11/87).

Human symptoms of exposure to cadmium include [940]:

A. Inhalation (an asymptomatic period of 4-8 hr may precede the clinical illness). 1. Metallic taste in the mouth and headache. 2. Shortness of breath, chest pain, cough with foamy or bloody sputum. Pulmonary rales and related physical signs. 3. Weakness, leg pains. 4. An asphyxial death from intense pulmonary edema. 5. Gradual resolution of pulmonary edema (over a period of a few days) and development of fever, with persistence of cough, chest pain and dyspnea for one or more weeks. Physical signs of pneumonic consolidation. 6. Late kidney and/or liver damage has followed respiratory exposures in industry. B. Ingestion (an asymptomatic period of 1/2-1 hr may precede the clinical illness). 1. Severe nausea, vomiting, diarrhea and abdominal cramps and salivation. 2. Headache, muscular cramps, vertigo, and perhaps convulsions (rarely). 3. Exhaustion, collapse, shock and death, usually within a period of 24 hr. 4. The gradual evolution of signs and symptoms of liver and kidney damage should be anticipated but are rarely seen in man (Gosselin, R.E., R.P. Smith, H.C. Hodge. Clinical Toxicology of Commercial Products. 5th ed. Baltimore: Williams and Wilkins, 1984.,p. III-81) [940].

Inhalation of cadmium dusts, salts & fume over a number of years result in chronic cadmium poisoning, a disease characterized by distinctive, nonhypertrophic emphysema with or without renal tubular injury. Further inhalation overexposure results in irreversible renal tubular damage, which may progress into complete Fanconi syndrome with decreased tubular reabsorption of proteins, glucose, amino acids, calcium, phosphorus, & with decreased ability to acidify & concentrate the urine. Other toxic effects include anemia, eosinophilia, anosmia, chronic rhinitis, yellow discoloration of teeth, & bone changes (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. 87) [940].

Many nonfatal cases of "food poisoning" followed ingestion of food kept for brief periods in cadmium coated containers, such as ice cube trays & metal pitchers. Welding (or cutting with acetylene torch) cadmium-plated or cadmium containing metal objects constitute very significant & potentially lethal hazard after short exposures (same ... For brazing or silver-soldering with cadmium-containing rods or wires). Some silver solders contain more than 20% cadmium. In early stages this syndrome may be confused with a much more benign illness caused by exposure to fumes of zinc & some other metals (Gosselin, R.E., R.P. Smith, H.C. Hodge. Clinical Toxicology of Commercial Products. 5th ed. Baltimore: Williams and Wilkins, 1984.,p. III-77) [940].

ATSDR has prepared a toxicological profile for cadmium which summarizes human health effects via various exposure routes [908]. Due to lack of time, important highlights from this ATSDR document have not yet been completely incorporated into this entry. EPA has a (several page) health advisory on this compound, available through the Office of Drinking Water, EPA, Washington, D.C. or through NTIS.

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

Information from EPA 1996 IRIS [893]:

> Weight-of-evidence classification:
> Classification -- B1; probable human carcinogen by inhalation; based on limited evidence from epidemiologic studies and sufficient evidence of carcinogenicity in rats and mice by two routes [893].
>
> Human carcinogenicity data: Limited. A 2-fold excess risk of lung cancer was observed in cadmium smelter workers. Studies of human ingestion of cadmium are inadequate to assess carcinogenicity [893].
>
> Animal carcinogenicity data: Exposure of Wistar rats by inhalation to cadmium as cadmium chloride at concentrations of 12.5, 25 and 50 ug/cu.m for 18 months, with an additional 13-month observation period, resulted in significant increases in lung tumors. Intratracheal instillation of cadmium oxide did not produce lung tumors in Fischer 344 rats but rather mammary tumors in males and tumors at multiple sites in males. ...Seven studies in rats and mice where cadmium salts (acetate, sulfate, chloride) were administered orally have shown no evidence of a carcinogenic response [893].

IARC Summary and Evaluation [940]:

> Evaluation: There is sufficient evidence in humans for the carcinogenicity of cadmium and cadmium compounds. There is sufficient evidence in experimental animals for the carcinogenicity of cadmium compounds. There is limited evidence in experimental animals for the carcinogenicity of cadmium metal. In making the overall evaluation, the Working Group took into consideration the evidence that ionic cadmium causes genotoxic effects in a variety of types of eukaryotic cells, including human cells. Overall evaluation: Cadmium and cadmium compounds are carcinogenic to humans (Group 1). [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. 58 210 (1993)].

There is some evidence relating cadmium exposure to prostate cancer in men and animal studies [1025].

Cadmium has been implicated in the increase in prostate cancer incidence in men exposed to high levels. A decrease in zinc and a concomitant increase in cadmium levels in the human prostate has been shown. The role and mechanism of cadmium action in prostate carcinogenesis is not clear. Selenium, on the other hand, has been shown to inhibit carcinogenesis in several animal systems. Results show that cadmium stimulates the growth of human prostatic epithelium in vitro between 10(-9) M and 10(-7) M concentrations. Selenium, at concentrations between 10(-12) M and 10(-7) shows no growth stimulatory or inhibitory effects on these cells. However, when present at 10(-8) M level, selenium inhibits the growth stimulation induced by cadmium (Webber MM; Biochem Biophys Res Commun 127, 3: 871-7 (1985) [940].

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

Cadmium is listed as having some endocrine disruptive activities [572]. Cadmium has been shown to cause birth defects in mammals [61].

Mammals and birds consuming cadmium-contaminated food have experienced lowered sperm counts, kidney damage, increased mortality of young, elevated blood sugar, and anemia [57]. From a variety of studies using mice and bacteria as models, it appears likely that cadmium has mutagenic effects [379].

Cadmium exposed, estradiol injected male and female flounders showed depressed blood levels of vitellogenin [982].

There are very few reports of cadmium-induced injury to wildlife [838]. Incidents of cadmium poisoning in humans and domestic animals have frequently been overlooked or incorrectly diagnosed as something else due to the multitude of interactions of cadmium with other essential and toxic elements. The main clinical signs of cadmium toxicity in animals are anemia, retarded gonad development, enlarged joints, scaly skin, liver and kidney damage, and reduced growth [838].

Evidence of gonadal effects from cadmium; microscopic changes consisting of depression & maturation of spermatocytes, associated with high levels of cadmium, were found in testes of men exposed to cadmium fumes (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. 1569) [940].

Studies observed reproductive impairment to Ceriodaphnia dubia at 6.0 ug/L cadmium [838]. One author has stated that reproductive problems in fish may occur when tissue concentrations exceed 0.1 mg/kg [57], but it is not clear from the citation which kinds of tissues were meant. The same paper discussed both whole body and edible tissue data.

In rats, oral doses of cadmium given on days 6-19 of gestation increased fetal resorption and caused skeletal, kidney, and heart abnormalities in fetuses, stillborn, and offspring. The incidence and intensity of skeletal defects increased with cadmium dosage (Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 83) [940]. For more details, see Tis.Wildlife section below.

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

Cadmium forms only bivalent compounds, which form coordination compounds with other ions and molecules [333]. Cadmium does not breakdown in the environment, but it may be affected by physical and chemical processes that modify its mobility, bioavailability, and residence time in different environmental media [907]. The environmental fate and transport of cadmium is greatly dependent upon the local conditions and processes [838].

Cadmium tends to bioaccumulate in fish [57], clams [90,95], and algae [95], especially in species living in close proximity to sediments contaminated by cadmium [95]. The mobility and bioavailability of cadmium in aquatic environments is enhanced under conditions of low pH, low hardness, low suspended matter levels, high redox potential, and low salinity [907].

For many metals, alkalinity is sometimes a more important co-factor for toxicity than hardness (Pat Davies, Colorado Division of Wildlife, personal communication, 1997). Some recent research (1990) has focused on the tendency of low-alkalinity (less than 50 ueq/L) waters to have a relatively high potential for acid deposition effects and increased bioaccumulation of cadmium in fish [383]. See also the Bio.Detail section below.

The movement of cadmium in soil and potential accumulation in biota is enhanced by low pH, low organic matter content, large soil particle size, and high soil retention [907]. Soils generally function as a major sink for most of the cadmium released into the terrestrial environment [748]. In an experiment conducted to follow the transfer of cadmium from a terrestrial to an aquatic ecosystem, most (94 to 96%) of the cadmium remained in the soil. Cadmium in the water accumulated more rapidly in the sediments than in living organisms. Twenty percent of the cadmium in water was found in suspended particles [838].

A study of highway runoff indicated slight reductions of cadmium in water after it had run through a sedimentation pond and slightly more reduction after going from the detention pond through a wetland [220].

Biological Half-Life [366]:

An accumulation of cadmium occurs in many tissues and particularly long half-times, 10-30 years, have been reported for muscles, kidneys and 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 130].

Synonyms/Substance Identification:

KADMIUM (GERMAN) [366]
C I 77180 [366]
Colloidal cadmium [366]

Molecular Formula [366]:
Cd

Associated Chemicals or Topics (Includes Transformation Products):

Selenium seems to have some properties as an immuno-potentiating agent, an agent which can bind mercury and cadmium compounds to make them more biologically inert. See Br.Car above for interactions between selenium and cadmium.

See also individual entry:

Mercury
Selenium

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

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

A monitoring study of wastewater effluents from a waste oil re-refinery in the United States (location not specified) found that mean concentration of metals varied from 0.34 mg/L for cadmium to 271 mg/L for lead [752].

Environmental accumulation: groundwater contamination from electroplating operations has been reported to cause concentrations of up to 3.2 mg/l cadmium (National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 212) [940].

W.Typical (Water Concentrations Considered Typical):

Recent developments in new analytical methods, as well as increased attention to sample preparation, have resulted in reporting lower cadmium concentrations in surface waters in the past decade (mid-1980s and 1990s) [838]. For example, a study reported that cadmium concentrations in contaminated lakes in the Sudbury area ranged from 3 to 20 ug/l, but more recent measurements suggest levels ranged as low as 0.08 ug/l [838]. In the same trend, typical freshwater concentrations were reported by EPA in 1981 to be 0.08 mg/l (80 ug/L) [83]. However, it is now understood that 80 ug/L is too high to be "typical" [838].

Recent (1990s) measurements suggest that average total cadmium concentrations in rivers, streams, and lakes are in the range of less than 0.01 to 0.07 ug/l [838].

Reported background levels of cadmium in uncontaminated compartments extend over several orders of magnitude (all values in ug/L) [379]:

Freshwater	0.05 to 0.2
Coastal seawater	up to 0.05
Open ocean seawater	0.01 to 0.1
Riverine and lake sediments	up to 5000
Marine sediments	30 to 1000
Soils of nonvolcanic origin	10 to 1000

Typical Ocean Concentrations of Cadmium: EPA 1981: 0.00011 mg/l (0.11 ug/L) [83].

1971: A median concentration of 1 ug/L for U.S. surface waters was reported (only 4% of samples exceeded 10 ug/L, the older recommended limit for irrigation or drinking water) [190].

USGS 1974-1981: The 50th percentile of 285 (not especially clean) NASQWAN and NWQSS river sites in the U.S. was <2 ug/l; as were the 25th and the 75th percentiles, with concentrations trending upward more often than downward, possibly partly due to atmospheric deposition from fossil fuel combustion [219].

California, 1986: Ambient background level for water was 0.01 ug/l [222].

Great Lakes, 1990s: Total background cadmium concentrations ranged from less than 0.02 to 0.10 ug/l. Filtered total cadmium concentrations ranged from less than 0.001 to 0.068 ug/l. The ratio of filtered to unfiltered cadmium concentrations ranges from about 20 to 98% [838].

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

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

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

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

EPA 1996 IRIS Database [893]:

Ambient Water Quality Criteria for Aquatic Organisms

Acute Freshwater: 3.9E+0 ug/L 1-hour avg [893].

Older References to same value: Freshwater Acute Criteria: 3.9 ug/L [689,649]. Hardness dependent criterion rounded to second integer (100 mg/L CaCO3 used) [689]. The equation is Criteria = e to the power of (1.128[ln(hardness)]-3.828), where "e" = exponential [649]. Further clarification:

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

Chronic Freshwater: 1.1E+0 ug/L 4-day avg [893].

Older References to same value: Freshwater Chronic Criteria: 1.1 ug/L ([649,689]. Hardness dependent criterion rounded to second integer (100 mg/L CaCO3 used) [689]. The equation is Criteria = e to the power of (0.7852[ln(hardness)]-3.490), where "e" = exponential [649]. Further clarification:

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

Marine Acute: 4.3E+1 ug/L 1-hour avg [893].

Older Reference to same value [446].
Marine Chronic: 9.3E+0 ug/L 4-day avg [893].

Older References to same value: [446].

Reference: 50 FR 30784 (07/29/85) [893].

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

Discussion: Criteria were derived from a minimum data base consisting of acute and chronic tests on a variety of species. 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 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 benchmarks (ug/L) [649]:

For CAS 7440-43-9, the cadmium benchmarks are (ug/L) [649]:

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 3.9

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:

The Criteria is equal to: e(1.128[ln(hardness)]-3.828), where "e" = exponential [649]. Note: Same as IRIS 1996 EPA equation given above [893]. Further clarification:

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

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: 1.1

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:

The criteria is equal to: e to the power of (0.7852[ln(hardness)]-3.490), where "e" = exponential [649]. Note: Same as IRIS 1996 EPA equation given above [893]. Further clarification:

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

SECONDARY ACUTE VALUE: no information found

SECONDARY CHRONIC VALUE: no information found

LOWEST CHRONIC VALUE - FISH: 1.7

LOWEST CHRONIC VALUE - DAPHNIDS: 0.15

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: no information found

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 2

LOWEST TEST EC20 - FISH: 1.8

LOWEST TEST EC20 - DAPHNIDS: 0.75

SENSITIVE SPECIES TEST EC20: 0.013

POPULATION EC2O: 4.3

Other Concern Levels for Water Concentrations:

Florida's water quality standard applied to some wetland sites was 0.8 ug/l [220].

A State of California recommendation based on direct toxicity was that 0.05 ug/L be the water quality criteria (0.2 ug/l was an adverse effects level) [222].

Canada's Interim Assessment Criterion for cadmium in water is 1 ug/L [656].

NOTE: a) criterion is considered "Interim" since complete supporting rationale do not exist.

Canada's Remediation Criteria for cadmium for freshwater aquatic life is 0.2-1.8 ug/L (guideline changes with hardness) [656].

Other notes related to water standards [366]:

The ocean dumping, or transportation for dumping, of materials containing cadmium or cadmium compounds as other than trace contaminants will not be approved on other than an emergency basis [40 CFR 227.6(3) (7/1/88)].

Toxic pollutant designated pursuant to section 307(a)(1) of the Clean Water Act and is subject to effluent limitations [40 CFR 401.15 (7/1/88)].

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, such as 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 7440-43-9, CADMIUM, the benchmark is 0.05 mg/L (groundwater or porewater).

Canada's Remediation Criteria for cadmium for irrigation water is 10 ug/L [656].

NOTE: This value is for total concentrations in an unfiltered sample, and applies to all soils. Guideline changes with hardness.

LC50 for various algae 0.06 to 0.16 mg/L [970].

W.Invertebrates (Water Concentrations vs. Invertebrates):

LC50 Daphnia magna 0.01 mg/L [970].

ACUTE: Reported 48-h acute toxicity values for invertebrates range from 7.0 to 34,600 ug/L [838]. Cladocerans are particularly sensitive to cadmium. The 48-hr LC50 for Daphnia magna is in the range of 34 to 60 ug/L in moderately hard water. The acute toxicity of cadmium to D. magna was lower in water with higher hardness. The lowest invertebrate acute LC50 (7.0 ug/L) was reported for Simocephalus serrulatus in wellwater [838].

CHRONIC: Adverse effects to aquatic invertebrates are documented at relatively low cadmium concentrations (0.28 to 3.0 ug/L), both in laboratory and field studies. The 10-day LC50 for the chironomid Tanytarsus dissimilis was 3.8 ug/L. Studies observed reproductive impairment to Ceriodaphnia dubia at 6.0 ug/L and suggest a Maximum Allowable Toxicant Concentration (MATC) for this species of 2.2 ug/L [838].

Some aquatic insects and crayfish demonstrate a marked tolerance to cadmium relative to other invertebrate species [838]. Cadmium concentrations as high as 238 ug/L had little or no effect on the survival of caddisfly (Hydropsyche betteni) and stonefly (Pteronarcys dorsata). The 96-hr LC50 for the mayfly Ephemerella grandis was 28,000 ug/L [838].

W.Fish (Water Concentrations vs. Fish):

ACUTE: The 96-hr LC50 for rainbow trout parr in soft (23 mg/L as CaCO3) water was 1.0 ug/L [838,970]. The reported 96-hr LC50 for small (0.2 g) brook trout was 2.4 ug/L compared with 5080 ug/L for 100-g brook trout. The toxicity of cadmium to juvenile coho salmon was reduced in the presence of organic complexing material [838].

The reported 96-h LC50 for fathead minnows ranged from 11.7 to 7160 ug/L. Much of the variation is related to the sensitivity of newly hatched fry compared with older fish. For example, the 96-hr

LC50 for 1-day-old fry was in the range of 11.7 to 54.2 ug/L, compared with 1280 to 7160 for adult (30+ -day-old) fathead minnows [838].

CHRONIC: Several studies reported chronic effects of cadmium to fish at concentrations as low as 0.5 to 1.0 ug/L [838].

The subacute toxicity of cadmium to fish varies greatly among species. Exposure to cadmium concentrations from 0.5 to 5.2 ug/L for 168 to 408 hours caused 50% mortality in some stages of rainbow trout, and coho and chinook salmon. Survival and growth of sensitive life stages of rainbow trout are often as sensitive and more meaningful indicators of exposure to cadmium than are biochemical or histological indices [838].

The toxic effects of cadmium are greatly influenced by fish life stage. Embryos and newly hatched alevins are more resistant to cadmium than are older alevins or juveniles [838].

The lowest cadmium concentrations affecting growth and survival of fathead minnows in exposures ranging from 8 to 32 days were between 14.5 and 41.4 ug/L. Long-term exposure (126+ days) to cadmium reduced growth and survival of brook trout at 3.4 ug/L and 3.8 ug/L, respectively [838].

The 96-hr and 168-hr LC50s for 2- to 3-g steelhead trout were less than 0.5 ug/L in water with a hardness of 25 mg/L. Others report a 200-hr LC50 for steelhead fry of 1.3 ug/L in water of similar hardness, but a higher calcium content (2.3 mg/L calcium vs. 6.1 mg/L calcium).

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

To protect livestock/cattle use, cadmium levels should be less than 0.01 mg/L [671].

Canada's Remediation Criteria for cadmium for livestock watering is 20 ug/L (guideline is for total concentrations in an unfiltered sample) [656].

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

CAS 7440-43-9 CADMIUM (AS SOLUBLE SALT)

SPECIES	WATER CONCENTRATION (ppm)
Mouse (test species)	0.00000
Short-tailed Shrew	1.09300
Little Brown Bat	1.88900
White-footed Mouse	0.70600
Meadow Vole	1.23600
Cottontail Rabbit	0.58600
Mink	0.60700
Red Fox	0.43400
Whitetail Deer	0.24300

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 IRIS database information [893]:

Maximum Contaminant Level Goal

Value: 0.005 mg/L Status/Year: Final 1991 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 56 FR 3526 (01/30/91) [893].

Contact: Health and Ecological Criteria Division / (202)260-7571 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: Cadmium has been classed as a Category III contaminant with an MCLG of 0.005 mg/L based upon reports of renal toxicity in humans. The MCLG is based upon a DWEL of 0.018 mg/L and an assumed drinking water contribution (plus aquatic organisms) of 25 percent. An uncertainty factor of 10 was also applied. [893].

Maximum Contaminant Level (MCL)

Value: 0.005 mg/L Status/Year: Final 1991 Econ/Tech?: Yes, does consider economic or technical feasibility Reference: 56 FR 3526 (01/30/91) [893].

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

Discussion: EPA has promulgated an MCL equal to the established MCLG of 0.005 mg/L. [893].

Ambient Water Quality Criteria for Human Health [893]:

Water & Fish: 1E+1 ug/liter [893].

Older Values: Human Health Risk Level for Carcinogens (risk of one additional case in 1 million, 1E-06) (ug/L): Published Criteria for Water and Organisms: 10 [446]. Published Criteria for Water and Organisms: 10 ug/L (this value is based on the MCL; the toxicity-based value calculated from CWA 304(a) = 29) [689]. IRIS Recalculated (7/93) Criteria for Water and Organisms: 14 [689].

Fish Only: None [893].

Older Values: Human Health Risk Level for Carcinogens (risk of one additional case in 1 million, 1E-06) (ug/L): Published Criteria for Organisms Only: None [446,689]. Previous IRIS Recalculated (9/90) Criteria for Organisms Only: 170 ug/L [446]. Previous IRIS Recalculated (7/93) Criteria for Organisms Only: 84 ug/L [689].

Criteria Federal Register Notice Number: 50 FR 30787, see also: USEPA; Ambient Water Quality Criteria Doc: Cadmium (1985) EPA 440/5-84-032.

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

[893].

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

Discussion: The criteria is the same as the existing standard for drinking water. [893].

Other EPA National Benchmarks [893]:

Drinking Water Crit. Dose: 0.005 mg/kg-day;
RfD: 5E-4 mg/kg-day Confidence: High [893].

EPA 1995 Region 9 PRG Tap Water Preliminary Remediation Goal: 18 ug/L [868].

Other Drinking water benchmarks [859]:

The Maximum Acceptable Concentration (MAC) in drinking water for Ontario's Ministry of the Environment is 0.005 mg/L (5 ug/L).

The U.S. EPA lifetime health advisories for a 70-kg adult assuming, first, that 100% of a person's exposure to the substance is from drinking water, and second, that only 20% of a person's exposure to the substance is from drinking water, are 18.0 ug/L and 5.0 ug/L, respectively.

The U.S. EPA 1-day, 10-day, and 7-year health advisories for a 10-kg child consuming 1 L of water per day are 43.0 ug/L, 43.0 ug/L, and 5.0 ug/L, respectively.

The U.S. EPA 7-year health advisories for a 70-kg adult consuming 2 L of water per day is 18.0 ug/L.

The European Economic Community's Maximum Admissible Concentration (MADC) for cadmium is 5.0 ug/L.

The World Health Organization's Guideline Value (GV) for cadmium is 0.005 mg/L.

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

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

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

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

Camp host: 155 ug/L
Child Camper: 142 ug/L
Boater: 553 ug/L
Swimmer: 239 ug/L

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

Child resident (living on properties adjacent to BLM lands): 0.2 ug/L
Camp host: 2 ug/L
Child Camper: 5 ug/L
Worker: 4 ug/L
Surveyor: 39 ug/L

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

Elevated cadmium concentrations have been reported in lower trophic levels in acidified lakes [838]. This had led to speculation that piscivorous or predatory animals could be exposed to higher cadmium concentrations in acidified watersheds. Studies in the U.S., Canada, and Sweden report that lake cadmium concentrations were inversely correlated with lake pH. An inverse relationship between cadmium concentrations and lake pH has been observed for yellow perch, bluegill sunfish, suckers, and various invertebrate species [838].

Cadmium can enter surface waters from the natural sources and from a variety of manufacturing operations that involve either cadmium itself or zinc that contains a cadmium impurity. Cadmium can enter the water environment from the plating operations when spent plating solutions are discarded. The production of refined cadmium metal is a potential source of cadmium in nearby surface waters from ore tailings and washings (IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT, Multivolume work,.,p. V2 80, 1973) [940].

Total vs. dissolved water concentrations:

> 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):

No information found.

Sed.High (Sediment Concentrations Considered High):

Texas: The statewide 90th percentile value for this compound was 3.0 mg/kg dry weight [7].

Great Lakes Harbors, EPA 1977: Sediments having sediment concentrations higher than 6.0 mg/kg dry weight were classified as "heavily polluted [145]."

Illinois EPA, 1984: Sediments having sediment concentrations higher than 1.0 mg/kg dry weight were classified as "elevated" [145].

NOAA National Status and Trends Program (1984-1990) [698]: High concentration for cadmium in fine-grained sediment (n=233) = 1.2 ug/g dry weight at 4.6% TOC dry weight. The above concentration was adjusted for sediment grain-size in the following way: the raw concentrations were divided by the fraction of particles less than or equal to 64 um. "High" NOAA concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].

> NOTE: Fine-grained sediment would typically contain more cadmium than course-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more cadmium 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.

Cadmium was detected in 89% of urban-bay samples from the Puget Sound area. The mean concentration was 1.8 mg/kg dry weight (ppb), while the median concentration was 0.6 mg/kg (ppm) [852].

> NOTE: The above values are not normalized for total organic carbon (TOC) content.

Gradient Monitoring Levels: Cadmium showed a general tendency to increase from upstream to downstream in Trinity River sediments [201]. The same trend was shown in sediment samples in a 1977 study by the Texas Water Quality Board. Elevated concentrations of cadmium have been found in sediments from downstream of Dallas [42,74]. Sediments from Beltline Road (6.5 miles downstream of our site 11) were 12.0 mg/kg, the highest recorded in the State at that time [74]. The highest levels of cadmium (7.0 to 12.0 mg/kg) were found in sediment samples from sites 9 through 12 (using our site numbers), with much lower concentrations upstream [74]. Sediment concentrations of cadmium from polluted Trinity River sites exceeded the statewide 90th percentile level, 3.0 mg/kg, in at least 50% of the historical records from 1974 to 1985 [7]. Cadmium has also been reported to have been highly elevated in sediments as far south as highway 31 near Trinidad [91]. A cycle of biomobilization of sedimentary cadmium by algae, followed by movement of the algae downstream and return of the cadmium to the sediments when the algae dies, may play a role in moving cadmium downstream [95].

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of cadmium was 32.2 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985). The median for Cadmium was 8.1 ppm of the dry weight. The range for cadmium was 1.7-320 ppm of the dry weight [347].

Sed.Typical (Sediment Concentrations Considered Typical):

The International Joint Commission considered <0.6 mg/kg as a background sediment level [145]. The control site in one Great Lakes study had a sediment concentration of 0.32 mg/kg dry weight [145].

NOAA National Status and Trends Program (1984-1990) [698]: Geometric mean for cadmium in fine-grained sediment (n=233) = 0.48 ug/g dry weight at 1.4% TOC dry weight. The above concentration was adjusted for sediment grain-size in the following way: the raw concentrations were divided by the fraction of particles less than or equal to 64 um.

NOTE: Fine-grained sediment would typically contain more cadmium than course-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more cadmium 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.

Cadmium was detected in 96.8% of non-urban-bay samples from the Puget Sound area. The mean concentration was 0.9 mg/kg dry weight (ppb), while the median concentration was 0.28 mg/kg (ppm) [852].

NOTE: The above values are not normalized for total organic carbon (TOC) content.

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

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

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

CAS 7440-43-9, CADMIUM

LOWEST EFFECT LEVEL (ONTARIO MOE): 0.6
EFFECTS RANGE - LOW (NOAA): 1.2
EFFECTS RANGE - MEDIAN (NOAA): 9.6

Other Concern Levels for Cadmium Sediment Concentrations (Dry Weight):

Guidelines for the pollution classification of Great Lakes harbor sediments (1977): Guidelines have not been established for nonpolluted or moderately polluted but the guideline for heavily polluted water is greater than 75 ppm (dry weight) [347].

Wisconsin interim criteria for sediments from Great Lakes harbors for disposal in water (1985): Cadmium should not exceed 1.0 ppm (dry weight) [347].

EPA Region 6, 1973: The cadmium concentration proposed by EPA Region 6 as a guideline for determining acceptability of dredged sediment disposal was 2.0 mg/kg [143].

Ontario, 1978, 1986: The cadmium concentration proposed by the Ontario Ministry of the Environment as a threshold for evaluations of dredging projects was 1.0 mg/kg [145]. Ontario Ministry of the Environment guidelines for open lake disposal of sediments (1986): the guideline for cadmium is 1 ppm [347].

International Joint Commission, 1988: The IJC suggested sediment concentrations of cadmium not exceed background levels of 0.6 mg/kg [145].

AET 1988: The apparent effects threshold concentrations for cadmium in sediments proposed for Puget Sound ranged from 5.1 mg/kg dry weight (benthic species) to 9.6 mg/kg dry weight (microtox) [416].

> NOTE: Although the authors of the Puget Sound AETs have cautioned that Puget Sound AETs may not be appropriate for comparison with data from other

geographic areas, so few concern levels for this chemical have been published that the proposed Puget Sound concern level is included in this text as an item of interest.

NOAA 1995 Concern Levels for Coastal and Estuarine Environments: After studying its own data from the National Status and Trends Program as well as many literature references concerning different approaches to determining sediment criteria, NOAA suggested that the potential for biological effects of this contaminant sorbed to sediments was highest in sediments where its concentration exceeded the 9.6 ppm dry weight Effects Range-Median (ERM) concentration and was lowest in sediments where its concentration was less than the 1.2 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	6.6
ERL-ERM	36.6
>ERM	65.7

Ontario Ministry of the Environment Freshwater Sediment Guidelines, 1993: Lowest effect level: 0.6 mg/kg dry weight. Severe effect level: 10 mg/kg dry weight [761].

St. Lawrence Interim Freshwater Sediment Criteria, 1992: No effect: 0.2 mg/kg dry weight. Minimal effect: 0.9 mg/kg dry weight. Toxic effect: 3 mg/kg dry weight [761].

Environment Canada Interim Sediment Quality Assessment Values, 1994: Threshold Effect Level: 0.596 mg/kg dry weight. Probable Effect Level: 3.53 mg/kg dry weight [761].

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs.

Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

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

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

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

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

Deer/Mouse: 1 mg/kg
Rabbit: 3 mg/kg
Bighorn Sheep: 6 mg/kg
Whitetailed Deer: 2 mg/kg
Mule Deer: 2 mg/kg
Elk: 2 mg/kg
Mallard: 3 mg/kg
Canada Goose: 3 mg/kg
Trumpeter Swan: 3 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 needed [715]. Exceedances of the criteria should be interpreted as follows [715]:

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

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

Camp host: 155 mg/kg
Child Camper: 71 mg/kg
Boater: 553 mg/kg
Swimmer: 239 mg/kg

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

Acid volatile sulfides (AVS) have been proposed as a sediment normalization measure to help in data interpretation related to the sediment toxicity of metals and mixtures of metals. It has been proposed that the extent to which metals bind to sediments is related to the acid volatile sulfide concentrations. It has been shown that acid volatile sulfides is the sediment phase that determines the extent of cadmium toxicity in fresh water sediments (see abstract listed below). Our ability is to use acid volatile sulfide normalization of sediment toxicity is better for marine waters than for freshwaters.

In freshwater, use of AVS for data interpretation is still in the developmental stage, and usually requires that total organic carbon (TOC) also be measured; acid volatile sulfide normalization is thus far more useful for predicting no toxicity than in predicting exactly what the toxicity will be (Bill Brumbaugh, Columbia National Fisheries Contaminant Research Center, Fish and Wildlife Service, personal communication).

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).

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].

Relevant Abstract: Di Toro DM; Mahony JD; Hansen DJ; Scott KJ; Hicks MB; Mayr SM; Redmond MS AF, Environ. Eng. and Sci. Program, Manhattan Coll., Bronx, NY 10471, USA Toxicity of cadmium in sediments: The role of acid volatile sulfide. ENVIRON. TOXICOL. CHEM.; vol. 9, no. 12, pp. 1487-1502; 1990:

> The toxicity of chemicals in sediments is influenced by the extent that chemicals bind to the sediment. It is shown that acid volatile sulfide (AVS) is the sediment phase that determines the LC50 for cadmium in the marine sediments tested. Although it is well known that metals can form insoluble sulfides, it apparently has not been recognized that AVS is a reactive pool of solid phase sulfide that is available to bind with metals. Amphipod sediment toxicity tests were conducted in the laboratory and the observed amphipod LC50s on a normalized cadmium concentration basis, (Cd)/(AVS), is the same for sediments with over an order of magnitude difference in dry weight normalized cadmium LC50s.

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

Soil.Low (Soil Concentrations Considered Low):

The lowest average cadmium content is found in highly leached spodosols (0.37 ppm) [699].

Soil.High (Soil Concentrations Considered High):

The highest average cadmium content is found in organic soils (0.78 ppm) [699].

Cadmium in German Gulch (Upper Clark Fork Superfund Site Area, Montana) samples ranged from 1.3 to 5.1 ppm and averaged 3.0 ppm [699].

A detailed investigation of cadmium levels in a Montana valley contaminated with cadmium from a zinc smelter reported that upper-soil cadmium levels decreased from 27.3 ug/g at 1.5 miles distant from the smelter to 1.5 ug/g at 21.0 miles away [838].

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of cadmium was 32.2 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985). The median for Cadmium was 8.1 ppm of the dry weight. The range for cadmium was 1.7-320 ppm of the dry weight [347].

Soil.Typical (Soil Concentrations Considered Typical):

Level of cadmium in surface soils worldwide [855]: 0.1 -1.0 ug/g; mean 0.62 ug/g

Reported background levels of cadmium in uncontaminated soils of non-volcanic origin [379]: 0.010 to 1.0 ppm

EPA 1981: 0.06 mg/kg dry weight not considered elevated [83]. Igneous Rocks (Earth's Crust) Concentrations not Considered Elevated: EPA 1981: 0.2 mg/kg dry weight [83]. Another reference stated the national average concentration for cadmium in U.S. soils is 5 mg/kg [98].

Average soil concentrations of cadmium in the United States range between 0.005 and 2.4 ppm (Alloway, 1990) [699].

The calculated worldwide mean of cadmium in surface soils is 0.53 ppm (range 0.005-2.4 ppm) [699].

Western U.S. Soil Median Concentrations [715]: 0.32 mg/kg

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):

Proposals for Maximum Acceptable Concentrations (MAC) of Cadmium in Agricultural Soils as Given by Various Authors (ppm dry weight) [719]:

Other MAC levels: 3 ppm dry weight (Stuttgart, Germany), 3.5 ppm dry weight (London).

Proposal of European Economic Commission for MAC in soils treated with sewage sludge: 1 (3) ppm dry weight (London).

NOTE: The value in parentheses is a mandatory concentration.

Proposal of Ontario Ministry of Agriculture and Food for MAC in soils treated with sewage sludge: 1.6 ppm dry weight (published in Tokyo; work done for Ontario).

Cadmium: A facility or practice concerning application of solid waste to within one meter (three feet) of the surface of land used for the production of food-chain crops shall not exist or occur, unless in compliance with requirements given in 40 CFR 257.3-5, which limit cadmium content in the solid waste. /Cadmium containing solid waste/ (40 CFR 257.3-5, 7/1/88) [366,940].

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act (1982): background concentrations is soil or detection limits 1 ppm, moderate soil contamination 5 ppm, threshold values that require immediate cleanup 20 ppm [347].

Soil cleanup criteria for decommissioning industrial sites in Ontario (1987): Cadmium should not exceed 1-6 ppm for agricultural land, 4 ppm for residential/parkland, 8 ppm for commercial/industrial land [347].

Suggested cleanup guidelines for inorganic contaminants in acidic soils in Alberta (1987). Acceptable level of cadmium for acidic soils (pH<6.5) is 1.0 ppm [347].

Quebec soil contamination indicators that differ from those of the Netherlands (1987): Background concentrations in soil or detections limit of cadmium is 1.5 ppm, moderate soil contamination is 5 ppm, threshold value that requires immediate cleanup is 20 ppm [347].

Maximum cumulative addition of metals (kg/ha) from sewage sludge to Maryland agricultural soil (1986): For a soil with a cation exchange capacity (CEC) of <5 meq/100g cadmium should not be added at greater than 5 kg/ha. For a soil with a CEC of greater than 5 meq/100g cadmium addition should not exceed 10 kg/ha [347].

Maximum cumulative addition of metals (kg/ha) from sewage sludge to Massachusetts agricultural soil (1983): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100g addition of cadmium should not exceed 5 kg/ha. For a soil with a cation exchange capacity of greater than 5 meq/100g cadmium addition should not exceed 5 kg/ha [347].

Maximum cumulative addition of metals from sewage sludge that may be added to Minnesota soils used for growing food crops (1987): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100g cadmium should not be added at greater than 5 kg/ha, for a soil with a CEC between 5 and 15 cadmium should not be added at greater than 10 kg/ha, for a soil with a CEC of greater than 15 meq/100g cadmium should not be added at greater than 20 kg/ha [347]. These values are also the same for the maximum cumulative addition of metals (kg/ha) from sewage sludge recommended for privately owned Missouri (1988) and Oregon (1984) farmland [347].

Cumulative amounts of metals per hectare that may be added to New York State soils with sewage sludge (1988): For more productive agricultural soils it is 3.4 kg/ha and for less productive agricultural soils it is 4.5 kg/ha. For dedicated lands (forests) is 11 [347].

The maximum cumulative additions (kg/ha) of metals from sewage sludge that may be added to Vermont soils by soil texture (1984): For loamy sand it is 6 kg/ha, fine sandy loam is 11 kg/ha, and clay loam, clay or silty clay is 22 kg/ha [347].

The maximum cumulative addition (kg/ha) of cadmium from sewage sludge that my be added to Wisconsin soils (1985): With a pH less than 6.5 if the soil cation exchange capacity is less than 5 meq/100g cadmium should not be added at greater than 5 kg/ha. If the CEC is between 5 and 15 meq/100g cadmium should not be added at greater than 5 kg/ha. If the CEC is greater than 15 meq/100 g cadmium should not be added at greater than 5 kg/ha. For soils with a pH greater than 6.5 and a CEC less than 5 meq/100 g cadmium should not be added at greater than 5 kg/ha. For a soil with a CEC between 5 and 15 meq/100g cadmium should not be added at greater than 10 kg/ha. For a soil with a CEC of greater than 15 meq/100g cadmium should not be added at greater than 20 kg/ha [347].

Soil limit values for cadmium 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): 1-3 ppm [347].

The 1987 soil (clean up) criteria given by the New Jersey Department of Environmental Protection for cadmium: 3 mg/kg dry weight [347,386].

In 1981 the U.S. Environmental Protection Agency proposed 25 ppm as an upper limit for cadmium for sewage sludges suitable for land application [391].

Soil.Plants (Soil Concentrations vs. Plants):

Levels of cadmium (ppm dry weight) considered phytotoxic: 5 (Vienna), 3-5 (Warsaw), 3 (Warsaw), 8 (Ontario) [719].

Minimum soil concentration causing phytotoxicity: 3-5 ppm [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 in mg/kg (ppm) [651]:

> For CAS 7440-43-9, (Cadmium) the Soil Benchmark is 3 mg/kg.

In general, it has been found that for many soils, the concentration of cadmium in plants shows a positive correlation with the level of cadmium present in or added to the soil [748]. The relationship holds even at very low rates of cadmium addition to the soils. In terms of cadmium uptake, it thus appears that there is no known threshold for safe concentration of cadmium in the soil [748].

Soil pH is particularly important in determining the amount of cadmium taken up from the soils [748]. A reduction in pH often enhances the cadmium uptake by plants. Other physicochemical properties of soils that affect the uptake of cadmium by crops include 1) the oxidation-reduction potential of soils, 2) soil temperature, 3) clay content and cation exchange capacity, 4) concentrations of iron, manganese, and aluminum oxides and hydroxides, 5) presence of anions that can immobilize the cadmium, 6) organic matter concentration, and 7) interactive effects of zinc, copper, nickel manganese, and selenium [748].

In a village in Japan where the agricultural soil was contaminated by tailings from an old zinc mining operation the vegetables grown there showed cadmium concentrations that were about 15 times above the normal values [748].

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

A detailed investigation of cadmium levels in a Montana valley contaminated with cadmium from a zinc smelter reported that upper-soil cadmium levels decreased from 27.3 ug/g at 1.5 miles distant from the smelter to 1.5 ug/g at 21.0 miles away. About 99% of the cadmium present in the ecosystem was contained in the soil compartment, with decreasing amounts at higher trophic levels. The levels of cadmium in grasshoppers (1.0-2.3 ug/g) were two to three times the levels present in vegetation [838].

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

See Sed.Wildlife section above.

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 = 78 mg/kg for ingestion pathway [952].

SSL = 1800 mg/kg for inhalation pathway [952].

SSL = 0.4 to 8 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: 38 mg/kg wet wt.
Industrial Soil: 850 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:

6 mg/Kg dry weight [903].

Maximum Acceptable Concentration (MAC) trigger (concern) concentration of cadmium for domestic gardens and playing fields: 3-15 ppm dry weight (London) [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 needed [715]. Exceedances of the criteria should be interpreted as follows [715]:

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

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

Child resident (living on properties adjacent to BLM lands): 2 mg/kg
Camp host: 52 mg/kg
Child Camper: 36 mg/kg
ATV Driver: 726 mg/kg
Worker: 77 mg/kg
Surveyor: 774 mg/kg

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

Cadmium toxicity to plants is moderate [951].

Soils generally function as a major sink for most of the cadmium released into the terrestrial environment [748]. Soils which are located close to urban areas, major roadways, arable fields, or point sources (such as smelter, incinerators, and power plants) generally receive large inputs of pollutant cadmium. The technology for decontaminating such soil has yet to be developed [748].

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:

Cadmium is generally less toxic to plants than to consumers, thus cadmium accumulation in plants represents a potential pathway to herbivorous wildlife [699].

Aquatic macrophytes can accumulate cadmium and may act as a source of cadmium to grazing herbivores such as moose. This possible link stirred up concern about elevated levels of cadmium in moose tissues from acidified areas for human consumption [838].

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

Cadmium levels in filamentous algae (Cladophora glomerata) were 1.4 to 3.9 ug/g dry weight. Cadmium levels in macrophytes ranged from 0.1 to 16 ug/g dry weight from Ontario lakes of various cadmium contamination [838].

Plant tissue concentrations of cadmium at the Smelter Hill site (Upper Clark Fork Superfund Site Area, Montana) averaged 2.35 ppm. Nationwide levels of cadmium in plants are generally less than 1 ppm (Kabata-Pendias and Pendias, 1984 as cited in PTI, 1991a) [379,699]. Cadmium is generally less toxic to plants than to consumers, thus cadmium accumulation in plants represents a potential pathway to herbivorous wildlife [699].

See also [748] info in Soil.Plants section above.

Tis.Invertebrates:

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

Earthworms from a golf course which used composted sewage sludge contained 48 ppm dry wt. cadmium. When fed to quail as 50% of their diet, the quail accumulated 14-18 ppm dry weight in their kidneys, levels well above what would be expected in control quail [347].

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:

Studies report cadmium levels of 3.8 to 7.3 ug/g dry weight in cladoceran zooplankton from Lake Huron [838]. Benthic mollusks accumulated higher levels of cadmium in their hepatopancreas and digestive tract than in their exoskeleton, abdominal muscles, or viscera. Cadmium concentrations in mollusks in Ontario ranged from 1.0 to 51.3 ug/g dry weight. Cadmium concentrations in the amphipod Hyalella azteca ranged from 0.13 to 56.6 ug/g dry weight in 69 Ontario lakes. Tissue cadmium concentrations were positively correlated with aqueous cadmium levels and inversely related to water calcium and dissolved organic carbon levels [838].

Earthworms concentrate this metal more than most other metals relative to soil concentrations. Concentrations of cadmium as high as 100 ppm (dry weight, a hazardous level for wildlife that eat worms) were detected in earthworms from soil containing only 2 ppm cadmium [179].

The following information summarizes data gathered from the NOAA National Status and Trends (NS&T) Program for the year 1990 [697]:

> For cadmium in mussels and oysters combined (n=214), the Geometric Mean was 2.7 ug/g dry and the "high" concentration was 5.7 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):

Legal Limits for Concentrations in Fish and Fishery Products: The lowest legal limit was 0.0 mg/kg (Venezuela) [216,418]. Six countries have limits less than or equal to 0.5 mg/kg, but the U.S. apparently has no limit [216,418].

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

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

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

Child resident (living on properties adjacent to BLM lands): 78 ug/kg
Camp host: 161 ug/kg
Child Camper: 444 ug/kg

EPA Region 3 Risk Based Concentration (RBC) in fish Tissue: 0.68 mg/Kg [903].

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

No information found.

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

Cadmium concentrations in various freshwater fish species from Canada were generally less than 0.4 ug/g. Cadmium concentrations in edible salmonid tissue from Lake Ontario ranged from 0.04 to 0.21 ug/g dry weight [838].

Predator Protection Level (Tissue Concentrations): Cadmium whole-body levels above 0.5 mg/kg are considered to be harmful to fish and predators [20].

Edible Fish Tissue (Usually Fillet) Concentrations:
The highest concentrations of cadmium in 5 studies of edible fish tissues in several states was 5.34 mg/kg wet weight [57]. The highest level in all but one of these 5 studies was 1.70 mg/kg wet weight [57].

Mean NCBP Levels (Tissue Concentrations): The geometric mean of (wet-weight) whole-body concentrations of fish in national surveys (1976-1984) was 0.03 mg/kg cadmium [23,384].

Eisler suggested that cadmium residues in vertebrate kidney or liver that exceed 10 ppm (ug/g) fresh (wet) weight or 2 ppm (ug/g) whole body fresh (wet) weight should be viewed as evidence of probable cadmium contamination [379]. However, it is harder to find concern levels for muscle or fatty tissue samples. Residues of 200 ppm (ug/g) fresh (wet) weight kidney, or more than 5 ppm (ug/g) whole body fresh (wet) weight are probably life-threatening to the organism [379].

One author has stated that reproductive problems in fish may occur when tissue concentrations exceed 0.1 mg/kg [57], but it is not clear from the citation which kinds of tissues were meant. The same paper discussed both whole body and edible tissue data in a nearby section.

Tissue Concentrations in Texas: The geometric mean of whole-body cadmium concentrations in fish in a 1980-1981 national survey was 0.03 mg/kg [23], a level exceeded in 24 of 77 Trinity River samples. Included in this group were a large variety of fish, turtle, and clam species. However, since this group included a variety of non-fish samples, it is not directly comparable to the NCBP means for fish only. None of the samples above 0.03 mg/kg were from the control/reference site. A Trinity River (Texas) sample from a polluted site exceeded 0.5 ppm: a composite whole-body sample of mosquitofish was 0.71 mg/kg wet weight.

Gradient Monitoring Levels: Cadmium showed a general tendency to increase from upstream to downstream in Trinity River mosquitofish. The same trend was shown in sediment samples in a 1977 study by the Texas Water Quality Board. Elevated concentrations of cadmium have been found in sediments from downstream of Dallas [42,74]. Sediments from Beltline Road (6.5 miles downstream of our site 11) were 12.0 mg/kg, the highest recorded in the State at that time [74]. The highest levels of cadmium (7.0 to 12.0 mg/kg) were found in sediment samples from sites 9 through 12 (using our site numbers), with much lower concentrations upstream [74]. In Trinity River study, the two highest concentrations of cadmium in mosquitofish were both from suburban creek sites (sites 17 and 20) [201]. Cadmium was the only contaminant for which this was true.

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):

Predator Protection Level (Tissue Concentrations): Cadmium whole-body levels above 0.5 mg/kg are considered to be harmful to fish and predators [20].

Concentrations of cadmium as high as 100 ppm (dry weight, a hazardous level for wildlife that eat worms) were detected in earthworms from soil containing only 2 ppm cadmium [179].

Dietary studies (using oral doses high enough to cause relatively quick toxicity) feeding cadmium chloride to a bird species, place it in the "slightly toxic" category for quick (acute) toxicity [185]. However, much lower levels may be a problem for long-term (chronic) exposure.

In rats, oral doses of 40 mg cadmium/kg body weight per day as cadmium chloride given on days 6-19 of gestation increased fetal resorption and caused skeletal, kidney, and heart abnormalities in fetuses, stillborn, and offspring. The incidence and intensity of skeletal defects increased with cadmium dosage, but the renal and cardiac abnormalities were not dose-related. /Inorganic cadmium/ [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 83].

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 7440-43-9, CADMIUM (AS SOLUBLE SALT)

SPECIES	NOAEL (mg/kg/day)	FOOD CONCENTRATION (ppm)
Mouse (test species)	0.19130	0.00000
Short-tailed Shrew	0.24000	0.40100
Little Brown Bat	0.30200	0.90700
White-footed Mouse	0.21200	1.37100
Meadow Vole	0.16900	1.48400
Cottontail Rabbit	0.05700	0.28700
Mink	0.06000	0.43900
Red Fox	0.03700	0.36600
Whitetail Deer	0.01600	0.51600

> 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).

Apparently protected from the deleterious effects of high metal body burdens by metallothioneins, birds and mammals are comparatively resistant to the biocidal properties of cadmium [379]. For example, adult drake mallards fed up to 200 ppm cadmium in the diet for 90 days all survived with no loss of body weight (kidney cadmium exceeded 130 ppm fresh (wet) weight under this regimen). Ducks contained the highest levels of metallothioneins of all groups examined. The lowest oral dose producing death was 250 mg/kg body weight of cadmium (as fluoroborate) in rats, and 150 mg/kg body weight of cadmium (as cadmium fluoride) in guinea pigs [379].

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

It has been suggested that cadmium concentrations in vertebrate kidney and liver exceeding 10 ug/g wet weight may be viewed as evidence of cadmium contamination, and residues exceeding 200 ug/g may be viewed as life threatening [379,838]. However, significant accumulation of cadmium has been demonstrated in wildlife, particularly birds, remote from point sources of contamination. For example, cadmium levels in several species of seabirds from the south Atlantic Ocean contained up to 112 ug/g wet weight in their kidneys [838].

Eisler suggested that cadmium residues in vertebrate kidney or liver that exceed 10 ppm (ug/g) fresh (wet) weight or 2 ppm (ug/g) whole body fresh (wet) weight should be viewed as evidence of probable cadmium contamination [379]. However, it is harder to find concern levels for muscle or fatty tissue samples. Residues of 200 ppm (ug/g) fresh (wet) weight kidney, or more than 5 ppm (ug/g) whole body fresh (wet) weight are probably life-threatening to the organism [379].

In one study where the soil contained 6.0 ppm cadmium, earth worms contained 79 ppm dry weight cadmium, moles had 294 ppm dry weight in their kidneys and 227 ppm in their livers [347].

In another study, earthworms from a golf course which used composted sewage sludge contained 48 ppm dry wt. cadmium. When fed to quail as 50% of their diet, the quail accumulated 14-18 ppm dry weight in their kidneys, levels well above what would be expected in control quail [347].

Earthworms concentrate this metal more than most other metals relative to soil concentrations. This is one potential hazard of birds feeding on sewage sludge amended soils [179].

A Trinity River (Texas) sample which exceeded 0.5 ppm included a fatty tissue sample (0.65 mg/kg wwt) from a composite sample of three Mississippi map turtles [201].

The average kidney cadmium level in deer collected less than 8 km from a Pennsylvania zinc smelter was 310 ug/g dry weight compared with 15.5 ug/g dry weight in deer collected more than 100 km from the smelter. One deer with a renal cadmium level of 600 ug/g dry weight had lesions in joints, similar to those observed in nearby horses diagnosed as suffering from zinc poisoning [838].

Studies report cadmium-induced lesions in tissues of the common shrew trapped near a copper/cadmium alloying factory. Tissue cadmium concentrations ranging from 300 to 1000 ug/g dry weight in liver, and 150 to 560 ug/g dry weight in kidney are among the highest recorded in terrestrial wildlife [838].

For information on alligator residues of cadmium, see: Delany, M.F., J.U. Bell, and S.F. Sundlof.

1988. Concentrations of contaminants in muscle of the American alligator in Florida. J. Wildl. Dis. 24:62-66. Florida Game and Fresh Water Fish Comm., Wild. Res. Lab., 4005 South Main St., Gainesville, FL 32601.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found.

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):

Crit. Dose: 0.005 mg/kg-day [Study 1 NOAEL] UF: 10 MF: 1 [893].

RfD: 5E-4 mg/kg-day Confidence: High [893].

EPA Region 3 Risk Based Concentration (RBC) in fish Tissue: 0.68 mg/Kg [903].

See also Tis.Fish, A) section above.

> NOTE: Because of the highly selected accumulation of cadmium in the visceral organs (that is, internal organs), the animal body, in general, tends to serve as a filter for cadmium transfer to human foods [748]. With the exception of liver, humans tend to eat more muscle tissues than visceral organs.

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

Information from the HSDB [366]:

To assess the pathophysiologic significance of increased body burdens of cadmium (Cd), cross-sectional evaluation of renal function and calcium, phosphorus and vitamin D metabolism was carried out in 38 industrial workers exposed to Cd for 11-37 yr. Average airborne concentrations of Cd ranged from 5 - 229 ug/cu m. Mean kidney Cd burden was 7.4 +/- 4.4 mg in nonsmokers and 12.3 +/- 7.2 mg for smokers. Mean liver Cd in nonsmokers was 4.5 +/-2.6 ug/g and 7.9 +/-4.9 ug/g in smokers. Liver or kidney Cd burden was considered elevated in 31% of the workers. Creatinine clearance was normal in all workers. Maximal urinary concentrating ability was abnormal in a significant fraction (52%) of the men. [Greenberg A et al; Arch Environ Health 41 (2): 69-76 (1986)].

In man/ about half of total body burden is found in liver & kidneys. Cadmium in these organs is mainly bound to a low molecular weight protein, in form of a metallothionein [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 90 (1973)].

Tis.Misc. (Other Tissue Information):

Elevated cadmium concentrations have been reported in lower trophic levels in acidified lakes [838]. This had led to speculation that piscivorous or predatory animals could be exposed to higher cadmium concentrations in acidified watersheds. Studies in the U.S., Canada, and Sweden report that lake cadmium concentrations were inversely correlated with lake pH. An inverse relationship between cadmium concentrations and lake pH has been observed for yellow perch, bluegill sunfish, suckers, and various invertebrate species [838].

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

Preliminary data suggests the potential for bioaccumulation or bioconcentration of cadmium is high for the following biota: mammals, birds, fish, mosses, lichens, algae, mollusks, crustacea, lower animals, and higher plants [83]. The best potential mediums for biological monitoring appear to include animal hair, clams, algae, mosses, lichens, and higher plants [83]. In fish, cadmium accumulates in the gill, liver, and kidney [488,838]. Irwin found mosquitofish to be acceptable for gradient monitoring of cadmium [201].

Cadmium accumulates in microorganisms, plant tissue, and animal tissue. Median bioconcentration factors for cadmium in macrophytes are less than 50 times, and generally less than 100 times for fish. Whole-body bioconcentration factors for food-exposed rainbow trout and whitefish are less than one. Bioconcentration factors of 900 to 4000 are reported in some mollusks [838,849]. It is generally reported that although cadmium accumulates in freshwater organisms, it does not biomagnify in the food chain [838].

Because of the highly selected accumulation of cadmium in the visceral organs (that is, internal organs), the animal body, in general, tends to serve as a filter for cadmium transfer to human foods [748]. With the exception of liver, humans tend to eat more muscle tissues than visceral organs.

Cadmium is sequestered in metallothionein complexes [838]. The metallothionein compounds have a high proportion of sulfur-containing amino acids that bind with cadmium such that it becomes unavailable for interaction with intracellular receptor sites. Tissue accumulation and distribution of cadmium is dependent upon the route of exposure (food or water vector) [838].

For information on cadmium in sediments vs. AVS and SEM, see Sed.Misc. section.

Earthworms versus Cadmium:

> Earthworms concentrate this metal more than most other metals relative to soil concentrations. This is one potential hazard of birds feeding on sewage sludge amended soils [179]. Concentrations of cadmium as high as 100 ppm (dry weight, a hazardous level for wildlife that eat worms) were detected in earthworms from soil containing only 2 ppm cadmium [179].
>
> In one study where the soil contained 6.0 ppm cadmium, earth worms contained 79 ppm dry weight cadmium, moles had 294 ppm dry weight in their kidneys and 227 ppm in their livers [347].
>
> In another study, earthworms from a golf course which used composted sewage sludge contained 48 ppm dry wt. cadmium. When fed to quail as 50% of their diet, the quail accumulated 14-18 ppm dry weight in their kidneys, levels well above what would be expected in control quail [347].
>
> The concentration factor for cadmium in earthworms relative to soils containing a few ppm is 21; however, it takes a while for the cadmium to build up in the worms, so short-term experiments may give misleading results [347].

Interactions:

The mobility and bioavailability of cadmium in aquatic environments is enhanced under conditions of low pH, low hardness, low suspended matter levels, high redox potential, and low salinity [907]. Some recent research (1990) has focused on the tendency of low-alkalinity (less than 50 ueq/L) waters to have a relatively high potential for acid deposition effects and increased bioaccumulation of cadmium in fish [383]. See also the Bio.Detail section below.

For information on cadmium in sediments and bioconcentratrion vs. AVS and SEM, see Sed.Misc. section.

Water hardness is governed by calcium and magnesium salts combined with bicarbonate and carbonate. Cadmium toxicity is moderated at increasing water hardness by either (1) complexation with carbonate, or (2) competition with calcium ions [838]. Low water pH also reduced cadmium toxicity to algae and to fish in some studies. It is suggested that the reduced toxicity is due to competition between H+ ions and free metal cations for transport mechanisms or cellular binding sites [838].

Studies suggest that humic acid or other complexing materials have a varying effect on cadmium toxicity [838]. The presence of complexing materials in water decreased cadmium uptake and toxicity in fish, but had mixed effects on toxicity to invertebrates. Monthly tests demonstrated that cadmium toxicity in river water varied by a factor of three or more over the year due to fluctuating levels of suspended solids [838].

Soil pH is particularly important in determining the amount of cadmium taken up from the soils [748]. A reduction in pH often enhances the cadmium uptake by plants. Other physicochemical properties of soils that affect the uptake of cadmium by crops include 1) the oxidation-reduction potential of soils, 2) soil temperature, 3) clay content and cation exchange capacity, 4) concentrations of iron, manganese, and aluminum oxides and hydroxides, 5) presence of anions that can immobilize the cadmium, 6) organic matter concentration, and 7) interactive effects of zinc, copper, nickel manganese, and selenium [748].

Female Swiss mice were exposed to cadmium in the drinking water at concentrations ranging from 0 to 50 ppm for 105 or 280 day time periods. In the 105 day study, the effect of cadmium on urethan induced pulmonary adenoma formation was evaluated. Urethan induced sleeping times observed following ip injection of urethan after 3 weeks of cadmium exposure were not affected by cadmium indicating that chronic cadmium exposure did not alter the elimination of urethan. Pulmonary adenoma formation which was evaluated 84 days later was not affected by cadmium. The size and number of tumors remained unchanged. Immunosuppressive actions of cadmium do not influence urethan induced adenoma formation. In the 280 day study the effects of cadmium on the incidence of spontaneous murine lymphocytic leukemia was evaluated. Mice exposed to 10 or 50 ppm cadmium experienced 33% more deaths from the virus. The average time till death was unaffected. Immunosuppressive effects of cadmium impair immunosurveillance mechanisms that control expression of the murine lymphocytic leukemia virus. (Blakely BR; Appl Toxicol 6, 6: 425-9, 1986) [366].

Cadmium and zinc are often found together (see Uses/Sources section).

Information on cadmium + zinc from 1994 National Society of Risk Assessment Annual Meeting Paper Entitled "An Evaluation of Potential Interactions of Zinc and Cadmium at a Former Zinc Smelter Site." by authors G. Evans, R. A. Schoof and L. Keill, PTI Environmental Services, Bellevue, WA:

> Extensive literature is available regarding the protective (or antagonistic) effects of zinc on cadmium toxicity. Simultaneous administration of zinc with cadmium has been found to protect against several aspects of cadmium toxicity, including proteinuria, the critical effect used as the basis for the cadmium oral reference doses (RfDs). The potential for interactions between cadmium and zinc is of particular significance at sites where increased environmental concentrations of zinc are found in conjunction with increased concentrations of cadmium...Animal studies provide strong evidence that potential antagonistic interactions between zinc and cadmium at the site may protect against the toxic effects of cadmium. However, available data from studies on various human populations supporting the derivation of the cadmium

RfDs appear insufficient to determine the extent to which antagonism of cadmium toxicity by zinc may have occurred in these populations. Consequently, it was concluded that although zinc exposures at the site may be protective of potential cadmium toxicity, there are currently insufficient data to support any quantitative change in the assessment of cadmium toxicity at the site.

Uses/Sources:

Cadmium has been used in preparation of embalming fluids [490]. Thus, like arsenic, it is one contaminant to look for around old cemeteries (see arsenic entry). It is also used in engraving [490].

Cadmium is used in metal plating and in batteries [335]. Air pollution sources of cadmium include smelters, incinerators, oil furnaces, and coal combustion. About 75% of all cadmium produced is used for cadmium plating of easily corroded metals such as iron and steel [333]. Metal platers, scrap yards, batteries, television tubes, solar cells, fungicides, and various industrial discharges constitute additional sources [57]. Because of its low melting point, cadmium is used in special alloys such as aluminum solder (40% cadmium, 50% lead, 10% tin); Wood's metal (50% bismuth, 25% lead, 15% cadmium, 10% tin), which has a melting point of 70 deg C; and related alloys that are used, for example, in sprinkler installations and other fire-protection systems [333]. In some localities, significant amounts of cadmium are also present in sewage sludges [61,94] and in leachates from municipal landfills [46,80].

Cadmium is also used in nickel-cadmium batteries, to absorb neutrons in the control rods and shielding of nuclear reactors, and in the manufacture of artists' pigments, automobile enamels, vinyl plastics, and phosphors for color television tubes [333].

Cadmium compounds (the metal does not occur naturally in the free state) are almost always found together with zinc compounds, so that the two metals are always mined together [333].

Plants take up cadmium from soil, groundwater, sewage sludge, biocides, and air pollution [83]. Animals take up cadmium from drugs, biocides, industrial sources, contaminated water, and contaminated food [83].

Major Uses [940]:

1. In electroplating of automotive, aircraft & electronic parts; marine equipment & industrial machinery; in prepn of cadmium sulfides, cadmium selenides & mixt containing these salts for use as pigments (incl phosphors) [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V11 44 (1976)].

2. As soft solder & solder for aluminum; deoxidizer in nickel

plating; process engraving; photometry of uv sun-rays; in electrodes for cadmium vapor lamps, photoelectric cells [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 223].

3. In fire protection systems, machinery enamels, baking enamels; weston standard cell; photography & lithography; mfr fungicide [Sax, N.I. and R.J. Lewis, Sr., eds.,. Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 196].

4. Plating & coating agent-eg, for transportation equipment [SRI].

5. Component of batteries-eg, nickel-cadmium batteries [SRI].

6. Chem int for plastic stabilizers-eg, cadmium stearate [SRI].

7. Component of alloys-eg, for bearings & control rods [SRI].

8. Analytical reagent-eg, for determination of nitrate [SRI].

9. Chem int for other cadmium cmpds-eg, cadmium chloride [SRI].

10. A constituent of easily fusible alloys, eg, lichtenberg's, abel's, lipowitz', newton's, and wood's metal. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 223].

11. In low-melting alloys. [ITII. Toxic and Hazarous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 95].

12. In brazing alloys. [ITII. Toxic and Hazarous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 95].

13. In solar ... batteries. [ITII. Toxic and Hazarous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 95].

14. In television phosphors. [ITII. Toxic and Hazarous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 95].

15. Neutron absorber in nuclear reactors. [Sittig, M. Handbook of Toxic And Hazardous Chemicals. Park Ridge, NJ: Noyes Data Corporation, 1981. 119].

16. Stabilizer for polyvinyl chloride. [Sittig, M. Handbook of Toxic And Hazardous Chemicals. Park Ridge, NJ: Noyes Data Corporation, 1981. 119].

17. Amalgam in dentistry. [Sittig, M. Handbook of Toxic And Hazardous Chemicals. Park Ridge, NJ: Noyes Data Corporation, 1981. 119].

18. Charging Jones reactors. [Sittig, M. Handbook of Toxic And Hazardous Chemicals. Park Ridge, NJ: Noyes Data Corporation, 1981. 119].

Natural Sources [940]:

1. Coal and other fossil fuels contain cadmium and their combustion releases the element into the environment. [Gilman, A.G., L.S.Goodman, and A. Gilman. (eds.). Goodman and Gilman's The Pharmacological Basis of Therapeutics. 7th ed. New York: Macmillan Publishing Co., Inc., 1985. 1617].

2. Occurs in a greenockite (cadmium sulfide) ore containing zinc sulfide also with lead and copper ores containing zinc. /Found/ in Canada, central and western USA, Peru, Australia, Mexico and Zaire. [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 196].

3. The principal cadmium-bearing mineral in primary deposits is sphalerite which also contains zinc. [Nat'l Research Council Canada; Cadmium p.16 (1979) NRCC No. 16743].

4. Among sedimentry rock types, the carbonaceous shales, formed under the reducing conditions, contain the most cadmium. [Nat'l Research Council Canada; Cadmium p.16 (1979) NRCC No.16743].

5. Cadmium content: Peat: <1-3 ppm based on 10 samples; Coal: <1-20 ppm based on 12 samples; bitumens, solid hydrocarbons, asphalts <1-3 ppm based on 6 samples. [Nat'l Research Council Canada; Cadmium p.30 (1979) NRCC No.16743].

6. Cadmium concentrations in: phosphatic rock: up to 100 mg/kg; igneous rock: 0.001 mg/kg. [Korte F; Ecotoxicol Environ Safety 7 (1): 3-8 (1983)].

7. Volcanic action is considered to be the major natural source of cadmium. This is related to the very large quantities of particulate matter emitted, together with high enrichment of cadmium in volcanic aerosols. An investigation into trace element emissions from Mount Etna in Sicily estimated that 2.8 x 10-2 tons/day, or about 10 tons/year of cadmium was discharged into the atmosphere. [Baut-Menard P, Arnold M; Geophys Res Lett 5: 245-248 (1978)].

8. Cadmium content /in/: sphalerite: 0.0001-2%; greenockite: 77.8%; hawleyite: 77.8%; chalcopyrite: < 0.4-110 ppm; marcasite: <0.3-<50 ppm; arsenopyrite: < 5 ppm; galena: < 10-3000 ppm; pyrite: < 0.06-42 ppm; pyrrhotite: trace;

tetrahedrite: 80-2000 ppm; magnetite: 0-0.31 ppm; cadmium oxide: 87.5%; limonite: <5-1000 ppm; wad and manganese oxides: <10-1000 ppm; anglesite: 120- >1000 ppm; barite: < 0.2 ppm; anhydrite and gypsum: < 0.2 ppm; calcite: < 1-23 ppm; smithsonite: 0.1-2.35%; otavite: 65.18%; pyromorphite: < 1-8 ppm; scorodite: <1-5.8 ppm; beudantite: 100-1000 ppm; apatite: 0.14-0.15 ppm; bindheimite: 100-1000 ppm; silicates: 0.03-2.8 ppm. [Nat'l Research Council Canada; Cadmium p.17 (1979) NRCC No.16743].

Artificial Sources [940]:

1. Liberation during smelting and refining of ores where it is a by-product of zinc, lead and copper-bearing ores. Liberation during recovery of metal by processing scrap; during melting and pouring of cadmium metal; during casting of alloys for cadmium-copper, cadmium-lead, cadmium-bismuth, cadmium-silver, cadmium-nickel, cadmium-lead-silver, cadmium-lead-silver-nickel, cadmium-lead-bismuth-tin, and cadmium-gold products used for coating telephone cables, trolley wires, welding, electrodes, automatic sprinkling systems, steam boilers, fire alarms, high pressure/temperature bearings, starting switches, aircraft relays, light duty circuit breakers, low temperature solder, and jewlery. Liberation during fabrication of metal, alloys, or plated steel. Liberation during casting and use of solders; during melting of cadmium ingots for paint and pigment manufacture used for coloring of plastics and ceramic glazes, electroplating, and in chemical synthesis. Liberation during coating on metals by hot dipping or spraying. Liberation during manufacture of nickel-cadmium batteries for use in radio-portable telephones, convenience appliances, and vented cells used in airplanes, helicopters, and stand-by power and lighting. /Cadmium, cadmium oxide/ [Mackison, F. W., R. S. Stricoff, and L. J. Partridge, Jr. (eds.). NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) PublicationNo. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981. 3].

2. All of the cadmium and/or its salts ... Used as stabilizers and pigments in plastics could enter the environment, a process particularly facilitated by incineration. Thus, disposal of plastics could contribute to pollution by cadmium. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V11 50 (1976)].

3. Ceramic artists can be exposed to many hazardous materials, generally related to dry clays, glazes and kiln use. Glazes can contain lead, antimony, arsenic, barium, beryllium, boron, chromium, cobalt, cadmium, copper, vanadium and other materials which all have potential toxic effects. [Hart C; J Environ Health 49 (5): 282-86 (1987)].

4. Forms readily from contact of cadmium vapor with air ... Found where cadmium is present in emissions from thermal processes / [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V2 82 (1973)].

Forms/Preparations/Formulations:

Cadmium forms many compounds in nature, such as:

Water-soluble compounds [907]:

Cadmium chloride
Cadmium bromide
Cadmium iodide
Cadmium nitrate
Cadmium sulfate

Water-insoluble compounds [907]:

Cadmium oxide
Cadmium sulfide
Cadmium carbonate
Cadmium orthophosphate
Cadmium fluoride

Radionuclides:

The symbol for Cadmium-109 is 109Cd, the atomic number is 48, the half-life is 462 days, and X-ray emission is the major form of decay [674].

The symbol for Cadmium-113m is 113mCd, the atomic number is 48, the half-life is 13.7 years, and beta emission is the major form of decay [674].

The symbol for Cadmium-115m is 115mCd, the atomic number is 48, the half-life is 44.6 days, and beta emission is the major form of decay [674].

The symbol for Cadmium-115 is 115Cd, the atomic number is 48, the half-life is 54 hours, and beta emission is the major form of decay [674].

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

Melting point: 321 degrees C [907,908,940].

Boiling point: 767 degrees C [908].
Boiling Point [940]:

760... 5 DEG C [The Merck Index. 10th ed. Rahway, New

Jersey: Merck Co., Inc., 1983]. 223:

Density: 8.65 g/cm3 at 20 degrees C [907].
Density/Specific Gravity [940]:

8.65 AT 25 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 223].

Solubility: Insoluble (sic) in water [849,908,940].

NOTE: Hardly anything is totally insoluble, just relatively insoluble (Roy Irwin, National Park Service, personal commuication, 1996).

Vapor pressure: 1 mmHg at 394 degrees C [849,908,940].

Molecular weight: 112.4 g/mol [907,908].

Color:

Blue-white [907,908].
Silver-white, blue-tinged, lustrous metal; distorted hexagonal closed-packed structure [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 223 [940].

Other Chemical/Physical Properties [940]:

1. MALLEABLE [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-78].

2. Heat capacity: 6.22 Cal/mole-deg at 25 deg c & constant pressure; readily cut with knife [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 223].

3. Tarnishes in moist air. [ITII. Toxic and Hazarous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 95].

4. Cadmium becomes brittle at 80 deg C. [ITII. Toxic and Hazarous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 95].

5. Eight stable isotopes of cadmium (Cd) are known in nature with conventional abundances as follows: (106)Cd: 1.21%; (108)Cd: 0.88%; (110)Cd: 12.39%; (111)Cd: 12.75%; (112)Cd: 24.07%, (113)Cd: 12.26%; (114)Cd: 28.86%; (116)Cd: 7.58%. [Nat'l Research Council Canada; Cadmium p.15 (1979) NRCC No.16743].

6. The electrical conductivity of cadmium is less than that of silver or copper, but greater than that of iron.

[Chizhikov DM; Cadmium (1966) as cited in NIOSH; Criteria Document: Cadmium p.7 (1976) DHEW Pub. NIOSH 76-192].

7. Cadmium (Cd) has two radioisotopes: (109)Cd and (115)Cd. [Mennear JH; Cadmium Toxicity p.1 (1979)].

8. SOL IN ACID, AMMONIUM NITRATE & HOT SULFURIC ACID [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-78

Odor [940]:

1. Odorless [Mackison, F. W., R. S. Stricoff, and L. J. Partridge, Jr. (eds.). NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) PublicationNo. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981. 1].

Corrosivity [940]:

1. Highly corrosion resistant [Sittig, M. Handbook of Toxic And Hazardous Chemicals. Park Ridge, NJ: Noyes Data Corporation, 1981. 119].

Spectral Properties [940]:

1. INDEX OF REFRACTION: 1.8 AT 578 NM & 20 DEG C/D [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V11 41 (1976)].

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

For information on cadmium in sediments and bioconcentratrion vs. AVS and SEM, see Sed.Misc. section.

Volatilization from Water/Soil [940]:

Cadmium can enter the air from natural sources. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V2 79 (1973)].

Biological Half-Life [940]:

An accumulation of cadmium occurs in many tissues and particularly long half-times, 10-30 years, have been reported for muscles, kidneys and 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 130].

Absorption, Distribution and Excretion [366]:

Cadmium is poorly absorbed from the gastrointestinal tract ... Absorption from the respiratory tract appears to be more complete; cigarette smokers may absorb 10-40% of inhaled cadmium. After absorption, cadmium is transported in blood, bound mainly to blood cells and albumin. After distribution, approx 50% of the total body burden is found in the liver and kidney. [Gilman, A.G., L.S.Goodman, and A. Gilman. (eds.). Goodman and Gilman's The Pharmacological Basis of Therapeutics. 7th ed. New York: Macmillan Publishing Co., Inc., 1985. 1618].

In the blood, a small-molecular weight plasma protein known as metallothionein binds cadmium. The elimination half-life of cadmium is long (16-33 yr) ... [Ellenhorn, M.J. and D.G. Barceloux. Medical Toxicology - Diagnosis and Treatment of Human Poisoning. New York, NY: Elsevier Science Publishing Co., Inc. 1988. 1018].

When exposure is excessive, the concentration of of cadmium in liver may be up to 100 times greater than normal. In many cases kidney concentrtions are very high, but when kidney damage has occurred ... Excretion incr considerably. This explains fact that in most severely poisoned workers ... Kidney levels, in contrast to liver ... Are low ... /Cadmium/ [Friberg, L., G.R. Nordberg, and V.B. Vouk. Handbook on the Toxicology of Metals. New York: Elsevier North Holland, 1979. 361].

Irrespective of mode of admin, cadmium crosses placental barrier in pregnant rats & hamsters, as shown by detectable amt in liver, brain & digestive tract of newborn. More than 2.5 Times the amt was found in livers of ... Test animals ... Than in control ... However, there is efficient placental barrier against cd in goats. [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 78].

Blood cadmium equilibrates with any given level of exposure within a year, while total amt in body keeps accum over a period of decades. Much the same situation has been noted in ... Urinary excretion of cadmium. [Doull, J., C.D. Klaassen, and M. D. Amdur (eds.). Casarett and Doull's Toxicology. 2nd ed. New York: Macmillan Publishing Co., 1980. 431].

Significance of inhalation exposure depends on concn, particle size, & solubility of particulate matter, & physiologic parameters such as rate & depth of resp. [Casarett, L.J., and J. Doull. Toxicology: The Basic Science of Poisons. New York: MacMillan Publishing Co., 1975. 469].

About 5% of cadmium ingested by human ... Is absorbed, but calcium and iron deficiency may incr this amount. Portion of inhaled cadmium absorbed is dependent on particle size & solubility. Absorbed cadmium is mainly stored in kidneys & liver. Excretion is slow, less than 0.01% Of body burden/day. [Friberg, L., G.R. Nordberg, and V.B. Vouk. Handbook on the Toxicology of Metals. New York: Elsevier North Holland, 1979. 355].

When renal damage has occurred, cadmium excretion by urine incr dramatically ... [Friberg, L., G.R. Nordberg, and V.B. Vouk. Handbook on the Toxicology of Metals. New York: Elsevier North Holland, 1979. 363].

In many species, including mice, rats, guinea pigs, rabbits, dogs & monkeys, about 10-40% of cadmium is retained after inhalation of cadmium cmpd. ... Studies in mice indicate that less than 10% of oral dose is absorbed ... [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 87 (1973)].

(115)Cadmium was found to accumulate selectively in rat kidney cortex. (109)Cadmium given sc to rats immediately appeared in blood plasma & then disappeared rapidly; after 6 days only 2% of dose was excreted in feces. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 87 (1973)].

Excretion via feces of normal humans is about 30-50 ug/day. Retention of ingested cadmium varied between 4.7-7% In five adult men. Only very small proportion of daily absorbed dose will be excreted ... Normal urinary excretion in humans ... 1-2 UG PER DAY. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 89 (1973)].

In mammals, cadmium will accumulate especially in liver & kidneys ... Studies in mice using aerosols of cadmium cmpd showed that particles of less than 2 microns were found in lungs & were also absorbed & concentrated in kidneys. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 87 (1973)].

After a yr of feeding 1 ppm cadmium (Cd) (as cadmium sulfate or cd contained in roll shell liver) in calcium-deficient diet of female rats, accum rate in liver & kidney was 0.33-0.48%, Whereas that of water-sol cd compd & cd fed as cd-polluted rice was 0.43-0.57%. [Sakamoto M; Juzen Igakkai Zasshi 83 (4): 533 (1974)].

Cadmium (Cd) concn in blood & urine of exposed & non-exposed workers was measured. Significant pos correlation observed. Concn in blood related to environ cd over 30 mug/cu m of exposure. Over 6 mo exposure to same level suddenly incr cd-urine excretion. [kono K ET AL; Proc Int Congr Occup Health 19th 1 (Chem Hazards): 207 (1980)].

Absorption of cadmium from soils by rice plants incr with incr solubility of cadmium cmpd, in order of: cadmium chloride being more sol than cadmium nitrate followed by cadmium oxide, cadmium carbonate, metallic cadmium, cadmium hydroxide, cadmium phosphate, cadmium sulfate. Calcium silicate plus phosphate prevented cadmium absorption. [Ueta H et al; Tottori-ken Nogyo Kenkyu Hokoku 13: 17 (1973)].

Cadmium accumulates in the liver and kidneys, perhaps because these two organs contain low molecular weight (about 10,000 daltons) proteins called metallothionein. [Gosselin, R.E., R.P. Smith, H.C. Hodge. Clinical Toxicology of Commercial Products. 5th ed. Baltimore: Williams and Wilkins, 1984.,p. III-78].

The absorption of cadmium cmpd through skin is negligible, the main routes of exposure for humans being via respiration and ingestion. Between 10 and 50% of inhaled cadmium will be absorbed, the absorption being greater for small particles and fumes than for large particle dust. In humans, about 5% of ingested cadmium is absorbed. A low intake of calcium or iron increases absorption. In individuals with iron deficiency, the gastrointestinal absorption rate may be as high as 20%. [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. VII-130].

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% 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 (Cd), iron (Fe), methylmecury (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% eliminated on the first day. Cu, Tl, Pb, and Zn were excreted at a slower rate, with 30.6 to 38.3% 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% 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)].

Baseline data on Cd 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 Cd concentrations were measured by flame absorption spectrometry. On a wet basis, the mean Cd concentration in muscle, liver, kidneys, and the whole body of fetuses (gestation age 0.3-0.7 yr, N= 13) was <1.0 ng/g; in fawns (age 0.0-0.5 yr, N= 12) was 18, 29, 60, and 22 ng/g, respectively; in yearlings (age 0.5-2.5 yr, N= 6)was 9, 51, 60, and 31 ng/g, respectively; in adults (age 2.5 to 10 yr, N= 42) was 16, 130, 950, and 42 ng/g, respectively; and in adults (age 10 to 17.5 yr, N= 17) was 20, 131, 1080, and 52 ng/g, respectively. The mean Cd concentration in fleece of fawns, yearlings, and adults (age 2.5 to 10 yr) was 55, 37, and 28 ng/g, respectively. The Cd levels in bone samples form two adult serows ranged from 0.4 to 0.8 ug/g. The body burdens of fetuses were low (<1%) compared with those of their mothers. The placental transfer of Cd was negligible; after birth, Cd levels increased each year. There was a significant difference in Cd concentration between collection locations, which was attributed to direct intake of Cd in soil. [Honda K et al; Arch Environ Contam Toxicol 16: 551-61 (1987)].

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

Laboratory and/or Field Analyses:

While a number of different techniques (including polarography, ion chromatography, and mass spectroscopy) are available to measure concentrations of cadmium in solutions such as natural waters and the acid digests of solid materials [861,907], the most common methods use atomic absorption spectrometry (AAS) and inductively-coupled plasma emission spectrometry (ICP) [907].

Low concentration criteria or benchmarks may require relatively rigorous methods such as graphite furnace AAS rather than ICP methods, and detection limits should be no higher than comparison benchmarks or criteria for various media (water, sediments, soil, tissues, etc), some of which are low (see sections above). For critical risk assessment applications, the water detection limit may need to be very low since sensitive species benchmarks are as low as 0.013 ug/L (ppb) [649]. EPA method 1640 (see details below) allows a water MDL detection limit of 0.0024 ug/L [1001]. EPA method 1637 allows a water MDL detection limit of 0.0075 ug/L [1003] to 0.0074 ug/L [1001]. Lowest EPA water quality criterion is 0.32 ug/L [1001,1003].

For other routine monitoring when benchmark or criteria comparisons do not require lower levels, the ICP detection limits should usually not exceed the following default concentrations often recommended by the Fish and Wildlife Service and the National Park Service (Roy Irwin, National Park Service, Personal Communication, 1996):

0.10 ppm dry weight in tissues,
0.20 ppm in sediments and soils, and
0.0005 ppm in water.

> Note: Routine Atomic absorption (AA) detection limits for water can be as low as 0.0001 mg/L (40 CFR Part 141.23, part of the Drinking Water Regulations).

Older detection limits for instruments measuring cadmium in solution were 1 ug/L for flame AAS, 0.001 ug/L for graphite furnace AAS, 800 ug/L for flame emission spectrometry, 2 ug/L for ICP, and 0.2 ug.L for ICP-mass spectrometry [907].

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). 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]:

> Cadmium conversion for acute or chronic criteria: 0.850 (that is, total recoverable metals criteria x 0.850 = dissolved metals criteria).

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

> Cadmium conversion at a hardness of 50 mg/L: 0.973 for the Criterion Maximum Concentration (CMC).
>
> Cadmium conversion at a hardness of 50 mg/L: 0.938 for the Criterion Continuous Concentration (CCC).
>
> Cadmium conversion at a hardness of 100 mg/L: 0.944 for the Criterion Maximum Concentration (CMC).
>
> Cadmium conversion at a hardness of 100 mg/L: 0.909 for the Criterion Continuous Concentration (CCC).
>
> Cadmium conversion at a hardness of 200 mg/L: 0.915 for the Criterion Maximum Concentration (CMC).
>
> Cadmium conversion at a hardness of 200 mg/L: 0.880 for the Criterion Continuous Concentration (CCC).
>
>> Note: None of these "generic" conversion factors work well for all areas. Both total and dissolved concentrations should be checked at new locations before relying on generic conversion factors (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Filtration and Acidification of Water Samples:

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

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

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

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

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

Sources of potential variation in contaminants data:

Variation in concentrations of contaminants may sometimes be due to differences in how individual investigators treat samples in the field and lab rather than true differences in environmental concentrations. See also notes in disclaimer section at the top of this file. It was recognition that collectors and labs often contaminate samples that led EPA to develop the 1600 series of water protocols for low detection limit applications [1001,1002,1003,1004]. In comparing contaminants data from different labs, different states, and different agencies, one should keep in mind that they are often not very comparable. They may be as different as apples and oranges since:

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

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

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

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

> A) The protocol phrases "As soon as practical or as soon as possible."

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

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

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

Filter—0.45-um, 15-mm diameter or

larger, tortuous-path capsule filters, Gelman Supor 12175, or equivalent [1003].

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

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

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

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

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

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

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

> "Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls. The sample pH should be verified as <2 immediately before withdrawing an aliquot for processing or direct analysis. If, for some reason such as

> > high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2" [1003].

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

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

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

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

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

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

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

5) Although the above examples are mostly related to water samples, variability in field and lab methods can also greatly impact contaminant concentrations in tissues, soil, and sediments. Sediment samples from different microhabitats in a river (backwater eddy pools vs. attached bars, vs. detached bars, vs. high gradient riffles vs. low gradient riffles, vs. glides, etc.) tend to

have drastically different concentrations of metals as well as very different data variances (Andrew Marcus, Montana State University, personal communication, 1995). Thus, data is only optimally comparable if both data collectors were studying the same mix of microhabitats, a stratified sampling approach which would be unusual when comparing random data from different investigators.

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

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

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

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 bioconcentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

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

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

> Highlights from EPA Lab Method 1640: Determination of trace elements in ambient waters by on-line chelation preconcentration and inductively coupled plasma-mass spectrometry:
>
> > This method is for the determination of dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using on-line chelation preconcentration and inductively coupled plasma-mass spectrometry (ICP-MS) [1003]. It may also be used for determination of total recoverable element concentrations in these waters [1003]. This method was developed by integrating the analytical procedures contained in EPA Method 200.10 with the quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels [1003]. This method contains QC procedures that will assure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (the "Sampling Method") [1003]. The Sampling Method is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process [1003].
> >
> > This method is applicable to the following elements:
> >
> > > Cadmium (Cd), Copper (Cu), Lead (Pb), and Nickel (Ni) [1003].

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Highlights from EPA Method 1637: Determination of Trace Elements in Ambient Waters by Off-Line Chelation Preconcentration and Stabilized Temperature Graphite Furnace Atomic Absorption [1003]:

This method, proposed by EPA in 1996, provides procedures for the determination of dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using off-line chelation preconcentration and stabilized temperature graphite furnace atomic absorption (GFAA) [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 200.13 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].

EPA method 1637 allows a water MDL detection limit of 0.0075 ug/L [1003]. EPA method 1640 allows a water MDL detection limit of 0.0024 [1003]. Lowest EPA water quality criterion is 0.32 ug/L [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.

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].

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].

Information related to older drinking water methods from EPA 1996 IRIS database [893]:

Monitoring Requirements: Ground water systems monitored every 3 years; surface water systems monitored annually; systems out of compliance must begin monitoring quarterly until system is reliably and consistently below MCL.

Analytical Methods: Atomic absorption/ furnace technique (EPA 213.2; SM 304); inductively coupled plasma (200.7): PQL= 0.002 mg/L.