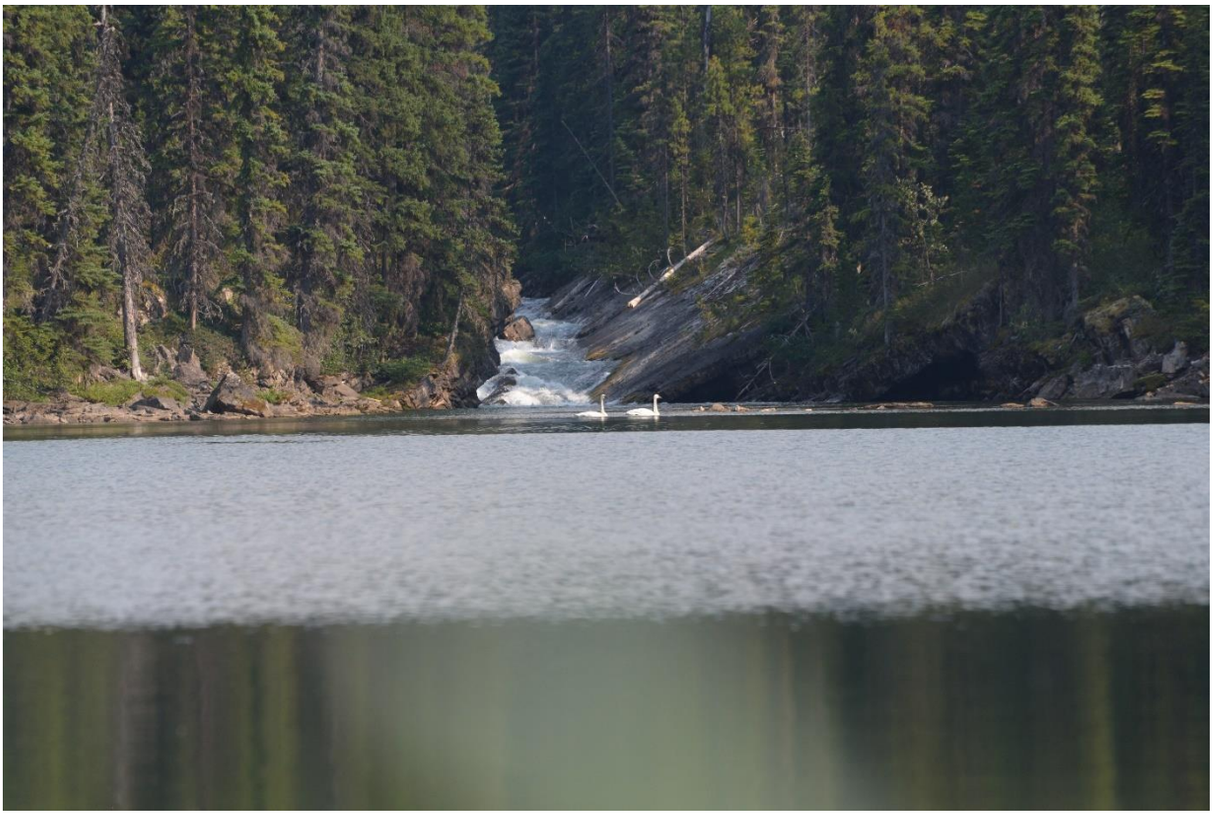
WATER QUALITY GUIDELINE SERIES

Mercury Water Quality Guidelines (Reformatted Guideline from 1989)

Technical Appendix

Ministry of Environment and Climate Change Strategy
Water Protection & Sustainability Branch



No. WQG-13

The Water Quality Guideline Series is a collection of British Columbia (B.C.) Ministry of Environment and Climate Change Strategy water quality guidelines. Water quality guidelines are developed to protect a variety of water values and uses: aquatic life, drinking water sources, recreation, livestock watering, irrigation, and wildlife. The Water Quality Guideline Series focuses on publishing water quality guideline technical reports and guideline summaries using the best available science to aid in the management of B.C.'s water resources. For additional information on B.C.'s approved water quality parameter specific guidelines, visit:

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Notes on Reformatted Version:
Sections of this report on industrial water use, drinking water and recreation have been removed. B.C. adopts Health Canada drinking water and recreation guidelines and no longer develops or supports guidelines for industrial water use. Fish tissue guidelines for human consumption have been removed due to out-of-date derivation methods. The current recommendation is to use a risk-based approach to develop human health-based fish/shellfish tissue guidelines for human consumption; these guidelines are referred to as screening values (SVs). Screening values are derived using Health Canada's general equation for calculating the ingested contaminant dose via consumption of contaminated food (Health Canada 2010).

Cover Photograph:
Location: Upper Blue Lake, B.C.

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1. INTRODUCTION

Mercury is a non-essential element for plant and animal nutrition. It is used widely in industry. This document discusses the effects of mercury on various water uses which include drinking water, aquatic life, wildlife, livestock water supply, irrigation, recreation and aesthetics, and industrial water supplies.

Since aquatic organisms can bioaccumulate mercury to levels which may be dangerous to the health of consumers, a large portion of this document focuses on effects of mercury on aquatic life. Standards, objectives, and criteria from national and international jurisdictions are reviewed. These, in conjunction with other information available from the literature, provided a basis for criteria recommended to protect water uses in British Columbia from anthropogenic mercury.

Because of the extensive amount of literature on mercury, a large portion of the information presented in this document has been extracted from recent reviews on the subject. The pertinent information available from up-to-date research papers and reports was also considered. The intent was to focus on the most applicable information which could be used to formulate defensible criteria for British Columbia waters.

2. FORMS AND TRANSFORMATIONS IN THE ENVIRONMENT

The discussion in this section is based on information presented in NAS (1978), Moore and Ramamoorthy (1984), and Adriano (1986).

2.1 Mercury in Natural Waters

There are three stable oxidation states of mercury in the environment: the elemental (Hg°), mercurous (Hg^{+}), and mercuric (Hg^{++}) state. The nature of the species and their abundance depend upon several factors, including the pH, redox potential, and nature and concentration of the anions which form stable complexes with mercury. In well-aerated waters, for instance, mercuric species will predominate, whereas elemental mercury and sulphide complexes of mercury prevail under reducing conditions.

In aquatic environments, mercury forms strong associations with inorganic ligands, organic ligands, and particulate matter, and also undergoes transformations by methylation and demethylation processes. Among the inorganic anions, chlorides of mercury are regarded as the most mobile and persistent compounds. Mercury also hydrolyses to form $Hg(OH)_2$ in waters at pH 4. The abundance of $HgCl_2$, $Hg(OH)_2$, and other intermediate chloro-hydroxy species of mercury is dependent on pH and chloride ion concentration.

The −SH, −COOH, and −N functional groups in organic ligands are considered to be responsible for complexing mercury. However, the sulphur-containing organic ligands form the strongest complexes. The organic-mercury complexes may occur in both soluble and colloidal forms. Dissolved organic mercury fractionates among compounds of molecular weight ranging from 500 to 100 000 (Ramamoorthy and Kushner, 1975). Salinity of water has a negative effect on organic-mercury complexing processes.

Mercury is strongly bound to suspended particulate matter in natural waters. The extent of the association depends on water quality characteristics such as pH, salinity, redox potential, and the presence of organic ligands. Partition coefficients of 134 000 to 188 000 for mercury, between suspended solids and water, have been determined from field and laboratory measurements. Sorption to suspended solids and subsequent sedimentation play an important role in the removal of mercury from the water column.

2.2 Mercury in the Sediments and Soils

Mercury in soils and sediments may be immobilized by (i) forming complexes with sulphhydryl groups of the organic fraction, (ii) incorporating within crystal lattices, (iii) co-precipitating with ferromanganese oxides, and (iv) forming insoluble mercuric sulphide, depending upon the redox potential of the medium. The rate and the amount of mercury sorbed by the solid phase are determined by the specific surface area of the solid phase, organic matter content, cation exchange capacity, and grain size.

The release of mercury sorbed by the sediment or the soil phase to bulk (or interstitial) water is a function of pH, redox potential, chloride ion concentration, and the presence of organic chelating agents. Little desorption of mercury was reported for clays, organics, and sands (Reimers and Krenkel, 1974). Sediments leached with solutions of NaCl and NTA (a surfactant and a strong chelating agent in commercial detergents) have been shown to release significant amounts of sorbed mercury (Ramamoorthy and Rust, 1976 and 1978). Overall, desorption of mercury is a slow process, thus posing a long-term problem even after the sources of pollution are eliminated or reduced.

2.3 Transformations of Mercury

Mercury is discharged into the environment mainly in elemental and inorganic forms; a variety of organo-mercury compounds are also discharged into the environment as a result of human activities. All forms of discharged mercury are subject to chemical, biological, and photochemical reactions.

Two groups of organic mercurial compounds are formed in the environment: (i) the amphiphilic (e.g.,R-Hg-X) group in which Hg is bonded to an organic radical through a covalent bond and an inorganic radical through an electrovalent bond, and (ii) the lipophilic (e.g.,R-Hg-R) group in which mercury is covalently bonded with two organic radicals. The first group, e.g., methylmercury ion (CH_3Hg^+), is characterized by its water and lipid solubility, whereas the second group is non-polar, almost insoluble in water, and extremely volatile.

In contaminated waters, almost all mercury in fish is methylmercury. Methylation of mercury is both a biological and an abiological reaction and requires the presence of a free mercuric ion and a methyl donor molecule(s). Biological methylation could occur in aerobic as well as anaerobic environments and involves both enzymatic and non-enzymatic processes. The efficiency of methylation is determined by the metabolic state of the organisms, availability and concentration of mercuric ion, temperature, pH, redox potential, and the presence of organic complexing agents. The production of methylmercury is enhanced if a means of methylmercury clearance is introduced into the system. In aquatic environments, for instance, methylmercury diffuses through the cells of higher organisms and binds rapidly to sulphhydryl groups thereby maintaining a concentration gradient across the membrane. As a consequence, even a low concentration of methylmercury in water leads to an elevated concentration in fish (Moore and Ramamoorthy, 1984).

Microbial degradation, or demethylation of methylmercury to· the elemental state or mercuric ion, occurs in sediments of fresh as well as marine waters. Two enzyme systems consisting of a hydrolase and a reductase enzyme have been shown to be responsible. Under ideal conditions demethylation is several orders of magnitude slower than the methylation reaction. Because of its degradation and rapid intake by aquatic organisms, methylmercury measurements in sediments do not necessarily indicate the total amount of methylmercury produced in the environment (Moore and Ramamoorthy, 1984).

Methyl derivatives of lead, tin, and silicon may be involved in transmethylation of mercury. Photochemical alkylation of mercury could occur with methyl donors such as acetic acid, propionic acid, methanol, and ethanol.

Methylation of mercury also occurs in terrestrial environments under both aerobic and anaerobic soil conditions (Beckert et al., 1974; Rogers, 1977). Methylated mercury was found in desert soils amended with mercuric nitrate, and in alkaline agricultural soils under a variety of conditions. Methylation of mercury in soils could, in part, be abiotic and is a direct function of clay content, moisture content, temperature, and concentration of inorganic mercury (Rogers, 1976 and 1977).

Mercury can be mobilized by volatilization, leaching, and biotic uptake. Volatilization of mercury is a result of chemical reaction, microbial activity, or both. It is considered to be the dominant pathway in loss of mercury from soils.

3. OCCURRENCE IN THE ENVIRONMENT

3.1 Natural Environment

The earth's crust contains approximately 0.05 ug Hg/g, mainly as sulphide (Adriano, 1986). The actual content of mercury, however, varies with the type of rock. In general, sedimentary rocks (0.005 to 3.25 ug Hg/g) tend to contain more mercury than igneous rocks (0.005 to 0.25 ug Hg/g); shales high in organic matter are particularly enriched in mercury (NRCC, 1979). Mercury minerals consist of cinnabar (mercuric sulphide), metacinnabar, or both (polymorphs of mercuric sulphide), and one or more of native Hg, stibnite, native S, quartz, fluorite, and carbonates (NRCC, 1979). Mercury is also found in coal, marine phosphate, and in the vicinity of gold, molybdenum, and base metal deposits. The areas of high mercury content over the globe have been arranged into belts and generally correspond to zones of instability, and volcanic and thermal activity; however, there are areas of high mercury content which fall outside the mercuriferous zones (Moore and Ramamoorthy, 1984).

In British Columbia, economic grade deposits of mercury are commonly associated with sedimentary rocks such as limestone and sandstone of the Palaeozoic to Recent age (Jonassen and Sangster, 1974). The province's richest mercury deposits are in the Pinchi Lake fault zone which extends from Fort St. James northwest to Omineca River (Reid and Morley, 1975). Other major areas of mercury mineralization in British Columbia include Kamloops Lake, Bridge River, and Yalakom River. Significant enrichment has been detected in rocks from lead-zinc base metal deposits throughout the province and mercury occurrences in the Bluebell mineral claim area near Kootenay Lake are associated with gold anomalies.

Mercury is released naturally into the environment through volcanic and geothermal activities, weathering of rocks, and degassing from water and earth surfaces. Mercury in air is re-deposited in terrestrial and aquatic environments through precipitation, snowfall, and fall-out of dust particles. It is generally assumed that mercury can remain in the atmosphere for long periods (Charlebois, 1977).

Disturbances exposing sediments to air (e.g., tidal changes, dredging, redeposition of dredged materials, etc.) release mercury into the water column. For instance, high levels of mercury in fish collected from new impoundments have been measured. It was shown that mercury 1evels in freshly inundated soils were much higher than those of original lake bottoms and the rate of methylation increased after flooding. It was also suggested that sediments of older reservoirs develop reducing conditions, thus binding mercury to sulphur compounds and thereby reducing its availability to the food chain (Abernathy and Cumbie, 1977; Cox et al., 1979).

3.2 Anthropogenic Sources

Metallic mercury is widely used in industry for the manufacture of chemicals, mercurial compounds, scientific equipment, electrical equipment, power generation, dental amalgams, and metallurgical gold.

The mercurial compounds, on the other hand, have found applications in paints, drywall compounds, scientific supplies, pharmaceuticals, fungicides, and bactericides.

Some anthropogenic sources responsible for the release of mercury into the environment are listed below.

(i) the FMC chlor-alkali plant near Squamish is probably the largest user of metallic mercury in B.C. The FMC plant uses mercury cells in the electrolysis of brine to produce chlorine and caustic soda. Mercury losses from such a plant could occur through liquid effluent discharges, air emissions, solid wastes, and plant products;

(ii) the pulp and paper industry is the main user of chlorine and caustic soda. Caustic soda produced at a chlor-alkali plant is often contaminated with mercury. In 1978, six B.C. mills used mercury-contaminated caustic soda (Garrett et al., 1980). Most of the mercury associated with caustic soda in the pulp and paper industry reaches the environment through air emissions**,** effluent discharges, and plant products;

(iii) the major users of mercurial compounds in B.C. are the paint and drywall industries. The mercurial compounds are used as fungicides and preservatives in latex paints, outdoor oil-based paints, marine paints, drywall joint cements, fillers, and ceiling textures. During paint manufacture, mercury is lost to the environment in process water, in sludge water, from spillage, and through volatilization. Upon application Hg is lost to the environment through volatilization;

(iv) mercury present in an ore body is released into the environment during mining, milling, and smelting via the mine and mill process water and smelter vapour emissions. The Island Copper Mine on Vancouver Island, the Afton copper smelter near Kamloops, and the Cominco smelter/fertilizer plant at Trail, are examples of such sources (as total mercury) in British Columbia;

(v) combustion of coal and oil is also known to contribute mercury to the B.C. environment, but mostly as atmospheric emissions (MacLaren, 1973);

(vi) no electrical company in B.C. produces mercury- containing apparatus. However, mercury-based electrical equipment, e.g., mercury arc rectifiers used for power generation/transmission by industries and electrical utilities in B.C., could be a cause of concern when disposed of or serviced;

(vii) spillage and vaporization of metallic mercury occurs during refilling or breakage of industrial scientific equipment (e.g., thermometers, barometers, manometers, diffusion pumps, Coulter counters, etc.). Mercurial reagents and catalysts used in laboratories and hospitals can be a source of mercury release into the environment;

(viii) 50% of the total amount(~4 800 kg/y) of mercury used in dentistry in B.C. between 1976 and 1978, was thought to have been released to sewer systems or discarded in landfills (Garrett et al., 1980);

(ix) mercury compounds used in disinfectants, antiseptics, diuretics, and other pharmaceuticals are potential sources of mercury in the environment. Many of the Hg-based pharmaceutical products are no longer on the market;

(x) mercurial compounds have been used in agriculture to control seed and soil-borne fungal diseases. In 1977, Agriculture Canada cancelled the registration of mercurial seed treatment under the Pest Control Product Act. However, the use of mercurials is still permitted in the treatment of seed for quarantine purposes. In British Columbia mercurial compounds may be purchased and used by special permit only. No permit for the use of mercurial compounds has been issued in B.C. for the past five years. Mercuric chloride is used in B.C. for the control of fungal diseases;

(xi) landfills, sewage treatment plants, incinerators, and ocean dumping sites are areas where contaminants, including mercury, are concentrated. Mercury from these sites is released to the environment through leaching, surface runoff, and vaporization.

3.3 Levels in Water, Sediment, and Biota

3.3.1 *Water*

Mercury strongly associates with organic and suspended sediment fractions and, as a result, settles to the bottom of the water column. Because of these characteristics and the volatility of some mercury compounds, the concentration of mercury in natural waters is generally low. Concentrations of dissolved mercury ranging from 0.01 to 0.1 ug/L have been reported for unpolluted lakes and rivers in Canada (D'Itri, 1972). The maximum concentration of total mercury in the fresh waters of British Columbia was generally 0.10 ug/L, with the 95th percentile concentration 0.05 ug/L (the usual minimum detection limit) and the 99th percentile concentration 0.10 ug/L (B.C. Ministry of Environment, 1988). Elevated mercury concentrations were**,** however, reported in certain freshwater systems: (i) up to 36.5 ug/L in Stoney Creek and 0.27 ug/L in the Columbia River near the Cominco smelter/fertilizer complex at Trail (these levels occurred prior to installation of the Hg removal plant in Trail and the drainage water treatment plant in Kimberley, and do not represent present conditions), (ii) up to 3.3 ug/L in Pinchi Lake in the vicinity of extensive mercury mineralization and the past site of a mercury mine, (iii) up to 4.5 ug/L in St. Mary River and various creeks near a mining operation at Kimberley, and (iv) > 0.2 ug/L in the industrialized lower portion of the Fraser River and its tributaries (Garrett et al., 1980; Garrett, 1985). The highest concentration of mercury in the Yakoun River and its tributaries was found to be 0.7 ug/L around the proposed Cinola Gold Project on Graham Island (Queen Charlotte Islands) (I.E.C. Beak, 1982). Streams and rivers near mercury deposits may contain up to 100 ug/L mercury (Jonassen and Boyle, 1971).

The natural concentration of mercury in oceans and seas may range from < 0.001 to 0.005 ug/L (Gill and Fitzgerald, 1985; Olafsson, 1982, 1983). Lu et al. (1986) noted that the mercury concentration of Saanich Inlet (British Columbia) varied with the depth and the season, and ranged between 0.0003 and 0.003 ug/L in the upper water column.

Elevated concentrations of mercury, 0.14 to 0.4 ug/L, were noted occasionally in Kitimat Arm, Ucluelet Inlet, Bamfield Inlet, and Quatsino Sound (Garrett et al., 1980; Garrett, 1985). The maximum concentration in Kitimat Arm on the west coast of British Columbia was reported to be > 400 ug Hg/L (Thomas et al., 1986); it most probably originated from the Alcan Aluminum smelter (Warrington, 1987).

3.3.2 *Sediment*

The mercury content of natural sediments (reported on dry weight basis unless indicated otherwise) in a catchment basin varies widely with the nature of the bedrock, physiographic conditions, and climate (Jonassen, 1978). Within an aquatic environment, mercury content of sediment is determined by its physical, chemical, and biological characteristics. The mercury concentrations in geologically recent sediments of streams, rivers, and lakes range from 0.01 to 0.70 ug/g, with an average value equal to 0.073 ug/g (Jonassen and Boyle, 1971).

In British Columbia, the maximum concentration of total mercury in sediments of unpolluted lakes and rivers was recorded at 0.90 ug/g, and the 90th percentile was 0.2 ug/g (B.C. Ministry of Environment, 1988; Derksen, 1985). Elevated levels were reported in fresh water sediments subject to mercury pollution: Port Clements (1.3 to 26 ug/g) on mining property containing mercury anomalies, Pinchi Lake (2 to 117 ug/g) in an area of extensive mercury mineralization and past site of a mercury mine, and the Columbia River at Trail (0.26 to 2.52 ug/g) near a smelter/fertilizer complex (Garrett, 1985).

Elevated levels of mercury are found in ocean and estuarine sediments near industrialized areas. In British Columbia, these include: Howe Sound (<0.01 to 20 ug/g in the vicinity of a mercury-cell chlor-alkali plant), Victoria Harbour (0.078 to 4.98 ug/g), Powell River (<0.02 to 21 ug/g near a pulp and a paper mill), Point Grey (0.975 to 1.4 ug/g), Sturgeon Bank (0.01 to 1.5 ug/g) (Garrett, 1985; Thompson et al., 1980), and

Alice and Hasting Arms (42 to 381 ug/g) (Thomas et al., 1986). An average of 630 ug/g mercury was recorded in Minimata Bay (Japan) sediments polluted with mercury (Matida and Kumada, 1969). The natural (unpolluted) sediments of the East Pacific Rise (Hawaii) contained mercury levels ranging from 0.02 to 0.24 ug/g, with an average value of 0.06 ug/g (Cox and McMurtry, 1981).

3.3.3 *Biota*

The concentration and/or accumulation of mercury in aquatic organisms depends on several factors. These include: (i) size**,** sex, age, trophic level, general biology, and feeding habits of the organisms, (ii) the concentration and the chemical form of mercury in the aquatic environment, (iii) availability of food, and (iv) the physical, chemical, and biological characteristics of the environment (Garrett, 1985). Non-migratory, predatory, bottom-feeding species, and filter-feeding bivalves are perhaps the most reliable indicators of local mercury contamination (Phillips, 1977; Smith et al., 1975).

The average concentration of mercury in the muscle tissue of salmon, herring, anchovies, eulachons, and tuna caught from British Columbia waters, was less than the maximum concentration of 0.5 ug/g wet wt. recommended for the edible portion of fish used for human consumption (Health and Welfare Canada, 1971; Garrett et al., 1980; Thomas et al., 1986). This, in part, resulted from the fact that these species of fish were not exposed to mercury for extended periods due to their migratory and pelagic habits. In several fish species collected from pristine lakes of British Columbia, the concentration of mercury in the muscle tissue varied from 0.05 to 1.5 ug/g wet wt. with the 90th percentile concentration exceeding the critical level of 0.5 ug/g wet wt. only in cutthroat (0.57 ug/g wet wt.) and lake trout (0.575 ug/g wet wt.). The slightly elevated levels in cutthroat and lake trout were thought to be the result of bias in collecting bigger and mature fish, although these are also the ones which are likely to be caught for human consumption (B.C. Ministry of Environment, 1988).

Although the mercury concentration in freshwater species was generally low in British Columbia, elevated levels (0.5 ug/g wet wt.) were recorded in several instances. These include: (i) several species of fish including squawfish, suckers, sculpin, and sturgeon from both industrialized and non-industrialized portions of the lower Fraser River (Singleton, 1983; Northcote et al., 1975), (ii) nearly all species of fish from Pinchi Lake, an area of rich mercury deposits and the site of an abandoned mercury mine (Fimreite et al.,1971; Petersen et al., 1970; Reid and Morley, 1975), and (iii) squawfish and perch in the Okanagan region, due perhaps to past agricultural applications of mercury-containing compounds, and municipal sewer discharges (Garrett et al., 1980). Elevated concentrations of mercury ranging from 0.24 to 0.91 and 0.16 to 0.55 ug/g wet wt. were also measured in the muscle tissues of squawfish and walleye, respectively, caught in the lower Columbia River (Smith, 1987).

Pacific halibut and other species of groundfish, including several commercially important species of rockfish and cod caught off the B.C. coast, registered high mercury concentrations (ranging from 0.19 to 1.02 ug/g wet wt.). The average concentration in sablefish muscle exceeded the critical (0.5 ug/g wet wt.) level in several areas of B.C. coastal waters, namely those in the vicinity of Queen Charlotte Islands and Queen Charlotte Sound, and Bute, Jarvis and Toba Inlets (Garrett et al., 1980; Thomas et al.; 1986). No anthropogenic sources of mercury were, however, recognized in these areas. Whereas mercury contamination of rockfish (maximum concentration = 1.13 ug/g wet wt.) from Port Alberni was most likely due to phenylmercuric acetate used in the pulpmill operation from 1959 to 1970, the high concentrations in sculpins (up to 1.62 ug Hg/g wet wt.) and flounders (up to 2.4 ug/g wet wt.) in Howe Sound near Squamish were attributed to the chlor-alkali plant in the area (Garrett et al., 1980; Harbo and Birtwell, 1978).

Among the cartilaginous fish species from the B.C. coastal waters, the mercury concentration in ratfish and skate ranged between <0.02 and 0.69 ug/g wet wt.(muscle), but were generally below the critical level. On the other hand, the mercury concentration in spiny dogfish and other sharks (e.g., six gill and

blue) ranged between 0.08 to 2.23 ug/g wet wt.(muscle), with values often exceeding 1.0 ug/g wet wt. (Garrett et al., 1980). The highest concentration was found in dogfish from Howe Sound in the early 1970's. Elevated levels (>0.5 ug/g wet wt.) of mercury in dogfish sampled from the Strait of Georgia, between Point Grey and the U.S.A. border, were attributed to the influence of industrial contamination in the Fraser River (Forrester et al., 1972).

4. AQUATIC LIFE

4.1 Effects on Algae and Other Aquatic Plants

4.1.1 *Freshwater Plants*

Aquatic plants remove mercury from water primarily by direct absorption rather than by uptake from the sediments. The uptake of mercury is essentially passive and depends upon the duration of the exposure and the concentration in water (Glooschenko, 1969; Mortimer and Kudo, 1975). The total mercury concentration in aquatic plants (0.03 to 2.0 ug/g dry wt.) is generally low, even in polluted areas (Moore and Ramamoorthy, 1984): however, it has been shown that an aquatic weed, *Elodea*, may accumulate between 10 000 to 60 000 times more mercury in its tissues than in the surrounding waters (Mortimer, 1977).

Freshwater (and marine) macrophytes appear to be more resistant to mercury effects than algae (U.S. EPA, 1985b). As low as 5 ug/L of mercury (as $HgCl_2$) caused chronic effects (incipient inhibition) in blue-green algae, *Microcystis aeruginosa* (Bringmann, 1975; Bringmann and Kuhn, 1976; 1978a,b; 1979). Toxic effects of $HgCl_2$ at 5 ug Hg/L were also noted for another species of algae, *Ankistrodesmus* sp. (Baker et al., 1983). The alga, *Chlorella vulgaris*, appears to be one of the most resistant species (LC 5 0 = 100 to 1 000 ug Hg/L) to the toxic effects of inorganic mercury (U.S. EPA, 1985b).

The pH, phosphate, and calcium content of water are often correlated with mercury toxicity to aquatic plants (Moore and Ramamoorthy, 1984). A larger reduction in the growth and the photosynthetic activities in *Ankistrodesmus* sp. by mercury at pH 5 than at pH 7, was demonstrated by Baker et al. (1983).

In general, the freshwater algae are more sensitive to organic mercury than inorganic mercury. After a 15-day exposure, Rai et al. (1981) noted a 50% reduction in the growth of *Chlorella vulgaris* by $HgCl_2$ at concentrations ranging from 443 to 592 ug Hg/L in water; a similar reduction was noted with methylmercury (MeHg) at 0.8 to 4 ug Hg/L. The EC_{50} (growth) values for another species of algae, *Anabaena* flos-*aguae*, with $HgCl_2$, MeHg, and phenylmercuric acetate were 53, 6.0, and 2.8 ug Hg/L, respectively (Thomas and Montes, 1978). The most sensitive freshwater alga to MeHg appears to be *Chlamydomonas* sp. (Chlorophyta); severe retardation in the growth of *Chlamydomonas* sp. was observed at 0.02 ug Hg/L (as MeHg) by Lock (1975).

4.1.2 *Marine Plants*

As in freshwater plants, the concentration of mercury in water causing toxicity to marine aquatic plants varied widely. Boney et al. (1959) recorded a 7-day LC_{50} of 3170 ug Hg/L (as $HgCl_2$) for red algae (*Plumarla elegans*) sporelings. On the other hand, a concentration of 10 ug Hg/L (as $HgCl_2$) was noted to reduce (i) chlorophyll £ synthesis in the marine alga, *Thalassiosira aestivalis*, (Hollibaugh et al., 1980), and (ii) growth by 50% after 5 days in the diatom, *Ditylum brightwellii* (Canterford and Canterford, 1980). As little as 0.08

ug Hg/L (as $HgCl_2$) was shown to reduce cell density in the diatom *Skeletonema costatum* (Cloutier-Mantha and Harrison, 1980).

Again, organomercurials retarded the growth and viability of several species of marine algae more effectively than inorganic mercury (Mora and Fabergas, 1980; Boney et al., 1959). Using planktonic algae (*Nitzchia acicularis* W.Sm. and *Tetraselmis suecica* Butch.), Mora and Fabergas found that the minimum toxic concentration of $HgS0_4$ was 150 to 200 ug Hg/L, but the corresponding levels for phenyl mercuric acetate and for MeHgCl were 25-50 and 25 ug Hg/L, respectively. An EC_{50} (photosynthesis) of 0.4 ug Hg/L was noted for the diatom, *Nitzchia delicatissima*, after an exposure for 24 hours to methylmercuric dicyandiamide in water (Harriss et al., 1970).

4.2 Effects on Invertebrates

4.2.1 *Freshwater Invertebrates*

(a) Acute Toxicity

Acute toxic effects of mercury to invertebrates in freshwater (and marine) depend upon species, developmental stage, and environmental conditions (Moore and Ramamoorthy, 1984). Based on the data reviewed in its report, U.S. EPA (1985b) concluded that the difference in the sensitivity between different species of invertebrates to a particular mercury compound is far greater than the difference in sensitivity of a particular species to various compounds. The most sensitive species to acute effects of inorganic mercury appeared to be *Daphnia* sp.: LC_{50} = 1.4 to 4.4 ug Hg/L (as $HgCl_2$) for *Daphnia magna*, and 2.2 ug Hg/L (as $HgCl_2$) for *Daphnia pulex* (Canton and Adema, 1978; Barera and Adams**,** 1983).

Increasing hardness of water reduced the acute toxicity of mercury compounds to freshwater invertebrates (Buikema et al., 1974; Brkovic-Popovic and Popovic, 1977). However, the degree of antagonism due to the hardness of water was considerably lower than that reported· for many other metals; e.g., the acute toxic concentration of mercury (as $HgCl_2$) to *Tubifex tubifex* at water hardness equal to 34.2 and 261 mg/L $CaC0_3$ (pH~ 7.2) increased only by about 1.2 times (from 82 to 100 ug Hg/L; Brkovic-Popovic and Popovic, 1977). In comparison, the maximum concentrations of Cu and Pb (which, if exceeded, could cause acute toxicity to freshwater aquatic life) between the same range of water hardness increased from 5 to 10 times (Singleton, 1987; Nagpal, 1987).

The data for acute toxicity of MeHg and other organic mercury compounds to freshwater invertebrates are limited. It is evident,·however, that freshwater invertebrates accumulate higher levels of Hg in their tissues from water containing organic than from water containing inorganic mercury compounds (Zubaric and O'Connor, 1978). A 4-day LC_{50} of 200 to 500 ug Hg/L (as MeHgCl) was recorded for *Dugesia dorotocephala* (Best et al., 1981).

(b) Chronic Toxicity

In chronic toxicity tests with *Daphnia magna*, adverse effects of inorganic mercury, as $HgCl_2$, were found at concentrations ranging from 0.72 to 1.82 ug Hg/L. However, methylmercury was more toxic resulting in chronic toxicity at concentrations < 0.04 ug Hg/Las MeHgCl. Tests with other invertebrates showed relatively higher chronic values for both inorganic and organic mercury (U.S. EPA, 1985b).

The extent to which organisms accumulate Hg from water depends upon the form of mercury, time of exposure, and a variety of environmental and biological characteristics of the media and the respective organisms. Organic mercury is absorbed faster and to a higher degree from food and water than inorganic mercury (Hannerz, 1968; Zubarik and O'Connor, 1978). For instance, in amphipods (*Gammarus* sp.) exposed to $HgCl_2$ and MeHg for seven days, bioconcentration factors (BCF) of 2 500 and 8 000,

respectively, were obtained· (Zubarik and O'Connor, 1978). The rate of accumulation, however, may increase with temperature and chelator concentration in water (Ribeyre et al., 1980). Also, whereas no direct correlation was obtained between an invertebrate's Hg burden and its trophic level, Hanne rz (1968) observed that predacious insect larvae such as dragonflies and alderflies (*Sialis*) accumulated more mercury than organisms which feed on decaying plants and detritus. Chang et al. (1983) reported that low pH retarded accumulation of Hg in crayfish, *Orconectes virilis*, either (i) by inhibiting the uptake of Hg in its cationic form, or (ii) by promoting absorption of mercury to particulate matter. An antagonistic effect of hardness of water on Hg toxicity (as $HgCl_2$) to the protozoan Tetrahymena pyriformis was also noted by these investigators.

4.2.2 *Marine Invertebrates*

(a) Acute Toxicity

As in freshwater, sensitivity of marine invertebrates to mercury compounds varies widely. Mysids, *Mysidopsis bahia*, appear to be one of the most sensitive species to acute effects of inorganic Hg, showing a 96-h LC_{50} of 3.5 ug Hg/L (as HgCl2) (Gentile et al., 1982, 1983; Lussier et al., 1985). In static acute toxicity tests with the softshell clam, *Mya arenaria*, in saline water, Eisler and Hennekey (1977) obtained a 96-h LC_{50} of 400 ug Hg/L (as $HgCl_2$); however, the 168-h LCS0 was 100 times smaller at 4.0 ug Hg/L. Much larger LC_{50}, 6, ranging from 8 700 to 10 000 ug Hg/L (as HgCl2), were obtained for the estuarine clam, *Rangia cuneata* (Olson and Harrel, 1973).

Larvae of invertebrates are generally more sensitive to mercury than adults (Connor, 1972; Thain, 1984). It was noted that a safety factor from 10 for *Crepidula fornicata* (Thain, 1984) to > 1 000 for the green crab, *Carcinus maenas*, (Connor, 1972) must be applied to toxicity data for adults, to protect the most sensitive stage in the life cycle of the organisms from acute effects of $HgCl_2$. A safety factor of 100 is generally assumed to give a good estimate of the safe level (FAO, 1977). The 96-h and 48-h $LC_{50's}$ for bay mussel (*Mytilus edulis*) and eastern oyster (*Crassostrea virginica*) embryos were 5.8 and 1.0 ug Hg/L (as HgCl2), respectively (Martin et al., 1981; Calabrese et al., 1973).

(b) Chronic Toxicity

Based on the data of Gentile et al. (1982, 1983) and Lussier et al. (1985), U.S. EPA (1985b) calculated a chronic value of 1.131 ug Hg/L for the mysids, *Mysidopsis bahia*, exposed to $HgCl_2$ for 36 days. Whereas the time to spawn and productivity of the organisms exposed to 1.6 ug Hg/L were significantly different from the control, no statistically significant effect on reproduction processes was detected at 0.8 ug Hg/L.

Thain (1984) found that Hg-equilibrated algal suspensions containing 0.25, 0.42, and 1.0 ug Hg/L (as $HgCl_2$) in solution reduced the growth and condition of the slipper limpet, *Crepidula fornicata*, in a 16-week period. Reproduction rates and larval survival to settlement were also reduced over the first three spawnings when the exposed pairs reached sexual maturity. Because of the impairment of reproductive capacity of the organisms at the lowest level of exposure, Thain suggested that even concentrations lower than 0.25 ug Hg/L may cause measurable impairment of reproduction in *Crepidula*. On examining the most recent review (U.S. EPA 1985b), *Crepidula fornicata* appears to be the most sensitive species of marine invertebrates to mercury.

Riisgard and Famme (1986) studied absorption of mercury by the shrimp, *Crangon crangon*. In the organisms exposed for three weeks to seawater containing 0.98 ug Hg/L (as Hg^{++}) and 0.02 ug Hg/L (as CH_3Hg^{+}) simultaneously, absorption of organic mercury was much higher than that for inorganic mercury; after 25 days of exposure, the organic and inorganic forms of mercury accumulated by the organisms were 0.05 and 0.01 ug/g wet wt., respectively. In practice, the character of the mercury pollution i.e., massive

versus chronic pollution, and the chemistry of the pollutants may determine accumulation and speciation of mercury in marine invertebrates (Riisgard et al., 1985). These investigators noted that the biological half-lives of mercury were 293 days for *Mytilus edulis* from the chronically polluted area in c6ntrast to only 53 days for the mussels from a temporarily massively polluted area near a chemical deposit. The seasonal, geographical, and size-induced variability in the mercury content of *Mytilus edulis* was studied by Cossa and Rondeau (1985).

4.3 Effects on Fish

4.3.1 *Freshwater Fish*

(a) Acute Toxicity

A recent review by the U.S. EPA (1985b) suggested that the acutely toxic concentrations of inorganic mercury varied widely among species of freshwater fish, while lying within the toxic range observed for freshwater invertebrates. Also, the sensitivity between different species to a particular mercury compound was far greater than the difference in the sensitivity of a particular species to various compounds.

Organic mercury compounds are considerably more toxic than inorganic compounds (Matida et al., 1971; Wobeser, 1975; Lock and van Overbeeke, 1981). The 96-h $LC_{50's}$ of 275 and 24 ug Hg/L, respectively were reported for the juvenile rainbow trout, *Salmo* ga*irdneri*, exposed to $HgCl_2$ and MeHgCl (Lock and van Overbeeke, 1981). Among the organic mercury compounds, phenylmercuric acetate yielded the lowest 96-h LC_{50} of 5.0 ug Hg/L in tests with the juvenile rainbow trout (Matida et al., 1971).

(b) Chronic Toxicity

Chronic and sublethal toxicity in fish shows several clinical symptoms. They include: (i) inhibition of enzymes and protein synthesis in liver, kidney, and brain, (ii) structural alterations of fish epidermal mucus, (iii) reduction in sperm viabilty, embryogenesis, and survival of second generation fry, (iv) reduction in olfactory response, vision, and respiration, (v) reduction in fin regeneration time, and (vi) decreased ability to osmoregulate. None of these changes, however, would result in drastic or immediate changes in fish stock (Moore and Ramamoorthy, 1984).

The chronic toxic concentration of inorganic Hg affecting the fathead minnow, *Pimephales promelas*, in its early life stage or in partial life cycle tests, was reported to be< 0.23 ug Hg/L (Call et al., 1983), and< 0.26 ug Hg/L (Snarsky and Olson, 1982). These chronic values for the fathead minnow were about 650 times lower than the reported acute values. Birge et al. (1979, 1980) reported a 28-d EC_{50} of< 0.1 ug Hg/L (as $HgCl_2$) causing death and deformity in embryos and larvae of the rainbow trout, *Salmo gairdneri*.

In studying long-term effects of MeHgCl on three generations of brook trout, *Salvelinus fontinalis*, McKim et al. (1976) found no significant effects on the survival, growth, or reproduction of the second generation trout at 0.03, 0.09, and 0.29 ug Hg/L (The mercury concentration in the muscle tissue of the first generation fish at the end of 39 weeks of exposure was 1.0, 1.9, and 4.9 ug Hg/g wet wt., respectively). The young third generation trout were not affected by these concentrations of MeHgCl in the 12-week period after hatching. The estimated total weights of 12-week-old young from females were similar in most cases, although the ratios of the mean estimated weights of 12-week-old young/female were less than the control at al1 concentrations tested. Matida et al. (1971) found that MeHgCl in water at concentrations ranging from 0.0037 to 0.037 ug Hg/L, inhibited the growth of rainbow trout, *Salmo gairdneri*.

The minimum mercury concentration in the larvae of pink salmon (*Oncorhynchus gorbuscha*) causing a harmful metabolic effect (i.e., a reduction in respiration rate) was 1.0 ug/g live weight, which was achieved by maintaining the larvae for 60 days in a medium containing 1.0 ug Hg/L (Storozhuk and Smirnov, 1982).

Several environmental and biological factors affect mercury toxicity and accumulation in fish. Whereas the sensitivity of fish to mercury may increase with an increase in water temperature, Hg toxicity is inversely related to the pH, dissolved oxygen level, and size of the organism (Verma et al., 1985). The prehatch (egg) state appears to be the most susceptible to mercury effects (Akiyama, 1970; Servizi and Martens, 1978); e.g., Servizi and Martens found that the 168-h LC_{50} of inorganic mercury for the eggs of sockeye salmon was 4 ug/L as compared 180-220 ug/L for the fry and smelt.

The dependence of mercury accumulation by fish on a variety of environmental, biological, and lake morphometric characteristics has been studied by several investigators (MacCrimmon et al., 1983; Mathers and Johansen, 1985: Wren and MacCrimmon, 1983). As expected, the mercury concentration was reported to be much higher in fish exposed to MeHg than in fish exposed to $HgCl_2$ (Nagashima et al., 1984; Boudou and Ribeyre, 1985). In general, factors causing higher mercury toxicity are responsible for higher accumulation of mercury in fish.

During an exposure to sublethal concentrations of mercury, Rogers and Beamish (1983) found that the relative efficiency of MeHg uptake by *Salmo gairdneri* in soft water (hardness= 30 mg/L $CaCO_3$) was more than double that measured in hard water (hardness = 385 mg/L $CaCO_3$). It was suggested that calcium-dependent changes in gill permeability were responsible for elevated MeHg residues in fish from lakes of low alkalinity and pH. It was also noted that when $HgCl_2$ was added with waterborne MeHg, the uptake of MeHg was further increased, but similar values were obtained in soft and hard waters. Tabata (1969) did not find any significant effects of water hardness on the toxicity of Hg^{++} to *Daphnia*, rainbow trout, carp, or Japanese killifish.

4.3.2 *Marine Fish*

(a) Acute Toxicity

As with the freshwater fish, the acute toxicity of mercury varies widely in marine fish (U.S. EPA, 1985b). Among the lowest acutely toxic concentrations, a 96-h LC_{50} of 36 ug Hg/L (Hansen, 1983) and an 168-h LC_{50} of 20 ug Hg/L (Eisler and Hennekey, 1977) as HgCl2 were reported for the juvenile spot, *Leiostomus xanthurus*, and adult starfish, *Asterias forbesi,* respectively.

Sharp and Neff (1980) found that MeHgCl (96-h LC_{50} = 51.1 ug Hg/L) was more toxic to the embryo of the mummichog, *Fundulus heteroclitus*, than HgCl2 (96-h LC_{50} = 67.4 ug Hg/L). Similar results were reported for himedaka, *Oryzias latipes*; however, himedaka were about 5 times more sensitive to MeHgCl (48-h LC_{50} = 155 ug Hg/L) than to HgCl2 (48-h LC_{50} = 700 ug Hg/L) (Nagashima et al., 1984).

(b) Chronic Toxicity

Dawson et al. (1977) observed that respiration activity in adult striped bass (*Morena saxatillis*) decreased after 30 days of exposure to 5 ug Hg/L (as $HgCl_2$). Adult winter flounder (*Pseudopieuronectes americanus*) were less sensitive and showed a decrease in respiration activity when exposed to 10 ug Hg/L (as HgCl2) for 60 ·days (Calabrese et al., 1973).

Teratologic effects were reported for the embryo of mummichog (*Fundulus heteroclitus*) exposed to 50 ug Hg/L (as MeHgCl) for 7 days (Weis et al.,1981). The striped mullet (*Mugil cephalus*) was more sensitive to MeHgCl, which inhibited fin regeneration in fish exposed to 1.0 ug Hg/L for 13 days (Weis and Weis, 1978).

4.4 Interactions with Metals

Mercury in mixtures with other metals displays a different behaviour. Copper in a mixture, for instance, seems to protect against the toxicity of MeHg to the blue gourami, *Trichogaster trichopterus*, (Roales and Perlmutter, 1974). The addition of $ZnSO_4$ was noted to decrease the relative efficiency of MeHg uptake by rainbow trout, *Salmo gairdneri* (Rogers and Beamish, 1983). The action of $ZnSO_4$ was suggested to be the result of a competition between inorganic zinc and methylmercury for sites of uptake on the fish gills. Rogers and Beamish also noted that waterborne MeHg was more efficiently absorbed by the fish in the presence of inorganic $HgCl_2$.

In studying uptake of metals in rainbow trout (*Salmo gairdneri*) Ramamoorthy and Blumhagen (1984) obtained somewhat different results. It was shown that the rainbow trout accumulated more than double the amount of mercury in the presence of zinc and cadmium than when exposed to mercury alone. High levels of zinc and cadmium were also accumulated, suggesting the possible existence of multiple binding sites in fish.

In a rare example of synergistic action between mercury and selenium, Huckabee and Griffith (1974) found that the percentage of carp (*Cyprinus carpio*) eggs hatched when exposed to mercury and selenium combined, was lower than that hatched when exposed to the same concentrations of either mercury or selenium alone. In most studies, however, antagonistic effects of selenium on mercury toxicity were attributed to inverse relationships between selenium and mercury concentrations in fish (Rudd et al., 1980; Speyer, 1980; Turner and Rudd, 1983; Klaverkamp et al., 1983). Kim et al. (1977) found an increase in retention, but lower toxicity to fish, of each element in presence of the other.

Aquatic organisms adapt to heavy metal pollution by synthesis of metallothionein, a small thio-rich protein which has been found to bind several metals in a number of fish species (Bourquegneau, 1979). However, metallothionein was not recognized to be a significant factor in mercury tolerance in mummichog (*Fundulus heteroclitus*) adults, had a questionable role in embryonic and larval tolerance to Hg^{++}, and no role regarding the more toxic methylmercury (Weis and Weis, 1983; Weis, 1984).

4.5 Criteria from the Literature

4.5.1 *Criteria from Other Jurisdictions*

4.5.1.1 *Freshwater Aquatic Life*

Table 1 lists the most up-to-date mercury criteria for aquatic life from various jurisdictions. Alberta and Saskatchewan set maximum water quality guidelines for surface waters at 0.1 ug/L total mercury, to protect for the most sensitive use. Aquatic life was assumed to require the highest quality of water.

Inland waters Directorate (Environment Canada) recommended a water quality objective of 0.2 ug/L total mercury to protect aquatic life when fish are not eaten. A more stringent water quality objective of 0.1 ug/L total mercury was recommended (to try and meet 0.5 ug Hg/g wet wt. in fish) to protect consumers of fish. The IWD chose to express its criteria in terms of total mercury concentration. It was argued that many forms of mercury can be present in an aquatic environment, and one form of mercury alone cannot be used for recommending a limit.

The Australian criterion of 0.1 ug/L total mercury was -set to ensure the protection of aquatic ecosystems from toxic effects of mercury, and to ensure that species consumed by humans did not accumulate mercury to levels that might endanger human life.

Table 1. Mercury Criteria for Freshwater Aquatic Life

Criteria Statements	Criteria Values (ug Hg/L)	Jurisdiction	Date	Reference
Maximum concentration for total Hg in surface water,	0.1	Saskatchewan	1975	SSWQO (1975)
Maximum concentration for total Hg in surface water,	0.1	Alberta	1977	ASWQO (1977)
To protect aquatic life, total Hg in water should not exceed 0.2 ug/L; to prevent undesirable accumulation of Hg in fish (0.5 ug/g) for human consumption, Hg in water should not exceed 0.1 ug/L;	0.2	Inland Waters Directorate	1979	Reeder et al. (1979)
	0.1	(Environment Canada)		
Recommended criterion for protection of aquatic ecosystems,	0.1	Australia	1982	Hart (1982)
Maximum acceptable concentration to protect cool and cold water aquatic life,	0.00057	Manitoba	1983	MDEWSH (1983)
Concentration of total Hg in filtered water should not exceed,	0.2	Ontario	1984	OME (1984)
To protect freshwater aquatic organisms and their uses 4-d average concentration of total Hg should not exceed 0.012 ug/L, and 1-h average concentration should not exceed 2.4 ug/L,	0.012 (4-d av.)	U.S. EPA	1985	U.S. EPA (1985b)
	2.4 (1-h av.			
Concentration of total Hg in water should not exceed,	0.1	Canada	1987	CCREM (1987)

Ontario, on the other hand, determined that to protect aquatic life the concentration of total mercury in filtered water samples should not exceed 0.2 ug/L; also, to protect humans, the concentration of total mercury in a whole fish should not exceed 0.5 ug/g wet wt.

Manitoba adopted one of the strictest criteria for total mercury (0.00057 ug/L) in the aquatic environment fashioned after the U.S. EPA (1980). Since then, however, the U.S. EPA (1985b) has come up with new 1-h average (2.4 ug Hg/L) and 4-d average (0.012 ug Hg/L) criteria for freshwater aquatic life, which are much higher than the criterion recommended in 1980. The U.S. EPA (1985b) criteria were expressed in terms of total recoverable mercury in water with the recommendation that acid-soluble mercury be measured in the future rather than total mercury. The procedure for acid-soluble mercury measurement is being developed.

As compared to the other jurisdictions (except Manitoba for reasons given above), the recommended 4-d average criterion for mercury for freshwater (0.012 ug/L) aquatic life by U.S. EPA (1985b) was the lowest (Table 1). The U.S. EPA criterion was based on the action level of 1.0 ug/g wet wt. total mercury for fish/shellfish consumed by humans, and the bioconcentration factor of MeHg in freshwater fish of 81 700. The use of the bioconcentration factor associated with the MeHg uptake resulted in the low 4-d average criterion recommended by the U.S. EPA. MeHg in water is absorbed very efficiently by aquatic organisms, yielding a bioconcentration factor 10 to 20 times higher than that for inorganic Hg in water (U.S. EPA, 1985b). Most of the mercury discharged to the environment, however, is metallic, inorganic, or in forms other than MeHg.

CCREM (1987) recommended a criterion of 0.1 ug/L total mercury.

4.5.1.2 *Marine Aquatic Life*

U.S. EPA (1985b) was the only jurisdiction which recommended mercury criteria for marine aquatic life. To protect marine aquatic life from acute toxic effects of mercury, the maximum (1-h average)

concentration is 2.1 ug Hg/L. As in freshwater, the chronic (4-d average) criterion of 0.025 ug Hg/L for marine aquatic life was designed to protect consumers of fish and shellfish as outlined in section 4.6.1.1.

4.5.2 *Forms of Mercury for Criteria*

All forms of mercury are recognized to be toxic. However, mercury criteria for aquatic life have been expressed in terms of dissolved Hg, total Hg, total recoverable Hg, and acid-soluble Hg. The total Hg and total recoverable Hg include all forms of dissolved, particulate, and inorganically and organically bound Hg in unfiltered samples, depending upon the completeness of the digestion step. Acid-soluble Hg is operationally defined as the Hg that passes through a 0.45 um membrane filter after the sample is acidified to pH 1.5 to 2 with $HN0_3$. It measures in ambient water all forms of mercury that are toxic to aquatic life or can be converted to toxic forms under natural conditions, including complexed forms of mercury (such as the EDTA complex of Hg++) which have low toxicities to aquatic life. This measurement does not measure Hg that is non-toxic or is not likely to become toxic under natural conditions (e.g., Hg occluded in minerals, clays, and sands) or is strongly sorbed to particulate matter (U.S. EPA, 1985b).

Organic mercury (e.g., MeHg) is more toxic to aquatic life than inorganic mercury. Biological and abiological production of MeHg in the environment is evident from the literature see section 2.3). The lack of mercury criteria for aquatic life in terms of MeHg concentration in water may have been due to several factors: (i) MeHg concentrations in both water and sediment are very low (<1% of total mercury) (Moore and Rarnamoorthy, 1984; Thompson et al.,1980), (ii) although MeHg content may be on occasion up to 100% of the total mercury in freshwater, a large variability has been observed in the MeHg concentration with season and site (Jackson et al., 1982), and (iii) the methylated mercury produced in the environment is subject to (a) microbial degradation and demethylation, and (b) rapid uptake by aquatic organisms (e.g., fish) which have been shown to accumulate high levels of MeHg from waters containing very low concentrations of MeHg. A measurement of MeHg concentration in sediment and water is therefore expected to yield a measure of net methylation, or rate of MeHg synthesis, rather than a true concentration of MeHg in the environment (Moore and Ramamoorthy, 1984).

4.5.3 *Mercury Mixed with Other Metals*

Synergistic and antagonistic effects of mercury in a mixture with other metals (e.g., copper, zinc, selenium, cadmium, etc.) on aquatic life have been reported in the literature (section 4.4).

Because of inconsistent results and inadequate data in the literature, U.S. EPA (1985b) did not consider the influence of mixtures of metals in the development of their mercury criteria for aquatic life. It is generally agreed that, for most metal mixtures and other commonly occurring constituents of sewage and industrial wastes, an additive model is adequate to describe the joint effect of toxicants in the mixture.

The IJC (1981) has outlined an approach to deal with metals in the Great Lakes, using an additive model. The EIFAC (1980) and Alabaster and Lloyd (1982) agree with the concentration-addition concept for metal mixtures; however, they concluded that it was not necessary to adjust the criteria for a single metal downward when the concentrations of metals in the mixture were lower than the EIFAC- recommended values. Neither EIFAC nor Alabaster and Lloyd have recommended criteria for mercury at this time.

4.6 Recommended Criteria

4.6.1 *Freshwater Aquatic Life*

(a) The average concentration of total mercury in water over a 30-day period (based on 5 weekly samples) should not exceed 0.02 ug/L. This level will protect freshwater aquatic life from the chronic effects of mercury.

(b) To protect freshwater aquatic life from acute effects of mercury, the maximum concentration

of total mercury in water should not exceed 0.1 ug/L.

4.6.2 *Marine and Estuarine Aquatic Life*

(a) The average concentration of total mercury in water over a 30-day period (based on 5 weekly samples) should not exceed 0.02 ug/L. This level will protect marine and estuarine aquatic life from the chronic effects of mercury.

(b) To protect marine and estuarine aquatic life from acute effects of mercury, the maximum concentration of total mercury in water should not exceed 2.0 ug/L.

4.6.3 *Application of Criteria*

4.6.3.1 *Forms of Mercury*

Toxicity of mercury has been expressed in terms of both total and soluble forms of mercury. However, total mercury is recommended for setting water quality objectives for a given waterbody. The advantage of expressing toxicity on the basis of total mercury concentration are several fold: (i) all the mercury that may potentially be toxic is included in the measurement. If the total Hg concentration in water is within the criteria limits, then it is safe to conclude that no Hg pollution exists; (ii) for comparison purposes, there is a considerable amount of historical information available for total Hg; (iii) total Hg measurement is routine and relatively inexpensive. Mercury in aquatic organisms (e.g., fish) should also be measured when investigating Hg contamination problems.

The main disadvantage of using total Hg to assess water quality could be that a large fraction of Hg may become biologically unavailable by forming complexes with the organic and suspended solid fractions of water. Nevertheless, given favourable environmental conditions, mercury complexed *in* such a manner will be released into the environment in readily available forms, becoming part of the food chain.

4.6.3.2 *Assessment of Existing Water quality*

The criteria recommended in this document are primarily based on laboratory bioassays, which usually are performed using soluble forms of Hg under controlled conditions. Aquatic organisms in a natural environment, however, obtain their mercury burden from both water and food. Also, Hg associated with the sediment fraction could become available to the organisms under favourable environmental conditions. Irrespective of the source, biomagnification of Hg in an aquatic environment occurs, with maximum bioconcentration at the top of the food chain. Thus measurements of total Hg in water alone cannot confirm that a Hg problem exists in a waterbody, even if the measurement exceeds the criteria. Other assessment techniques include measurement of mercury in fish, and long-term bioassays with resident species using local water. Whereas mercury in fish may prove to be a very useful measurement in the assessment of existing water quality, alternative methods like long-term bioassays are complex and costly, and should be reserved for waterbodies with high fisheries values which are threatened by a controllable source.

4.7 Rationale

4.7.1 *Freshwater Aquatic Life*

(a) 30-day Average Concentration

The 30-d average criterion for total mercury in water, based on 5 weekly samples, was chosen to be 0.02 ug/L. Two approaches, independent of each other in assumptions, were used in justifying this choice.

A. The first approach used the following assumptions and information from the literature.

1. Most of the anthropogenic Hg discharged to the environment is inorganic mercury. However, MeHg constitutes most of the total Hg in fish.

2. The maximum safe intake of mercury for humans from fish ranges between 10 and 20 ug Hg/d (Table 2).

3. Fish is the main source of Hg in the diet of the 'meat, poultry, fish, and eggs' category of food groups for some Canadians. A daily consumption of 200 g of fish (70% of the national average rate of 285 g/d for 20-39 year old adults; Nutrition Canada, 1975) containing as little as 0.10 ug Hg/g wet wt. will provide mercury equal to the upper limit of the amounts recommended in assumption 2.

4. Both water (through gills) and food (through the digestive tract) contribute to fish Hg burden (Jernelov and Lann, 1971; Norstrom et al., 1976; Phillips and Gregory, 1979; Mathers and Johansen, 1985). Therefore, mercury residue in tissues will be higher in organisms exposed via both routes than via either route separately (Boudou et al., 1979; Akielaszek and Haines, 1981; Phillips and Buhler, 1978). Mercury released from bottom sediments due to biotic or abiotic methylation can also be taken up by the aquatic life (Jernelov, 1970; Weis et al., 1986).

5. Bioconcentration factors (BCF) for waterborne MeHg ranging from about 10 000 to 86 000, have been reported for various species of freshwater fish (Olson et al., 1975; Mckim et al., 1976; Boudou and Ribeyre, 1984; Niimi and Lowe-Jinde, 1984). Although MeHg is rapidly and more efficiently absorbed by aquatic species, its concentration in the environment is relatively low (< 1% of total Hg) and depends largely upon the environmental conditions (Moore and Ramamoorthy, 1984; Jackson et al.,1982; Riisgard et al., 1985). Also, inorganic mercury constitutes a larger proportion of the anthropogenic mercury discharged to the environment. A maximum BCF of ~5 000 obtained with the fathead minnow in water containing 0.26 ug Hg/L mercuric chloride (Snarski and Olson, 1982), was assumed in this document.

6. Based on the information and assumptions noted above, the 30-day average criterion was calculated as below:

(0.10 ug Hg/g(fish)] x [1/5 000] x [1 000 g(water)/1.0 L(water)] = 0.02 ug/L (Total Hg)

B. In studying effects of mercury in fish, Birge et al. (1979) found greater than 50% mortality in 6 days in the eggs and embryos of rainbow trout (Salmo gairdneri) exposed to inorganic Hg in water containing 0.1 ug Hg/L. Based on Birge's results, the minimum concentration of mercury which may cause acute toxic effects in aquatic life was chosen to be 0.10 ug/L. Although no specific value for rainbow trout was available from the literature, it has been shown that the acute-to-chronic ratio for various species of aquatic life exposed to inorganic Hg varied widely from 3.0 in mysid to> 650 in fathead minnow (U.S. EPA, 1985b). Obviously, the maximum concentration of mercury in water which may· result in chronic toxic effects in aquatic life will be 0.03 ug/L.

(b) Maximum Concentration

The maximum concentration permitted at any time was designed to protect aquatic life from short-term lethal (acute) effects of mercury in water. An examination of the data reviewed by the U.S. EPA (1985b) suggested that the U.S. EPA did not consider all of the data available from the literature in the derivation of their acute criterion (2.4 ug Hg/L). Whereas various reasons were given for rejecting data from several sources, no specific reason was stated for rejecting the Birge et al. (1979) results, which formed the basis for the maximum criteria in this document.

Birge et al. (1979) reported that, in a flow-through system, the median lethal concentrations (LC_{50}) were 0.3 and 0.7 ug Hg/L for the catfish (total exposure time= 10 days) and goldfish (total exposure time= 7 to 8 days) embryos, respectively. In these tests the fish were exposed to inorganic Hg immediately after spawning to 4 days after hatching. Also, measurable reductions in survival were observed for the catfish (23%) and goldfish (11%) embryos at hatching time (total exposure time 6 and 3 to 4 days, respectively), at concentrations ranging down to 0.19 to 0.23 ug Hg/L. Trout eggs, on the other hand, exhibited> 50% mortality after 6 days (total exposure time) at a concentration of 0.1 ug/L. In view of these additional data, the maximum concentration of total mercury in freshwater is recommended not to exceed 0.1 ug/L at any time.

The guideline of 0.1 ug/L total mercury recommended by CCREM (1987) to protect freshwater aquatic life and consumers of fish/shellfish, is the same as the maximum concentration recommended in this document, but much higher than the 30-day average concentration of 0.02 ug/L total mercury recommended in this report. The CCREM guideline was based on the Inland Waters Directorate (Reeder et al., 1979) guideline which was issued in the year Birge et al. (1979) published their results.

4.7.2 *Marine Aquatic Life*

(a) 30-day Average Concentration

The 30-day average criterion for marine aquatic life, based on 5 weekly samples, was also designed to protect consumers of seafood; as a result, the assumptions and considerations which led to the establishment of this criterion were the same as in section 4.7.1. The bioconcentration factors for inorganic Hg in marine and estuarine aquatic life were noted to be 129 for the American lobster and 10 000 for the eastern oyster, from the literature reviewed by the U.S. EPA (1985b). No bioconcentration factor (BCF) was given for marine fish species. As for freshwater species, a BCF of 5 000 was assumed for marine and estuarine aquatic life.

The 30-day average criterion for marine and estuarine aquatic life, based on 5 weekly samples, was therefore calculated to be 0.02 ug/L total mercury, as in the case of freshwater aquatic life.

(b) Maximum Concentration

To protect marine and estuarine aquatic life from the short-term lethal (acute) effects of mercury in water, the maximum concentration at any time should not exceed 2.0 ug/L total mercury. This is similar to the one-hour (acute) criterion recommended by the U.S. EPA (1985b).

4.7.3 *Forms of Mercury*

Although organic mercury compounds are more toxic to aquatic life than all inorganic compounds, all forms of mercury have been shown to affect aquatic life. Also, because Hg has a strong affinity for suspended matter, the concentrations of mercury in natural waters are generally low. However, even in waters containing very low levels of mercury <0.03 ug/L), aquatic organisms, especially those at the top of the food chain (e.g., fish), could accumulate undesirable levels (0.5 ug Hg/g wet wt.) of mercury in their tissues (MacCrimmon et al., 1983). Furthermore, in addition to the concentration of mercury in water, the uptake of mercury by fish is influenced by several biotic and abiotic factors (e.g., fish growth and metabolic rate, body size, concentration of Hg in fish diet, water temperature, alkalinity, pH, hardness, lake morphometric parameters, etc.) (Rogers and Beamish, 1981; Suns et al., 1980, Wren and MacCrimmon, 1983, MacLeod and Pessah, 1973; Scheider et al., 1979). It is, therefore, recommended that the total mercury concentration in both water and aquatic species at the top of the food chain or consumed by humans be measured in order to assess the impact of mercury on a water body.

4.7.4 *Mercury Mixed with Other Metals*

In view of the discussion presented in sections 4.4 and 4.6.5, no separate criterion for mercury mixed with other metals has been recommended here. It is believed that mercury in mixtures will behave like other heavy metals. At levels recommended in section 4.7, mercury should not contribute to the toxicity of a mixture of toxicants, especially at the average level.

Table 2. Mercury Uptake from Air, Water, And Food

STEP	COMMENT
1	Daily permissible intake of MeHg from food, air, and water without excessive Hg body-burden in humans is 30 ug/d, according to WHO (1976).
2	Assuming daily water consumption of 1.5 L by an adult, MeHg constituting 10% of total Hg, and the concentration of total Hg in drinking water maintained at the maximum allowable level of 1.0 ug/L, the maximum Hg body-burden from drinking water will be= 0.15 ug/d, as MeHg.
3	Assuming an air intake of 15 m^3 /d for an adult engaged in light physical activity and Hg concentration in air at the objective level of 1.0 ug/m^3 (B.C. Ministry of Environment, 1979), the maximum Hg body burden from air will be 15.0 ug/d or 3.0 ug MeHg/d (assuming MeHg is 20% of the total Hg in air; Johnson and Braman, 1974).
4	Maximum allowable intake of MeHg from food sources may range, therefore, from 22.5 − 3 − 0.15 = 19.35 ug/d to 30 - 3 − 0.15 = 26.85 ug/d.
5	Assuming an average total Hg content of 0.05 ug/g in all foods (except fish) (Somers, 1971), a daily national consumption of food (except meat, poultry, fish, and eggs) of 1552 g (for 20-39 year-old adults; Nutrition Canada, 1975), and MeHg content of foods (except fish) at 13% of the total Hg (Cappon, 1987), MeHg uptake from all foods, except fish, can be calculated at: 1552 g/d × 0.05 ug/g × 0.13 = 10.09 ug/d. Therefore, the maximum allowable MeHg intake from the 'meat, poultry, fish, and eggs' group of food will be 19.35 − 10.09 = 9.3 to 26.85 − 10.09 = 16.8 ug/d.

5. WILDLIFE

5.1 Effects

The intake of mercury in wild birds almost exclusively occurs via contaminated foods (Nriagu, 1979). Fish, aquatic insects, and seeds treated with mercury fungicides have been shown to contribute significantly to the mercury burden of wild birds, snakes, and furbearing mammals (Keith and Gruchy, 1971; Fimreite et al., 1971; Heinz et al., 1980; Sheffy and St. Amant, 1982; Kucera, 1983; Powell, 1983). The herbivorous mammals and the birds feeding on vegetation and terrestrial invertebrates, on the other hand, accumulate much lower levels of mercury in their body tissues (Fimreite, 1974; Ford and Prince, 1975; Sheffy and St. Amant, 1982; Powell, 1983).

Kirk (1971) reported that a diet containing 1 ug Hg/g (dry wt.) proved fatal to domestic mink in two months. Juvenile starlings, *Sturnus vulgaris*, fed a diet containing 1.1 ug Hg/g (dry wt.) accumulated 21.6 to 65.2 ug Hg/g (dry wt.), sufficient to cause kidney lesions within 8 weeks (Nicholson and Osborn, 1984). Studies with black and mallard ducks fed foods contaminated with methylmercuric dicyandiamide over two to three generations, demonstrated reduced hatching success and juvenile survival. The concentrations in the natural succulent foods of the black and mallard ducks were estimated to be

equivalent to 0.5 and 0.1 ug Hg/g wet wt. (as MeHg), respectively (Finley and Standell, 1978; Heinz, 1979). Delayed testicular development was noted in young quail exposed to 2 ug Hg/g (dry wt.) in their diet (Hill and Soares, 1984). In a comprehensive field study, Barr (1986) suggested a strong negative relationship between the successful use of territories by breeding loons (*Gavia immer*) and the degree of environmental pollution; egg laying and territorial fidelity were impaired at Hg concentrations of 0.3 to 0.4 ug/g wet wt. in prey.

In studying levels and interactions of metals in sea birds· from Svalbard (in the Arctic circle, Norway) and the Antarctic, the highest concentration (7.5 ug/g wet wt.) was observed in brown skua, *Catharacta lonnbergi*, from Bouvetoya in South Atlantic (Norheim, 1987). This concentration was considered to be well below the level (20 ug/g wet weight) considered to be lethal by Froslie et al. (1986), based on Oehrne's (1981) observations. Upon analyzing for mercury levels in white-tailed eagles found dead in the northern district of East Germany, Oehme (1981) had reported a geometric mean of 0.8 ug/g wet wt. in the liver of specimens collected in 1967-76. Helander et al. (1982) concluded that a mercury concentration in eggs up to 1.0 ug/g wet wt. is not likely to cause reproductive failure in the white-tailed eagle.

Methylated mercury appears to be more toxic than inorganic mercury (Scott et al., 1975). MeHg has also been shown to be teratogenic in birds; as little as 0.5 ug Hg within fertile mallard eggs increased the incidence of malformations, while 4 ug resulted in increased embryonic mortality (Hoffman and Moore, 1979). The safe level of MeHg in the diet of birds was assumed to be close to 0.5 ug Hg/g (wet wt.) (Reeder et al., 1979; IJC, 1976), although the results cited above indicated significant effects at 0.1 to 0.5 ug Hg/g (wet wt.).

No direct evidence of mercury toxicity from drinking water to terrestrial species of wildlife such as ungulates and carnivores has been found in the literature. However, the toxicity to domestic birds exposed to mercury in drinking water alone, at concentrations of 250 mg/L, has been demonstrated (Parkhurst and Thaxton, 1973; Grissom and Thaxton, 1985).

5.2 Criteria from the Literature

To protect fish-consuming animals, the Inland Waters Directorate (Reeder et al., 1979) recommendedthat total mercury in fish should not exceed 0.5 ug/g on a wet wt. basis. However, in drinking water of terrestrial wildlife, such as ungulates and carnivores, they recommended a maximum concentration of 3 ug/L total mercury. CCREM (1987) did not recommend guidelines for wildlife, although it did recommend a guideline of 3 ug/L total mercury for livestock watering.

5.3 Recommended Criteria

Due to the lack of sufficient relevant information in the literature, specific water quality criteria to protect wildlife from the harmful effects of mercury in drinking water were not developed.

Instead, the criterion to protect wildlife from harmful effects of mercury in water was adopted from that specified for livestock watering in section 6.3.

The maximum concentration of total mercury in water for wildlife use should not exceed 3 ug/L.

5.4 Rationale

The use of livestock criteria for wildlife in waters devoid of sensitive or desirable aquatic life is based on the assumption that, in all likelihood, the safe concentration for mercury for both groups of animals is similar in magnitude. See section 6.4 for the rationale for the 3 ug Hg/L criterion for wildlife. Note that 3 ug/L mercury in water could lead to> 0.1 ug Hg/g wet wt. in aquatic organisms in that water. The

concentration of total mercury in fish/shellfish and other aquatic species to protect their wildlife consumers was based on observations of Finley and Standell (1978), and Heinz (1979) (see section 5.1).

For waters inhabited by aquatic life, the criteria recommended to protect relatively sensitive aquatic life appear more than adequate to protect wildlife.

The CCREM (1987) did not recommend criteria for wildlife; however, the livestock criterion that we chose to recommend for wildlife is the same as the CCREM (1987) guideline for livestock watering.

6. LIVESTOCK WATER SUPPLY

6.1 Effects

The toxicity of mercury to livestock depends upon its chemical form. As in humans, organic mercurials, especially methylmercury, are the most toxic compounds of mercury (Neathery and Miller, 1975). Characteristics such as (i) the ability to cross cell membranes barriers, and (ii) high sorption combined with low elimination rate from body tissues, contribute to the high toxicity of organic mercurials. For instance, Sell and Davison (1975) found that only 14% of mercuric chloride administered via gastrointestinal tracts was absorbed by lactating cows and goats, whereas the sorption of methylmercury was around 70%. Also, the estimated half-life for methylmercury in humans and animals is much higher than that for inorganic ($HgCl_2$) mercury (Neathery and Miller, 1975). Scott et al. (1975) found that inorganic mercury ($HgSO_4$ or $HgCl_2$) fed to Japanese quail and chickens at a dietary level up to 200 ug/g (dry wt.) had little effect on egg production, hatchability, egg shell strength, morbidity, and mortality, whereas methylmercury chloride at 10 or 20 ug Hg/g diet (dry wt.) severely affected all these parameters.

Parkhurst and Thaxton (1973) showed that the addition of mercury to the drinking water of newly hatched chicks at 250 mg/L resulted in a general toxicity (reduced weight gains, reduced feed and water consumption, increased mortality, etc.). Grissom (1982) suggested that reduced feed and water consumption could contribute to the other toxicity symptoms noted in the Parkhust and Thaxton study. Grissom and Thaxton (1984, 1985) showed that ingestion of mercury from drinking water and water deprivation in chickens were interrelated, thus suggesting that the toxicity that has been attributed solely to the metal, could actually be a result of an interaction of the effects of the metal per se and a dehydration-nutrition inadequacy.

The distribution and accumulation of mercury in tissue depends upon the chemical form of mercury, route of entry, dosage, and the animal species. In farm animals, the highest concentration of mercury is associated with kidneys, with the possible exception of chickens in which liver and kidney may have similar concentrations (Neathery and Miller, 1975; Palmer et al., 1973; March et al., 1974; Al-Fayadh et al., 1976). Although the normal mercury concentrations in tissues of farm animals are low (<0.01 to 0.3 ug/g wet weight), the concentration of Hg in the tissues could exceed the recommended concentration of 0.5 ug/g wet weight in foods for human consumption (Health and Welfare Canada, 1971) without being harmful to animals (Puls, 1981). Boyd (1985) noted that 3 of 17 hereford cattle fed phenyl mercuric acetate-treated seed barley, at the rate of 275 ug Hg/kg body weight/d, died. The results of the tissue analysis on affected animals revealed that the mercury concentrations in livers and kidneys were 3.5 to 11.7 ug/g (wet wt.) and 43.5 to 55.7 ug/g (wet wt.), respectively.

Dietary selenium counteracts the toxicity of both inorganic and organic mercury compounds to animals (Froseth et al., 1974). The protective effect of selenium towards methylmercury intoxication was found in rats (Ohi et al., 1976; Hill, 1975), chicks (Hill, 1973), swine and pigs (Froseth et al., 1974), and Japanese quail (Ganther et al., 1972).

6.2 Criteria from the Literature

The livestock drinking water quality criteria for mercury from various jurisdictions are shown in Table 3.

The provinces of Alberta and Saskatchewan recommended the lowest levels at 0.1 ug/L total mercury. These jurisdictions, however, did not establish water use categories while setting water quality criteria for surface waters. It is probable that the 0.1 ug Hg/L criterion is for a more sensitive water use (e.g., aquatic life - see section 4, Table 1) than livestock watering.

Table 3. Mercury Criteria for Livestock Water Supply

Criteria Statements	Criteria Values (ug Hg/L)	Jurisdiction	Date	Reference
Recommended upper limit of Hg in water for live-stock,	10.0	U.S. EPA	1973	U.S. EPA (1973)
Maximum concentration of total Hg in surface water,	0.1	Saskatchewan	1975	SSWQO (1975)
Maximum concentration of total Hg in surface water,	0.1	Alberta	1977	ASWQO (1977)
Concentration of total Hg in livestock water supply should not exceed,	3. 0	Canada	1979	Reeder et al. (1979)
95 and 99 percentile, respectively, for Hg in livestock water are,	2.0 and 3. 0	England	1983	AWA (1983)
Maximum acceptable concentration of total Hg in livestock water supply,	3. 0	Manitoba	1983	MDEWSH (1983)
Water quality criteria for livestock watering,	10.0	Ontario	1984	OME (1984)
Concentration of Hg in livestock drinking water,	3.0	Canada	1987	CCREM (1987)

The water quality criterion for total mercury of 3.0 ug/L (maximum) recommended by Canada (CCREM, 1987) and the province of Manitoba, was adopted from the Inland Waters Directorate (Reeder et al., 1979). A similar criterion, at the 99th percentile, was recommended by the Anglian Water Authority (1983).

Among all jurisdictions, the criterion of 10 ug/L for total mercury in livestock drinking water supply proposed by the U.S. Environmental Protection Agency (1973) and the province of Ontario (OME, 1984), was the highest.

6.3 Recommended Criterion

It is recommended that the concentration of total mercury in livestock water supply should not exceed 3.0 ug/L.

This is the same as that proposed by the Canadian Council of Resource and Environment Ministers (1987).

6.4 Rationale

The concentration of total mercury in cattle, pigs, poultry, and sheep tissues (e.g., kidney, liver, and muscle) ranges from 1.0 to 146 ug/g wet weight, without being toxic to the animals (Puls, 1981). These concentrations are much higher than the maximum concentration of 0.5 ug Hg/g wet weight in edible portions of food recommended for human consumption (Health and Welfare Canada, 1971). Thus, the criterion for mercury in livestock water supply was based on its accumulation in animal tissues rather than on its toxicity to livestock. The accumulation of mercury in poultry was chosen to derive the criterion for

the livestock water supply, since poultry appeared to be one of the most, if not the most, sensitive species of livestock to mercury effects (Puls, 1981).

In chickens, daily administration of 1.0 ug Hg/kg body weight (as fish meal mixed with feed) for one year resulted in a mercury concentration in the kidney of 0.2 to 0.4 ug/g wet weight (March et al., 1974). Assuming an average mercury content of feed of 0.03 ug/g dry matter and a daily requirement for feed of 0.07 g/g body weight/d (Agriculture Canada, 1978), chickens will ingest 2.1 ug Hg/kg body weight/d from feed (Note that the assumed concentration of mercury in chicken feed (grain) is more than the concentration in barley, wheat, and oat grains grown in soil containing 0.023 ug Hg/g, and less than the concentration in the fruits of *C. sparsiflorus* and *A. maxicana* grown in soil containing 10 ug Hg/g; the critical concentration of mercury in soils was set at 1.0 ug/g - see section 7.4 and Table 5). Given that (i) methylmercury is the most toxic form of mercury and 100% of methylmercury ingested from feed is absorbed in animal tissues, (ii) methylmercury constitutes about 15% of total mercury in feed (Cappon, 1987), and (iii) 10% of inorganic and other (than methylmercury) organic forms of mercury in the feed are absorbed in animal tissues, the total intake of mercury actually absorbed by chickens from feed could be estimated at:

$$[2.1 \text{ ug Hg/kg b.w./d} \times 0.15 \times 1.0] + [2.1 \text{ ug Hg/kg b.w./d} \times (1-0.15) \times 0.1) = 0.49 \text{ ug Hg/kg b.w./d}$$

Thus, based on a maximum allowable intake of 1.0 ug Hg/kg b.w./d from food sources, the maximum mercury intake by chickens from water supply is limited to 1.0 − 0.49 = 0.51 ug/kg b.w./d. Assuming an average daily water requirement of 0.13 L/kg b.w. (Agriculture Canada, 1978), a livestock water supply containing 3 ug Hg/L would contribute about 0.4 ug Hg/kg b.w./d to chickens. The contribution of air to total mercury intake by chickens was considered to be small.

It is, therefore, recommended that the concentration of total mercury in livestock water supply should not exceed 3.0 ug/l at any time. Since the proportion of methylmercury in water is naturally- low, holding the maximum concentration of mercury at 3.0 ug/L in livestock water supply will provide added protection against accumulation of mercury in the livestock tissue to undesirable levels.

The maximum daily intake of 1.0 ug Hg/kg b.w. above was based on chickens fed fish meal mixed with feed. Considering that (a) most of the mercury in the fish portion of the feed was MeHg, and (b) MeHg is absorbed efficiently in the body tissue of the animals, it could be assumed that the accumulation of mercury in kidney (0.2 to 0.4 ug/g wet wt.) of the birds was more than in the birds fed grain only. The feed consisting of grain only would, therefore, provide further protection against undesirable accumulation of mercury in the livestock tissue.

The Inland Waters Directorate (Reeder et al., 1979) used two different approaches and came up with the same criterion for the livestock water supply as above. The starting point (i.e., the maximum recommended intake by chickens of 1.0 ug/kg b.w./d) was**,** however, the same as above. In the first approach it was assumed that (a) 25% of the mercury intake by the birds came from the water supply, and (b) the daily water intake of a bird was ~8% of its body weight. In comparison, our calculations above assumed daily intake of water by the birds at 13% of the body weight while indicating that ~40% of the birds' mercury burden may come from the water supply.

The second approach by Reeder at al. was based on the formula provided by Kitamura et al. (1976). In addition to assumptions (a) and (b) above, it was assumed that (c) the biological half-life of MeHg in chickens was 70-d and (d) the ratio of the mercury levels in kidney/whole body was 4. CCREM (1987) used the same basic data and the second approach to justify its criteria.

For waters inhabited by aquatic life, the criteria recommended to protect relatively more sensitive aquatic life would appear more than adequate to protect livestock, especially in situations where methylmercury may be up to 100% of the total mercury during certain periods of the year (Jackson et al., 1982).

7. IRRIGATION

7.1 Effects

7.1.1 *Plant Uptake and Accumulation*

Mercury and its compounds are absorbed by plants mainly through the roots. There is a general tendency for mercury to accumulate in the root with limited translocation from soil to aerial parts of the plant (Hogg et al., 1978a,b; Gracey and Stewart, 1974a,b; Beauford et al., 1977; Fang, 1978). There are exceptions, however.

Table 5 shows the mercury content of plants grown in Hg-treated soils. Soils treated with 10 ug Hg/g, as methylmercury dicyndiamide, caused high concentrations of mercury in stems and leaves of potatoes (1.045 ug/g fresh weight) and tomatoes (0.341 ug/g fresh weight) and in edible portions of carrots (0.279 ug/g fresh weight), potatoes (0.327 ug/g fresh weight, and onions (1.044 ug/g fresh weight) (Bache et al., 1973). Mushrooms (*Agaricus edulis*) grown on soils containing 0.3 ug Hg/g registered mercury concentrations in the carpophores of 4 to 10 ug/g dry weight (Stijve and Besson, 1976). Siegel et al. (1987) noted that specific local environmental factors strongly influence the accumulation of mercury even when the soil concentrations are the same.

In studying the distribution of mercury in the tissues of plants collected around a chlor-alkali plant, Shaw and Panigrahi (1986) noted a significant correlation between the concentration in the soil and the plant tissues, especially when the concentration of mercury in the soil was low or limiting. Accumulation in leaves was the highest followed by the stem and the root, and in some cases, the root and the stem. The concentration of mercury in soils and in the leaves of *Croton sparsiflorus*, *Jatropha gossypifolia*, and *Argemone mexicana* grown in these soils, ranged from 2.13 to 660 ug/g dry wt. and 0.51 to 7.7 ug/g fresh wt., respectively. Shaw and Panigrahi also found that sheep and· goats grazing on these plants accumulated very high levels of mercury in their liver (46.3 and 51.5 ug/g wet wt., respectively) and muscle (2.91 and 2.86 ug/g wet wt., respectively).

Beyer et al. (1985) found that adding methylmercury to soil at 1.3 ug Hg/g wet wt. resulted in a mercury concentration of 27 ug/9 wet wt. in earthworms (*Eisenia foetida*). No mercury toxicity to *E. foetida* was found at this soil concentration; however, predators feeding on earthworms containing such high levels of mercury may be harmed. As little as 0.1 ug Hg/gin feed (wet wt.) has been shown to interfere with reproduction of mallard ducks (Heinz, 1979).

Table 4. Mercury Content of Plants in Hg-Treated or Contaminated Soils

Soil/Crop	Crop Part	Mercury Content (ug/g dry weight)*		References
		Range	Mean	
Soil		0.012 - 0.060	0.023	Gracey and Stewart (1984b)
Alfalfa	Foliage	0.015 - 0.057	0.039	
Barley	Straw	0.067 - 0.089	0.080	
	Grain	0.005 - 0.017	0.012	
Wheat	Straw	0.027 - 0.047	0.036	
	Grain	0.007 - 0.015	0.011	
Oats	Straw	0.027 - 0.042	0.033	
	Grain	0.004 - 0.019	0.009	
Flax	Straw	0.009 - 0.033	0.019	
	Seed	not detected		
Rape	Straw		0.024	
	Seed	not detected		
Rutabagas	Tops		0.051	
	Tubers		0.040	
Soil		(as $HgCl_2$)	10.0	Bache et al. (1973)
Potatoes	Stems, leaves		1.045	
	Edible parts		0.130	
Tomatoes	Stems, leaves		0.231	
	Edible parts		0.013	
Onions	Edible parts		1.087	
Soil			0.3	Stijve & Besson (1976)
Mushrooms (*A. edulis*)	Carpophores	4.00 - 10		
Soil		2.13 - 660		Shaw and Panigrahi (1986)
C. sparsiflorus	Leaves	2.32 - 27.9		
	Stems	2.93 - 10.43		
	Fruit	0.39 - 3.52		
Soil		3.87 - 5.20		
A. maxicana	Leaves	3.44 - 4.27		
	Stems	3.02 - 3.82		
	Fruit	2.77 - 3.82		
Soil		9.20 - 503.33		
J. gossypifolia	Leaves	2.32 - 18.25		
	Stems	1.38 - 16.33		
Soil		0.184 - 0.326		Cappon (1981)
Cabbage	Edible parts		0.014	
Lettuce	Head		0.033	
Lettuce	Leaf		0.041	
Soil			0.423	Cappon (1987)
Lettuce	Head		0.139	
Lettuce	Leaf		0.074	
Spinach	Edible parts		0.073	
S. chard	Edible parts		0.064	
Broccoli	Cole		0.050	
Cabbage	Cole		0.064	
Tomato	Fruit		0.024	

* Mercury concentrations in plant parts by Bache et al., are on fresh weight basis

The availability and stability of mercury and mercurial compounds in a soil-plant-water system are functions of pH, texture including clay type, organic matter content, soil moisture content, oxidation-reduction potential, and the form of mercury (Adriano, 1986). High pH, clay content, and organic matter content favour sorption of mercury by soils however, organic matter is the most effective sorbent for mercury in acid (pH <4) soils, whereas iron oxides and clay minerals could become more effective sorbents at higher pH (>5.5) (Andersson, 1979). Hogg et al. (1978a, b) noted that adsorption of methylmercury chloride (MeHgCl), phenylmercuric acetate (PMA), and mercuric chloride ($HgCl_2$) by soils increased iri the order MeHgCl < PMA < $HgCl_2$; as a result, mercury levels in bromegrass foliage were significantly higher from the MeHgCl-treated soil than from either the PMA- or $HgCl_2$- treated soils. Rogers (1976) found that methylation of mercury in soils was directly proportional to the clay content, moisture content, temperature, and mercury concentration.

7.1.2 *Phytotoxicity of Mercury*

The concentration of mercury in the soil-plant-water system and its toxicity to plants is summarized in Table 5.

Table 5. Toxicity of Mercury to Plants

Crop	Form and Concentration of Mercury*		Observed Effect	Reference
Onions	Metallic Hg	100 ug/g (soil)	No effect on plant emergence	Booer (1951)
Carrots & Lettuce	Compounds of mercury	50 ug/g (soil)	Severe pre-emergence losses	Booer (1951)
Dwarf beans	Phenyl mercuric acetate	110 ug/L (nutrient solution)	50% reduction in seedling biomass	Pickard & Martin (1959)
Velvet bentgrass	Organic Hg fungicide originated	450 ug/g (soil)	No effect	Estes et al. (1973)
Pisum sativum & *Mentha spicata*	Mercuric chloride	5 000 ug/L (nutrient solution)	Affected growth, physiological, & biochemical processes	Beauford et al. (1977)
Barley	Mercuric chloride	3.0 ug/g(plant tissue) and 4 000 ug/L (nutrient soln.)	Yellowing of leaves and presence of reddish stems (Critical level)	Davis et al. (1978)
Rice	?	0. 5 ug/g (stems and leaves) & 1 000 ug/g (roots)	Critical level	Chino (1981)
Lucerne, Raska, & Okra	Mercuric chloride	10.0 ug/L (nutrient solution)	Reduced yield and chlorophyll contents	Mhatre & Chaphekar (1984)

*concentrations in soil and plant tissues are on dry weight basis

Metallic mercury and compounds of mercury in soils have been reported to retard plant growth (Booer, 1951). Concentrations causing severe pre-emergence losses in sensitive species like lettuce and carrots (Booer, 1951), and reduced growth in bermudagrass (Weaver et al., 1984) have been reported at 50 ug Hg/g in soil.

In sand culture experiments, Davis et al. (1978) found that the critical level of mercury in the dry matter tissue of barley was 3 ug/g dry wt., whereas the critical concentration of mercury in solution was 4 000 ug/L. For the rice plant, Chino (1981) reported the critical concentration of mercury was 0.5 ug/g (dry wt.) in stems and leaves, and 1 000 ug/g (dry wt.) in roots.

In solution culture, Beauford et al. (1977) found that 5 000 ug/L of mercury as HgCl2, inhibited growth of higher plants (*Pisum sativum* and *Mentha spicata*) and affected both physiological and biological processes in the plants. More recently, young plants of *Pennisetum typhoideum* (a cereal crop), *Medicago sativa* (a forage crop), and *Abelmoschus esculenuts* (a vegetable crop) exhibited mercury toxicity at 10 ug Hg/L, as $HgCl_2$, in a nutrient culture (Mhatre and Chaphekar, 1984).

7.2 Criteria from the Literature

The Anglian water Authority (1983) recommended 95th and 99th percentiles of 1.3 and 2.0 ug/L, respectively for mercury in water used for spray irrigation of field crops. Criteria for mercury in irrigation water from other jurisdictions, including Canada and the United States of America, were not found in the literature.

7.3 Recommended Criterion

It is recommended that the maximum concentration of total mercury in irrigation water should not exceed 2.0 ug/L.

7.4 Rationale

Two factors were considered in establishing the criterion for mercury in irrigation water: (i) toxicity of mercury to crops, and (ii) accumulation of mercury in edible portions of the plant used for human and animal consumption. The data relating mercury toxicity to plants to the mercury concentration in soil, plants, and water are limited both in number and/or field tests. Also, perceptions of mercury toxicity based on laboratory tests are not in accord with the results of field data, where far higher levels of Hg-tolerance are reported (Siegel et al., 1987).

Based on the daily intake of mercury from ambient air and dust, ingestion of fish and other foods, and ingestion of soil, the allowable concentration of mercury in soil was calculated to be 12 ug/g dry wt. (Bashor and Turri, 1986). However, at 10 ug/g mercury in soil (dry wt.), certain vegetable crops (e.g., onions in Table 4) accumulate mercury up to twice the maximum allowable concentration of 0.5 ug/g wet wt. in food (e.g., fish) for human consumption (Health and Welfare Canada, 1971) or ten times the value (0.1 ug Hg/g wet wt. in fish) recommended for humans consuming large quantities of fish in their diet. Therefore, it is desirable that the concentration of mercury in vegetables and cereals be much lower than O .1 ug/g wet wt. A mercury content of 0.03 ug/g dry feed (grain) was used to derive the criterion for the livestock water supply (see section 6.4). The question, however, is what would be the corresponding concentration of mercury in soil? Recently, Beyer et al. (1985) found that soil containing about 2.0 ug/g dry wt. results in undesirable levels of mercury in earthworms (27 ug/g wet wt.) which could cause harmful effects to wildlife and other predators. Gracey and Stewart (1974b) observed that oats grown in soil containing 0.012 to 0.06 ug Hg/g (with a mean value of 0.023 ug Hg/g dry wt.) accumulated 0.004 to 0.019 ug Hg/g (dry wt.) in their grains (Table 4). Obviously, in order for plants and other organisms (e.g., earthworms) to not accumulate undesirable levels of mercury in their tissues, a concentration between 0.023 and 2.0 ug Hg/g (dry wt.) in soil is desirable.

The maximum allowable concentration of total mercury in soils was set at 1.0 ug/g dry wt. This concentration of mercury is higher than the average concentration of mercury in uncontaminated Canadian soils of about 0.08 ug/g (McKeague and Kloosterrnan, 1974),

0.023 ug/g (Gracey and Stewart, 1974b), and 0.44 ug/g (Moore, 1977), but much lower than those in the contaminated (Griffin, 1976; FMC Chemicals, 1971; Frank et al., 1976) and mineralised areas (John et al., 1975). Assuming that: (i) the maximum irrigation rate is 1.0 rn /rn 2/y, (ii) the bulk density of cultivated soil is 1 500 kg/m3, and (iii) the mercury in irrigation water is absorbed within 0.15 rn of the soil surface,

it will take over 100 years for a cultivated soil to accumulate 1.0 ug Hg/g dry wt. from irrigation water containing 2.0 ug Hg/L, as shown below:

Annual accumulation of Hg = 2.0 ug Hg/L x 1m3/m2/y × 1 000 L/m3 × (1/1 500 kg soil/m3) × (1/0.15 m soil) ×1 kg/1 000 g

= 0.0089 ug Hg/g soil.

Time period to accumulate 1.0 ug Hg/g = 1/0.0089 = 112.3 years.

These calculations assume that there would be no loss of mercury from the soil by crop uptake and removal, and volatilization (the dominant pathway in loss of mercury from soils- section 2.3), and thus is a very conservative estimate of the time needed to reach a soil level of 1.0 ug Hg/g dry wt.

It is, therefore, recommended that the concentration of total mercury in irrigation water should not exceed 2.0 ug/L.

8. RESEARCH AND DEVELOPMENT NEEDS

Several research needs were identified during preparation of this document. These are:

1. Prenatally exposed children are more susceptible to MeHg intake by mothers. However, data regarding mercury effects in prenatally exposed children at various stages of their reproductive years are scant.
2. Methylation of inorganic mercury has been shown to occur in the environment; however, concentration of methylmercury in aquatic environments has been found to be low and variable. Since methylated mercury is by far the most toxic form of mercury, further information regarding its role in bioconcentrating mercury in aquatic species in in-situ environments is required.
3. Although anthropogenic mercury discharged to the environment is mostly of inorganic and organic (other than MeHg) nature, it is the MeHg form which predominates in aquatic species. Why MeHg predominates in aquatic species is not clear from the literature and should be investigated.
4. Whereas pH, hardness of water, temperature etc. may affect mercury uptake and toxicity to aquatic organisms, the data demonstrating effects of such water quality parameters on aquatic life are too scant to account for their contribution in the mercury toxicity equation.
5. Sediment-bound mercury has been shown to contribute to the mercury burden of aquatic species. More information is, however, needed to set criteria to protect aquatic life from mercury in sediments.
6. Minimum daily intakes of mercury causing harmful effects in wildlife (e.g., ungulates) and livestock have not been well defined in the literature. Investigations with low doses of mercury are needed to define the minimum dose causing clinical and sub-clinical toxicosis in wildlife and livestock.
7. The uptake of mercury from treated soil and the presence of MeHg in the edible tissue of agronomic crops have been demonstrated in small scale studies. Since agronomic foods constitute a major proportion of the human diet, large-scale studies on a variety of crops, soil, and environmental conditions are desirable to evaluate the full impact of mercury in plant tissue on human health.

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