

ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

MERCURY ENTRY

July 1, 1997

COMPILERS/EDITORS:

ROY J. IRWIN, NATIONAL PARK SERVICE

WITH ASSISTANCE FROM COLORADO STATE UNIVERSITY

STUDENT ASSISTANT CONTAMINANTS SPECIALISTS:

MARK VAN MOUWERIK

LYNETTE STEVENS

MARION DUBLER SEESE

WENDY BASHAM

NATIONAL PARK SERVICE

WATER RESOURCES DIVISIONS, WATER OPERATIONS BRANCH

1201 Oakridge Drive, Suite 250

FORT COLLINS, COLORADO 80525

## **WARNING/DISCLAIMERS:**

Where specific products, books, or laboratories are mentioned, no official U.S. government endorsement is intended or implied.

Digital format users: No software was independently developed for this project. Technical questions related to software should be directed to the manufacturer of whatever software is being used to read the files. Adobe Acrobat PDF files are supplied to allow use of this product with a wide variety of software, hardware, and operating systems (DOS, Windows, MAC, and UNIX).

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

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

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

It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...

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

Differences in field and laboratory methods are also major issues related to (the lack of) data comparability from media other than water: soil, sediments, tissues, and air.

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

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it

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

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

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

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

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

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

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

on the internet or NTIS: 1998).

Mercury (Mercury in General, Hg, CAS number 7439-97-6)

**Brief Introduction:**

**Br.Class:** General Introduction and Classification Information:

This entry contains information on both elemental metallic mercury and mercury compounds. Unless stated specifically as a particular form of mercury, such as methyl mercury or specific mercury compounds, the text below refers to total mercury. Mercury in general, inorganic mercury, total mercury, or elemental mercury [Hg(0)] are most often associated with CAS number 7439-97-6 [617,893,903]. Methyl mercury is given CAS number 16056-34-1 [617] or 22967-92-6 [617,868,903]. Various other mercury compounds have a large number of different CAS numbers [617]. Most of the mercury in tissues is methyl mercury, but it usually analyzed as total mercury to maximize convenience and minimize expense (see details below).

Mercury is an element that occurs naturally in the environment in several forms [955]. In the metallic or elemental form, mercury is a shiny, silver-white, odorless liquid with a metallic taste. Mercury can also combine with other elements, such as chlorine, carbon, or oxygen, to form mercury compounds. These compounds are called "organic mercury" if they contain carbon, and "inorganic mercury" if they do not. In pure form, these mercury compounds are usually white powders or crystals. All forms of mercury are considered poisonous. One organic form of mercury, methylmercury, is of particular concern because it can build up in certain fish [955] (see Br.Fate section below).

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

Mercury is slowly increasing in concentration in lakes of SE Alaska that get most of their rainfall from the open Pacific Ocean, suggesting an increase in global atmospheric transport of mercury [916]. Coal combustion and municipal and medical waste incineration are the major anthropogenic sources to the atmosphere [999].

Jerry Keeler, University of Michigan presented the following information at the USGS Workshop on Mercury Cycling in the Environment held in Golden, Colorado, July 8-11, 1996 [999]:

Major sources to atmosphere include coal and oil fired powerplants (Hg is in the fuels), smelting of

metals, incineration of municipal waste, fossil fuel plants, landfills, natural emissions and re-emissions, CERCLA and RCRA sites, gold mining and manufacturing, sewage sludge burning, medical waste incinerators. Perhaps half or more of the mercury entering worldwide atmospheric transport comes Asia, with mainland China being an especially big source, and a high percentage of the rest comes from third world countries that do not have good controls on air pollution.

Mercury Highlights from U.S. EPA Press Release of Monday, August 28, 1995:

In a speech today to the American Fisheries Society in Tampa, Fla., U.S. Environmental Protection Agency Administrator Carol M. Browner said that in 1994, 46 states issued public health warnings advising citizens to avoid or limit fish consumption because of chemical contamination in thousands of water bodies across the country -- a 20 percent increase in such warnings since the previous year. Sixty percent of the health warnings against fish consumption were related to mercury contamination of the fish.

The largest source of the mercury contamination is air deposition, particularly from power plants burning coal, incineration of wastes that contain mercury or mercury-containing products and industrial facilities that use mercury in their processes. Once released into the atmosphere, mercury can be deposited in waters around a facility or transported over long distances and deposited in water directly or through runoff. Once in the water, the mercury is converted to methylmercury. Methylmercury is highly toxic and accumulates in fish flesh.

The general public can call state government agencies for specific state fish advisory information. In most cases, this is the state health department.

**Br.Haz:** General Hazard/Toxicity Summary:

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

Mercury is one of the few metals which strongly bioconcentrates and biomagnifies, has only harmful effects with no useful physiological functions when present in fish and wildlife, and is easily

transformed from a less toxic inorganic form to a more toxic organic form in fish and wildlife tissues [33]. It is a metal whose use should be curtailed as much as possible to prevent impacts to fish and wildlife [33]. Mercury is a cumulative poison [83] and is the heavy metal most toxic to fish [33].

For most aquatic ecosystems, atmospheric deposition is the primary source of mercury (although there are numerous instances of geologic and anthropogenic point-source contamination cases) and the resulting aqueous concentrations of mercury are generally less than 10 nanograms per liter [999]. Even in areas where there are no point sources, the mercury can still be high in fish tissues due to atmospheric sources [914]. However, except for the most polluted areas, mercury concentrations in water are often below lowest observed effect (LOEC) levels [914]. Therefore, water concentrations of mercury (by themselves) are often not the biggest threat to fish [914]. For fish, the harmful route of exposure is usually through the diet [914].

Certain fresh waters with fish-consumption advisories (i.e., high concentrations of mercury in sport fish) are lightly contaminated ecosystems in which inorganic Hg (II) is readily converted to methylmercury. These fresh waters include low-alkalinity lakes, newly flooded reservoirs, and certain wetland ecosystems [999].

Additional detail: In U.S. freshwaters, one should look for mercury problems in fish in mercury sensitive ecosystems such as the following [914]:

Recently flooded impoundments (mercury can remain high in such habitats for 3 to 5 decades);

Wetlands;

Note: Wetlands have high microbial degradation rates which favor production of methyl mercury [914]. In the Everglades, mosquitofish (*Gambusia affinis*) have very high (1 ug/g) mercury in tissues [914].

Low alkalinity lakes (Low alkalinity water is 50 to 100 micro equivalents per liter) [914];

The degree to which mercury will become a problem depends partly on cofactors such

as alkalinity and pH:

Alkaline streams in Oakridge National Lab had low mercury concentrations in fish despite high amounts of mercury put out into the environment, whereas low alkalinity lakes in Wisconsin with low inputs of mercury had high mercury in predatory fish [914].

Low-pH systems generally promote higher concentrations, mobility, and methylation of mercury [999].

See interactions section below for details on pH vs. bioaccumulation.

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 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 mercury in fish [383]. Edible fish tissue concentrations of mercury above the 0.5 to 1.0 ug/g wet weight values used for fish consumption advisories have been found even in relatively pristine (but low alkalinity) waters [383]. This takes on added importance since the 1989 "Mercury in Temperate Lakes" studies done by William Fitzgerald of the University of Connecticut and Dr. Carl Watras (Wisconsin Department of Natural Resources) indicated that atmosphere is the major source of mercury in many inland lakes and that sediments are the major sink.

Alkalinity, specific conductance, pH, and the concentration of calcium in waters are inversely correlated with concentrations of mercury in fish [383]. Also, some contaminants specialists who have looked at some of the human health and animal husbandry literature have wondered whether or not slight elevations of some forms of selenium in fish tissues may possibly be acting partly in a protective manner (to a greater degree than is commonly recognized) to humans and fish and wildlife predators consuming fish contaminated with harmful concentrations of heavy metals such as cadmium, mercury, and lead (Jerry Miller, U.S. Bureau of Reclamation, Salt Lake City, personal

communication). See also the Selenium entry, and the Interactions section below for a more detailed separate section on interactions between mercury and selenium, pH, eutrophication, etc.

Exposure risks for piscivorous (fish-eating) wildlife is maybe the area where additional concern is warranted [915]. Fish-eating birds, mammals, and reptiles in ecosystems with mercury-contaminated fish have high dietary exposure to methylmercury, vastly exceeding the exposure of human populations (as indicated by mercury concentrations in blood) [999].

As a constituent in the flesh or food of aquatic organisms, mercury has no known redeeming qualities. In this respect, there seems to be no good amount of mercury: the less mercury that aquatic organisms (or humans) ingest, the better.

There are increased potential effects of mercury to early life stages of fish [914]. Elevated concentrations of mercury in water are particularly toxic to many species of algae, crustaceans, and salmonids [180].

The general stress syndrome (GSS) produced the best estimates of overall risk for aquatic species exposed to mercury [970].

The most sensitive target of low-level exposure to metallic or organic mercury following short- or long-term exposures appears to be the nervous system. The storage of methyl mercury in fish muscle may be a defense against methyl mercury toxicity: storage in muscle seems to be functioning as a way to keep the mercury away from central nervous systems [914].

Mercury from natural sources is mostly elemental mercury which is less hazardous than methyl mercury [921]. Anthropogenic sources tend to produce cationic mercury which is more soluble. It is also more readily methylated by bacteria than elemental mercury [921].

Sulfate-reducing bacteria are important mediators of methylmercury production medium [999]. The sediment water interface (or other interfaces where oxic/anoxic boundaries are present) is a dominant site for methylmercury production [999].

Methyl mercury bound to sulfur is not stable and

will tend to change partners [34,921]. Methyl mercury can denature DNA [921] and can otherwise interact with both DNA and RNA to alter their structures [494].

One author has stated that there would not nearly as big a problem with mercury in aquatic systems in the U.S. if it were not for anthropogenic sources of cationic mercury; if the main sources were natural elemental mercury, bacteria would not be methylating it to the same degree [921].

Wren et al. provided a 1995 summary of biological effects of mercury and cadmium [838] (the highlights have not yet been summarized herein).

The molecular structure of the mercury compound, its stability in the organism & its routes of biotransformation & excretion will govern toxicological properties for the higher organisms. Thus each mercury compound has its own toxicology in relation to dose-effect & dose-response relationships (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. 389) [940].

The most sensitive target of low-level exposure to inorganic mercury appears to be the kidneys. Short-term exposure to high levels of mercury can have similar effects [955].

Until recently, attempts to unravel mercury environmental contamination problem have been frustrated by both sampling and analytical barriers [999]. Clean lab guidance has been provided by EPA [1004].

In announcing the establishment of an ultra-clean mercury lab capable of analyzing for aqueous concentrations of total mercury, methylmercury, dissolved elemental mercury, and reactive ionic mercury, at detection limits of about 0.00045 nanograms, the USGS provided the following summary of developing mercury issues (David Krabbenhoft, USGS, Wisconsin, personal communication, 1995):

Mercury contamination of aquatic ecosystems has become a problem of national and global extent. Currently, 37 States have posted one or more fish consumption advisories for mercury; 10 years ago there was none. In most areas, the source of the mercury is globally

or regionally distributed atmospheric deposition, which is deposited at very low-level rates (about 10 micrograms per square meter per year).

Due to recent great strides in sampling and analytical techniques, scientists can now routinely collect representative air, water, tissue, and sediment samples, and analyze for specific mercury species [999]. The resultant data have provided new insights into the processes controlling the transport, cycling, and fate of mercury in aquatic ecosystems [999]. In addition, new techniques that employ isotopic tracers have provided new insights about the specific processes at the root of this contamination problem: mercury methylation and demethylation [999].

#### Tolerance Factors for Mercury:

Populations of organisms chronically exposed to chemical pollutants may develop increased tolerance to those pollutants [177,493]. Some of the aquatic issues related to tolerance, interactions with other metals, and/or indirect impacts related to mercury were summarized by Rand and Petrocelli [177]. Development of tolerance to mercury does not appear to be without cost, however [493]. Resistance to a specific chemical pollutant (methylmercury) in the mummichog, for example, decreased the tolerance of eggs and embryos to salinity and HgCl<sub>2</sub> and resulted in slower growth and weakness as adults [493]. The effects noted in adults, including early reproduction, diminished growth and regeneration rate, reduced longevity, and less feeding, probably reflect the stress associated with living in a contaminated environment [493].

Increased synthesis of metallothionein in response to mercury exposure may help animals acquire a somewhat increased tolerance of this metal [180]. However, in fish, metallothionein and various barriers and internal defenses do not bind or work as well to protect against methyl mercury as they do for inorganic mercury [914].

#### Potential Hazards to Humans:

Human exposure to methylmercury is almost entirely due to consumption of fish [999]. Sources include tuna, marine shellfish, marine fish, and freshwater fish. Those eating these foods often may be among those most at risk. Such risks were summarized in 1994 (DOE/FDA/EPA Workshop on Methylmercury and Human Health, March 22-23, 1994 Publication #Conf-9403156, Brookhaven National Lab, Upton, New York).

Current standards for the issuance of fish-consumption advisories are intentionally conservative, and these standards should be kept in place as a protection barrier for the human health, or at least until we have improved information [999].

Methyl and alkyl mercury compounds are two of the most toxic classes of mercury compounds [83]. Potential impacts to human health are real and potentially great, as was demonstrated in case studies where severe mercury poisoning has occurred [999]. The impact from low-level exposure (commonly observed today) is unclear, but is potentially great for unborn children [999]. Unborn children are especially at risk, as it has been demonstrated recently that maternal blood mercury levels are magnified tenfold in the fetus. Current consumption advisory limits have been established without considering this phenomenon [999].

Mercury deposits in the brain cause many disorders and sometimes dementia in humans [173]. Although organic chemicals like PCBs may also be involved, lead and mercury are the main contaminants widely recognized to be potentially involved with human learning disabilities [977].

Exposures in the womb can be important [494]. Mercury moves readily across the placenta and into fetal tissue. Regardless of the chemical form administered, fetal tissues attain concentrations of mercury at least equal to those of the mother (Doull, J., C.D.Klassen, and M.D. Amdur, eds., Casarett and Doull's Toxicology. 3rd ed., New York: Macmillan Co., Inc., 1986. 606) [494,940].

Mercury deposits in human kidneys may lead to renal failure [173].

Mercury poisoning has occurred in the United States and in other countries. The most notorious episode, however, occurred in the 1950s at Minamata

Bay in Japan, where mercury in the effluent from a plastics factory was ingested (in the form of methyl mercury, an organic compound) by fish and, eventually, by people in the fishing communities on the bay [335].

In humans, mercury exposures have been associated with the following effects [940]:

Children and persons with a history of allergies or known sensitization to mercury, chronic respiratory disease, nervous system disorders, or kidney disorders are at increased risk to mercury poisoning].

Many mercury compounds are irritating to skin & may produce dermatitis with or without vesication [940].

Contact with eyes causes ulceration of conjunctiva & cornea [940].

Methylmercury is highly neurotoxic, damaging the central nervous system [999]. The most consistent & pronounced effects of chronic exposure to elemental mercury vapor are CNS effects, both neurological & psychiatric, with common symptoms including depression, irritability, exaggerated response to stimulation (erethism), excessive shyness, insomnia, emotional instability, forgetfulness, confusion, & vasomotor disturbances such as excessive perspiration & uncontrolled blushing [940]. Tremors are also common. These are exaggerated when task is required but minimal when patient is at rest or asleep [940]. A fine trembling of fingers, eyelids, lips, & tongue may be interrupted intermittently by coarse shaking movements [940].

First phase symptoms after ingestion of inorganic mercury salts: 1) Burning pain, sense of constriction, and ashen discoloration of the mucous membrane in mouth and pharynx, occurring immediately after the ingestion of corrosive mercury salts [940]. 2) Within a few minutes intense epigastric pain, followed by diffuse abdominal pain and associated with almost continuous vomiting of mucoid material, which frequently contains blood and shreds of mucous membrane. 3) Severe purging, with liquid, bloody feces and considerable tenesmus. 4) Metallic taste, excessive salivation and thirst. 5) A rapid, weak pulse; Shallow breathing; Pallor; Prostration, collapse, and death. 6) Signs and symptoms listed

above are not encountered with mercury compounds of low irritancy or with portals of entry other than the mouth. In these cases the first clinical evidence of poisoning may be phase 2 [940].

Acute intoxication from inhaling mercury vapor in high concentrations used to be common among those who extracted mercury from its ores [940]. There is a metallic taste, nausea, abdominal pain, vomiting, diarrhea, headache, & sometimes albuminuria [940]. After few days, salivary glands swell, stomatitis & gingivitis develop, & a dark line of mercury sulfide forms on inflamed gums. Teeth may loosen, & ulcers may form on lips & cheeks. In milder cases, recovery occurs within 10-14 days, but in others, poisoning of chronic type may ensue [940].

Possible renal damage may occur in connection with chronic exposure to mercury vapor [940].

Brain damage: The brain is critical organ in humans for chronic mercury vapor exposure; in severe cases, spongy degeneration of brain cortex can occur as a late sequela to past exposure [940].

Effects from elemental mercury include contact dermatitis from mercury amalgam fillings & mercury sensitivity occurring among dental students [940].

Permanent changes to affected organs and organ systems from either acute or chronic exposure to mercury [940].

Acute poisoning due to mercury vapors affects the lung primarily, in the form of acute interstitial pneumonitis, bronchitis, and bronchiolitis [940].

In general, chronic exposure produces four classical signs: gingivitis, sialorrhea, increased irritability, and muscular tremors [940]. Rarely are all four seen in together in an individual case [940].

Human risk assessment, exposure factors for humans eating fish, and health effects of methyl mercury were summarized in 1994 (DOE/FDA/EPA Workshop on Methylmercury and Human Health, March 22-23, 1994 Publication #Conf-9403156, Brookhaven National Lab, Upton, New York).

A comprehensive toxicological profile for mercury and mercury compounds, especially as they relate to human health, is available from ATSDR [955]. Due

to a lack of time, important highlights from this ATSDR document have not yet been completely incorporated into this entry.

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

EPA 1996 IRIS database information [893]:

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

Classification: D; not classifiable as to human carcinogenicity

Basis: Based on inadequate human and animal data. Epidemiologic studies failed to show a correlation between exposure to elemental mercury vapor and carcinogenicity; the findings in these studies were confounded by possible or known concurrent exposures to other chemicals, including human carcinogens, as well as lifestyle factors (e.g., smoking). Findings from genotoxicity tests are severely limited and provide equivocal evidence that mercury adversely affects the number or structure of chromosomes in human somatic cells.

Human carcinogenicity data: Inadequate. A number of epidemiological studies were conducted that examined mortality among elemental mercury vapor-exposed workers. Conflicting data regarding a correlation between mercury exposure and an increased incidence of cancer mortalities have been obtained. All of the studies have limitations that complicate interpretation of their results for associations between mercury exposure and induction of cancer; increased cancer rates were attributable to other concurrent exposures or lifestyle factors.

Animal carcinogenicity data: Inadequate. No studies were located regarding cancer in animals after inhalation exposure to metallic mercury [955]. There is no evidence from epidemiological studies that indicated inhalation of metallic mercury produces cancer in humans [955]. No studies were located regarding cancer in humans following oral exposure to organic mercury. Results of a 2-year NTP (1991) study indicates that mercuric chloride may induce tumors in rats. No studies were located regarding cancer in humans or animals after dermal

exposure to mercury [955].

IARC Summary and Evaluation [940]:

Evaluation: There is inadequate evidence in humans for the carcinogenicity of mercury and mercury compounds. Overall evaluation: Metallic mercury and inorganic mercury compounds are not classifiable as to their carcinogenicity to humans (Group 3). [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. 58 324 (1993)].

Some references refer to mercury as a carcinogen:

Although mercury itself is generally considered a carcinogen, at least one mercury compound has been investigated as anti-cancer agent: Sodium 2-mercaptoethanesulfonate (Mesna), a cytoprotective thiol-containing agent, was marginally effective in decreasing the estradiol-induced kidney tumor incidence in hamsters (Roy D; Liehr JG, 1990. Inhibition of estrogen-induced kidney carcinogenesis in Syrian hamsters by modulators of estrogen metabolism. Carcinogenesis 11(4); P 567-70, Department of Pharmacology, University of Texas Medical Branch, Galveston 77550).

Mercury is a carcinogen [33].

However, some more recent sources say mercury is not classifiable as to its human carcinogenicity [893,940].

Neither inorganic nor methyl mercury have been treated as a carcinogen for model calculation purposes in some EPA risk-based (RBC and PRG) models, but this is for modeling purposes rather than for definitely stating these substances are not carcinogenic [868,903].

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

Continent-wide studies on common organisms (e.g., loons) are beginning to show strikingly similar results that suggest mercury impacts piscivorous wildlife, particularly reproduction rates [915]. These studies are difficult to conduct and more controlled, experimental research needs to be performed before definitive conclusions can be reached [915]. Recent studies that employ innovative methods, such "clean egg/dirty egg" swapping will be key for unraveling controlling

influences [915]. Nationwide and Canadian studies on the Common Loon suggest that mercury is having a significant negative effect on the reproductive rates of these fish-eating birds [999].

It is suspected that methylmercury adversely affects the reproductive success and developing young of fish-eating wildlife in ecosystems having fish with elevated mercury concentrations [999].

The developing young (early life stages) of vertebrate organisms (including humans) are much more sensitive than adults to methylmercury [999].

Recent deaths of three Florida panthers have been attributed to mercury poisoning, and the failure of any panthers to reproduce in the Everglades in the past seven years is thought to be attributable to mercury burden [999].

Mercury is an endocrine system disrupter [514]. Mercury is a mutagen and a teratogen [33].

Mercury, especially in organic forms, is a known neurodevelopmental toxin [955].

Mercury has been shown to cause negative effects on human spermatozoa [955]. Animal data suggest that mercury may alter reproductive function and/or success [955].

Whereas trimethyl tin is an indirect neurotoxin, methyl mercury is a direct neurotoxin whose distribution in brain and other neurological tissues corresponds with locations of lesions; methyl mercury mimics essential metabolites and causes numerous problems, including reductions in RNA production, reductions in protein synthesis, and eventual cell deaths (Louis Chang, University of Arkansas at Little Rock Medical Center, Department of Pathology, Personal Communication).

Long-term exposure to either inorganic or organic mercury can permanently damage the brain, kidneys, and developing fetus. Organic mercury in the body is similar to metallic mercury because it can reach most tissues including the brain and fetus [955].

Mothers exposed to elemental mercury through their dental work place showed significantly increased mercury content in their babies' placenta & membranes. Exposure limits for women of childbearing age & levels at which toxicity might be expected have been suggested. For fetus & newborn, the toxic level is given as 3 ug H g/g. (Shepard, T.H. Catalog of Teratogenic Agents. 4th ed. Baltimore, MD: Johns Hopkins University Press, 1983. 278)

[940].

Neonates have absorbed significant amounts of mercury after the breakage of elemental mercury switches in their incubators. (Ellenhorn, M.J. and D.G. Barceloux. Medical Toxicology - Diagnosis and Treatment of Human Poisoning. New York, NY: Elsevier Science Publishing Co., Inc. 1988. 1048) [940].

A review of human genotoxicity studies by ATSDR found that these studies could not be used to predict the potential genetic hazard to humans associated with exposure to mercury or mercury compounds [955]. However, the induction of primary DNA in mammalian and bacterial cells and weak mutagenesis in mammalian cells suggest that inorganic and organic mercury compounds have some genotoxic potential [955].

Aneuploidy and other chromosomal aberrations have been observed in lymphocytes from whole blood cultures of workers occupationally exposed to mercury, including people working with mercury amalgams. (USEPA; Mercury Health Effects Update p.5-11 (1984) EPA 600/8-84-019F) [940].

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

Recent studies have shown that several key environmental parameters are linked with high levels of mercury in fish [914]. However, this is a very complex area of research that is controlled by ecosystem parameters (e.g., water chemistry, wetlands presence/absence), aqueous mercury speciation, food-web structure, size, age, and growth rate of organisms, population size, etc [914]. The effect of source strength and point-source impacts are unclear, as was illustrated by examples from Oak Ridge, TN; Carson River, NV; and the Everglades [914].

The construction and flooding of new reservoirs increase mercury levels in fish by creating environmental conditions that greatly increase the microbial production of methylmercury from existing inorganic Hg (II) [999].

Re-emissions of mercury from terrestrial and marine environments to the atmosphere (due to past activities) may be continuing to impact current atmospheric mercury concentrations [917]. Additional detail:

Dated sediment cores are an effective way to infer historical trends in mercury accumulation rates, and potential point-sources releases, in deep water

lakes and reservoirs containing organic-rich sediments [917]. Cores taken over an area can be used to differentiate watershed versus atmospheric contributions to lakes and reservoirs, as well as regional trends in deposition [917]. Fine-scale sampling in well preserved cores show that atmospheric deposition rates of mercury may have already peaked, and in some local to regional areas are declining [917]. On the global scale, however, Hg emissions from developing areas (e.g., South America, Asia) are rising, which may reverse this trend [917].

The global mercury cycle is important to consider for mercury researchers, and one of the most elusive aspects of this cycle is the relative contributions of natural to anthropogenic sources [917]. Modeling efforts suggest that past uses (as long ago as the 1800's) of mercury by man may still be affecting the global mercury cycle [917].

Since the industrial revolution, anthropogenic mercury emissions have increased atmospheric mercury levels about threefold, causing corresponding increases in mercury levels in terrestrial and aquatic ecosystems [999].

The dominant food source of mercury in the human diet is fish and fish products. In terms of total mercury (Hg), the diet greatly exceeds other media, including air and water, as a source of human exposure and absorption of Hg (USEPA; Mercury Health Effects Update p.2-4 (1984) EPA 600/8-84-019F) [940].

Aqueous mercury is affected by photochemical processes (e.g., photo reduction) [999].

Microbes are largely responsible for mercury demethylation in the environment, and they accomplish this through the mer operon and oxidative processes [999].

Sedimentation and evasion (water-air exchange of reduced gaseous mercury) are the primary sinks for mercury from an aquatic ecosystem [999].

Mercury concentrations and speciation varies spatially and temporally (daily to seasonal) [999].

Mercury is generally found at very low concentrations and is extremely reactive in the environment. It readily undergoes phase, species, and redox changes [999].

Many biogeochemical processes operate under optimal conditions at the sediment/water interface, including

mercury methylation and demethylation [918]. Recent studies involving detailed investigations of the sediment/water interface show that in many cases the interface a relatively unimportant source of inorganic mercury, but a dominant site for methylmercury production and flux [918]. These studies need to place an equal emphasis on quantifying groundwater fluxes, which is the dominant transport vector is most littoral zones [918].

Many surface waters with fish-consumption advisories for mercury have no known industrial or waste discharge that could readily explain the mercury contamination of fishery resources. Recent advances in sampling and analytical methodology have enabled researchers to construct mercury budgets for a number of small lakes and streams. These budgets show that the atmosphere is a major source of mercury for certain aquatic ecosystems (James Wiener, National Biological Service, personal communication, 1996, summary statement electronically reporting on the USGS Workshop on Mercury Cycling in the Environment held in Golden, Colorado, July 8-11, 1996).

Mercury released into the environment stays there for a long time. Once in the environment, mercury can slowly be changed from organic to inorganic forms and vice versa by microorganisms and natural chemical processes. Methylmercury is the organic form of mercury created by these natural processes [955].

Certain methanogenic bacteria often found in sediments or soil can methylate inorganic mercury to the methyl mercury form. Methyl mercury is the more active form biologically; most of the bad press that mercury gets is due to methyl mercury rather than inorganic mercury. It is organic mercury (mostly methylmercury) which are most hazardous to fish [488]. Methyl mercury tends to bioconcentrate and cause many negative biological impacts.

Hg<sup>0</sup> (Hg<sup>0</sup>) may be converted by methane-generating bacteria to methyl mercury, which (like elemental mercury) is lipophilic. Methyl mercury is more lipophilic than inorganic forms which results in increases in mercury accumulation and mercury induced toxicity. Metallic mercury is the only metallic element that is a liquid at room temperature [190]. Its volatility tends to reduce its concentration in surface waters [190]. It can evaporate easily into the air and be carried a long distance before returning to water or soil in rain or snow [955].

The mercury in air, water, and soil is thought to be mostly inorganic mercury. This inorganic mercury can enter to air from deposits of ore that contain mercury,

from the burning of fuels or garbage, and from the emissions of factories that use mercury. Inorganic mercury may also enter water or soil from rocks that contain mercury, releases of water containing mercury from factories or water treatment facilities, and the disposal of wastes. Organic compounds of mercury may be released in the soil through the use of mercury-containing fungicides [955].

Mercury strongly associates with particulate matter, especially organic particulates [999].

The quality and quantity of DOC in an aquatic ecosystem can have a strong influence on the fate and transformation of mercury in the environment [999].

Organic forms of mercury can enter the water and remain there for a long time, particularly if there are particles in the water to which they can attach. If mercury enters the water in any form, it is likely to settle to the bottom where it can remain a long time. Mercury also remains in soil for a long time. Mercury usually stays on the surface of the sediments or soil and does not move through the soil to underground water [955].

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

Forests accumulate dry deposition in equivalence to wet deposition. Vegetation is a source to the atmosphere (evasion from leaf surfaces) and to watersheds (leaf litter and throughfall) [999].

In sediments, mercury is often bound to sulfides and other sulfur compound [366]. Mercury in bottom sediments is re-suspended during floods and carried further downstream. Such events have resulted in increased levels of mercury in fish, as noted in a previous Fish and Wildlife Service study in Montana [32]. Mercury is one of the few metals which accumulates in the axial muscles of fish, so fillet levels are typically closer to whole-body concentrations than for most other contaminants [27].

In biota, mercury is often bound to sulfhydryl and other sulfur compounds. Mercury readily forms covalent bonds with sulfur, and it is this property that accounts for most of the biological properties of the metal [366]. When sulfur is in form of sulfhydryl groups, divalent mercury replaces the hydrogen atom to form mercaptides [366]. Mercurials even in low concentrations are capable

of inactivating sulfhydryl enzymes and interfering with cellular metabolism & function [366]. Mercury also combines with other ligands of physiological importance, such as phosphoryl, carboxyl, amide & amine groups [366].

There has been considerable confusion on the subject of methyl mercury versus total mercury. Much of the mercury in sediments can be in the inorganic form, so that total and methyl mercury measures in the same sediments can result in very different concentrations (see the Laboratory and/or Field Analyses section below for details).

Another point of confusion related to total mercury versus methyl mercury is the notion that most inorganic mercury "locked up in the sediments" no longer represents a biological hazard. Like many other oversimplifications, this one contains a small amount of truth. It is true that inorganic mercury in sediments is often bound to sulfides and other compounds and generally represents less of an immediate biological hazard than organic (methylated) or other more mobile forms of mercury. However, it should not be forgotten that there are many mechanisms (flooding disturbances, bioturbation, release with sulfide gases, bacterial action, etc.) which tend to bring this presumably "locked up" mercury to the surface or up into the water column or even the atmosphere. Once this happens, methylation and uptake mechanisms tend to transform these relatively harmless "locked up" forms of mercury into more hazardous and more bioavailable forms. At least part of the mercury in sediments is vertically mobile, which is a factor needing more study. Methyl mercury moves from the sediments upwards into the water (paragraph summarized from numerous sources, Roy Irwin, National Park Service, personal communication, 1996).

When exposed to mercury in both mediums, fish accumulate more mercury from sediments than from water [95]. Lower pH levels (indicating increased acidification) are correlated with increased mercury accumulation in fish [120]. At low pH, there is typically a higher methyl mercury production than at higher pH levels. Primary productivity increases pH so there is typically a fall off later as the higher pH slows down the methyl mercury production. See the Interactions section below for more details.

Elemental mercury (mercury with no charge, Hg<sup>0</sup>) is lipid soluble. Elemental mercury may be oxidized in natural oxidizing environments or in various tissues to Hg<sup>+2</sup> (Hg II) [34,941]. In water or sediments, elemental mercury would be expected in extremely reducing environments, while HgCl<sub>2</sub> or Mercury Oxide (both Hg II) would be

expected in oxidizing environments [941].

At of REDOX of pE 7.5 or higher, all the mercury in water is Hg II, including the very soluble Hg<sub>2</sub>CL<sub>2</sub> and HgCL<sub>2</sub> [958]. This is important because Hg II tends to be more soluble and more readily methylated by bacteria than elemental mercury (Hg<sub>0</sub>) [921]. At pH of 5 to 9 and Eh less than 0.5 volts, the reduced mercury species elemental mercury (Hg<sub>0</sub>) or (the relatively insoluble HgS (cinnabar) are likely to occur [941,952]. The reduced HgS form is relatively insoluble, while the Hg II forms such as HgCL<sub>2</sub> tend to be relatively soluble [941].

Measures of total vs. acid soluble vs. dissolved mercury:  
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 mercury concentrations. For detailed discussion, see the Laboratory and/or Field Analyses section (far below).

The forms of methylmercury [e.g. CH<sub>3</sub>HgCl, CH<sub>3</sub>HgOH, (CH<sub>3</sub>)<sub>2</sub>Hg] that most readily cross biological membranes are still not completely understood [999].

Atmospheric Sources and Transport: Studies in this area of research are very scale dependent; the scale at which research questions are asked can dictate the information that is needed or will be attained, and the consequent interpretations. Although mercury contamination is truly a global pollution problem, regional, sub-regional, and local effects are clearly evident from recent studies [999].

Mercury emissions from electric power plants, atmospheric modeling, and global biogeochemical cycling issues for mercury were summarized in 1994 (DOE/FDA/EPA Workshop on Methylmercury and Human Health, March 22-23, 1994 Publication #Conf-9403156, Brookhaven National Lab, Upton, New York).

**Synonyms/Substance Identification:**

Metallic mercury [617,940]  
Quicksilver [617,940]  
KWIK (DUTCH) [940]  
LIQUID SILVER [940]  
MERCURE (FRENCH) [940]  
MERCURIO (ITALIAN) [940]  
NCI-C60399 [940]

QUECKSILBER (GERMAN) [940]  
Hydrargyrum [940]  
COLLOIDAL MERCURY [940]

Molecular Formula:  
Hg [940]

**Associated Chemicals or Topics (Includes Transformation Products):**

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

Copper  
Selenium

**Metabolism/Metabolites [940]:**

One of the pathways, if not the only pathway, by which elemental mercury (hg(0+)) is absorbed & converted in vivo is by its oxidation (in erythrocytes) to Hg(2+). Studies with acatalasemic red blood cells (RBCs) show that catalase-hydrogen peroxide system plays a determinant role in mercury uptake through this catalytic oxidation system; human acatalasemic RBCs had only 1/100 to 6/100 the uptake of mercury vapor found in normal RBCs with hydrogen peroxide. (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. 1784)].

Early studies indicated that microorganisms could methylate mercury & that dimethyl mercury formed. In other studies, a methanogenic bacterium, methanobacterium omelianskii, as well as soln of methylcobalamine, were capable of methylating mercury (Menzie, C. M. Metabolism of Pesticides, An Update. U.S. Department of the Interior, Fish, Wild-life Service, Special Scientific Report - Wildlife No. 184, Washington, DC: U.S. Government Printing Office, 1974. 240)].

Because sorption at the gill surface is a major pathway of mercury into an organism, increases in temperature and activity cause increases in metabolic rate and ventilation rate, and therefore, uptake rate. (USEPA; Ambient Water Quality Criteria Doc: Mercury p.11, 1984, EPA 440/5-84-026) [940, also update of 34].

Pregnant Hartley guinea pigs in late gestation were repeatedly exposed in a chamber to 0 or 0.2-0.3 mg/cu m mercury vapor mixed with fresh air for 2 hr per day until parturition. The mothers and their offspring were killed and their tissues were analyzed for mercury content. Mercury concentrations in whole blood of offspring was

lower than that of mothers. Mercury concentration ratios in neonatal brain, lung, heart, kidney, plasma, and erythrocytes were much lower than those of maternal organs and tissues, with the exception of neonatal liver, which showed a mercury concentration twice as high as that of maternal liver. In placental tissue, mercury levels were found to be higher than those in the blood of mothers and offspring. The results suggested that mercury vapor metabolism in fetuses was quite different from that in the mothers, and that mercury vapor was most likely oxidized and accumulated in the fetal liver as ionic mercury. (Yoshida M et al; Arch Toxicol 58: 225-8, 1986)].

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

**W.Low** (Water Concentrations Considered Low):

As a constituent in the flesh or food of aquatic organisms, mercury has no known redeeming qualities. In this respect, there seems to be no good amount of mercury: the less mercury that aquatic organisms ingest, the better. Perhaps partly for this reason, there do not appear to be many literature references on concentrations of mercury considered low.

**W.High** (Water Concentrations Considered High):

Anything over benchmark or concern levels (see section below).

**W.Typical** (Water Concentrations Considered Typical):

Typical Ocean Concentrations: EPA 1981: 0.0001 mg/l [83].

Typical Freshwater Concentrations: EPA 1981: 0.00008 mg/l [83].

Leland and Kuwabara, 1985: In non-polluted areas, baseline concentrations as low as 0.00001 mg/l have been recorded [177].

USGS 1985: Concentrations in filtered river water seldom exceed a few tenths of a microgram per liter [190].

USGS 1974-1981: the 50th percentile of 199 (not especially clean) NASQWAN and NWQSS river sites in the U.S. was 0.2 ug/l; the 25th percentile was 0.2 ug/l, and the 75th percentile was 0.3 ug/l, with concentrations trending upward more often than downward [219]. These riverine sites in the USGS study were mostly in (or

downstream of) agricultural and urban areas [219].

Concentrations in rainwater and fresh snow are generally below 0.2 ug/L. Water samples from lakes and rivers in the Ottawa, Ontario, region of Canada had total mercury concentrations of 3.5-11.4 ng/L with organic mercury constituting 22-37% of the total mercury [955].

The results of chemical analysis of water from the pump-out well, provided by SCM (Glidden Coatings and Resins Division), indicated the presence of mercury at < 0.001 ppm concn (USEPA; Subst Risk Notice, 8(e) p.51, 1982, EPA 560/2-83-001) [940].

Drinking Water (range): 5 to 100 ng Hg/l, estimated (USEPA; Mercury Health Effects Update p.3-19, 1984, EPA 600/8-84-019F) [940].

Drinking Water: In the Federal Republic of Germany, the mercury concn measured was approx 600 ng/l in a sample of potable water (WHO; Environ Health Criteria: Mercury p.59, 1976) [940].

Surface Water: The purest surface water (drinking quality) contains less than 30 ng/l based on over 700 samples collected from drinking reservoirs in the Federal Republic of Germany. Rivers believed to have low contamination, such as the Danube, and bodies of water such as the Boden Sea, have values close to 150 ng/l based on the analysis of 152 samples (Bouquiaux J; Proceedings of the Intl Symposium on the Problems of Contamination of Man and His Environment by Mercury and Cadmium p.23, 1974, as cited in WHO; Environ Health Criteria: Mercury p.58 (1976)).

Other Waters: In the Federal Republic of Germany, the mercury contamination was approx 400 ng/l in inland waters and between 100 and 1,800 ng/l in rivers (WHO; Environ Health Criteria: Mercury p.59, 1976) [940].

The baseline concentration of mercury in unpolluted marine waters has been estimated to be 0.005-0.006 ug/L [955].

The amount of mercury in the oceans has been calculated as 70 million ton using a figure for total ocean volume of  $1.37 \times 10^9$  cu km and taking the avg Hg content of ocean water as 50 ng/l (WHO; Environ Health Criteria: Mercury p.47, 1976) [940].

Natural Waters: Rainwater, snow 0.01-0.48 ppb; Normal stream, river, and lake waters 0.01-0.1 ppb; Coal mine waters (Donets Basin, USSR) 1-10 ppb; Stream and river waters near mercury deposits 0.5-100 ppb; Oceans and seas

0.005-5.0 ppb; Hot springs and certain mineral waters  
0.01-2.5 ppb; Normal groundwaters 0.01-0.10 ppb;  
Groundwaters and mine waters near polymetallic sulfide  
deposits 1-1000 ppb; Oil field and other saline waters  
0.1-230 ppb (Jonasson IR, Boyle RW; Bull Can Inst Min  
Metal 65: 32-9, 1972, as cited in Nat'l Research Council  
Canada; Effects of Mercury in the Canadian Environment  
p.40, 1979, NRCC No. 16739) [940].

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

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

Note: Measures of total vs. acid soluble vs.  
dissolved mercury: 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 mercury concentrations. For  
detailed discussion, see the Laboratory and/or  
Field Analyses section (far below).

EPA 1996 IRIS database information [893]:

Ambient Water Quality Criteria for Aquatic  
Organisms for Mercury, elemental, CAS Number  
7439-97-6:

Acute Chronic Freshwater Criterion:  
2.4E+0 ug/L 1 hour average [893].

Previous Gold Book Water Quality  
Criteria in ug/L was the same:  
Freshwater Acute Criteria: 2.4  
[689].

Chronic Freshwater Criterion: 1.2E-2 ug/L  
4-day avg [893]. Older Freshwater  
Chronic Criteria: 0.012 ug/L [689].

Marine Acute Criterion: 2.1E+0 ug/L 1  
hour average.

Older Marine Acute Criteria was the  
same: 2.1 ug/L [446].

Marine Chronic Criterion: 2.5E-2 ug/L 4-day avg [893].

Older Marine Chronic Criteria was the same: 0.025 ug/L [446].

Notes on IRIS Values [893]:

Econ/Tech?: No, does not consider economic or technical feasibility Reference: 45 FR 79318 (11/28/80); 50 FR 30784 (07/29/85)

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

Discussion: Criteria were derived from a minimum data base consisting of acute tests on a variety of species. Requirements and methods are covered in the reference to the Federal Register. The Agency recommends an exceedence frequency of no more than 3 years.

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

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

For CAS 7439-97-6 (Mercury, inorganic), the freshwater benchmark values in ug/L are [649]:

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 2.4

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

SECONDARY ACUTE VALUE: No information found.

SECONDARY CHRONIC VALUE: 1.30

LOWEST CHRONIC VALUE - FISH: < 0.23

LOWEST CHRONIC VALUE - DAPHNIDS: 0.96

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

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 5

LOWEST TEST EC20 - FISH: 0.87

LOWEST TEST EC20 - DAPHNIDS: 0.87

SENSITIVE SPECIES TEST EC20: 0.18

POPULATION EC20: 0.32

**W.Plants (Water Concentrations vs. Plants):**

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

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

For CAS 7439-97-6, MERCURY, the benchmark is 0.004 mg/L (groundwater or porewater).

LC50s for various algae 0.006 to 0.01 mg/L [970].

The uptake of mercury (Hg) and toxic effect of the metal on some biochemical parameters in the plant *Pistia stratiotes* were studied. The uptake of Hg by the plants gradually increased with incr in concn of Hg in the culture medium. Max accumulation of Hg

was noted within a day. Max removal (approx 90%) of Hg was < 20 ppm Hg. Accumulation of Hg in roots was approx 4 times higher than that in shoots. At 20 ppm, Hg promoted senescence of the plants by decreasing chlorophyll, protein, RNA, dry wt, and the activities of catalase and protease as well as increasing free amino acid content, peroxidase activity, and the ratio of acid to alkaline pyrophosphatase activity over control values. At Hg concn < 20 ppm, these constituents were least affected (De AK et al; Water, Air, Soil Pollut 24 (4): 351-60, 1985) [940].

**W. Invertebrates (Water Concentrations vs. Invertebrates):**

LC50s for Calanoida (copepod order) were 22 to 32 ug/L (ppb) (0.022 to 0.032 mg/L, ppm) for 48-hr exposures [998].

LC50s for *Acartia tonsa* (Calanoid copepod) ranged from 10 to 22 ug/L (ppb) for 24-, 48-, 72- and 96-hr exposures [998].

LC50s for *Amnicola* sp. (Spire snail) were 1.10 and 6.30 mg/L (ppm) for 24-hr exposures, and 2.10 and 0.08 mg/L for 96-hr exposures [998].

LC50 for *Aedes aegypti* (mosquito) was 0.29 mg/L for a 48-hr exposure [998].

LC50s for *Artemia salina* (brine shrimp) were 0.50 mg/L for a 24-hr exposure, and 0.25 mg/L for a 48-hr exposure [998].

LC50 for *Brachionus calyciflorus* (rotifer) was 60 ug/L (ppb) (0.060 mg/L, ppm) for a 24-hr exposure [998].

LC50s for *Chironomus plumosus* (midge) were about 3.18 mg/L for a 24-hr exposure, and 0.60 and 0.88 mg/L for a 96-hr exposure [998].

LC50s for *Chironomus tentans* (midge) ranged from 2.28 to 32.3 mg/L for a 24-hr exposure, with most values around 29 mg/L. LC50s ranged from 0.24 to 0.57 mg/L for a 96-hr exposure [998].

LC50s for Trichoptera (Caddisfly order) were 5.6 and 1.2 mg/L for 24-hr and 96-hr exposures, respectively [998].

LC50s for *Crangon crangon* (common shrimp) ranged from 4.80 to 10.0 mg/L (ppm) for 48-hr exposures,

with most values below 1.3 mg/L [998].

LC50 *Daphnia magna* 0.005 mg/L [970].

Note: mercury exposures changed zooplankton species compositions [970].

LC50 *Modiolus carvalhoi* (mollusk) 0.5 ppm/48 hr; 0.19 ppm/96 hr /Conditions of bioassay not specified/ (Ekanth AE, Menon NR; Fish Technol 20 (2): 84-9, 1983) [940].

**W.Fish** (Water Concentrations vs. Fish):

LC50 for various fish 0.005 to 0.150 mg/L [970].

LC50 for *Channa striata* (Snake-head catfish) was 6.148 mg/L (ppm) for a 72-hr exposure [998].

LC50 for *Carassius auratus* (goldfish) was 0.7 ug/L (ppb) (0.0007 mg/L, ppm) for an 8-day exposure [998].

LC50s for *Chrysophrys major* (Red sea bream) were 25, 16, 6 and 4 ug/L (ppb) for 24-, 48-, 72- and 96-hr exposures, respectively [998].

LC50s for *Cyprinus carpio* (common, mirror, colored, carp) ranged from 0.16 to 0.94 mg/L (ppm) for 96-hr exposures, with most around 0.65 mg/L [998].

LC50 for *Etheostoma spectabile* (orangethroat darter) was around 64 ug/L (ppb) (0.064 mg/L, ppm) for 96-hr exposures [998].

LC50s for *Morone saxatilis* (striped bass) were 0.22, 0.14 and 0.09 mg/L (ppm) for 24-, 48- and 96-hr exposures, respectively [998].

Toxicity values [940]:

Threshold of effect opercular rhythm on *Micropterus salmoides* (largemouth bass) 10 ug/l/21 days. [Morgan WSG; J Water Pollut Control Fed 51: 580 (1979) as cited in USEPA; Ambient Water Quality Criteria Doc: Mercury p.62 (1985) EPA 440/5-84-026].

LC50 Catfish 0.35 mg/l/96 hr. /Conditions of bioassay not specified/ [Spehar RL et al; J Water Pollution Control Federation 53 (6): 1028-1076 (1981) as cited in Environment Canada; Tech Info for Problem Spills: Mercury

(Draft) p.35 (1982)].

LC50 Rana hexadactyla (tadpoles) 0.051 ppm/96 hr /Conditions of bioassay not specified/ [Khangurot BS et al; Acta Hydrochim Hydrobiol 13 (2): 259-63 (1985)].

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

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

For CAS 7439-97-6 (Mercury) the benchmarks are [650]:

SPECIES	WATER CONCEN- TRATION (ppm)
Mouse (test species)	0.0000
Short-tailed Shrew	0.0820
Little Brown Bat	0.1420
White-footed Mouse	0.0530
Meadow Vole	0.0930
Cottontail Rabbit	0.0440
Mink	0.0460
Red Fox	0.0330
Whitetail Deer	0.0180

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

Note: Measures of total vs. acid soluble vs. dissolved mercury: 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 mercury concentrations. For detailed discussion, see the Laboratory and/or Field Analyses section (far below).

EPA 1996 IRIS database information [893]:

Ambient Water Quality Criteria for Human Health: Water & Fish Routes of Exposure: 1.44E-1 ug/liter [893].

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

Published Criteria for Water and Organisms: 0.144 ug/L [689].

IRIS Recalculated (7/93) Criteria for Water and Organisms: 0.14 ug/L [689].

Ambient Water Quality Criteria for Human Health: Fish Only Route of Exposure: 1.46E-1 ug/liter [893].

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

Published Criteria for Organisms Only: 0.146 ug/L [689].

IRIS Recalculated (7/93) Criteria for Organisms Only: 0.15 ug/L [689].

Maximum Contaminant Level Goal:

Value: 0.002 mg/L [893,952]

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

Discussion: EPA has promulgated a MCLG of 0.002 mg/L based on potential adverse effects (renal toxicity) in three major studies. The MCLG is based upon a DWEL of 0.01 mg/L and an assumed drinking water contribution of 20 percent [893].

Maximum Contaminant Level (MCL)[893]:

Value: 0.002 mg/L [893,952]

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

Discussion: EPA has set an MCL equal to  
the MCLG of 0.002 mg/L [893]. Older  
reference: Drinking Water MCL: 2.0 ug/L  
[446,940].

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

EPA Region 9 Preliminary remediation goals (PRGs)  
for tap water [868]: 3.7 ug/L for methyl mercury,  
none given for inorganic mercury.

EPA 1995 Region 3 Risk based concentration (RBC)  
for tap water for inorganic (total) mercury: 11  
ug/L [903].

Wisconsin has some drinking water criteria as low  
as 0.79 ug/L [955].

State Drinking Water Standards [940]:

(AL) ALABAMA 2 ug/l [USEPA/Office of Water;  
Federal-State Toxicology and Risk Analysis  
Committee (FSTRAC). Summary of State and  
Federal Drinking Water Standards and  
Guidelines (11/93)].

(AZ) ARIZONA 2 ug/l [USEPA/Office of Water;  
Federal-State Toxicology and Risk Analysis  
Committee (FSTRAC). Summary of State and  
Federal Drinking Water Standards and  
Guidelines (11/93)].

State Drinking Water Guidelines [940]:

(AZ) ARIZONA 3 ug/l [USEPA/Office of Water;  
Federal-State Toxicology and Risk Analysis  
Committee (FSTRAC). Summary of State and  
Federal Drinking Water Standards and  
Guidelines (11/93)].

(ME) MAINE 2 ug/l [USEPA/Office of Water;  
Federal-State Toxicology and Risk Analysis  
Committee (FSTRAC). Summary of State and  
Federal Drinking Water Standards and  
Guidelines (11/93)].

(MN) MINNESOTA 2 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

Other Occupational Permissible Levels [940]:

Water: Health and Welfare Canada recommends 0.001 mg/l Hg as a maximum acceptable concn in water; Air: The Ontario limit for airborne environmental Hg is 5 ug/cu m. [Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.34 (1982)].

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

Mercury is concentrated in the sludges from sewage treatment by a factor of several hundred to several thousand over the levels initially present in the raw sewage (Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.73, 1979, NRCC No. 16739) [940].

A plant in northwestern Ontario is estimated to have discharged 9 tons of mercury into local waters, with effects traceable 200 miles downstream (Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.84, 1979. NRCC No. 16739) [940].

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

**Sed.Low** (Sediment Concentrations Considered Low):

St. Lawrence River Interim Freshwater Sediment Criteria, 1992. No effect level: 0.05 mg/kg dry weight [761].

**Sed.High** (Sediment Concentrations Considered High):

If the mercury content is greater than 1 ppm the sediment is considered to be heavily polluted [347].

Analyses of sewage from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of mercury is 2.8 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The median for mercury was 3.9 ppm (dry weight), and the range was 0.6-130 ppm (dry weight) [347].

Sediment samples analyzed for NOAA's National Status and

Trends Program between 1984 and 1987, showed that 38 of 175 sites contained mercury concentrations in excess of 0.41 ug/g (ppm), the level considered to be indicative of sediment toxicity [955] (see Sed.General section below).

In a previous study by the Texas Water Quality Board downstream of Dallas, mercury levels in sediments from Beltline Road (6.5 miles downstream of our site 11) were the highest recorded in the State at that time [74]. Sediment concentrations of mercury from our site 12 exceeded the statewide 90th percentile level, 0.32 mg/kg, in 50% of the historical records from 1974 [7,201].

**Sed. Typical** (Sediment Concentrations Considered Typical):

Sediments taken from coastal areas off British Columbia, Canada, contained variable concentrations of mercury ranging from 0.05 ug/g (ppm) to 0.20 ug/g (ppm) [955].

**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 [652]:

EFFECTS RANGE - LOW (NOAA): 0.15 mg/kg (ppm)  
dry weight  
EFFECTS RANGE - MEDIAN (NOAA): 0.71 mg/kg  
(ppm) dry weight

Long 1992 [444]: After studying a large amount of data (including NOAA and AET data) on sediment concentrations versus toxic effects, Long concluded that mercury concentrations of about 1 ppm (dry weight) or more often have been associated with toxic effects. Effects in sediments were rare at mercury concentrations 0.026 to 0.38 ppm. From mercury concentrations of 0.41 to 0.7 ppm, 31% of the data entries suggested toxic effects associated with mercury. From mercury concentrations above 0.88 ppm dry weight, 73% of the data entries suggested toxic effects associated with mercury. However, ERL/ERM methods based on acute toxicity may be insufficient to determine safe levels for

biomagnifying compounds like mercury.

Wisconsin interim criteria for sediments from Great Lakes harbors for disposal in water (1985): Mercury should not exceed 0.1 ppm (dry weight) [347].

Ontario Ministry of the Environment guidelines for open lake disposal of sediments (1986): The guideline for mercury disposal is 0.3 ppm [347].

Ontario Ministry of the Environment Freshwater Sediment Guidelines, 1993. Lowest effect level: 0.2 mg/kg dry weight. Severe effect level: 2 mg/kg dry weight [761].

St. Lawrence River Interim Freshwater Sediment Criteria, 1992. No effect level: 0.05 mg/kg dry weight. Minimal effect level: 0.2 mg/kg dry weight. Toxic effect level: 1 mg/kg dry weight [761].

Environment Canada Interim Sediment Quality Assessment Values, 1994. Threshold effect level: 0.174 mg/kg dry weight. Probable effect level: 0.486 mg/kg dry weight [761].

Guidelines for the pollutional classification of Great Lakes harbor sediments (1977): If the mercury content is less than 1 ppm the sediment is considered to be nonpolluted. If the mercury content is 1 ppm the sediment is considered to be moderately polluted. If the mercury content is greater than 1 ppm the sediment is considered to be heavily polluted [347,761].

New York 1994 Freshwater Dredging Sediment Criteria. No appreciable contamination: less than 0.1 mg/kg dry weight. Moderate contamination level: 0.1 to 4 mg/kg dry weight. High contamination level: greater than 4 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):

No information found.

**Sed.Human** (Sediment Concentrations vs. Human):

No information found.

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

When exposed to mercury in both mediums, fish accumulate more mercury from sediments than from water [95].

Several investigators have found efficient production of methylmercury in wetland soils and sediments. (Jim Wiener, National Biological Survey, NBS, Personal Communication, 1997).

Most methyl mercury production was found to be within the top 10 cm of sediments, virtually all within the top 30 cm, most right at the top [918]. In some habitats, virtually all the mercury in the top 1 cm is methyl mercury [918]. Pore water methyl mercury tends to be highest in spring, decreasing in warmer periods [918]. Porewaters are not stagnant: they are often actively flowing [918]. The sediments are more constant [918].

Microorganisms convert elemental mercury into methyl mercury salt ( $\text{CH}_3\text{HgCl}$ ) & dimethyl mercury, which escape into the atmosphere [366]. Most of these reactions take place in sediments of river & ocean beds [366].

The conversion, in aquatic environments, of inorganic mercury compounds to methyl mercury implies that recycling of mercury from sediment to water to air and back could be a rapid process [366].

Mercury concentrations are typically higher in sediments, in eutrophic (nutrient and carbon rich) areas than in oligotrophic (nutrient and carbon poor) areas. This is thought to be due to the ability of organic compounds to bind mercury to sediments and to suspended organic particulates, as well as the tendency for the increased nutrients to stimulate the growth of the bacteria which methylate mercury.

Mercury in bottom sediments is resuspended during floods and carried further downstream. Such events have resulted in increased levels of mercury in fish, as noted in a previous Fish and Wildlife Service study in Montana

[32].

Mercury attached to sulfides and other sulfur containing bottom sediments in marshes can make its way from the sediments and even up into the atmosphere by way of bacterial action (methylation), bioturbation, transport on volatile compounds, and various other mechanisms, Although these are probably slow-rate mechanisms, they may also be happening over very broad time and geographical scales, so that the total amounts of mercury released into the overlying waters and atmosphere may be substantial.

The 1989 "Mercury in Temperate Lakes" studies done by William Fitzgerald of the University of Connecticut and Dr. Carl Watras (Wisconsin Department of Natural Resources) indicated that atmosphere is the major source of mercury in many inland lakes and that sediments are the major sink.

In Yatsushiro Sea & Minamata Bay, Japan, the croaker (*Argyrosomus argentatus*) was a good indicator of hg pollution [366]. Mercury migrated from sediment to the croaker by way of suspended particulate matter & zooplankton [366]. Conversion from inorganic to methylmercury occurs at the stage of zooplankton [366].

In those systems where the residence time of the water is low (rivers and streams), mercury (Hg) is in most cases removed quite quickly, perhaps by as much as 50% per yr: ie the half-life of the Hg would be of the order of 1 yr or more. The mechanisms largely responsible must be (i) ingestion or absorption and subsequent removal by biological materials and organisms, and (ii) transformation to a more volatile chemical form which can escape from the sediment and from the entire aquatic system (Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.81, 1979, NRCC No. 16739) [366]..

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

**Soil.Low** (Soil Concentrations Considered Low):

No information found.

**Soil.High** (Soil Concentrations Considered High):

Soils with more than 1,000 ppm must be considered toxic (Manual on Hazardous Substances in Special Wastes, Federal Environmental Agency Waste Management Division, 1976, as cited in Environment Canada; Tech Info for

Problem Spills: Mercury, Draft, p.43, 1982) [940].

Analyses of sewage from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of mercury is 2.8 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The median for mercury was 3.9 ppm (dry weight), and the range was 0.6-130 ppm (dry weight) [347].

Around mercury deposits there is usually 1 to 10 ppm mercury in soils [951].

**Soil. Typical** (Soil Concentrations Considered Typical):

EPA 1981: 0.03 mg/kg dry weight is typical [83].

Typical Igneous Rocks (Earth's Crust) Concentrations: EPA 1981: 0.08 mg/kg dry weight [83].

Volcanic exhalations: Soil air over mercury deposits 0-2000 ng/cu m; Soil and Glacial Deposits: Normal soils 20-150 ppb; Normal tills, glacial clay, sand, etc 20-100 ppb; Soils, tills, etc near mercury deposits, sulfide deposits, etc up to 250 ppm; Soil horizons (normal)- A (humic) 60-200 ppb, B 30-140 ppb, C 25-150 ppb; Soil horizons (near mercury deposits)- A (humic) 200-1860 ppb, B 140-605 ppb, C 150-554 ppb (Jonasson IR, Boyle RW; Bull Can Inst Min Metal 65: 32-9, 1972, as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.39, 1979, NRCC No. 16739) [940].

Approximate concn of all forms of mercury in the earth's crust is 80 ppb (Jonasson IR; Mercury in the Natural Environment: A Review of Recent Work: Geological Survey of Canada p.13-14, 1970) [940].

Concentration in soils: 0.01 ppm [951].

**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):

Note: Benchmark concentrations for Hg in soil or sediments should probably be used cautiously. A key factor affecting ecological and health risks of mercury contamination is

the conversion of inorganic Hg(II) to methylmercury, which is largely a microbial process. Some contaminated ecosystems have large inventories of Hg(II) in sediments or soils, but produce little methylmercury. Others have low inventories of inorganic Hg(II), but have high levels of methylmercury in upper trophic levels because of efficient methylation of inorganic Hg. Wet soils or sediments may be different than dry. Several investigators have found efficient production of methylmercury in wetland soils and sediments. (Jim Wiener, National Biological Survey, NBS, Personal Communication, 1997).

Other Maximum Allowable Concentration (MAC) levels for mercury (dry weight): 2 ppm (Stuttgart), 1 ppm (London) [719].

Proposal of European Economic Commission for MAC of mercury in soils treated with sewage sludge: 2 ppm dry weight (London) [719].

Proposal of Ontario Ministry of Agriculture and Food for MAC in soils treated with sewage sludge: 0.5 ppm dry weight (published in Tokyo; work done for Ontario) [719].

The 1987 soil (clean up) criteria given by the New Jersey Department of Environmental Protection for mercury is 1 mg/kg dry weight [347,386].

In 1981 the U.S. Environmental Protection Agency proposed 10 ppm as an upper limit for mercury for sewage sludges suitable for land application [391].

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act (1982): For background concentrations mercury equals 0.5 ppm, for moderate soil contamination mercury equals 2 ppm, and for threshold values mercury equals 10 ppm [347].

Soil cleanup criteria for decommissioning industrial sites in Ontario (1987): For agricultural land mercury should not exceed 0.5 ppm, for residential or parkland mercury should not exceed 1 ppm, and for commercial or industrial land mercury should not exceed 2 ppm [347].

Maximum allowable concentrations and tentative allowable concentrations of pesticides and other substances in soil in the Soviet Union (1984): The maximum allowable concentration of mercury is 2.1

ppm [347].

Maximum cumulative additions of metals from sewage sludge that may be added to Vermont soils, by soil texture (1984): For loamy sand mercury should not be added at greater than 6 kg/ha, for fine sandy loam mercury should not be added at greater than 11 kg/ha, and for clay loam mercury should not be added at greater than 22 kg/ha [347].

Soil limit values determined by the Council of European Communities for the addition of heavy metals from sewage sludge to soil with a pH of 6.0 to 7.0 (1986): The limit value of mercury is 1-1.5 ppm [347].

**Soil.Plants (Soil Concentrations vs. Plants):**

50 ppm of mercury in soil impairs growth of plants. Soils with more than 1,000 ppm must be considered toxic (Manual on Hazardous Substances in Special Wastes, Federal Environmental Agency Waste Management Division (1976) as cited in Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.43 (1982) [940].

Levels of mercury (dry weight) considered phytotoxic: 5 ppm (Vienna), 5 ppm (Warsaw), 2 ppm (Warsaw), 0.3 ppm (Ontario) [719].

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 benchmark for soil [651]:

For CAS 7439-97-6, MERCURY, the benchmark is 0.3 mg/kg dry weight in soil (WILL and SUTER, 1994).

See also Soil.Misc section below for additional information on mercury and plants.

**Soil.Invertebrates (Soil Concentrations vs. Invertebrates):**

No information found.

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

No information found.

**Soil.Human** (Soil Concentrations vs. Human):

EPA 1995 Region IX Preliminary remediation goals (PRGs) for cancer risk for methyl mercury only (none given for inorganic mercury) [868]:

Residential Soil: 6.5 mg/kg wet weight  
Industrial Soil: 68 mg/kg wet weight

NOTE:

- 1) Values are based on a one-in-one million cancer risk.
- 2) 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.
- 3) PRGs are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects [903].

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

None given for methyl mercury [903]. For inorganic mercury, the groundwater protection RBC for soil is 3 mg/kg mercury dry weight [903].

Acceptable level of mercury for production of healthy food: 2.1 ppm dry weight (Moscow) [719].

EPA soil screening level (SSL): none given [952].

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

Mercury is predominantly particle bound in contaminated water ways. [WHO; Environ Health Criteria: Mercury p.59 (1976) [940].

Mercury toxicity to plants is severe, and different plants vary in their ability to concentrate mercury [951].

In general, the availability of soil mercury (Hg) to plants is low and there is a root barrier to translocation of Hg to plant tops (Steward JWB et al; Joint FAO/IAGA Meetings: Publ IAGA Vienna p.23-4, 1975, as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.101, 1979, NRCC No. 16739) [940].

**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:

Maximum levels for mercury are recommended at 0.5 ppm for plant tissue and 0.15 in soil. These recommendations reflect human effects rather than plant responses (Britt DL, Hushon JM; Biological Effects, Criteria and Standards for Hazardous Pollutants Associated with Energy Technologies p. 6-39, 1976, ERDA E, 49-1, -3878) [940].

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

Mitra summarized body burden information in plants in 1987 [978]; due to lack of time, the results have not yet been quoted in this document.

Living organisms: Marine plants 0.01-37 ppb fresh wt; terrestrial plants 0-40 ppb fresh wt; Terrestrial plants in vicinity of mercury deposits 200-30,000 ppb fresh wt. (Jonasson IR, Boyle RW; Bull Can Inst Min Metal 65: 32-9, 1972, as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.39, 1979, NRCC No. 16739) [940].

Mercury and its compounds occur naturally in trace amounts in plants growing in soils with low mercury concentrations (<500 ppb) (OECD; Mercury and the Environment p.135-147, 1974) [940].

Typical Food Basket Concentrations [366]:

Cabbage, 0.09 mg/kg (natural), 0.57 mg/kg (abnormal). /Mercury Compounds/ [OECD; Mercury and the Environment p.135-141 (1974)].

Various kinds of cereal and flour (2,133 samples, taken from the Federal Republic of Germany and the United Kingdom) ranged from 0 to 20 ug/kg with most values being close to 3 ug/kg. Mercury levels in cereal products from the same countries (52 samples) ranged up to 50 ug/kg with most values close to 20 ug/kg. Vegetables and fruits (288 samples) from Belgium, the Federal Republic of Germany, and

the United Kingdom had mercury levels up to 50 ug/kg with most values close to 7 ug/kg. [Bouquiaux J; Proceedings of the Intl Symposium on the Problems of Contamination of Man and His Environment by Mercury and Cadmium p.23 (1974) as cited in WHO; Environ Health Criteria: Mercury p.59 (1976)].

**Tis.Invertebrates:**

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

No information found.

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

No information found.

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

No information found.

**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):

Human health standards for fish have included a 1.0 mg/kg U.S. FDA standard and a 0.5 mg/kg Canadian standard [32].

Legal Limits for Concentrations in Fish and Fishery Products: The lowest legal limit was 0.1 mg/kg (Venezuela) [216,418]. Eighteen countries (and some states like Colorado) have limits less than or equal to 0.5 mg/kg, but the U.S. limit is 1.0 mg/kg total mercury [216,418, see also note below].

Maine Department of Human Services Human consumption level of concern: 0.43 ppm mercury (The North American Task Force on Mercury Report entitled "The Status of Mercury in the United States." published 10 September 1996, available from the Commission for Environmental Cooperation; 393, rue St.-Jacques Ouest; Bureau 200; Montreal Quebec Canada, H2Y 1N9).

FDA Action Level for Mercury in Fish Tissue Used as

Human Food: The FDA action level for mercury for fish tissue to be consumed by humans is 1.0 mg/kg (ppm) wet weight [417]. This level includes consideration of mercury's effects on children.

NOTE: Although the FDA calls for methylmercury analyses, it often makes more sense to measure total mercury in fish tissues rather than methylmercury, since 1) virtually all of the mercury in fish tissue is methyl mercury [489,914], 2) more laboratories can accurately measure total mercury in fish tissues than can accurately measure methylmercury, and the methylmercury analysis is about five times more expensive than the total mercury analysis [489]. Therefore, it is easier and less expensive to simply analyze total mercury and to use this concentration as a fairly good estimate of methyl mercury in tissues.

For risk to human adults eating fish, separate carcinogenic and non-carcinogenic risk-based fish tissue concentrations were calculated [903]. The following EPA Region III fish tissue risk-based concentration (RBC) benchmark utilizes the lower of the two concentrations (non-carcinogenic), rounded to two significant figures [903]:

RBC for inorganic mercury = 0.41 mg/Kg wet weight of fish tissue (non cancer risk the lowest).

RBC for methyl mercury = 0.14 mg/Kg wet weight of fish tissue (non cancer risk the lowest).

Concentrations in edible fish should not exceed 0.5 ppm (Britt DL, Hushon JM; Biological Effects, Criteria and Standards for Hazardous Pollutants Associated with Energy Technologies p. 6-38 (1976) ERDA E, 49-1, -3878) [366].

EPA Cancer Criterion for Mercury in Fish Tissue Used as Human Food:

The EPA criterion for fish tissue to be consumed by humans for a 1:1,000,000 (1E+06) additional risk for carcinogens is a mercury concentration of 3.23 mg/kg (ppm) wet weight [417].

Predator Protection Level (Tissue Concentrations):  
The most recently recommended level for the

protection of avian predators which consume fish and other aquatic organisms is that total mercury in these food items should not exceed 0.1 mg/kg [33]. The author believes the 0.1 mg/kg alert level may be inadequate to protect fish and wildlife, since concentrations of 0.1 mg/kg fed to ducks reduced fertility and inhibited food conversion [34].

#### Predator Alert Level (Tissue Concentrations):

Due to mercury's potency, an argument could be made for applying an application factor to FDA's 1.0 mg/kg action level for mercury in fish used as human food. Assuming fish typically are eaten by humans at no more than 3 of 21 meals per week, and further assuming that fish usually account for no more than half of the food at each of those meals, a typical maximum percentage of fish in the human weekly diet could be estimated as  $3 \times 0.5$  divided by 21 meals or 7.14% of the diet.

On the other hand, predators such as bass may be eating other fish and wildlife exclusively, and the tendency of contaminants like mercury to bioaccumulate in predators or biomagnify up the food chain make a lower standard necessary. Fish and wildlife predators usually consume the entire body of a prey species rather than fillets.

Concentrations of metal contaminants in muscle tissue are typically 0.5 to 0.6 of the concentration of a whole-body sample [63]. Dividing the 7.14% level by 2 to compensate for the difference between whole-body and muscle concentrations would yield a fish and wildlife application factor of 0.036. Multiplying 0.036 by the 1.0 FDA action level would yield an alert level of 0.036 mg/kg.

The 0.036 mg/kg level is not much lower than concentrations fed to chickens (0.050 mg/kg) which resulted in chickens concentrating mercury to levels high enough to be of concern to human consumers [33]. However, each species is probably different in sensitivity to mercury, so more work would have to be done to definitively develop a predator alert level for mercury, so we have provided this simple derivation for illustrative and discussion purposes rather than for regulatory purposes.

The predator alert level derived above (0.036 mg/kg) was exceeded by 64 of 77 Trinity River samples.

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:

Mitra summarized body burden information in fish 1987 [978].

Lightly contaminated areas often have 0.6 to 4 ng/L mercury in fish flesh [914]. Areas heavily contaminated from direct sources have fish flesh in the following ranges: 4-100 ng/L (often 10-40 ng/L) [914]. Methyl mercury is often 0.01-0.8 (max 2) ng/L.

Some habitats typically have elevated concentrations of mercury in fish, included newly flooded reservoirs and low alkalinity lakes:

Fish tissues are typically 0.7 to 3 ug/g wwt in newly flooded reservoirs (there is often a 10 fold increase following inundation) [914]. This probably is the result of increases of organic carbon, as plants and other organics are microbially degraded [914].

Fish tissues are typically 0.5 to 0.9 ug/g wwt in low alkalinity lakes [914].

To put the above concentrations in perspective, 0.5 and 1 ug/g are most often used for human health advisories [914].

A concentration of 9-20 ug/g wet weight in mercury in muscle tissues of juvenile or adult fish results in harmful effects [914]. However, the young are more susceptible to harmful effects of mercury residues. In fish embryos or eggs, 0.07 to 0.10 ug/g wet weight can result in adverse effects [914].

Fish eggs in Lake Ontario have perhaps (speculative) high enough mercury concentrations (in the range of 0.011 ug/g wet weight) to be impacted [914].

NCBP Wet Weight Concentrations of Mercury in Whole-

Body Fish Samples. The 1976-1984 NCBP survey report gave the nationwide maximum mercury level as 0.37 mg/kg wet weight, the 85th percentile level as 0.17 mg/kg, and the geometric mean level as 0.10 mg/kg [384].

Very high value: At one time there was 6 ppm in bass in the everglades [920].

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

A muscle tissue level of 0.232 mg/kg has been shown to cause decreased swimming ability in fish [57].

Gradient Monitoring Levels: In mosquitofish, mercury showed a tendency to increase from upstream of Fort Worth to downstream at Malloy Road Bridge south of Dallas.

In a previous report, the Texas Parks and Wildlife Department reported that mercury was one of the few metals which appeared to increase in concentration as one progressed downstream [56].

In related findings, the Trinity River Authority indicated that high mercury concentrations were occasionally found at various stations downstream of Dallas, some quite a distance downstream [42]. The highest mercury level (2.318 mg/kg) was in shad muscle tissue from the Crockett area; the 0.5 mg/kg level was exceeded in 10 of 38 fish samples collected downstream of Dallas [42]. Algae may be playing a role in moving mercury downstream [95].

Mercury concentrations in water above recommended criteria have also been reported for the Trinity River [71]. At all three Trinity River stations sampled for water during the July fish kill of 1985, mercury was found to be elevated above levels which the Environmental Protection Agency recommends not be exceeded at any time [56].

In our study, the four highest mercury levels in mosquitofish were from sites 9, 10, 11, and 12 just downstream of Dallas. Mosquitofish samples from these four sites had significantly higher concentrations of mercury

than a group of mosquitofish samples from sites (1, 16, and 27) upstream of Fort Worth or Dallas.

Except for 5 sites below Dallas, Trinity River mosquitofish concentrations of mercury (0.025 to 0.065 mg/kg) were lower than those recorded for mosquitofish from Big Bend National Park, an area where mercury mining has occurred in the past [65].

#### Edible Tissue (Mostly Fillet) Concentrations for Mercury in Freshwater Fish:

The highest concentrations of mercury in 8 studies of edible fish tissues in several states (mostly eastern states and the studies included sites which were not especially clean) ranged from <0.002 to 3.1 mg/kg wwt [57]. Seven of the eight studies had maximum mercury concentrations below 0.84 ppm wwt [57].

#### Fish/Seafood Concentrations [940]:

Fish Concn (avg): 100-200 ng Hg/g fish (est) [USEPA; Mercury Health Effects Update p.2-4 (1984) EPA 600/8-84-019F].

Fish and shellfish /concn/ in the United States: Tuna (mainly canned) 0.24 ppm; Unclassified (mainly breaded, including fish sticks) 0.21 ppm; Shrimp 0.46 ppm; Flounder 0.10 ppm; Clams 0.05 ppm; Crabs/lobsters 0.25 ppm; Salmon 0.05 ppm; Oysters/scallops 0.04 ppm; Trout 0.42 ppm; Bass 0.21 ppm; Catfish 0.15 ppm; Sardines 0.06 ppm; Pike 0.61 ppm; Snapper 0.45 ppm; Whiting 0.05 ppm; All other classified 0.21 ppm. [USEPA; Mercury Health Effects Update p.3-16 (1984) EPA 600/8-84-019F].

Mercury content in muscle tissue of British Columbia fish: Crabs (Squamish) 1.55-13.4 ppm; Crabs (Fraser River Flats) 0.19 ppm; Crabs (West Vancouver) 0.14 ppm; Crabs (Tofino) 0.02 ppm; Dolly Varden (Carpenter Lake) 0.41-1.94 ppm; Dogfish (English Bay) 1.08 ppm; Flounder (Squamish) 1.00-1.42 ppm; Flounder (Fraser River Flats) 0.23 ppm; Flounder (Hecate Strait) 0.11 ppm; Herring (Squamish) 0.14-0.30 ppm; Herring (Prince Rupert) 0.07 ppm; Lake trout (Pinchi Lake) 2.86 ppm; Rainbow trout (Tezzeron Lake) 0.04 ppm. [Bligh EG, Armstrong

FAJ; Int Council Explor Sea Rep No. CM 1971/E34 p.13 (1971) as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.90 (1979) NRCC No. 16739].

Concentrations in edible fish should not exceed 0.5 ppm. /Mercury Compounds/ [Britt DL, Hushon JM; Biological Effects, Criteria and Standards for Hazardous Pollutants Associated with Energy Technologies p. 6-38 (1976) ERDA E (49-1)-3878].

**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:

Concentrations of 0.050 mg/kg fed to chickens resulted in chickens concentrating mercury to levels high enough to be of concern to human consumers [33].

Predator Protection Level: The most recently recommended level for the protection of avian predators which consume fish and other aquatic organisms is that total mercury in these food items should not exceed 0.1 mg/kg [33]. The author believes the 0.1 mg/kg alert level may be inadequate to protect fish and wildlife, since concentrations of 0.1 mg/kg fed to ducks reduced fertility and inhibited food conversion [34]. The 0.1 mg/kg level was exceeded in 17 of 77 Trinity River samples. Included in this group were a variety of fish and turtles, all from areas just downstream of Dallas or other highly polluted sites. The three highest levels (0.19 to 0.23 mg/kg) exceeding 0.1 but not 0.5 mg/kg, were all in fish from sites just south of Dallas, including composite samples of mosquitofish from site 12, carp from site 11, and smallmouth buffalo fish from site 24.

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): The most recently recommended level for the protection of avian predators which consume fish

and other aquatic organisms is that total mercury in these food items should not exceed 0.1 mg/kg [33]. The author believes the 0.1 mg/kg alert level may be inadequate to protect fish and wildlife, since concentrations of 0.1 mg/kg fed to ducks reduced fertility and inhibited food conversion [34].

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

For mercury CAS 7439-97-6, the benchmarks are [650]:

CONCEN- SPECIES	(mg/kg/day)	NOAEL TRATION (ppm)	FOOD
Mouse (test species)	0.0064		0.0000
Short-tailed Shrew	0.0180		0.0300
Little Brown Bat	0.0230		0.0300
White-footed Mouse	0.0160		0.1030
Meadow Vole	0.0130		0.1120
Cottontail Rabbit	0.0040		0.0220
Mink	0.0050		0.0330
Red Fox	0.0030		0.0280
Whitetail Deer	0.0010		0.0390

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

Note: Mercury vapor appears to be extremely toxic to sheep & cattle & is presumably absorbed by respiratory tract & other mucous membranes. Inhalation of mercury vapor causes dyspnea & coughing, nasal discharge, fever, & loss of appetite & condition, with sometimes bleeding of oral mucosa, dermatosis & nephritis. (Clarke, M. L., D. G. Harvey and D. J. Humphreys. Veterinary Toxicology. 2nd ed. London: Bailliere Tindall, 1981. 61) [940].

Mitra summarized body burden information in various birds 1987 [978].

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

Mercury concentrations above the detection limit (0.02 mg/kg) were found in 73 of 77 Trinity River samples.

Maximum Level: The highest mercury concentration, 0.85 mg/kg, was from a composite sample of fat dissected from three Mississippi map turtles from site 11. This was the only sample which exceeded the 0.5 mg/kg whole-body guideline previously proposed to avoid harm to fish, ducks, and predators [20,31]. For comparison, human health standards for fish have included a 1.0 mg/kg U.S. FDA standard and a 0.5 mg/kg Canadian standard [32]. A muscle tissue level of 0.232 mg/kg has been shown to cause decreased swimming ability in fish [57].

Concentrations of 0.1 mg/kg fed to ducks reduced fertility and inhibited food conversion [34].

Whole-body concentrations of 0.050 and 0.060 mg/kg mercury were found in softshell turtles from two comparatively rural Trinity River sites (sites 1 and 15). Concentrations of 0.18 mg/kg were found in whole-body samples of softshell turtles from two highly polluted sites (sites 11 and 18). The mercury level in one composite sample of softshell turtles from the Rio Grande River at Big Bend National Park was 0.073 mg/kg [65].

The effects of autumn molt on levels and distribution of mercury (Hg) between feathers and body tissues in juvenile, second-year, and adult Bonaparte's gulls (*Larus philadelphia*) in the Quoddy region, New Brunswick, Canada, are reported. A total of 222 birds were collected over 7 years and collectively pooled into 15 ten-day periods spanning the molting season. During their stopover, second-year and adult birds undergo complete molt, including sequential molt of the primary feathers. The juveniles undergo only partial molt. The mean Hg concentrations for all feathers including the primary feathers were lowest for juveniles (1.98 +/- 0.07 ug/g dry wt) and highest for adults (4.1 +/- 2.2 ug/g dry wt). After completion of the molt, the new feathers contained 93% of the Hg body burden. All tissues (liver, kidney, muscle, and brain) showed a progressive decrease in Hg concentration during the period of molt (data presented in graph). Juvenile gulls contained higher tissue concentrations than second-year and

adult birds before converging to a minimum asymptotic Hg level after molting. Second-year birds did not show any differences in tissue concentration over time. The percent distribution of total Hg (excluding feathers) in postmolt juveniles (N= 2), second-year (N= 2) and adult gulls (N= 12) was: In liver, 38.3 +/- 9.90, 32.3 +/- 4.67, and 36.4 +/- 6.57%, respectively; in kidneys, 6.2 +/- 0.14, 3.6 +/- 1.34, and 5.5 +/- 1.53%, respectively; in muscle, 6.1 +/- 2.26, 5.5 +/- 0.57, and 8.8 +/- 3.65%, respectively; in brain, 1.4 +/- 0.21, 0.7 +/- 0.07, and 0.9 +/- 0.25%, respectively; and in the carcass, 48.1 +/- 8.02, 58.0 +/- 6.59, and 48.4 +/- 8.19%, respectively (Braune BM, Gaskin DE; Arch Environ Contam Toxicol 16: 539-549, 1987) [940].

Baseline data on Hg 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 Hg concentrations were measured by flame absorption spectrometry. On a wet wt basis, the mean Hg concentration in muscle, liver, kidney, and whole body of fetuses (gestation age 0.3-0.7 yr, N= 13) were 1.9, 2.3, 2.0, and 2.2 ng/g, respectively; in fawns (age 0.0-0.5 yr, N= 12), 1.4, 9.1, 44.6, and 24.3 ng/g, respectively; in yearlings (age 0.5-2.5 yr, N= 6), 2.5, 11.2, 97.2, and 35.3 ng/g, respectively; in adults (age 2.5 to 10 yr, N= 42), 2.1, 13.2, 94.5, and 36.3 ng/g, respectively; and in adults (age 10 to 17.5 yr, N= 17), 2.0, 11.0, 87.9, and 33.3 ng/g, respectively. The mean Hg concentration in fleece of fawns, yearlings, and adults (age 2.5 to 10 yr) was 372, 377, and 350 ng/g. Bone samples of two adult serows contained 5.3 to 17.1 ug/g. The Hg burden of fetuses was very low (<1%) compared with those of their mothers. Although the Hg accumulation in muscle, liver, and kidney varied during the developmental stage, the age-related accumulation was similar to that in the whole body. In fleece, however, the Hg concentration remained constant throughout life. Fleece contained about 40% of the body burden, indicating that Hg is excreted by molting. The Hg uptake agreed well with the concentration found in food plants. There was no significant difference in Hg concentration between collection locations (Honda K et al; Arch Environ Contam Toxicol 16: 551-61, 1987) [940].

**Tis.Human:**

A) Typical Concentrations in Human Food Survey Items:

See also Tis.Fish, C) and Tis.Plants, B) sections above.

Milk Concentrations [940]:

Mercury levels in milk products (81 samples from the Federal Republic of Germany and the United Kingdom) ranged from 0 to 40 ug/kg with a medium value of 6 ug/kg. [Bouquiuoux J; Proceedings of the Intl Symposium on the Problems of Contamination of Man and His Environment by Mercury and Cadmium p.23 (1974) as cited in WHO; Environ Health Criteria: Mercury p.59 (1976)].

Food Survey Results [940]:

Levels in eggs (440 samples) taken from Denmark, the Federal Republic of Germany and the United Kingdom, ranged from 0 to 100 ug/kg with most of the values between 10 and 20 ug/kg. Levels in meat, meat products, and prepared meat products (318 samples from the United Kingdom) ranged from 0 to 50 ug/kg with most values lying between 10 and 20 ug/kg. Various kinds of cereal and flour (2,133 samples, taken from the Federal Republic of Germany and the United Kingdom) ranged from 0 to 20 ug/kg with most values being close to 3 ug/kg. Mercury levels in cereal products from the same countries (52 samples) ranged up to 50 ug/kg with most values close to 20 ug/kg. Vegetables and fruits (288 samples) from Belgium, the Federal Republic of Germany, and the United Kingdom had mercury levels up to 50 ug/kg with most values close to 7 ug/kg. [Bouquiaux J; Proceedings of the Intl Symposium on the Problems of Contamination of Man and His Environment by Mercury and Cadmium p.23 (1974) as cited in WHO; Environ Health Criteria: Mercury p.59 (1976)].

Tuna, 0.2 mg/kg (natural), 10.6 mg/kg (abnormal); eggs, 0.009 mg/kg (natural), 0.029 mg/kg (abnormal); cabbage, 0.09 mg/kg (natural), 0.57 mg/kg (abnormal). /Mercury Compounds/ [OECD; Mercury and the Environment p.135-141 (1974)].

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):

For risk to human adults eating fish, separate carcinogenic and non-carcinogenic risk-based fish tissue concentrations were calculated [903]. The following EPA Region III fish tissue risk-based concentration (RBC) benchmark utilizes the lower of the two concentrations (non-carcinogenic), rounded to two significant figures [903]:

RBC for inorganic mercury = 0.41 mg/Kg wet weight of fish tissue (non cancer risk the lowest).

RBC for methyl mercury = 0.14 mg/Kg wet weight of fish tissue (non cancer risk the lowest). Note: virtually all of the mercury in fish tissue is methyl mercury [489,914], so perhaps the benchmarks for total or inorganic mercury should be down in this range as well (Roy Irwin, National Park Service Personal Communication, 1996).

For comparison, human health standards for fish for total mercury or inorganic mercury have included a 0.5 mg/kg Canadian standard [32]. The legal Limits for Concentrations in Fish and Fishery Products: The lowest legal limit was 0.1 mg/kg (Venezuela) [216,418]. Eighteen countries (and some states like Colorado) have limits less than or equal to 0.5 mg/kg, but the U.S. limit is 1.0 mg/kg total mercury wet weight [216,417,418].

Maine Department of Human Services Human consumption level of concern: 0.43 ppm mercury (The North American Task Force on Mercury Report entitled "The Status of Mercury in the United States." published 10 September 1996, available from the Commission for Environmental Cooperation; 393, rue St.-Jacques Ouest; Bureau 200; Montreal Quebec Canada, H2Y 1N9).

Rfd for total (inorganic) mercury 3.0E-04 mg/kg/day [903,952].

Rfd oral for methyl mercury 1.0E-04 mg/kg/day [868,903].

Oral doses of 100-500 G have been given to man with little effect, because of poor absorption, although they occasionally resulted in diarrhea (National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 274) [940].

C) Body Burden Residues in Humans: Typical, Elevated, or

of Concern Related to the Well-being of Humans:

Mitra summarized body burden information in mammals, including extensive data on concentration in human organs, in 1987 [978]; due to lack of time, the results have not yet been quoted in this document.

Lethal Blood Level: The concn of inorganic mercury present in blood (serum or plasma) that has been reported to cause death in humans is: 0.04-2.2 mg%; 0.4-22 ug/ml. /Inorganic Mercury/ (Winek, C.L. Drug and Chemical Blood-Level Data 1985. Pittsburgh, PA: Allied Fischer Scientific, 1985) [940].

**Tis.Misc.** (Other Tissue Information):

Total concentrations of mercury in sediment, water, and biota in lower trophic levels (below fish) are not reliable predictors of methylmercury concentrations in fish [999]. Mercury concentrations in fish are low in some freshwater ecosystems having large inventories of inorganic mercury in sediments [999].

Mercury in fish is mostly (95-99%) methyl mercury [914,999]. There is no methylation of inorganic mercury (II) in tissues, and elimination of methyl mercury is slow so there are often increasing concentrations of methyl mercury in fish with age or size [914]. Methylation may occur in gut but this is not thought to be a significant source of methyl mercury [914]. Diet is the main source of mercury in fish, probably 90% of the source [914]. There is practically no elimination of methyl mercury from fish as documented in various studies in whole body as well as muscle [914]. Exposures to fish to inorganic mercury is mostly to mercuric chloride [914].

The tissue concentration ratio of mercury comparing predator to prey is often about 5 to 7 [914]. However, there are exceptions and overlap: if bass eat invertebrates rather than perch, the ratio from bass to perch does not hold up [914].

The mostly inorganic mercury in mayflies is not so toxicologically significant as methyl mercury [914]. However, some invertebrates may be able to mobilize mercury through bioturbation [914].

Pregnant Hartley guinea pigs in late gestation were repeatedly exposed in a chamber to 0 or 0.2-0.3 mg/cu m mercury vapor mixed with fresh air for 2 hr per day until parturition. The mothers and their offspring were killed

and their tissues were analyzed for mercury content. Mercury concentrations in whole blood of offspring were lower than that of mothers. Mercury concentration ratios in neonatal brain, lung, heart, kidney, plasma, and erythrocytes were much lower than those of maternal organs and tissues, with the exception of neonatal liver, which showed a mercury concentration twice as high as that of maternal liver. In placental tissue, mercury levels were found to be higher than those in the blood of mothers and offspring. The results suggested that mercury vapor metabolism in fetuses was quite different from that in the mothers, and that mercury vapor was most likely oxidized and accumulated in the fetal liver as ionic mercury (Yoshida M et al; Arch Toxicol 58: 225-8, 1986) [940].

Severe has been produced damage to kidneys, liver, brain, heart, lung & colon of rabbits exposed for single 4-hr period to mercury vapor at avg concn of 28.8 Mg/cu m, mild damage to most of these organs occurred from single hour exposure. ... Mercury vapor in repeated daily exposures for ... 83 Weeks ... /Produced/ severe damage to kidney, heart, lung & brain of rabbits after 6 weeks at 6 mg hg/cu m, but no microscopic indication of tissue damage or of altered kidney function in dogs after 83 wk of exposure at 0.1 Mg hg/cu m. Although intermediate level, 0.86 Mg/cu m, produced significant amt of brain & kidney injury at 6 wk, this disappeared on cessation of exposure (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. 1775) [940].

#### Additional Information on Mercury in Plants:

There is little or no active uptake (translocation through the roots) in some species of plants, although even in these plants there can be some mercury issues related to deposition on plant surfaces and uptake of gaseous mercury through stomata (John Huckabee, Electric Power Research Institute, personal communication, 1994). However, the literature is mixed, and some species of plants seem better at taking up mercury than others. Some literature references say there are root barriers to translocation of mercury, others say there is considerable relationship between environmental concentrations and plant concentrations. The BCF for mercury is the same for freshwater fish, marine plants, and freshwater plants [366].

Other references say that plants differ in their ability to uptake mercury, that some plants can develop a tolerance to mercury in soil, and that

translocation does occur in various plant tissues, including apple leaves to fruit, potato leaves to tubers, rice leaves to grains, and from wheat or pea seed to first generations seed [719].

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

Methylmercury bioaccumulates in fish and many other aquatic organisms and biomagnifies in food chains [999]. The fraction of total mercury existing as methylmercury typically increases up aquatic food chains from primary producers to fish [999]. It is suspected that most of the methylmercury (inventory) within an aquatic ecosystem at a given point in time resides in the fish [999]. However, the vast majority of mercury (presumably mercury in general, not just methyl mercury) in an aquatic ecosystem is found in the sediments [999].

Temperature may be a significant environmental variable affecting methylmercury production and uptake in fish and other biota in aquatic ecosystems [999].

Nearly all (95-100%) of the mercury present in fish is methylmercury, obtained mostly from the diet [999]. The structure of aquatic food webs can greatly influence mercury concentrations in fish [999]. Methylation and demethylation are key processes affecting concentrations of methylmercury in aquatic organisms in both grossly and lightly contaminated ecosystems [999].

Total concentrations of mercury in sediment, water, and biota in lower trophic levels (below fish) are not reliable predictors of methylmercury concentrations in fish [999]. Mercury concentrations in fish are low in some freshwater ecosystems having large inventories of inorganic mercury in sediments [999].

The biogeochemical processes of mercury methylation and demethylation are probably the most important bioaccumulative-controlling steps in the environmental mercury cycle [999]. Methylation is largely the result of intracellular processes of sulfate-reducing bacteria, although other microorganisms can methylate mercury as can some abiotic processes [999].

Demethylation of mercury is also microbially mediated [999]. There appear to be two pathways: the mer Operon (a lyase/reductase process), and an oxidative process [999]. Current research seeks to identify the organisms which mediate the demethylation processes, to quantify where and under what conditions each process dominates, and rates reactions [999].

Methyl mercury is very dangerous [368]. Organisms do not expel it fast enough to prevent accumulation [368]. Phenyl mercury and inorganic mercury are accumulated at slower rates [368]. Organo mercury develops in soil within 30-50 days after application [368]. And in the top 2 cm of bottom deposits [368].

Assimilation efficiency of fish assimilating mercury: high for gut (65-89 percent) whereas it is much lower (typically 12%) for waterborne assimilation across a gill [914]. Methyl mercury is rapidly transported to organs via red blood cells [914]. Mercury is highest in blood, spleen, liver, and kidney [914]. There is an

eventual redistribution in the tissues: mercury in fish is relocated to skeletal muscle tissue, associated with sulfhydryl groups and protein [914].

Preliminary data suggests the potential for bioaccumulation or bioconcentration of mercury is high to very high for the following biota: mammals, birds, fish, mollusks, crustacea, and lower animals [83]. It appears to be relatively low for mosses, lichens, algae, and higher plants [83]. The bioconcentration factors listed by EPA for freshwater organisms vary quite a bit, with methyl mercury BCFs of up to 85700 for rainbow trout and 81670 for fathead minnows, and 40000 for oysters [955]. The BCF for mercury is the same for freshwater fish, marine plants, and freshwater plants [366].

In birds: feathers have the most mercury, then the kidney, liver, blood, eggs, muscle, brain (high to low mercury concentration progression); in mammals, fur has the most mercury, then liver, kidney, muscle, and brain [915]. However, the mercury in the liver may be mostly inorganic, and the mercury in the feathers may be mostly sequestered [915].

Among birds, common loons are good indicator species for mercury (they nest even on mine seepage areas) [915].

There is storage of methyl mercury in fish muscle [914]. There is less of a loss rate for mercury in fish compared to birds [914]. The best potential mediums for biological monitoring (including gradient monitoring) appear to include animal hair, mammal livers, bird feathers, bird livers and kidneys, fish, and clams [83]. Irwin found mosquitofish to be acceptable for gradient monitoring of mercury in an urban river [201]. Crayfish contained the highest concentrations of mercury of any invertebrate taxa sampled in Clay Lake, Ontario [180].

One rodent study suggested that more selenium is accumulated if methyl mercury is present. Selenium accumulation in all organs (especially the kidney) was accelerated (8-fold increase in 41 days in the kidneys) in rats treated with mercury and selenium [488].

Mercury in the monatomic state is distributed primarily to alveolar bed upon inhalation. The most important route of absorption is respiratory tract where percent deposition & retention are quite high (about 80% in man) [366,494]. Mercury is very poorly absorbed from GI tract, probably less than 0.01% [366,494]. The degree of skin absorption in man is not known with any precision [366,494]. Transfer of lipid-soluble  $\text{Hg}(0+)$  (elemental mercury) from blood to brain is sufficiently rapid to result in toxicologically significant differential distribution to that organ [366,494]. Subsequent oxidation of  $\text{Hg}(0+)$  in brain to  $\text{Hg}(2+)$  serves to trap it there [366,494]. A similar selective distribution occurs in fetus. The oxidative process is enzyme mediated, with the catalase complex being most likely site of oxidation. Administration of mercury stimulates synthesis of metallothionein, which may serve a protective role for the kidney by sequestering mercury [366,494].

Bioaccumulation in fish varies directly with pH [914]. Evasive loss of elemental mercury ( $\text{Hg}0$ ) higher in higher pH than in lower pH [914]. In Wisconsin where 0.5 ppm wet wt fish tissue is used as a human health standard:

In low pH or even moderate pH waters, fish can exceed the standard [914].

There is a big increase in the number of lakes having advisories [914].

One of the pathways, if not the only pathway, by which elemental mercury ( $\text{Hg}(0+)$ ) is absorbed & converted in vivo is by its oxidation (in erythrocytes) to  $\text{Hg}(2+)$ . Studies with acatalasemic red blood cells (RBCs) show that catalase-hydrogen peroxide system plays a determinant role in mercury uptake through this catalytic oxidation system; human acatalasemic RBCs had only 1/100 to 6/100 the uptake of mercury vapor found in normal RBCs with hydrogen peroxide. (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. 1784) [940].

Mercury has been detected in fish eating birds in concentrations which may pose a problem for predatory bald eagles [189]. In humans, mercury accumulates principally in the brain and kidneys [173].

Mitra summarized bioconcentration and fate in 1987 [978]; due to lack of time, the results have not yet been quoted in this document.

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

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

Information relating to the bioavailability and fate of various forms of mercury in humans [955]:

Mercury can easily enter your body when you breathe in air containing metallic mercury. Most of the mercury that gets

into your lungs as metallic mercury goes rapidly to other parts of the body. Metallic mercury that you might swallow does not enter your bloodstream very easily, and most of it leaves the body in the feces. Some metallic mercury may stay in your body, mostly in the kidney and brain. Metallic mercury can also easily reach the fetuses of pregnant women. Metallic mercury that you breathe in will leave your body in urine, feces, and breath [955].

Inorganic salts of mercury (mercurous or mercuric chloride, for example) that are inhaled do not enter your body as easily. However, these inorganic forms of mercury, if swallowed, enter the body more easily than metallic mercury. Inorganic mercury can also enter the bloodstream directly through the skin. However, only a small amount would pass through your skin compared with breathing or swallowing inorganic mercury. After entering the body, inorganic compounds of mercury can reach many tissues. Some may stay in the body, mostly in the kidneys. However, inorganic mercury cannot reach the brain as easily as metallic mercury. Inorganic mercury leaves your body in the urine or feces after several weeks or months.

Organic compounds of mercury can probably enter your body easily through the lungs. Organic mercury in contaminated fish or other foods that you might eat enters your bloodstream easily and goes rapidly to other parts of your body. It can also enter the bloodstream directly through the skin, but only a small amount would pass through your skin. Organic mercury in the body is similar to metallic mercury because it can reach most tissues including the brain and fetus. Organic mercury can change into inorganic mercury in the brain and remain there a long time. Organic mercury that you swallow or breathe leaves your body in the feces, mostly as inorganic mercury, within weeks [955].

Bioconcentration [940]:

Mercury bioaccumulates and concentrates in food chain. The concentration may be as much as 10,000 times that of water. [Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.42 (1982)].

Bioconcentration factors of 63,000 for freshwater fish and 10,000 for salt water fish have been found. [Sittig M Ed; Priority Toxic Pollutants, Health Impacts and Allowable Limits, p.266-271 (1980) as cited in Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.43 (1982)].

As the tissue concn approaches steady-state, net accumulation rate is slowed either by a reduction in uptake rate, possibly due to inhibition of membrane transport, or by an increase in depuration rate, possibly

because of a saturation of storage sites, or both. [USEPA; Ambient Water Quality Criteria Doc: Mercury p.10 (1984) EPA 440/5-84-026].

Bioconcentration Factors for Mercury: Marine Plants 1,000; Marine Invertebrates 100,000; Marine Fish 1,670; Freshwater Plants 1,000; Freshwater Invertebrates 100,000; Freshwater Fish 1,000. [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 14-10].

Specimens (195) of higher fungi and their substrata collected in the mercury mining area of Amiata and around Siena (central Italy), were analyzed for their total mercury (Hg) content. Wood decomposers and many species of mycorrhizal fungi accumulated the metal at a very low rate; some mycorrhizal species and all the humus decomposers may accumulate up to 100 ug/g/l dry weight of Hg and in the least contaminated sites, up to 63 times as much Hg as the substratum. In mineralized areas, the concn factor rarely exceeded 1. The methylmercury content of 35 /specimens/ (almost all edible), ranged between 0.01 and 3.7 mug/g/l dry weight. [Bargagli R, Baldi F; Chemosphere 13 (9): 1059-72 (1984)].

Fish can accumulate mercury (Hg) to very high levels because accumulation is rapid and elimination is slow. Predators achieve higher concn than do fish lower in the food chain. In Canadian freshwaters, the highest Hg levels are found in lake trout, pike and walleye. In the sea, high Hg concn are found in sharks, swordfish, tuna, and halibut. [Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.89 (1979) NRCC No. 16739].

Acidification of a body of water might also increase mercury residues in fish even if no new input of mercury occurs, possibly because lower pH increases ventilation rate and membrane permeability, accelerates the rates of methylation and uptake, affects partitioning between sediment and water, or reduces growth or reproduction of fish. [USEPA; Ambient Water Quality Criteria Doc: Mercury p.12 (1984) EPA 440/5-84-026].

Accumulation of mercury in the terrestrial and aquatic food chains results in risks for man mainly through the consumption of: fish from contaminated waters; especially predator species, tuna fish, swordfish and other large oceanic fish even if caught a considerable distance off shore; other seafoods including muscles and crayfish; fish-eating birds and mammals; and eggs of fish eating birds. [WHO; Environ Health Criteria: Mercury p.55

(1976)].

#### Biological Half-Life [940]:

The biological half-life of mercury in fish is approx 2 to 3 yr. [USEPA; Ambient Water Quality Criteria Doc: Mercury p.10 (1984) EPA 440/5-84-026].

The whole body half-time of mercury in man is approximately 50 to 70 days. A rapid component in blood has a half-time of about three days, and a slower component has a half-time of about 30 days. A rapid component in the brain has a half-time of about 21 days. There is evidence of a much slower component in brain with a half-time on the order of several years. [USEPA; Mercury Health Effects Update p.2-4 (1984) EPA 600/8-84-019F].

For pike, mercury (Hg) concn in muscle after 70-90 days were 1000-1500 times that in water. ... The half-life for elimination of Hg from contaminated pike placed in clean water was 65-70 days. [Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.89 (1979) NRCC No. 16739].

#### **Interactions:**

Mercury, like selenium, has many interactions with sulfur compounds. This affinity for sulfur compounds may account for some of the many synergistic and antagonistic interactions between mercury and selenium. Also like selenium, mercury chemistry, transformations, and interactions with other contaminants are complex. Due to these complexities, generalizations about mercury should be approached with caution. For more details, see separate section below entitled: Interactions between selenium and mercury.

#### Highlights of interactions of dissolved organic carbon (DOC) vs. mercury [919]:

Dissolved organic carbon (DOC) is an effective complexing ligand for many trace metals including mercury [919]. Recent studies have shown strong correlative relations between DOC and total and methylmercury content in a variety of aquatic ecosystems [919]. The precise mechanisms for this relation are still poorly understood [919]. Researchers need to place more emphasis on the quality of the DOC (elemental makeup, functional and sulfhydryl group concentrations, humic/fulvic fractions, etc.) to clarify the role of DOC in the environmental mercury cycle [919].

Mercury is redox sensitive, and DOC has a role a role in that [919].

DOC can be 90% acidic (often organic acids) and includes all organic carbon smaller than .45 microns (operational definition) DOC includes a vast array of sometimes poorly defined matter, including colloids, fatty acids and many other acids [919]. Components range from high to low molecular weights and have different reactivities [919].

DOC is a mixture of many things, some that bind mercury strongly, some that do not [919]. Organic sulphur is complicated [919]. When considering DOC, one needs to determine, did it come from crude oil or the breakdown of algae, or some other source?

DOC is very important in the Everglades, which is like a giant solar collector, 100 miles wide, 2 feet deep [919]. Photochemistry: DOC is consumed in light and decreased over one week when exposed to sun [919].

Mercury is a soft ion which tends to interact with ligands that contain sulphur [919]. DOC and Mercury tend to be correlated with mercury concentrations, but nobody knows why [919]. Mercury is attracted to sulfides, but DOC can interfere [919]. Common ligands like citric acids can bind mercury [919]. So can EDTA [919].

#### Relationships between pH and Mercury:

Lower pH levels (indicating increased acidification) are correlated with increased mercury accumulation in fish [120].

At low pH, there is typically a higher methyl mercury production than at higher pH levels (John Rudd, Freshwater Institute, personal communication). Primary productivity increases pH so there is typically a fall off later as the higher pH slows down the methyl mercury production (John Rudd, Freshwater Institute, personal communication).

Acidification of a body of water might also increase mercury residues in fish even if no new input of mercury occurs, possibly because lower pH increases ventilation rate and membrane permeability, accelerates the rates of methylation and uptake, affects partitioning between sediment and water, or reduces growth or reproduction of fish (USEPA; Ambient Water Quality Criteria Doc: Mercury p.12, 1984, EPA 440/5-84-026) [366].

Some recent research 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 mercury in fish [383].

Adjusting acidity is one recommended method of controlling mercury, by precipitating mercury as mercuric sulfide [368].

#### Relationship between Mercury Concentrations and Nutrients, Organic Materials, TOC, DOC, and other Eutrophication-Related Factors:

Mercury concentrations are typically higher in sediments, in eutrophic (nutrient and carbon rich) areas than in oligotrophic (nutrient and carbon poor) areas. This is thought to be due to the ability of organic compounds to bind mercury to sediments and to suspended organic particulates, as well as the tendency for the increased nutrients to stimulate the growth of the bacteria which methylate mercury. Some of these trends are being seen in south Florida, where mercury levels sediments of the relatively oligotrophic western sites are lower than the mercury levels in the relatively eutrophic central and northern parts of the study areas.

The relationship between eutrophication and fish concentrations of mercury is often not so clear. For example, fish from offshore often have higher concentrations of mercury than nearshore estuarine fish. Offshore there is less carbon, less eutrophication, yet more mercury in the fish. Large, long-lived offshore predators tend to build up high levels of mercury, and whatever mercury is out there is perhaps more available (less bound to organic or sulfur compounds in the water column).

The relative importance of binding factors (factors tending to bind mercury to sulfur and organic compounds) versus stimulation factors (feeding nutrients to bacteria and increasing methylation rates) vary at different locations. For example, in Florida just SE of Lake Okeechobee, the sediments contain higher concentrations of mercury while the fish only moderately elevated, suggesting that the binding factors may be playing a bigger role in that highly eutrophic area than the nutrient factors. Fish movement may also be a factor. The nutrient factors tend to stimulate bacteria to methylate more mercury, but there is perhaps a lag in this stimulation factor. This may explain why it appears to be happening to a greater extent farther downstream than in the areas with the highest mercury concentrations in the sediments.

Eutrophic lakes tend to have a lot of particulates in the water; particulates tend to scavenge mercury out of water and tend to transport the mercury to the bottom (Jerry Stober, EPA/ESD, Region III, Athens, Georgia, personal communication). In the Everglades, stimulation factors

related to eutrophication may be important, if only as a slow-rate function which happens steadily over a large areas.

There are only 7 or 8 things which are known to influence mercury methylation rates. Phosphorus is not the only suspect. If one adds glucose, or soy broth, to certain aquatic environments, one will see an initial bursts of productivity and methyl mercury production (John Rudd, Freshwater Institute, personal communication).

Enclosed experiments have provided insight into mercury/eutrophication relationships. Experimentally adding nutrients to fish habitats stimulated production; as primary production went up, the methylation went up into the medium range (mercury concentration in the fish went up) then mercury concentrations went back down in the highest range for nutrients, but stimulation also increased the size of the fish (John Rudd, Freshwater Institute, personal communication).

Thus indirect factors are important. Increasing the growth rate can increase the rate at fish grow and larger fish have eaten more and may contain more mercury. Growth of fish is stimulated by nutrients, which indirectly increases mercury concentrations in the fish (bigger fish which have eaten more tend to contain more mercury, John Rudd, Freshwater Institute, personal communication).

At low pH, there is typically a higher methyl mercury production than at higher pH levels. Primary productivity increases pH so there is typically a fall off later as the higher pH slows down the methyl mercury production (John Rudd, Freshwater Institute, personal communication).

#### Interactions between Copper and Mercury:

In water, copper acts synergistically with other common urban contaminants such as ammonia, cadmium, mercury, and zinc to produce an increased toxic effect on fish [26,47].

Copper and mercury are antagonistic at lower concentrations, additive at intermediate concentrations, and synergistic at higher concentrations [488]. Evaluation of hatchability of trout embryos shows synergistic, additive, and antagonistic relationships between Cu and Hg. As with Cu and zinc, synergistic interaction exists at high Cu and Hg concentrations in the water [488]. Additive effects are noted at an intermediate level of about 0.03 ppm of equal proportions of either

element. Antagonism is noted at low levels ( $<0.01$  ppm of equal proportions of each metal). Moreover, the complexity of elemental interactions is confirmed in such comparisons, although Cu-Hg interactions seem less complicated for channel catfish (*Ictalurus punctatus*) and goldfish (*Carassius auratus*) than for largemouth bass (*Micropterus salmoides*) and rainbow trout (*Salmo gairdneri*). The LC50 values show Hg to be twenty-five times more toxic than Cu to bass, trout, catfish, and goldfish under conditions of this series of studies [488].

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

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

Metal selenides are formed with cadmium, copper, and mercury [445].

#### Interactions between Selenium and Mercury:

Dietary selenium can reduce toxic effects of methyl mercury in humans [494].

Some of the interactions between selenium and mercury were mentioned in the Brief Introduction above. These are important enough that they are repeated here with additional information:

Selenium, like mercury, has many interactions with sulfur compounds. This affinity for sulfur

compounds may account for some of the many synergistic and antagonistic interactions between mercury and selenium (see details below). Also like mercury, selenium chemistry, transformations, and interactions with other contaminants are complex. In fact, selenium is one of the most complex elements in these regards. Due to these complexities, generalizations about selenium should be approached with caution.

Antagonism/Synergism: Four studies have suggested that the presence of selenium reduces the toxicity of (is antagonistic to) mercury (Hg), cadmium (Cd), arsenic (As), and silver (Ag) [488]. The exact mechanism of action for selenium induced protective effects of vertebrates has not been elucidated [488]. Sorenson (1991) suggested caution in attempting to use selenium supplementation to decrease the severity of point-source mercury contamination, since synergistic interactions have also been observed, and since synergistic interactions on even a single life stage (as demonstrated on carp by Huckabee and Griffith) have a potential of eliminating an entire population of fish [488]. Although selenium and mercury interacted synergistically rather than in an antagonistic (protective) fashion, the author of the study which showed synergistic effects cautions that it was an early lab study and should not totally override all later field studies (John Huckabee, Electric Power Institute, personal communication, 1993).

Nevertheless, most mercury and selenium experts suggest caution in using selenium to treat surface waters in an effort to reduce mercury problems, since there is such a small safety window between too little and too much selenium. Interactions are known to be concentration (dose) dependent [488]. Interactions between Se and mercury can be synergistic at low aqueous mercury concentrations (< or = 0.07 ppm) and antagonistic at high mercury levels (> or = 0.10 ppm) and high selenium levels [488]. In Sweden, selenium supplementation was tried as a remedy for mercury problems in lakes and some reduced mercury concentrations seemed to be the result; however, too much selenium was eventually used and negative effects on fish reproduction was eventually seen (John Rudd, Freshwater Research Institute, Winnipeg, Manitoba, personal communication, 1993). Moderate selenium toxicity to adult fish may be irrelevant if the larval fish are much more sensitive to selenium toxicity and thus the fish do not make it to

adulthood.

One rodent study suggested that more selenium is accumulated if methyl mercury is present. Selenium accumulation in all organs (especially the kidney) was accelerated (8-fold increase in 41 days in the kidneys) in rats treated with mercury and selenium [488].

Selenium has been referred to as an agent which can bind mercury and cadmium compounds to make them more biologically inert, as a protective agent against mercury induced lipid peroxidation, as an element which can detoxify various metals by chelating them [484,486].

Under some circumstances, selenium may interact in an antagonistic or protective manner with mercury and several other contaminants [445]. Some contaminants specialists who have looked at some of the human health and animal husbandry literature have wondered whether or not slight elevations of some forms of selenium in fish tissues may possibly be acting partly in a protective manner (to a greater degree than is commonly recognized) to humans and fish and wildlife predators consuming fish contaminated with harmful concentrations of heavy metals such as cadmium, mercury, and lead (Jerry Miller, U.S. Bureau of Reclamation, Salt Lake City, personal communication). However, care should be taken in generalizing, and the many risks associated with bioconcentration, reproductive risk, and other potential risks of selenium cannot be ignored.

Dietary sulfate, which can have a protective effect on selenate toxicity, does not affect the toxicity of selenite or organoselenium; dimethyl selenide (normally not very toxic) has a synergistic effect with some mercuric salts; and although drinking water containing arsenic can ameliorate the toxic effects of dietary selenium, their toxic effects can be additive when provided together in drinking water (NRC-Subcommittee on Selenium, 1976) [445].

Metal selenides are formed with cadmium, copper, and mercury. Many organic selenides also are common [445].

Mercury binds to selenium (Se) & tellurium (Te) with mutually antagonistic effect on their toxicities (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. 1786) [366].

Gary Heinz and Dave Hoffman of the Patuxent Fish and Wildlife Research Center in Laurel, MD, believe that, as of November 1993, there is usually not enough data available to tell exactly what various combinations of various forms of selenium and mercury mean as body burdens in various life stages of waterfowl. Organic selenium (typically organoselenium compounds such as Se-methionine) combined with organic mercury (typically methyl mercury) appears to be the most dangerous combination, but not all research has used these two. Some workers have suggested that a ratio of one mole of selenium/one mole of mercury can have protective effects for certain adult organisms, but ratios found in nature seldom work out to this exact ratio. Some preliminary experimental data from Patuxent seems to hint that certain doses of organic selenium combined with certain doses of organic mercury can have "more than additive" effects (deformities and death) on mallard duck embryos; however, the reverse (antagonism) may be true for adult ducks and the complexity of potential combinations of forms and concentrations of the two compounds makes generalizations difficult (Gary Heinz and Dave Hoffman, Patuxent Fish and Wildlife Research Center, National Biological Survey, personal communication, 1993).

Interactions between mercury, nitrogen, and periphyton [921]:

Periphyton is microalgae that coats submerged substrates; it includes algae growing on stream beds and rocks [921]. In the Everglades, periphyton is primary producer and covers everything [921]. It can look like brown or white foam, coats dead grass blades, but live grass puts out a natural herbicide that keeps periphyton from coating it [921]. Periphyton can play an important role in biogeochemistry of mercury [921].

In South Florida studies, the percent nitrogen in periphyton is directly related to the concentrations of total mercury and methyl mercury in the tissues [921]. There is a gradient from more to less mercury in tissues of periphyton from north to south [921]. The methyl mercury gradients for locations within the south Florida Water Conservation area or within Big Cypress National Preserve are influenced by water column pH with larger concentrations of methyl mercury in periphyton occurring when pH values are approximately neutral [921].

In periphyton, the more total mercury, the more methyl mercury [921]. This does not just happen in Florida

[921]. Algae can concentrate metals, can change the species of metals, and can transport metals [921].

Organic nitrogen had a better relationship with mercury concentrations than did organic carbon; the nitrogen fixing nitrogen cycle may be related to methyl mercury production [921].

In Fairfax, Virginia, dabbling ducks will eat algal mats when they can not find anything else and mercury. In this setting, mercury was found in concentrations of 0.4 ppm in pond scum and in significant concentrations in duck eggs [921].

Information from HSDB [940]:

Ethanol depresses conversion of inhaled elemental mercury into ionic form in blood. In addn, ethanol enhances pulmonary exhalation of absorbed mercury, with resultant effect of suppressing lung retention of mercury together with lowering blood mercury content. [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. 1784].

The concentration of NTA in surface waters had no interaction with barium, antimony, molybdenum, strontium, chromium, silver, tin, iron, lead, cadmium, copper, and mercury ... and not enough with nickel, zinc, manganese, cobalt, magnesium, and calcium ... to be of environmental concern. [Nat'l Research Council Canada; NTA (Nitrilotriacetic Acid)-An Ecological Appraisal p.20 (1976) NRCC No. 15023].

The suppressive effect of zinc on the toxicity of mercury was studied. [Yamane Y et al; Chem Pharm Bull 24 (4): 836-7 (1976)].

#### **Uses/Sources:**

About 10,000 U.S. tons of mercury are mined each year, half of which is lost into the environment [335]. There is growing concern from abandoned mines where metallic mercury from the extraction process, and oxidizing tailings or remnant ore present a potentially large contamination source [999].

Mercury's use in pesticides has been restricted [187].

Forests accumulate dry deposition in equivalence to wet deposition. Vegetation is a source to the atmosphere (evasion from leaf surfaces) and to watersheds (leaf litter and throughfall) [999].

Most depositing mercury is in the form of inorganic mercury, and the majority of that falls with precipitation [999].

Coal and oil combustion and municipal and medical waste

incineration are the major anthropogenic sources to the atmosphere. Abandoned mines and industrial effluents are unquantified point sources to aquatic ecosystems [999]. Natural emissions are important too (e.g., volatilization from the oceans and soils), but the natural: man-contributed ratio is still unresolved. Recent evidence suggests that Asian and South American countries are major contributors to the global atmospheric load [999].

Sources of mercury include batteries, vapor discharge lamps, thermometers, older-style seals in sewage treatment plants, sewage treatment plant discharges, the chloralkali industry, paints, pesticide compounds, switches, valves, dental labs and offices, pharmaceuticals, scientific and analytical laboratories, soil erosion, and air pollution deposition from fossil fuel combustion and smelters [33]. Other uses include: barometers, hydrometers, pyrometers, mercury arc lamps, florescent lamps, catalysts, and gold extraction [368]. Leachates of municipal landfills contain mercury [80], possibly due to the disposal of items such as mercury batteries, thermometers, and electrical switches. Scrap metal dealers who accepted mercury and laboratories analyzing soil samples have been a significant source of mercury in Dallas/Fort Worth Storm Drains (Ross Muir, Tarrant County Health Department, personal communication). Contact lens solutions containing thimerosal are an additional source of small amounts of mercury. Many sources of small amounts of mercury can have a cumulative impact on a small river, due to mercury's persistence.

Considerable amounts of mercury are coming down from the atmosphere in the NE U.S. in rain, and the deposition is also significant during dry periods [922].

Mitra summarized mercury sources in 1987 [978]; due to lack of time, the results have not yet been quoted in this document.

Misc. Unconfirmed News Media Report from National Journal's GREENWIRE (The Environmental News Daily), Tuesday, June 24, 1997:

ARCTIC: MERCURY RAIN FALLS EACH SPRING -- REPORT

"A toxic rain of mercury" falls on the Arctic each spring as ecosystems prepare for their "first burst of activity," according to a report by Environment Canada researchers published last week in the journal New Scientist. Although the cause of the rain of mercury -- "one of the earth's most poisonous substances" -- remains unclear, researchers "said the pattern almost exactly mimics" the timing of seasonal ozone depletion, suggesting that similar processes cause both phenomena (AP/mult., 6/20).

Major Uses Summarized in HSDB [940]:

In barometers, thermometers, hydrometers, pyrometers; in mercury arc lamps producing ultraviolet rays, in switches, fluorescent lamps; in mercury boilers; mfr all mercury salts, mirrors; catalyst in oxidn of org compd; extracting gold & silver from ores; electric rectifiers;

making mercury fulminate; for millon's reagent; as cathode in electrolysis, electroanalysis [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 843].

Pulp & paper mfr [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 271].

Component of batteries (eg, zinc-carbon & mercury cells), industrial & control instruments (eg, meters), & amalgams (eg, for dental preparations); agent in mfr of wire & switching devices (eg, oscillators); cathode in electrolytic mfr of chlorine & caustic soda; catalyst for urethane & epoxy resins; laboratory reagent; lubricant (eg, in turbines) [SRI].

Metallic mercury (quicksilver) has been employed in india to fumigate & protect grain in closed containers from ... Insect infestation. [Farm Chemicals Handbook 1983. Willoughby, Ohio: Meister Publishing Co., 1983.,p. C-150].

Used in pharmaceuticals, agricultural chemicals, antifouling paints, /SRP: as a wet chemistry method/, and many other uses. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 843].

#### Natural Sources [940]:

Mercury ore is found in rocks of all classes. Common host rocks are limestone, calcareous shales, sandstone, serpentine ( $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), chert andesite (soda lime feldspar), basalt, & rhyolite (alkaline feldspar & quartz). Mercury is recovered almost entirely from cinnabar ( $\alpha\text{-HgS}$ ), 86.2% Hg, although elemental mercury occurs in some ores. [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. 1769].

Joint FAO/WHO expert committee on Food Additives (1972) quotes the major source of mercury (Hg) as the natural degassing of the earth's crust ... in the range of 25,000-150,000 ton of Hg/yr. [WHO; Environ Health Criteria: Mercury p.43 (1976)].

The mercury (Hg) content of some common ore and gangue minerals as a result of its coexistence in a deposit with cinnabar, metacinnabar or other Hg minerals is as follows: Tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) 17.6-21%; Grey copper ores ( $\text{Cu,As,Sb}$ ) $\text{XSy}$  14%; Spalerite ( $\text{ZnS}$ ) 1%; Wurtzite ( $\text{ZnS}$ ) 0.03%; Stibnite ( $\text{Sb}_2\text{S}_3$ ) 1.3%; Realgar ( $\text{AsS}$ ) 2.2%; Pyrite ( $\text{FeS}_2$ ) 2%; Galena ( $\text{PbS}$ ) 0.02%; Marcasite ( $\text{FeS}_2$ )

0.07%; Native gold (Au) 60%; Native silver (Ag) 30%; Barite (BaSO<sub>4</sub>) 0.5%; Cerussite (PbCO<sub>3</sub>) 0.1%; Fluorite (CaF<sub>2</sub>) 0.01%; Calcite (CaCO<sub>3</sub>) 0.03%; Aragonite (CaCO<sub>3</sub>) 3.7%; Siderite (FeCO<sub>3</sub>) 0.01%; Pyrolusite (MnO<sub>2</sub>) 2%; Hydrated iron oxides Fe<sub>2</sub>O<sub>3</sub>nH<sub>2</sub>O 0.2%; Graphite (Carbon) 0.01%; and Coal 2%. [Jonasson IR, Boyle RW; Bull Can Inst Min Metal 65: 32-9 (1972) as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.32 (1979) NRCC No. 16739].

Fossil Fuels: Coal 10-8530 ppb; Coal in mercuriferous basins 20-300,000 ppb; Crude oils 20-2000 ppb; Petroleum crudes in mercuriferous belts 1900-21,000 ppb; Bitumens, solid hydrocarbons, asphalts, etc 2000-900,000 ppb. [Jonasson IR, Boyle RW; Bull Can Inst Min Metal 65: 32-9 (1972) as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.39 (1979) NRCC No. 16739].

Mercury is released into the environment from volcanoes and hot springs. [Miller DR, Buchanan JM; Atmos Trans of Mercury: Exposure Commitment and Uncertainty Calculations. MARC Report #14 p.1 (1979)].

#### Artificial Sources [940]:

Of greater significance currently in Canada is the mercury liberated from the working and smelting of ores of copper, gold, lead, silver and zinc which normally contain traces of mercury. [Jonasson IR, Boyle RW; Bull Can Inst Min Metal 65: 32-9 (1972) as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.62 (1979) NRCC No. 16739].

The average emissions of mercury stack losses for USA cinnabar (HgS) roasting operations was 2-3%. [Stahl QR; Dept of Health, Education and Welfare p.30 (1969) as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.62 (1979) NRCC No. 16739].

Maximum ground-level concn of Hg for 12 USA coal-fired power plants were 0.035-6.9 ug/cu m. [Vaugh WP, Fuller SR; Illinois Institute for Environmental Quality Rep ILEQ 71-3 (1971) as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.66 (1979) NRCC No. 16739].

Mercury (Hg) loss est from Canada fuel consumption and other Canadian sources: In 1974, approximately 12 ton Hg were discharged to the environment as a result of coal combustion. Approximately 90% was discharged to air as vapor, 9% was adsorbed onto fine particulate (controllable by particle-collecting devices) and

approximately 1% remained in the bottom or grate ash. [Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.66 (1979) NRCC No. 16739].

In general, industrial and domestic products, such as thermometers, batteries, and electrical switches which account for a significant loss of mercury to the environment, ultimately become solid waste in major urban areas. [British Dept of Environment; Pollution Paper No. 10 p.75 (1977) as cited in Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.77 (1979) NRCC No. 16739].

Anthropogenic sources of airborne mercury (Hg) may arise from the operation of metal smelters or cement manufacture. Water borne pollution may originate in sewage, metal refining operations, or most notably, from chloralkali plants. [Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.84 (1979) NRCC No. 16739].

Twenty thousand tons of mercury are released into the environment each year by human activities such as combustion of fossil fuels and other industrial release. [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. 387].

Concentrated local discharges associated with industrial activities and waste disposal. Diffuse discharges generally associated with combustion of fuels containing mercury impurities. Mercury is released in various chemical forms. [Miller DR, Buchanan JM; MARC Report: Atmos Trans of Mercury: Exposure Commitment and Uncertainty Calculations #14 p.1 (1979)].

Inadequate & improper disposal of industrial mercury wastes incr mercury levels in water & atmosphere. ... Microorganisms convert elemental mercury into methyl mercury salt ( $\text{CH}_3\text{HgCl}$ ) & dimethyl mercury, which ... Escape into the atmosphere. Most of these reactions take place in sediments of river & ocean beds. ... Major source of mercury contamination is disposal of industrial mercury wastes into water where the wastes settle as sediment, only to be recycled into the water & air. [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 87].

#### Air Pollution As a Source of Mercury in Surface Water:

Coal-fired power plants have recently (1993) been discovered to be a bigger source of mercury in the atmosphere than was previously realized, and it was

always realized that coal was an important source. For example, in 1974, approximately 12 tons of mercury were discharged to the environment as a result of coal combustion in Canada [366]. Approximately 90% was discharged to air as vapor, 9% was adsorbed onto fine particulate (controllable by particle-collecting devices) and approximately 1% remained in the bottom or grate ash [366]. Recent speculation is that ultra small mercury particulates, not just gaseous mercury, might be important in long distance transport, but many questions remain. For example, does the conversion to mercury<sup>2+</sup> occur in the dry atmosphere or in water droplets?

In the mercury contaminated areas of S. Florida, atmospheric sources of mercury are considered a prime suspect, including S. Florida urban sources (municipal waste burning, fossil fuel burning) as well as global transport via air pollution. Mercury can travel long distances in the atmosphere as a relatively inactive (slow to react) gas and attached to very fine particulate matter.

In the perched (98% of the water comes from rainfall) Savannah Marsh area of south Florida, mercury concentrations (ranging from 0.5 to 2.4 ppm) are thought to be mostly a result of precipitation of air pollution. A decrease in mercury concentrations has been reported from that particular area, about the only area where a decrease has been noted recently in S. Florida (Tom Atkerson, Florida DER, Tallahassee, personal communication).

Mercury attached to sulfides and other sulfur containing bottom sediments in marshes can make its way from the sediments and even up into the atmosphere by way of bacterial action (methylation), bioturbation, transport on volatile compounds, and various other mechanisms. Although these are probably slow-rate mechanisms, they may also be happening over very broad time and geographical scales, so that the total amounts of mercury released into the overlying waters and atmosphere may be substantial. Some researchers have seen some methylation of mercuric sulfide; although this process is slow, there is so much sulfide in the sediments that the slow, low release may still put quite a bit of mercury into the water column, biota, and eventually the atmosphere above.

The 1989 "Mercury in Temperate Lakes" studies done by William Fitzgerald of the University of Connecticut and Dr. Carl Watras (Wisconsin Department of Natural Resources) indicated that atmosphere is the major source of mercury in many inland lakes and that sediments are the major sink.

**Forms/Preparations/Formulations:**

Mercury occurs in metallic or elemental form (Hg) as well as several organic and inorganic forms [955]. Organic forms include: methylmercury (CH<sub>3</sub>Hg<sup>+1</sup>) and phenylmercury (C<sub>6</sub>H<sub>5</sub>Hg<sup>+1</sup>). Inorganic forms include: mercuric mercury (Hg<sup>+2</sup>) and mercurous mercury (Hg<sup>+1</sup>) [955]. Generally the vast majority of mercury in an aquatic ecosystem is in the inorganic form (about 95 to 99%) [999].

**Radionuclides:**

The symbol for Mercury-203 is <sup>203</sup>Hg, the atomic number is 80, the half-life is 47 days, and beta emission is the major form of decay [674].

The symbol for Mercury-206 is <sup>206</sup>Hg, the atomic number is 80, the half-life is 8.1 minutes, and beta emission is the major form of decay [674].

**Information from HSDB [940]:**

Blue pill; blue mass. Contains 32-34% metallic mercury. The rest is honey, licorice, althea, glycerol, and some mercury oleate. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 843].

Grades or Purity: Pure [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5.].

Available in commercial, instrument, redistilled, technical, and triple distilled grades. [Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.1 (1982)].

Typical commercial grade: 99.9% mercury [Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.3 (1982)].

USP mercury conforms to US Pharmacopeia specifications. Triple distilled mercury conforms to American Dental Association & National Formulary requirements and reagent grade conforms to the ACS specifications. [Considine. Chemical and Process Technol Encyc 1974 p.730].

**Chem.Detail:** Detailed Information on Chemical/Physical Properties:**Solubilities [940]:**

0.28 UMOLES/L of water at 25 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Sol in nitric acid; insol in the following: dilute hydrochloric acid, hydrogen bromide, hydrogen iodide, cold sulfuric acid [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-106].

Dissolves to some extent in lipids [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. 358].

2.7 MG/L in pentane [Doull, J., C.D. Klaassen, and M. D. Amdur (eds.). Casarett and Doull's Toxicology. 2nd ed. New York: Macmillan Publishing Co., 1980. 422].

0.002% g/100 g in water at 20 deg C [NIOSH. Pocket Guide to Chemical Hazards. 5th Printing/Revision. DHHS (NIOSH) Publ. No. 85-114. Washington, D.C.: U.S. Dept. of Health and Human Services, NIOSH/Supt. of Documents, GPO, Sept. 1985. 152].

Boiling Point [940]:

356.72 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Melting Point [940]:

-38.87 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Molecular Weight [940]:

200.59 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Critical Temperature and Pressure [940]:

1462 deg C and 1587 atm [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5.].

Density/Specific Gravity [940]:

13.534 AT 25 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Heat of Vaporization [940]:

14.652 KCAL/MOLE AT 25 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Surface Tension [940]:

484 DYNES/CM AT 25 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Vapor Pressure [940]:

2X10<sup>-3</sup> MM HG AT 25 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Viscosity [940]:

1.55 mPa.sec (15.5 millipoise) at 20 deg C [Considine DM Ed; Chemical and Processing Technology Encyclopedia (1974) as cited in Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.3 (1982)].

Corrosivity [940]:

The high mobility and tendency to dispersion exhibited by mercury, and the ease with which it forms alloys (amalgam) with many laboratory and electrical contact metals, can cause severe corrosion problems in laboratories. [Bretherick, L. Handbook of Reactive Chemical Hazards. 3rd ed. Boston, MA: Butterworths, 1985. 1218].

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

Color/Form [940]:

SILVER-WHITE, HEAVY, MOBILE, LIQUID METAL; SOLID MERCURY IS TIN-WHITE [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Odor [940]:

Odorless [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5.].

Other Chemical/Physical Properties [940]:

Ductile malleable mass which may be cut with a knife; atomic number 80; valences 1 & 2; group 2b element of periodic table; natural isotopes 202 (29.80%), 200 (23.13%), 199 (16.84%), 201 (13.22%), 198 (10.02%), 204 (6.85%) & 196 (0.146%); Electrical resistivity 95.76 Microhm cm at 20 deg c; forms alloys with most metals except iron & combines with sulfur at ordinary temp;

reacts with hno<sub>3</sub>, hot concn H<sub>2</sub>SO<sub>4</sub>, & ammonia solutions to form hg<sub>2</sub>noh (millon's base); std electrode reduction potential: eo (aq) hg/hg<sub>2</sub><sup>+</sup> equals -0.854 Volts; EO (AQ) 2 HG/2HG<sub>2</sub><sup>+</sup> EQUALS -0.789 VOLTS [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

HEAT CAPACITY (CP): 6.687 CAL/MOLE AT 25 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842].

Forms cmpd with org radicals, normally linking covalently to carbon atom [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 273].

Saturated atmosphere at 24 deg c contains approx 18 mg/cu m; the vapor exists in a monoatomic state [Doull, J., C.D. Klaassen, and M. D. Amdur (eds.). Casarett and Doull's Toxicology. 2nd ed. New York: Macmillan Publishing Co., 1980. 422].

Blue-gray mass /Mercury mass/ [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 843].

Reacts with HNO<sub>3</sub> and hot, concentrated H<sub>2</sub>SO<sub>4</sub>, does not react with dil hydrochloric acid, cold H<sub>2</sub>SO<sub>4</sub>, or alkalis. Reacts with ammonia solutions in air to form Hg<sub>2</sub>NOH, Millon's base. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 842]

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

The atmosphere is the dominant transport vector of mercury to most ecosystems that are not affected by point sources (which is the general case) [999]. Natural emissions are important too, including volatilization from the oceans and soils [999].

Mitra summarized mercury fate in 1987 [978]; due to lack of time, the results have not yet been quoted in this document.

Mercury flux changes on a seasonal and daily basis. In the Everglades, the following aspects were noted [920]:

Diurnal changes is dissolved gaseous mercury: peaks at noon, drops through night. Methyl mercury rises after a big rain event. Under intense sunlight, mercury near the surface can change to an "excited chemical state" and may become more mobile. Dissolved gaseous elemental mercury comes out of water whenever one turns on the light in a room. Diurnal studies show that the chemical concentrations of all mercury chemical species vary a lot (up to 8 times) during the day. To really get an

understanding of mercury flux in shallow, sunny habitats such as the Everglades would require sampling many times a day.

#### Environmental Fate [940]:

Environmental accumulation: two characteristics, volatility & biotransformation, make hg somewhat unique as environmental toxicant. Its volatility accounts for high atmospheric concn, 20 to 200 ug/cu m near areas containing high soil levels (10 ppm) as compared to normal atmospheric concn of 5 ug/cu m. ... Ground water concn in usa ... Below 1 PPB. [Doull, J., C.D. Klaassen, and M. D. Amdur (eds.). Casarett and Doull's Toxicology. 2nd ed. New York: Macmillan Publishing Co., 1980. 422].

In yatsushiro sea & minamata bay, the croaker (*argyrosomus argentatus*) was a good indicator of hg pollution. Mercury migrated from sediment to the croaker by way of suspended particulate matter & zooplankton. Conversion from inorganic to methylmercury occurs at the stage of zooplankton. [Nishimura H, Kumagai M; Water, Air, Soil Pollut 20 (4): 401 (1983)].

Aquatic Fate: In aquatic systems, mercury appears to bind to dissolved matter or fine particulates, while the transport of mercury bound to dust particles in the atmosphere or bed sediment particles in rivers and lakes is generally less substantial. [Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.78 (1979) NRCC No. 16739].

Aquatic Fate: Mercury can be desorbed into the water column, transported by water (probably bound or chelated to some fine particles or dissolved substances), and redeposited on the bed sediment. [Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.81 (1979) NRCC No. 16739].

Atmospheric Fate: 50% of volatile form is mercury (Hg) vapor with sizeable portion of remainder being Hg(II) and methylmercury, 25 to 50% of Hg in water is organic. Hg in the environment is deposited and revolatilized many times, with a residence time in the atmosphere of at least a few days. In the volatile phase it can be transported hundreds of kilometers. /Mercury Compounds/ [Miller DR, Buchanan JM; Atmospheric Transport of Mercury: Exposure Commitment and Uncertainty Calculations. MARC Report #14 p.3-6 (1979)].

Aquatic Fate: The conversion, in aquatic environments, of inorganic mercury cmpd to methyl mercury implies that recycling of mercury from sediment to water to air and back could be a rapid process. /Mercury cmpd/ [Callahan,

M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 14-11].

#### Volatilization from Water/Soil [940]:

In those systems where the residence time of the water is low (rivers and streams), mercury (Hg) is in most cases removed quite quickly, perhaps by as much as 50% per yr: ie the half-life of the Hg would be of the order of 1 yr or more. The mechanisms largely responsible must be (i) ingestion or absorption and subsequent removal by biological materials and organisms, and (ii) transformation to a more volatile chemical form which can escape from the sediment and from the entire aquatic system. [Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.81 (1979) NRCC No. 16739].

Much of the mercury deposited on land, appears to revaporize within a day or two, at least in areas substantially heated by sunlight. [Nat'l Research Council Canada; Effects of Mercury in the Canadian Environment p.78 (1979) NRCC No. 16739].

Volatilization of mercury from land and lakes was estimated to enhance the atmosphere concn over continental land masses by a factor of 45. [Miller DR, Buchanan JM; Atmospheric Transport of Mercury: Exposure Commitment and Uncertainty Calculations. MARC Report #14 p.67 (1979)].

#### Biodegradation [940]:

Methylmercury is formed naturally in aquatic & terrestrial environment from elemental mercury. ... Methylation is likely to occur in upper sedimentary layers of sea or lake bottoms. [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. 393].

Inorganic forms of mercury (Hg) can be converted to organic forms by microbial action in the biosphere. /Inorganic mercury/ [Schroeder WH; Envir Sci Tech 16 (7): 394A-400A (1982) as cited in Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.41 (1982)].

Certain bacteria, particularly of the genus *Pseudomonas*, can convert divalent mercury into metallic mercury. [WHO; Environ Health Criteria: Mercury p.49 (1976)].

Mercury resistant bacteria (eg, *Escherichia coli*), which

are able to reduce (sic) mercuric metallic mercury Hg(0+) were examined for their ability to remove wastewater aerobically. Growth studies in artificial medium indicated that mercury increases the lag phase, but does not affect the growth rate of these bacteria. Further studies demonstrated that growth was minimal during a phase of rapid Hg removal, after which growth resumed. Small but significant amounts of carbohydrates were required for the Hg(2+) reduction (sic). Prolonged periods of bacterial growth under nonsterile conditions was accomplished without the loss of the mercuric reducing ability of the culture. A continuous culture of the resistant organism was maintained on raw sewage for 2 wk, during which time relatively high concn of Hg (70 mg/l) were removed from the sewage at a rate of 2.5 mg/l/hr and at efficiencies exceeding 98%. [Hansen CL et al; Biotechnol Bioeng 26 (11): 1330-3 (1984)].

Upon entering an aqueous system, virtually any mercurial compd may be microbially converted to methyl mercury. /Mercury compd/ [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 14-9].

All forms of mercury (Hg) (metal, vapor, inorganic, or organic) are converted to methyl mercury. Inorganic forms are converted by microbial action in the atmosphere to methyl mercury. /Mercurial compd/ [Environment Canada; Tech Info for Problem Spills: Mercury (Draft) p.41 (1982)].

The mechanism of mercury elimination from wastewater was studied. The mercury-resistant bacterial Pseudomonas K62 strain at concn of  $6 \times 10^8$  cells/ml was incubated for 6 hr with 30 ppm mercuric nitrate. 0% added mercury was removed from culture medium in which Pseudomonas was not present; Whereas 47% of added mercury was removed in presence of Pseudomonas. Uptake of mercury was severely inhibited by sodium chloride, sodium sulfate, and mono- and dibasic potassium phosphate. [Menzie, C.M. Metabolism of Pesticides, Update II. U.S. Department of the Interior, Fish Wildlife Service, Special Scientific Report - Wildlife No. 212. Washington, DC: U.S. Government Printing Office, 1978. 174].

#### Absorption, Distribution and Excretion [940]:

As mentioned above, mercury moves readily across the placenta and into fetal tissue. Regardless of the chemical form administered, fetal tissues attain concentrations of mercury at least equal to those of the mother. [Doull, J., C.D.Klassen, and M.D. Amdur (eds.).

Casarett and Doull's Toxicology. 3rd ed., New York: Macmillan Co., Inc., 1986. 606].

Since/ vapor exists in monoatomic state it is ... Distributed primarily to alveolar bed upon inhalation. ... The most important route of absorption is respiratory tract. ... Percent deposition & retention are quite high ... /Approx/ 80% in man. ... It is very poorly absorbed from gi tract, probably less than 0.01%. ... The degree of skin absorption in man is not known with any precision. ... Transfer of lipid-soluble Hg(0+) (elemental mercury) from blood to brain is sufficiently rapid to result in toxicologically significant differential distribution to that organ. Subsequent oxidation of Hg(0+) in brain /to Hg(2+)/ serves to trap it there. A similar selective distribution occurs in fetus. The oxidative process is enzyme mediated, with the catalase complex being most likely site of oxidation. ... Admin of ... /Mercury/ stimulates synthesis of metallothionein. ... It may serve a protective role for kidney by sequestering mercury. [Doull, J., C.D.Klassen, and M.D. Amdur (eds.). Casarett and Doull's Toxicology. 3rd ed., New York: Macmillan Co., Inc., 1986. 606].

Ionic mercury is transported in plasma, while elemental mercury is transported in red cells. [Hayes, Wayland J., Jr. Pesticides Studied in Man. Baltimore/London: Williams and Wilkins, 1982. 12].

Diffusion & absorption of mercury into tissues from outer surface of eye have been demonstrated. Mercury metal in contact with conjunctiva has been shown in rabbits to be absorbed & ultimately ... Detectable in urine. [Grant, W.M. Toxicology of the Eye. 3rd ed. Springfield, IL: Charles C. Thomas Publisher, 1986. 587].

Elimination ... After exposure to ... Vapor occurs mainly by excretion of mercuric mercury, /Hg(2+)/. However, exhalations of small quantities of mercury vapor ... Demonstrated in animals. It is unclear whether this mercury vapor is result of reduction of mercuric mercury excreted into airways or by diffusion of vapor through alveolar membrane. Routes of excretion of mercuric mercury are ... Feces & urine, & by salivary, lacrimal & sweat glands. ... Rate of excretion is dose-dependent & considerable species difference has been observed. ... Limited data from human studies indicate that bulk of mercury is excreted with biological half-time of about 60 days. Part of mercury accumulated in brain is slowly eliminated with biological half-time which may exceed a year. [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. 398].

Fetal mercury determination in an aborted monkey whose mother had been exposed to mercury vapor at 0.5 Mg/cu m for about 20 weeks revealed that mercury crossed the placenta & was present in ... 9 Tissues & organs analyzed except amniotic fluid, indicating no apparent elimination ... By fetus. ... /Comparison of/ relative concn in 9 tissues ... /Of mother revealed that liver is/ only fetal tissue that ... Concentrate mercury over & above that found in mother. [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. 1780].

The distribution of mercury within a fish is the result of the movement of mercury from the absorbing surfaces (gills, skin, and gastrointestinal tract), into the blood, then to the internal organs, and eventually either to the kidney or bile for recycling or elimination, or to muscle for long-term storage. [USEPA; Ambient Water Quality Criteria Doc: Mercury p.10 (1984) EPA 440/5-84-026].

Distribution of mercury appeared to be complete within 24 hr for most regions of the body except for the head, where peak radioactivity was not attained until two to three days later. [USEPA; Mercury Health Effects Update p.4-2 (1984) EPA 600/8-84-019F].

Therapeutic or Normal Blood Level: The concn of inorganic mercury in blood (serum or plasma) following therapeutically effective dosage in humans is: 0.018-0.062 mg%; 0.18-0.62 ug/ml. [Winek, C.L. Drug and Chemical Blood-Level Data 1985. Pittsburgh, PA: Allied Fischer Scientific, 1985.].

Slow elimination of /mercury/ ... Is ... Characteristic of nucleus dentatus. Inorg mercury is selectively accumulated by lysosomal system. ... Steadily accumulates in kidneys where it is bound in part to sulphydryl groups. [Doull, J., C.D.Klassen, and M.D. Amdur (eds.). Casarett and Doull's Toxicology. 3rd ed., New York: Macmillan Co., Inc., 1986. 485].

Inorganic mercury has a markedly nonuniform distribution after absorption. The highest concentration of mercury is found in the kidneys, where the metal is retained longer than in other tissues. Concn of inorganic mercury are similar in whole blood and plasma. Inorganic mercurials do not readily pass the blood-brain barrier or the placenta. The metal is excreted in the urine and feces. /Inorganic mercury cmpd/ [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. 1612].

In view of animal data, other organs or cells /besides kidney/ where mercury is likely to accumulate are liver, mucous membrane of intestinal tract, & epithelium of skin, spleen, interstitial cells of testicles, & some parts of brain. In animal expt, placenta & fetal membrane ... Accumulate & retain mercury. [Friberg, L., G.R. Nordberg, and V.B. Vouk. Handbook on the Toxicology of Metals. New York: Elsevier North Holland, 1979. 517].

Mercuric mercury is excreted by ... Sweat glands, lacrimal glands, mammary glands, & salivary glands. Major part ... Is excreted in urine & feces. Partition between these two routes is dose-dependent & data indicate a larger fraction excreted by urine upon admin of larger doses. [Friberg, L., G.R. Nordberg, and V.B. Vouk. Handbook on the Toxicology of Metals. New York: Elsevier North Holland, 1979. 517].

Absorption from intestinal tract is greater with inorg than org form of mercury. By inhalation of inorg mercury ... Conc'n ranging from 2.91 To 26.18 Mg/cu m, an avg of 24.16% Of that inhaled was absorbed. [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 227].

Dimethyl Hg is (relatively) insoluble [368]. It volatilizes to surface, is broken down by sun and returns to upper layer of water as methyl mercury [368].

#### **Laboratory and/or Field Analyses:**

Many methods have been used or are available for the analysis of mercury [861,955,1001,1002,1003,1005,1006]. Historically, EPA has published separate methods and protocols in 40 CFR and various publications for applications related to the Clean Water Act, the Resource Conservation and Recovery Act, the the Comprehensive Environmental Response, Compensation and Liability Act. If the application was drinking water, the standard method has historically been Manual cold vapor technique (EPA 245.1; ASTM D3223- 80; SM 303F); automated cold vapor technique (EPA 245.2) [893].

The new (1996) EPA Method 1631: Mercury in Water by Oxidation, Purge and Trap, and CVAFS [1003], was developed for the collection of samples to be measured at or near the water quality criteria levels, can also be used for drinking water applications and applications related to the Resource Conservation and Recovery Act and the Comprehensive Environmental Response, Compensation and Liability Act when used along with EPA field protocol methods 1669 (see details below) [1003].

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

There are advantages to expressing aquatic life criteria

for mercury in terms of acid soluble mercury, and EPA criteria are essentially equivalent to acid-soluble mercury. Acid soluble metals are generally those that pass through a 0.45 um membrane filter after the sample is acidified to pH 1.5 to 2 with acid). In 1984, EPA gave 10 detailed reasons why Acid Soluble mercury (the mercury that passes through a 0.45 um membrane filter after the sample is acidified to pH 1.5 to 2 with acid) is probably the best measure to compare with water quality criteria. However, total mercury is more often used, there is no ideal measurement for acid soluble mercury, and there might be cause for concern if total mercury is much above an applicable criteria or other limit (USEPA; Ambient Water Quality Criteria Doc: Mercury p.11, 1984, EPA 440/5-84-026) [1984 update of publication 34].

Along these same lines, 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]:

Mercury II (inorganic Hg+2) conversion for acute and chronic criteria: 0.858 (for example, total recoverable chronic mercury II criteria x 0.858 = dissolved chronic mercury II criteria).

Note: This conversion factor may not hold up for many areas. Both total and dissolved concentrations should be checked at new locations before relying on this conversion factor (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

#### Recommended Detection Limits for mercury:

Sampling and analytical methods have rapidly developed over the past decade to include reliable sub part per trillion quantification of several mercury species in a variety of environmental samples (e.g., water, sediments, air, aerosols). These developments were a key reason for the interpretive power of many recent mercury studies [999]. Sampling and analytical methods are continuing to

evolve at a rapid rate [999,1001].

ICP methods are generally inappropriate because lower detection limits are needed.

Detection Limits for water:

A typical historical routine detection limit was 0.2 ug/L (ppb) using the following methods:

For the examination of ground and surface waters, domestic and industrial waste effluents, and treatment process samples: Method 245.1 for the determination of Mercury employs manual cold vapor technique. The detection limit is 0.2 ug Hg/l. Standard deviation at 0.35 level was +/- 0.16. Percent recoveries at the three levels were 89, 87, and 87% respectively (USEPA; Methods for Chemical Analysis of Water and Wastes p.245.1-1, 1983, EPA-600/4-79-020) [940].

Mercury in Liquid Waste (Manual Cold Vapor Technique) Method 7470 is a cold vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. Based on the absorption of radiation at 253.7 nm by mercury vapor. Typical detection limit is 0.0002 mg/l (USEPA; Test Methods for Evaluating Solid Waste. Physical/Chemical Methods 3rd Ed, 1986 EPA, 955-001-00000-1) [940].

However, by 1997, lower water detection limits were often required for comparison to lower water benchmarks (for example, EPA Chronic Freshwater Criterion: 0.12 ug/L 4-day avg [689,893,1001]:

The establishment of an ultra-clean mercury lab means the USGS is capable of analyzing for aqueous concentrations of total mercury, methylmercury, dissolved elemental mercury, and reactive ionic mercury, at detection limits of about 0.00045 nanograms (per liter) (David Krabbenhoft, USGS, Wisconsin, personal communication, 1995).

Using EPA method 1631, the minimum level (ML) has been established as 0.5 ng/L [1003]. An MDL as low as 0.05 ng/L (0.00005 ug/L) can be achieved for low Hg samples by using larger sample sizes, lower BrCl levels (0.2%), and extra caution in sample handling [1003].

## Detection Limits for Soils, Sediments and Tissues:

In the past, for soils, sediments, and tissues, cold vapor atomic absorption methods have been recommended by federal agencies such as the Fish and Wildlife Service, with mercury detection limits 0.20 ppm dry weight in tissues, sediments, and soils (Roy Irwin, personal communication, 1994). However, lower criteria and benchmarks, some in the area of 0.01 ppm (see media sections above) mean that detection levels at least as low as 0.01 ppm need to be used for many hazard or risk assessments in 1996. If required, tissue detection levels as low as 0.1 to 0.84 ng/g (ppb) are available using CVAAS [955]. See also: clean lab discussion above.

Acceptable containers (after proper cleaning per EPA protocols) for mercury: Fluoropolymer or borosilicate glass bottles with fluoropolymer or fluoropolymer-lined caps [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].

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

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

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

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to 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.

#### Filtration and Acidification:

In the past, EPA has recommended the following protocols:

1) For metals water samples, EPA recommends the following (40 CFR Part 136, Appendix C, pertaining to ICP analyses using method 200.7, 1994 edition of CFR Part 40): 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. However, other EPA guidance before and after 1994 has been different, stressing field preservation to a lesser degree:

In previous 1991 guidance for this same method 200.7 (which applies to mercury), EPA stated that if field acidification was not done because of sampling limitations or transport restrictions, that the sample should be acidified upon receipt with nitric acid in the laboratory and held in pH of less than 2 for at least 16 hours prior to analysis [1005]. In a similar way, for method 200.2 for total metals, EPA in 1991 recommended nitric acid, but said it could be done in the lab and that following acidification the sample should be held for 16 hours before analysis [1005].

However, 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). EPA specified the use of a particular kind of nitric acid in guidance for for some metals but not for Hg in method 1631, the use of "Nitric acid-concentrated (sp gr 1.41), Seastar or equivalent" [1003].

"Mercury samples should be shipped by overnight courier and preserved when received at the laboratory" [1003].

"Preservation recommendations For Mercury: Total: Add 0.5% high-purity HCl or 0.5% BrCl to pH < 2; Total & Methyl: Add 0.5% high-purity HCL; preserve on-site or immediately upon laboratory receipt" [1003].

However, in a different part of Method 1669, EPA recommended [1003]:

It is recommended that 1 mL of ultrapure nitric acid be added to each vial prior to transport to the field to simplify field handling activities [1003].

Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample [1003]. This will be sufficient to preserve a neutral sample to pH <2 [1003].

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 acid to a pH of 2 or less (40 CFR Part 136, Appendix C, pertaining to ICP analyses using method 200.7, 1994 edition of CFR Part 40).

Note: the acid (ultrapure, or pre-tested, or triple distilled, or nitric, or HCL, or BrCL, etc.) 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). Conclusion: many different types of acids are apt to be used for preservation of mercury water samples at various stages, contributing to data variability (see more detailed discussion related to data variability below).

2) 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 (40 CFR Part 136, Appendix C, pertaining to ICP analyses using method 200.7, 1994 edition of CFR Part 40).

Misc. sources of potential variation in contaminants data:

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

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

Note: Even "Standard EPA Methods" which are supposedly widely used by consultants, industry, and academia, have been variable over time and between application category (Drinking Water vs. NPDES, vs. RCRA, vs. CERCLA, vs. Water-Quality Based permits, etc.).

Preservation and other details of various EPA lab and field protocols have changed over the years, just as they have at USGS and various States and other agencies. USGS data from 30 years ago may be

different than USGS data today due to differences (drift) in lab and field protocols rather than differences in environmental concentrations.

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

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

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

B) Differences in numerous other details of the method used can drastically change the results. Some cold, wet, hurried, or fire ant-bitten collectors might decide that it is not "practical" to filter and acidify quite so immediately in the field, and may decide the shore, a vehicle, a motel room, or even a remote lab are more "practical" locations. Filtering and acidifying in the field immediately has been thought of as a

better option for consistency (see copper and silver entries for examples of what can happen if there is a delay). However, in recent methodology designed to prevent some the contamination sources listed above, EPA has recently suggested that waiting until the sample arrives at the lab before acidifying is OK [1003]. In EPA method 1631 for mercury, EPA states that "Samples may be shipped to the laboratory unpreserved if they are (1) collected in fluoropolymer bottles, (2) filled to the top with no head space, (3) capped tightly, and (4) maintained at 0-4°C from the time of collection until preservation. The samples must be acid-preserved within 48 h after sampling" [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 and 1631:

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

D) Sometimes acidification with standard field units of acid is not sufficient, depending on alkalinity and other factors. What field collectors sometimes (often?) do is just use standard pop tabs of acid and hope for the best rather than checking to see that the acidity has been lowered to below a pH of two. How many field collectors take a specially pure HCL to the field for separate Hg samples vs. how many just use nitric as they do for other samples? Although in one part of Method 1669 EPA suggests that "Mercury

samples should be shipped by overnight courier and preserved when received at the laboratory... with HCL or BrCL, in another part of method 1669 EPA suggests Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample [1003]. This will be sufficient to preserve a neutral sample to pH <2 [1003].

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].

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 or pre-tested preservation 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. EPA's method 1631 calls for using pretested (or, in another place "ultrapure") HCL or BrCL to insure they contain no mercury [1003]. It also calls for the use of ultrapure de-ionized water [1003]. In another place, method 1631 calls for "Hydrochloric acid—trace-metal purified reagent HCL containing less than 5 pg/mL Hg. The HCL should be pre-analyzed for Hg before use" [1003]. Other passages in 1631 state that "The acids used in this method should be reused as practicable by purifying by electrochemical techniques" [1003]. As mentioned above, although EPA method 1631 does not call for mercury water sample preservation with nitric acid, one area of the Method 1669 protocol, which is supposed to be used with 1631, actually suggests the use of nitric acid for all metals other than trivalent and hexavalent chromium [1003]. The bottom line: in the real world of the

field and the lab investigators are preserving mercury water samples with various types of acids, at various times, creating potential variability between different data sets.

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). Maximum holding time for mercury: 28 days (40 CFR Part 136.3, table II). Maximum holding time for mercury in water was also given as 28 days in 1984 (Federal Register, Friday, October 26, 1984, Vol. 49). In the 1994 version of the CFR, NPDES holding times for mercury was also listed as 28 days (40 CFR, Part 136.3, Table 2, page 397, 1994). However, not all investigators may be following the 28 day guideline.

The degree to which a water sample is re-acidified, re-checked for pH, 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.

Method 1631 states that "Samples that are acid-preserved may lose Hg to coagulated organic materials in the water or condensed on the walls. The best approach is to add BrCl directly to the sample bottle at least 24 hours before analysis. If other Hg species are to be analyzed, these aliquots must be removed prior to the addition of BrCl. If BrCl cannot be added directly to the sample bottle, then the bottle must be shaken vigorously prior to sub-sampling" Other methods have different suggestions [1003]. This is in contrast to EPA's previous 1991 recommendation that for method 200.2 for total metals, that nitric acid could be used in the lab and that following acidification the sample should be held for 16 hours before analysis [1005].

G) This brings up another question related to data variability vs. "standard methods": 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.

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).

EPA method 1669 says samples can be shipped to the lab prior to acidification "if they are sent with no head space" [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].

There has been considerable confusion on the subject of methyl mercury versus total mercury. Much of the mercury in sediments can be in the inorganic form, so that total and methyl mercury measures in the same sediments can result in very different concentrations.

However, the situation is much different for edible (muscle) tissues of fish and invertebrates. Rigorous laboratory analyses performed using "ultra-clean techniques" have indicated that the chemical form of mercury in edible (muscle) tissues of fish and marine invertebrates is virtually all (99%) in the form of methylmercury (CH<sub>3</sub>Hg) [489]. Whether the actual level is 98 or 100% was judged to be impossible to assess in 1992, given the analytical uncertainty in the methods available [489]. It generally makes more sense to measure total mercury in fish tissues rather than methylmercury, since 1) virtually all of the mercury in fish tissue is methyl mercury [489], 2) more laboratories can accurately measure total mercury in fish tissues than can accurately measure methylmercury, and the methylmercury analysis is about five times more expensive than the total mercury analysis [489]. Therefore, it is easier and less expensive to simply analyze total mercury and to use this concentration as a fairly good estimate of methyl mercury in tissues.

Part of the confusion between methylmercury and total mercury

measures in fish tissues has arisen because of the different ways the two have typically been analyzed:

The FDA methyl mercury method is very elaborate and complex and tends to underestimate the mercury present unless all the lab procedures are done very carefully; the cold vapor method for total mercury which has typically been done by the Fish and Wildlife Service and others tends to slightly overestimate (up to 10%) the mercury (Tom Atkerson, Florida DER, Tallahassee, Florida, personal communication). When the two errors are compounded, one can approach 30% error and the situation where methyl mercury is higher than total. A third kind of analysis, a state-of-the-art analysis done in "clean labs" typically shows less of difference in concentrations of methyl mercury versus total mercury in fish and other biological tissues than some of the older literature references would tend to indicate (Gary Gill, Texas A. and M. University, personal communication).

Hightlights of information about EPA Method 1631: Mercury in Water by Oxidation, Purge and Trap, and CVAFS [1003]:

Note: 1600 series methods are for water quality based applications at low detection limits [1001].

This method is for determination of mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS) [1003]. This method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act [1003]. The method is based on a contractor-developed method and on peer-reviewed, published procedures for the determination of mercury and in aqueous samples, ranging from sea water to sewage effluent [1003].

This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (Sampling Method) [1002,1003]. The Sampling Method is necessary to preclude contamination during the sampling process [1002,1003].

This method is designed for determination of Hg in the range of 0.5-100 ng/L and may be extended to higher levels by selection of a smaller sample size [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 part-per-billion (ppb) range, whereas ambient mercury concentrations are normally in the low part-per-trillion (ppt) 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].

The detection limit and minimum level of quantitation in this method are usually dependent on the level of background elements rather than instrumental limitations [1003]. The method detection limit (MDL; 40 CFR 136, Appendix B) for mercury has been determined to be 0.2 ng/L when no background elements or interferences are present [1003]. Ambient water quality criteria are as low as 12 ng/L [1003]. The minimum level (ML) has been established as 0.5 ng/L [1003]. An MDL as low as 0.05 ng/L (0.00005 ug/L) can be achieved for low Hg samples by using larger sample sizes, lower BrCl levels (0.2%), and extra caution in sample handling [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 [1003,1004]. These terms are not used in this method because they lack an exact definition [1003]. However, the information provided in this method is consistent with the summary guidance on clean and ultraclean techniques [1003].

Sample preparation includes pouring a 100-mL aliquot from a thoroughly shaken, acidified sample, into a 125-mL fluoropolymer bottle [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].

Samples may be shipped to the laboratory unpreserved if they are (1) collected in fluoropolymer bottles, (2) filled to the top with no head space, (3) capped tightly, and (4) maintained at 0-4°C from the time of collection until preservation. The samples must be acid-preserved within 48 h after sampling" [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].

EPA 1996 Drinking Water Monitoring Requirements [893]:

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.

EPA 1996 Drinking Water Analytical Methods [893]:

Manual cold vapor technique (EPA 245.1; ASTM D3223- 80; SM 303F); automated cold vapor technique (EPA 245.2): PQL=0.0005 mg/L.