AN ABSTRACT OF THE THESIS OF

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Lawrence R. Curtis

Two Oregon reservoirs contaminated by different mercury sources were compared for mercury distribution in sediment and bioaccumulation by fish. The average mercury concentration in the sediment of Cottage Grove reservoir (0.67 ± 0.05 µg/g dry wt) was higher than for Dorena Reservoir (0.12 ± 0.01 µg/g dry wt). Sediment mercury in the main tributary of Cottage Grove Reservoir, which drains the tailing of past mercury mining activities, was ten fold higher than mercury in sediment from other reservoir tributaries with no evidence of mining. However, there were no significant differences between sediment mercury concentrations in the tributaries of the Dorena Reservoir, which has no mercury mining history within its watershed. Three fish species (largemouth bass, bluegill, crappie) from Cottage Grove Reservoir had significantly higher levels of mercury than the same species from Dorena Reservoir. These results indicated that a point source, Black Butte Mine,

contributed amounts of mercury in excess of natural deposits based on differences in bioaccumulation among fish populations from these two systems.

Cottage Grove Reservoir was examined for environmental evidence of point source mercury pollution. High mercury concentrations were found at various points around the suspected source, the Black Butte Mine area. The highest concentration occurred close to the kiln. The mercury concentration in the sediments of a creek below the mine dump was up to ten times higher than that of the sediments of a creek from a watershed adjacent to the watershed of the mine area. Two sediment cores from the deep area were collected to assess for pollution history profiles. These showed mercury loading in Cottage Grove Reservoir was consistent with the past mercury production in Black Butte Mine. Therefore most of mercury in Cottage Grove Reservoir was believed to be of Black Butte Mine origin. Mercury contents in pore water and food web indicated that continuing mercury transportation from the point source create a management problem in Cottage Grove Reservoir.

Point and Nonpoint Source Mercury Pollution of Oregon Reservoirs

by

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APPROVED:

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Major Professor, representing Toxicology

Redacted for Privacy

Chairman of Toxicology Program

Redacted for Privacy

Dean of Graduate School

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POINT AND NONPOINT SOURCE MERCURY POLLUTION OF OREGON RESERVOIRS

I. Introduction

SOURCES OF MERCURY IN THE ENVIRONMENT

Mercury (Hg) is a ubiquitous metal, occurring in different concentrations in the soils, rocks, air and water through-out the world. But attention has recently focused on regions having dilute, relatively unproductive waters (Hakanson et al., 1990). Elevated concentrations of mercury in surface water can be derived from many sources, including natural processes and anthropogenic releases. Natural processes include volcanic and atmospheric deposition, degassing, surface runoff, and erosion of mercuric soil. Anthropogenic sources include mercury mining and processing of gold and silver ores, smelting incineration, energy related activities, pesticide application, and chlor-alkali operation (Nriagu, 1979)

A major use of mercury is as a cathode in the electrolysis of sodium chloride solution to produce caustic soda and chlorine gas. Mercury is widely used in the electrical industry (discharge lamps, rectifiers, mercury battery cell, and switches) and in other laboratory and

medical instruments (thermostats, barometers, manometers, diffusion lamps, air pumps, mercury jet electrode, and western standard cells) (US WHO, 1990). The quantity of mercury used for the recovery of gold and silver has dwindled into insignificance. But it is still used for mercury amalgams in dental fillings. Considerable quantities of organomercurial compounds are used as bactericide and fungicide products in the paint industry and agricultural application to control fungal infections of seeds, bulb plants, and vegetation (US WHO, 1990).

ENVIRONMENTAL TRANSPORT AND DISTRIBUTION

Mercury exists in the natural environment in three oxidation states: as the native element, in the +1 (mercurous) state, and in the +2 (mercuric) state (Fig. I-1). The nature of the species which occur in a given assemblage, or predominate in solution, depends upon the redox potential, temperature, and pH of the environment (US EPA, 1979a).

During the last decade a new pattern has emerged with regard to mercury pollution, particularly in North America and the Nordic countries (Iverfeldt, 1991; Lindqvist, 1991)). Fish, mainly from nutrient-poor lakes, have often been found to contain high concentrations of mercury. Elevated

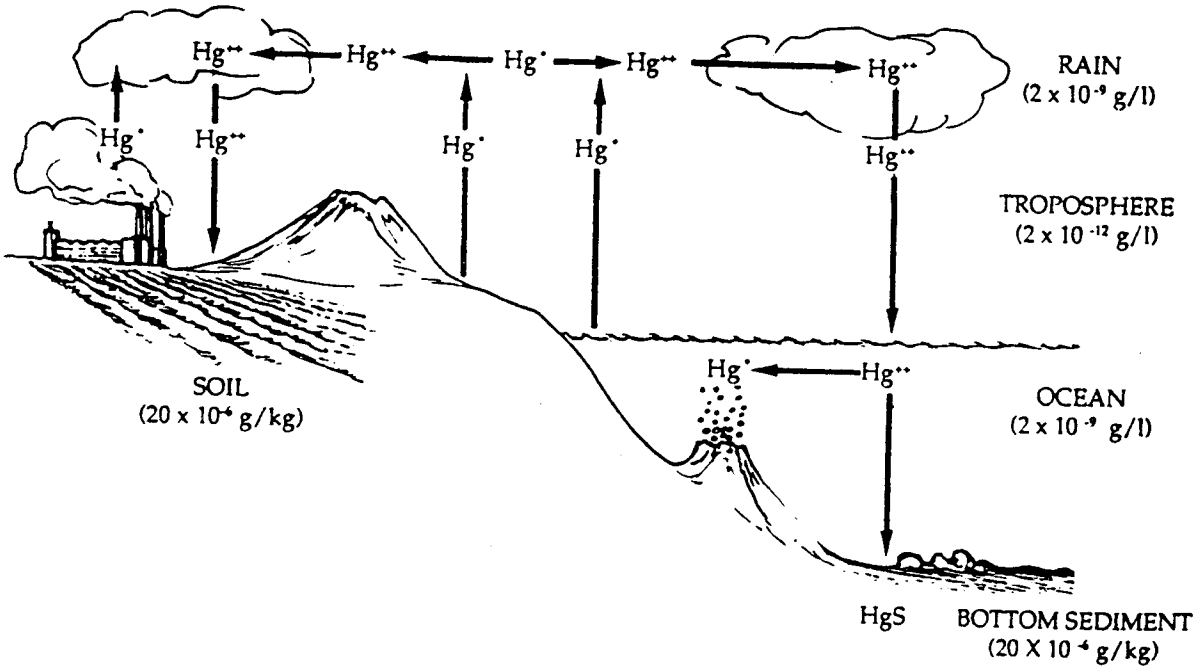

Fig. I-1. The global cycle of mercury

concentrations have also been found in marine fish. Contamination cannot be linked to point source emissions of elemental mercury, but appear due to more widespread air pollution.

Two cycles may be involved in the environmental transport and distribution of mercury. One is global in scope and involves the atmospheric circulation of elemental mercury vapor from sources on land to the ocean. The other cycle is local in scope and depends upon the methylation of inorganic mercury mainly from anthropogenic sources. The vapor of environmental mercury is released into the atmosphere from a number of natural sources. Man-made emissions, mainly from the combustion of fossil fuels, form about 25% of the total emissions to the atmosphere. Elemental mercury and dimethyl mercury ($(CH_3)_2Hg$), as a result of their air/water distribution coefficients, are most likely to be found in atmosphere (Lindqvist er al.,1984). The solubility of mercury vapor in water is not high enough to account for the concentrations of mercury found in rain water. A small fraction of mercury vapor is converted to a water soluble species, probably inorganic mercury (mercuric form, Hg^{2+}), which is deposited on land and water in rain. Atmospheric deposition or input from the watershed are the major sources

of mercury to remote lakes without point source pollution (Evans, 1986; Johnson, 1987).

Inorganic mercury readily adsorbs to inorganic and organic particulates as well as dissolved organic carbon in lakes (Miller, 1975). In the presence of hydrogen sulfide, mercuric ion precipitates as mercuric sulfide (HgS). This is generally assumed to render the mercury unavailable for methylation (Fagerstrom & Jernelov, 1971). The bottom sediment of the oceans is thought to be the ultimate sink where mercury is deposited in the form of the highly insoluble mercuric sulfide.

Mercuric ion is also reduced to elemental mercury (Hg°) in lake water which volatilizes to the atmosphere. This emission, deposition, and re-emission creates difficulties in tracing the movement of mercury from its source. Mercuric ion can be methylated abiotically (Lee et al., 1985) and biotically (Jensen & Jernelov, 1969). Abiotic methylation of mercuric ion involves the non-enzymatic methylation by methylcobalamin (Berman et al., 1990; Rednell & Tunlid, 1991), methyltin compounds (Byrd & Andreae, 1982; Cerrati et al., 1992; Chau et al, 1987; Han & Weber, 1988; Maguire et al., 1986), and humic matter (Alberts et al., 1974; Allard & Arsenie, 1991; Jackson 1988; Nagase et al., 1982; Wilson & Weber, 1979). Numerous experiments by microbiologists

suggest that biotic sediments are major sites for methylation of inorganic mercury and that sulfate reducing bacteria contribute considerably to methylmercury production. The enzymology of CH_3Hg^+ hydrolysis and mercuric ion reduction is now understood in some detail, as is the oxidation of mercury vapor to Hg^{2+} by an enzyme that is critical to the oxygen cycle (catalase) (Begley et al., 1986).

ACCUMULATION OF MERCURY IN AQUATIC ORGANISMS AND HUMANS

Interest in the biogeochemical cycle of mercury in the environment has dramatically increased in recent years because of observations that fish tissue mercury levels are elevated in acid-impacted pristine lakes (Bloom et al., 1991; Grieb et al., 1990). The global cycle of mercury mostly involves inorganic forms which do not accumulate in human food chains. Therefore, the change in speciation from inorganic to organic forms (methylmercury) is the first step in the aquatic bioaccumulation process.

Methylmercury is more mobile, more toxic, and more readily bioaccumulated because of its ability to transfer mercury across biological membranes, greater solubility in lipid tissues, and a tendency to bioconcentrate (Weber, 1993). Bloom (1992) found that almost all (>95%) of the mercury in

fish is in the form of methylmercury which is also the case for many other types of aquatic organisms.

Bacterial action in sediments of fresh water, estuarine, and marine ecosystems converts inorganic mercury to methylmercury which accumulates in fish via food chain transfer (WHO, 1990). Consumption of contaminated fish is clearly the dominant route of exposure of humans to methylmercury (WHO, 1990). It is certain that wildlife which depend on fish as a primary food source are at equivalent and probably greater risk of methylmercury accumulation humans.

Methylmercury is one of the few compounds documented to produce poisonings in humans subsequent to trophic transfer through aquatic food chains. The Minamata Bay disaster is the most extreme example (Mishima, 1992). Trophic transfer of industrial mercury contamination via fish and shellfish in coastal Japan during the 1950's poisoned thousands of humans.

The central nervous system toxicities of methylmercury on the visual cortex and cerebellum of the brain produced blindness, gross motor and mental impairment in adults. Infants born to methylmercury poisoned mothers suffered markedly increased instance of cerebral palsy and other neural dysfunction.

There are reports of less severe instances of human poisonings due to consumption of methylmercury contaminated

fish from Canada and New Zealand. McKeown-Eyssen and Ruedy (1983a; 1983b) reported neurological abnormalities in Cree Indian adults from Northwestern Quebec, Canada with lifetime histories of contaminated fish consumption.

While the severity of poisoning was mild or even questionable, some consider it the first example of an endemic disease due to trophic transfer of methylmercury. Kjellstrome et al.(1986) found evidence of developmental retardation in four-year old New Zealand children associated with maternal consumption of methylmercury contaminated fish.

MERCURY METABOLISM

Mercury can exist in three forms, elemental, inorganic, and organic, and all are toxic. However, the toxicity of the three forms of mercury are different, mainly as a result of differences in tissue distribution.

Absorption

Elemental mercury (Hg°) may be absorbed by biological systems as a vapor. Elemental mercury vapor is relatively lipid soluble and is readily absorbed from the lungs following inhalation and is oxidized in the red blood cells to inorganic

mercury (Hg^{+2}). Ionic mercury is very poorly absorbed from the gastrointestinal tract, however.

Inorganic mercury, existing as monovalent (mercurous) or divalent (mercuric) ions is relatively poorly absorbed from the gastrointestinal tract (7% in humans). After absorption inorganic mercury accumulates in the kidney. Organic mercury is the most readily absorbed (90-95% from the gastrointestinal tract), owing to lipid solubility (Timbrell, 1991; WHO, 1990).

Distribution and metabolism

The distribution of mercury varies considerably, depending on the chemical form and on the route of administration. Elemental mercury is rapidly oxidized to Hg^{2+} and organic mercury compounds are also metabolized to varying degrees to yield Hg^{2+}.

While chronic mercury poisoning due to intake of Hg^{2+} is essentially a renal problem, chronic mercury poisoning due to inhalation of Hg^{0} is a disease of the central nervous system.

The disposition of organic mercury compounds is quite unlike that of Hg^{2+}. This is particularly true of methylmercury. Although methylmercury and Hg^{2+} distribute preferentially to the kidney, the concentration in the brain and blood is substantially higher in the case of methylmercury. Toxic manifestations of inorganic mercury are

renal whereas those for methylmercury poisoning are neurologic.

Mercury is a reactive element and its toxicity is probably due to interaction with proteins. Mercury has high affinity for sulfhydryl groups in proteins (Simpson, 1961; Bach & Weibel, 1976) and a methylmercury glutathione (GSH) complex has been detected in several animal tissues (Omata etal.,1978; Thomas & Smith, 1979; Urano, 1988).

GSH is the most abundant naturally occurring thiol in mammalian tissues and is transported from tissues into the extracellular environment. Plasma GSH is predominantly released from the liver (Bartoli & Sies, 1978; Hahn et al., 1978; Ookhtens et al., 1985) and extracted mainly by the kidneys (Hanh et al., 1978).

Consequently methylmercury is an inhibitor of various enzymes such as membrane ATPases, which are sulphydryl dependent. Brain pyruvate metabolism is known to be inhibited by mercury, as are lactate dehydrogenase and fatty acid synthetase.

The accumulation of mercury in lysosomes increases the activity of lysosomal acid phosphatase which may be a cause of toxicity as lysosomal damage releases various hydrolytic enzymes into the cell, which can then cause cellular damage.

Mercury accumulates in the kidney and is believed to cause uncoupling of oxidative phosphorylation in the mitochondria of the kidney cells. Thus, a number of mitochondrial enzymes are inhibited by Hg^{2+}. These effects on the mitochondria will lead to a reduction of respiratory control in renal cells and their functions such as solute reabsorption, will be compromised.

Excretion

Fecal elimination of mercury from the body is the dominant route of excretion. Some methylmercury has been found in a complex with GSH in the cytosol (Omata et al., 1978) and in the bile (Refsvik & Norseth, 1975). In vitro conversion of methylmercury GSH to methylmercury cysteine has been demonstrated by bile enzymes (Hirata & Takahashi, 1981).

The process of fecal elimination begins with the biliary secretion of both methylmercury and Hg^{2+}, complexed mainly with GSH (Refsvik & Norseth, 1975) or other sulfhydryl peptides (Norseth & Clarkson, 1971; Ohsawa & Magos, 1974).

Inorganic mercury is poorly absorbed across the intestinal wall so that most (approximately 90%) of the inorganic mercury secreted in bile passes directly into the feces. Methylmercury is secreted into the bloodstream and may

subsequently contribute to biliary secretion, thereby forming a secretion-reabsorption cycle (North & Clarkson, 1971).

This enterohepatic circulation increases the amount of methylmercury passing through the intestinal contents and thus provides a continuous supply of methylmercury to serve as a substrate for the intestinal microflora. These microorganisms are capable of converting methylmercury to inorganic mercury, which then becomes the major contributor to total fecal elimination in the rat (Rowland et al., 1980).

OBJECTIVES

In western Oregon, mercury ore deposits are scattered within a belt 20 miles in width, extending from Lane, Douglas, and Jackson counties in the Southern Coast Range to the California border. In Lane County, past production of the Black Butte and Bonanza mines accounts for about one-half of Oregon's quicksilver production (Orr et al., 1992).

The abandonded site of the second largest mercury mine ever operating in Oregon, Black Butte Mine, is located 15 miles south of and within the drainage basin of Cottage Grove Reservoir basin. Active intermittently from 1882 to 1966, this mine produced 18,156 flasks of mercury (Brooks, 1971).

Mercury directly associated with mining enters the environment from mining wastes and via atmospheric deposition

of mercury emitted from the roasting of cinnabar. In this process elemental mercury vapor, obtained by the thermal dissociation and oxidation of cinnabar (HgS), was condensed in cooling towers to obtain liquid mercury. Exhausted cinnabar ore was disposed of at and around the smelting plant and in a few principal dumps of roasted cinnabar. These deposits and atmospherically-deposited metallic mercury residues in the soil, particularly in the vicinity of roasting plants and condensers, jointly with natural emissions related to geological anomalies, have contributed to the elevation of atmospheric mercury concentrations (Bargagli, 1990).

Though there is no history of mercury mining within the Dorena Reservoir basin, the Oregon Department of Environmental Quality (DEQ) has reported that gold mining was a historical feature of this drainage basin (Personal communication). The amalgamation process used in the recovery of gold and silver, until recently considered to be insignificant to the global mercury cycle, is an important source of mercury contamination (Andren & Nriagu, 1979; Lane et al., 1988).

Mercury concentrations in some Oregon reservoir fish have exceeded the 1.0 µg/g limit established by the U.S. Food and Drug Administration (FDA) for human consumption (Allen-Gil et al., 1995; Lowe et al., 1985; Worcester, 1979)(Table I-1). Two Oregon reservoirs with different mercury sources, Cottage

Table I-1. Differences in fish tissue mercury concentration in Cottage Grove and Dorena Reservoir.

Reservoir	Sampling year	Fish sp.	Age (yrs)	Hg (µg/g)
CG[a]	1970*[1]	L.M.Bass	-	1.23 (1.12-1.37)
CG	1974*[2]	L.M.Bass	0.9	0.72 (0.34-1.24)
CG	1987*[3]	L.M.Bass	-	0.47 (0.29-0.64)
CG	1992*[4]	L.M.Bass	2.6	0.96 (0.49-1.79)
CG	1992*[5]	L.M.Bass	3.5	0.86 (0.38-1.75)
CG	1970*[1]	B.Bullhead	-	0.79 (0.53-0.98)
CG	1974*[2]	B.Bullhead	1	0.32 (0.23-0.42)
CG	1974*[4]	B.Bullhead	1.4	0.38 (0.30-0.55)
CG	1975*[2]	B.Bullhead	1	0.24 (0.20-0.27)
CG	1987*[3]	B.Bullhead	-	0.63 (0.51-0.81)
CG	1994*[4]	B.Bullhead	-	0.55 (0.33-0.75)
Dorena	1994*[4]	L.M.Bass	4.7	0.56 (0.40-0.94)
Dorena	1994*[4]	B.Bullhead	-	0.31 (0.25-0.37)

[a] ; Cottage Grove Reservoir.
Compiled data from *[1]: D. R. Buhler, *[2]: Worcester, 1979, *[3]: Oregon st. Dept. Fish & Wildlife, *[4]: Oregon DEQ by personal communication, and *[5]; Allen-Gil et al., 1995.

Grove and Dorena Reservoirs, were examined, comparing mercury distribution and bioaccumulation.

Cottage Grove and Dorena Reservoirs are located within the same ecoregion (Fig. I-2). The drainage basin and limnological characteristics of the study reservoirs were built in the 1940's as part of a multi-purpose water project operated be the Corps of Engineers in the Willamette Valley, compared to other reservoirs within the ecoregion (Table I-2), and were considered to be representative of reservoirs of similar size for this ecoregion. Also both reservoirs were built in the 1940's as part of a multi-purpose water project operated by the Corps of Engineers in the Willamette Valley, Oregon.

SPECIFIC OBJECTIVES:

1. To investigate the probable mercury sources and their fate in the Cottage Grove Reservoir.
2. To compare mercury distribution in sediment and bioaccumulation by fish in two reservoirs.
3. To examine the characteristics of mercury contamination in Cottage Grove Reservoir.
4. To improve the detection limit of methylmercury, by using distillation method and GC-MS detection.

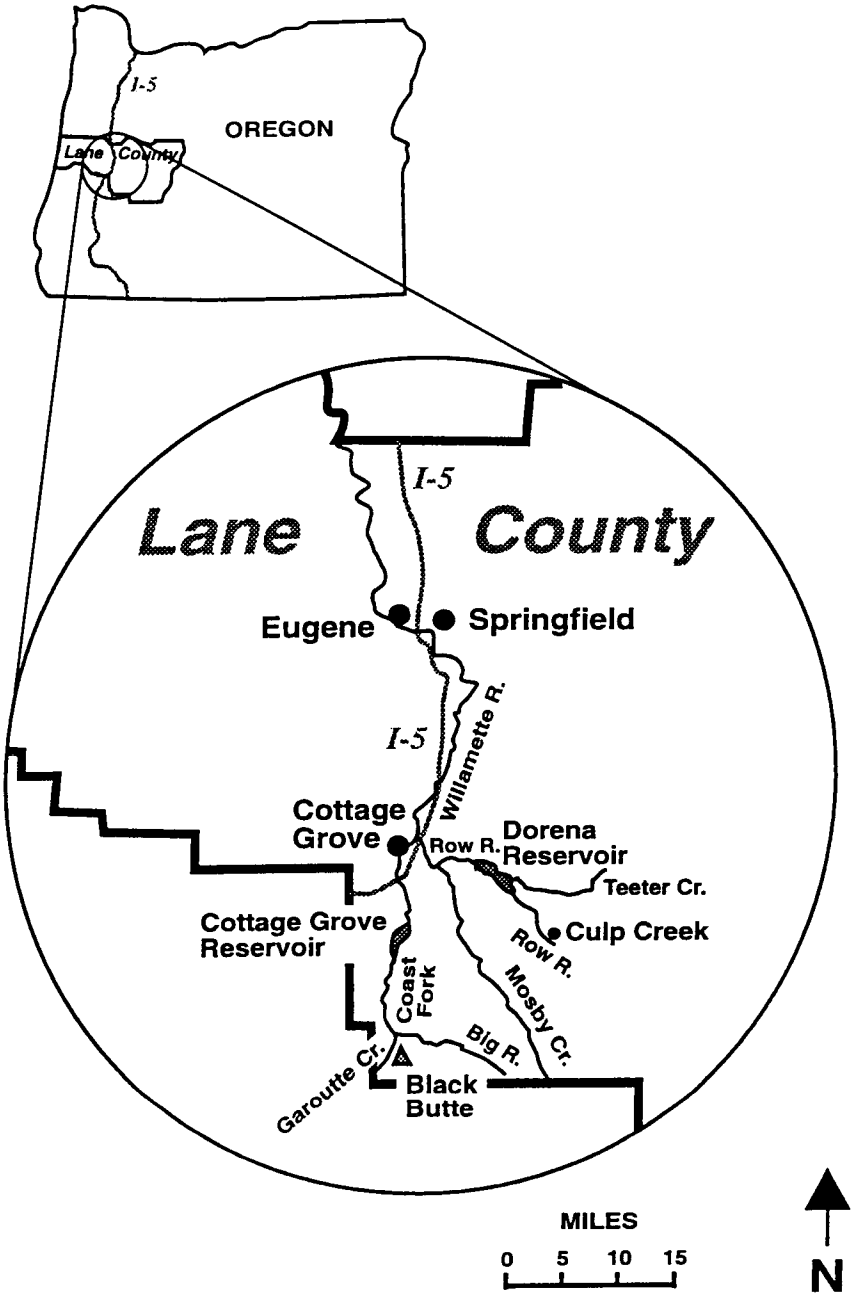

Fig. I-2. Location of Cottage Grove and Dorena Reservoir.

Table I-2. Characteristics of Cottage Grove and Dorena Reservoir.

Characteristics	Cottage Grove	Dorena
Drainage basin area (km^2)	257	655
Annual precipitation (cm)	122 - 157	127 - 203
Land use (% total area)		
Forest	96.5	97.0
Range	1.0	-
Surface area (ha)	461	745
Average depth (m)	9.0	12.9
Shoal area (%)	17	15
Retention time (month)	2	1.7
pH	7.7	7.9
Conductivity (µmhos/cm)	63	49
Sulfide (SO_4 mg/l)	1.2	1.9
Dissolved oxygen (mg/l)	7.2	9.0
Trophic status	Mesotrophic	Mesotrophic

Compiled from : Johnson et al., 1985

II. Mercury distribution in sediments and bioaccumulation by fish in two Oregon reservoirs: Point source and nonpoint source impacted systems

Jeong-Gue Park[1], Lawrence R. Curtis[2]

[1]Toxicology program, Oregon State University, Corvallis, OR 97331, USA

[2]Department of Environmental Health, East Tennessee State University, Johnson City, TN 37614, USA

ABSTRACT

Mercury pollution of sediment and accumulation by several fish species in two Oregon reservoirs of similar size, age, and location within the same ecoregion were compared. Cottage Grove Reservoir is distinguished by a history of mercury mining and processing within its watershed. Sediment mercury concentrations in the main tributary of Cottage Grove Reservoir, which drains the tailings of past mercury mining activities, was tenfold higher than mercury in sediments from other reservoir tributaries. However, there were no significant differences between sediment mercury concentrations in the tributaries of the Dorena Reservoir, which has no mercury mining history within its watershed. The average mercury concentration in the sediment of Cottage Grove Reservoir (0.67 ± 0.05 µg/g dry wt.) was higher than for Dorena Reservoir (0.12 ± 0.01 µg/g dry wt.).

At Cottage Grove Reservoir, maximum mercury concentrations exceeded the FDA limit of 1 µg/g wet wt. for largemouth bass (*Micropterus salmonides*) and bluegill (*Lepomis macrochirus*). All fish species (including largemouth bass, bluegill, crappie (*Pomoxis nigromaculatus*) from Cottage Grove Reservoir had significantly higher levels of mercury than the same species from Dorena Reservoir. Between summer and fall, mercury levels for largemouth bass showed a strong seasonal

fluctuation in both reservoirs. Fish ages were also positively correlated with mercury concentrations in both reservoirs. These results indicated that a point source, Black Butte Mine, contributed amounts of mercury in excess of natural deposits based on differences in bioaccumulation among fish populations from these two systems.

MATERIALS & METHODS

Field Sampling

Duplicate sediment samples were collected from 10 sites at each reservoir in March 1994 (Fig. II-1 and II-2). Three sediment samples (Sites G, I, and J) were collected from exposed sediment at drawdown and from inundated sediments at the same sampling sites in September, 1994 . All sediment samples were obtained using an Ekman™ dredge and placed in acid-pretreated I-Chem™ jars. All samples were frozen immediately and then stored until subsequent analysis.

Three species of fish, largemouth bass *(Micropterus salmoides)*, bluegill (*Lepomis macrochirus*), and crappie (*Pomoxis nigromacutus*), were collected at four times using electroshock methods at Cottage Grove Reservoir (June 1993,

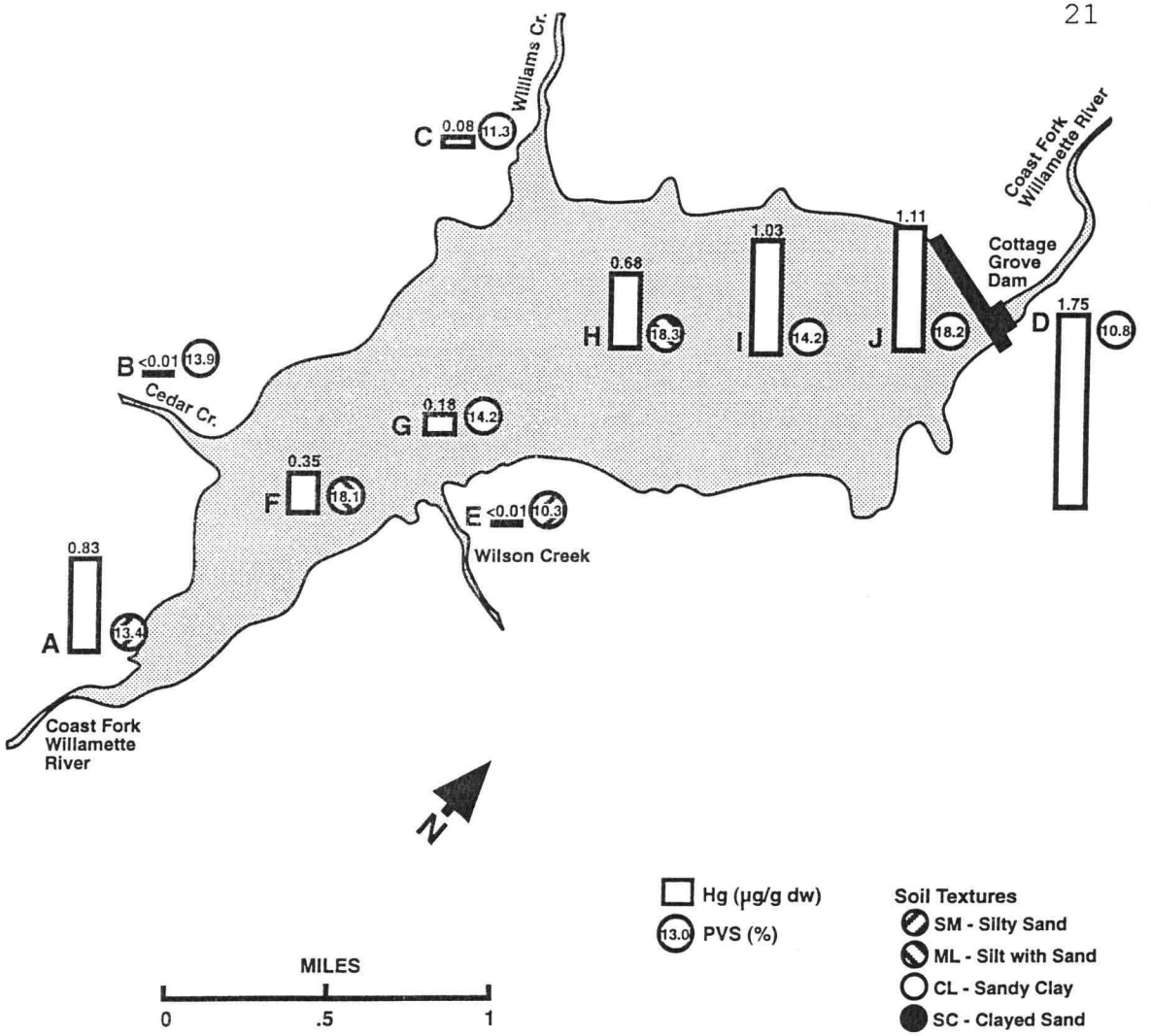

Fig. II-1. Mercury and percent volatile solids in sediment of Cottage Grove Reservoir and its tributaries. Two samples were collected at each sample site and each sample was analyzed in duplicate.

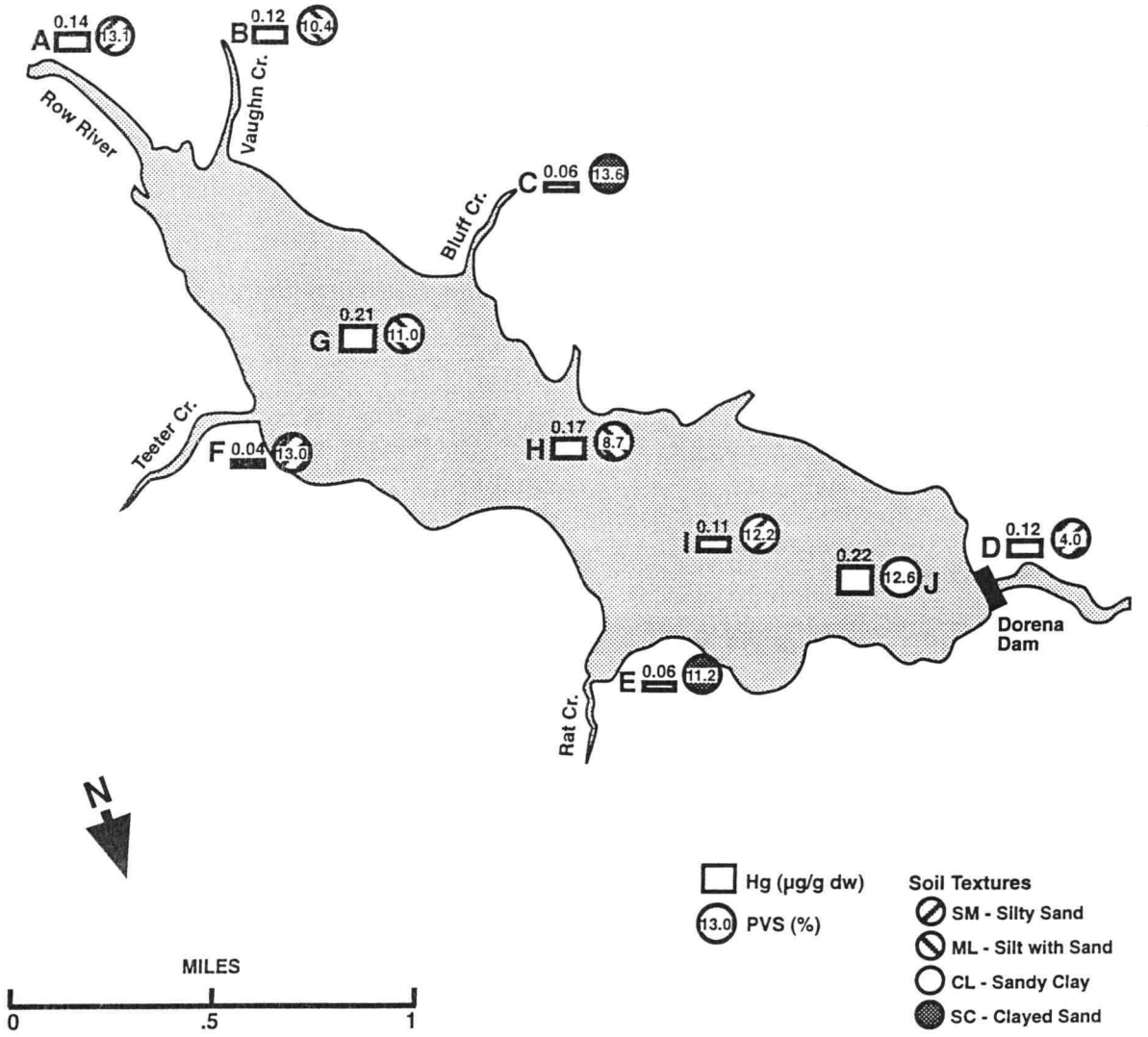

Fig. II-2. Mercury and percent volatile solids in sediment of Dorena Reservoir and its tributaries. Two samples were collected at each sample site and each sample was analyzed in duplicate.

September 1994, July 1995, and November 1995) and two times at Dorena Reservoir (August 1993 and September 1995). The fish were stored on ice in the field and then frozen and filleted in the laboratory.

Chemical Analysis

Total sediment mercury

Sediment samples were analyzed as outlined in Buhler *et al.* (1984). Sediment samples were dried at 50°C for three days, passed through a 1 mm sieve to remove coarse particles, ground with a porcelain mortar and pestle, and homogenized. Subsamples were weighed and transferred to glass 250 ml BOD bottles, to which 5 ml deionized H_2O and 5 ml aqua regia (3 vol. conc. HCl to 1 vol. conc. HNO_3) were added. Samples were placed in a 95°C water bath. After two min, 50 ml of deionized H_2O and 50 ml of 5% $KMnO_4$ were added to each sample. Samples were digested in the water bath for 30 min, and the cooled to room temperature.

Fifteen min prior to analysis, the samples were treated with 50 ml of deionized H_2O and 8 ml of 24% NaCl-hydroxlamine and placed in a hood to allow the evolved oxygen gas to escape. The samples were then transferred to 250 ml reaction flasks and 5 ml 0.5N SnCl in 0.5N H_2SO_4 was added. The flasks were supplied with flow-through nitrogen gas at 91.5 ml/min.

Mercury vapor was passed through a Coleman Model 50 mercury analyzer (Perkin-Elmer Co., Maywood, IL), connected to a Microscribe 4500 recorder set at 50 mv (The Recorder Company, San Marcos, TX).

Sediment mercury concentrations were determined, based on a standard curve of $HgCl_2$ in HNO_3 (0.01-1.0 ppm). The accuracy of this methodology was confirmed by comparison with standard materials purchased from the National Institute of Standards and Technology. All the recoveries were within 10% of complete recovery.All samples were analyzed in duplicate.

Sediment dry weight was determined by drying at 55°C to stable weight. Organic matter (% volatile solid) was determined by at 550°C for 5hr.

Total mercury in fish

Mercury concentrations in fish muscle was determined using heat-based digestion followed by cold vapor atomic absorption (Magos & Clarkson, 1972). Fillet samples (1 to 2 g each) were placed in screw-top test tubes, to which 2 ml 10 N NaOH was added. Samples were then heated for 30 min in a heat block (95°C) and cooled to room temperature. Total mercury was determined by placing 1 ml subsamples in reaction flasks, along with 3 ml 1% NaCl, 1 ml 1% cysteine, 4 drops octanol, 1 ml 50% $SnCl_2$ (w/v), and 10% $CdCl_2$ (w/v) in 4N HCl.

The flask opening was then covered with a septum, through which 4 ml 10 N NaOH was injectd by syringe. After 30 seconds, N gas was supplied at 1.5 l/min. The recorder was set at 50 mv.

Standards were prepared as mercury in HNO_3 (0.01 to 1.0 ppm), prepared from a commercially available standard (Johnson and Mathey, Seabrook, NH). The blank values for the reagents ranged between 5 ng and 7.5 ng. Age determinations were performed by scale analysis, as described by Jearld (1983).

Statistical Analysis

Means and standard errors were calculated from two mercury analyses for each duplicated sediment sample from each site. Mercury concentration of duplicate muscle analyses from each individual fish were grouped by species and age. Two-way analyses of variance (ANOVA) was used to compare the influence of fish age and year of sampling on muscle mercury concentrations for each fish species.

RESULTS

Sediment Mercury

Sediment mercury concentrations at the confluence of the Coast Fork of the Willamette River, which drains the tailings of the abandoned mercury mine in the area of the Cottage Grove Reservoir, was 0.83 ± 0.14 µg/g, 10 times higher than sediments from other tributaries to the reservoir (Fig. II-1).

Average mercury concentrations within the reservoir were 0.67 ± 0.41 µg/g, with elevated mercury contamination observed in the deepest areas of the reservoir (Fig. II-1, sites H, I, and J), which may have reflected the active deposition of particulate mercury concentrations. The highest mercury concentration (1.75 ± 0.1 µg/g) was downstream of the dam, more than twofold higher than mercury concentrations at the mouth of the Coast Fork of the Willamette River. There were no significant differences in sediment mercury concentrations between tributaries of Dorena Reservoir. The average mercury concentration for five tributaries was 0.08 ± 0.04 µg/g (Fig. II-2).

Mercury was associated with fine particulate matter (Fig. II-1 and II-2). The concentration of mercury in the sediment was correlated with the sediment type, and high concentrations

were found in clay-type sediments. The percent of volatile solids (PVS) was not correlated with mercury concentration for reservoir sediments.

The average sediment mercury concentration within the reservoir basin was 0.18 ± 0.05 µg/g. As seen from data in Figure II-3 and II-4, there were lower mercury concentrations in exposed sediments than in the inundated sediments in the fall of the year. Mercury concentrations in exposed sediments were approximately 65% of the inundated sedimentary mercury concentrations for Cottage Grove Reservoir and 73% for Dorena Reservoir.

Mercury in Fish

The lateral fillets of three fish species (largemouth bass, bluegill, and crappie) for each reservoir were analyzed for total mercury content. Maximum mercury concentrations exceeded the FDA limit of 1 µg/g wet wt for largemouth bass and bluegill from the Cottage Grove Reservoir (Fig. II-5), and the U.S. Environmental Protection Agency (EPA) limit of 0.6 µg/g was exceeded among 54% of largemouth bass, 89% of bluegill, and 50% of crappie.

Mercury concentrations in fish from the Dorena Reservoir were about one-third those among fish from the Cottage Grove

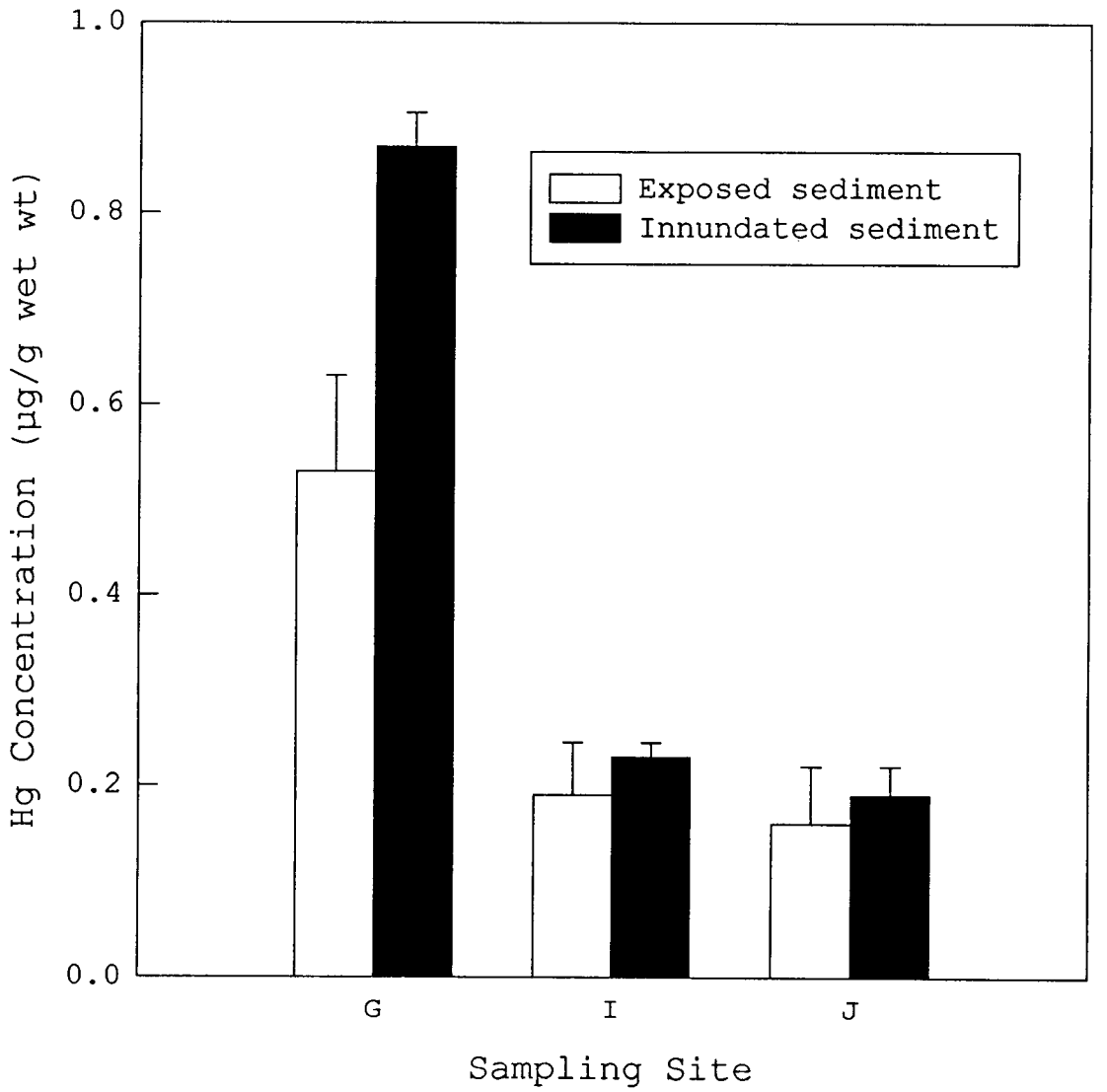

Fig. II-3. Comparison of mercury concentration in exposed and inundated sediment of Cottage Grove Reservoir.

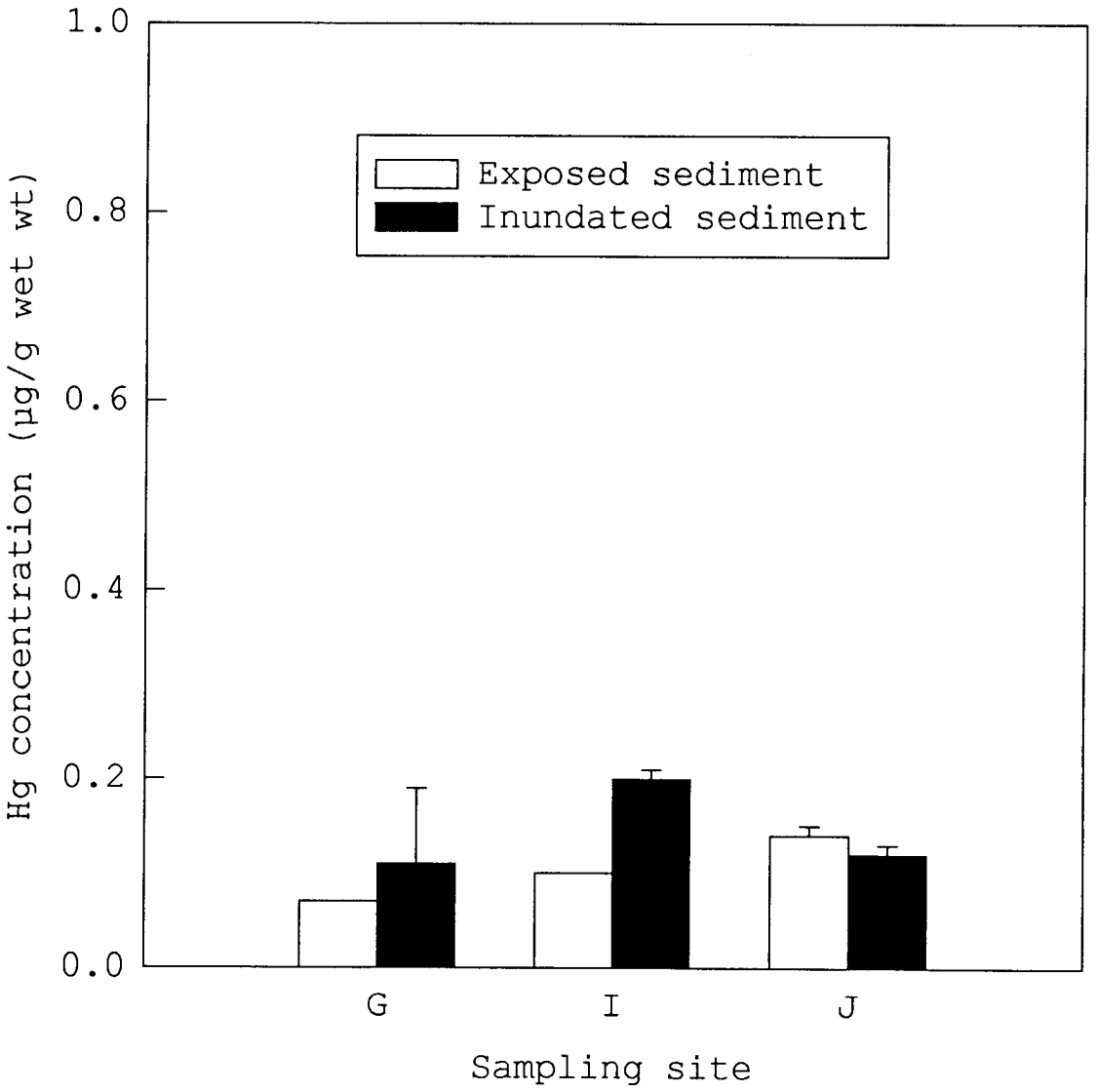

Fig. II-4. Comparison of mercury concentration in exposed and inundated sediment of Dorena Reservoir.

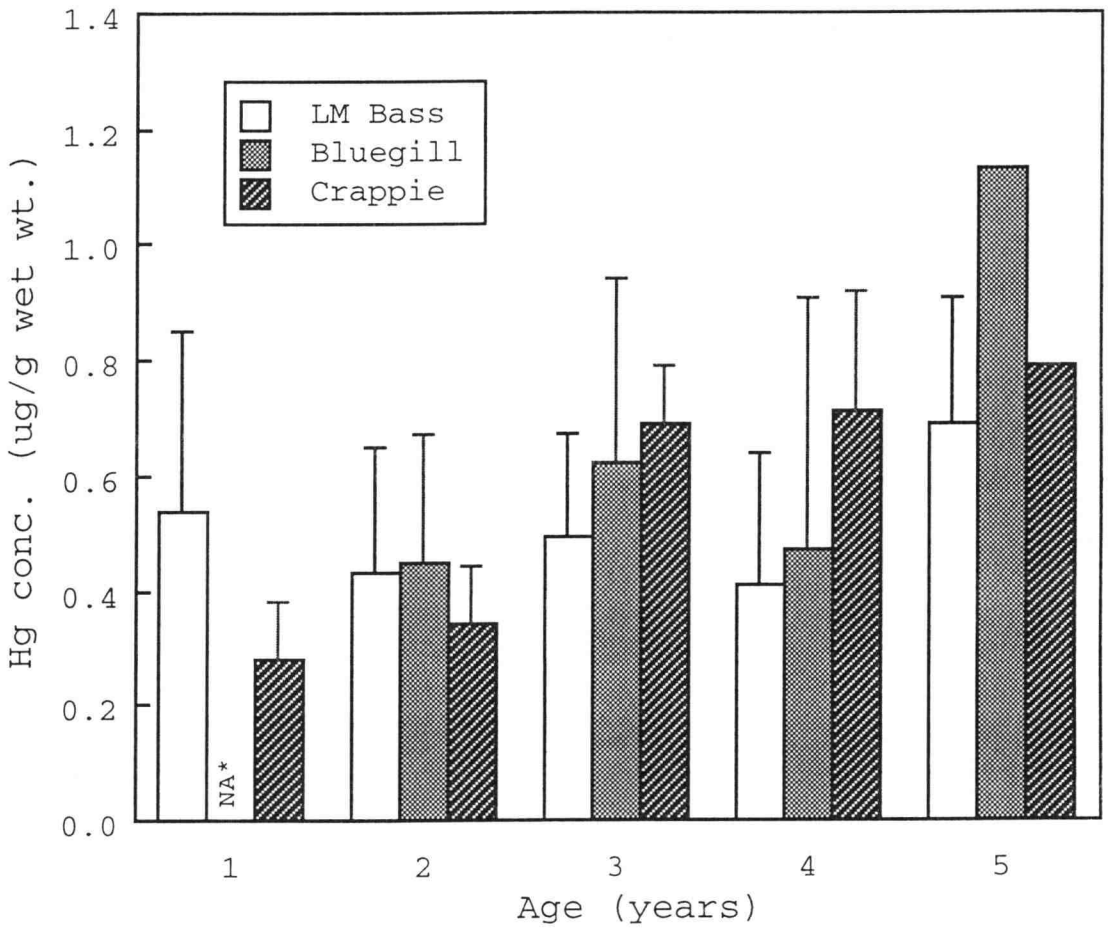

Fig. II-5. Mercury concentration in fish tissues by fish age for the three species from the Cottage Grove Reservoir. Results are mean ± SEM for all fish collected from June 1993 until November 1995.

Reservoir. No fish species from Dorena Reservoir exceeded the FDA and EPA limits (Fig. II-6).

Mercury concentrations in fish muscle increased with age for all Cottage Grove Reservoir species, but not for species from Dorena Reservoir. There were clear differences in mercury levels between year and fish age in each reservoir ($p < 0.0001$), as shown in Figures II-7 and II-8.

Mercury contents in fish muscle significantly increased with increase of the mercury concentration in the whole fish body in both reservoirs (Fig. II-9).

DISCUSSION

Sediment Mercury

With the exception of mercury concentrations from site A in Figure II-1, the mercury detected in each of the tributaries was similar for the two reservoirs. The data indicated that the main mercury inputs were from the Black Butte Mine, situated on the main tributary (Fig. II-1, site A) of the Cottage Grove Reservoir. There were no indications of point sources of mercury for the Dorena Reservoir (Fig. II-2).

Allen-Gil et al. (1995) reported that total mercury concentration in the sediments of Cottage Grove Reservoir was

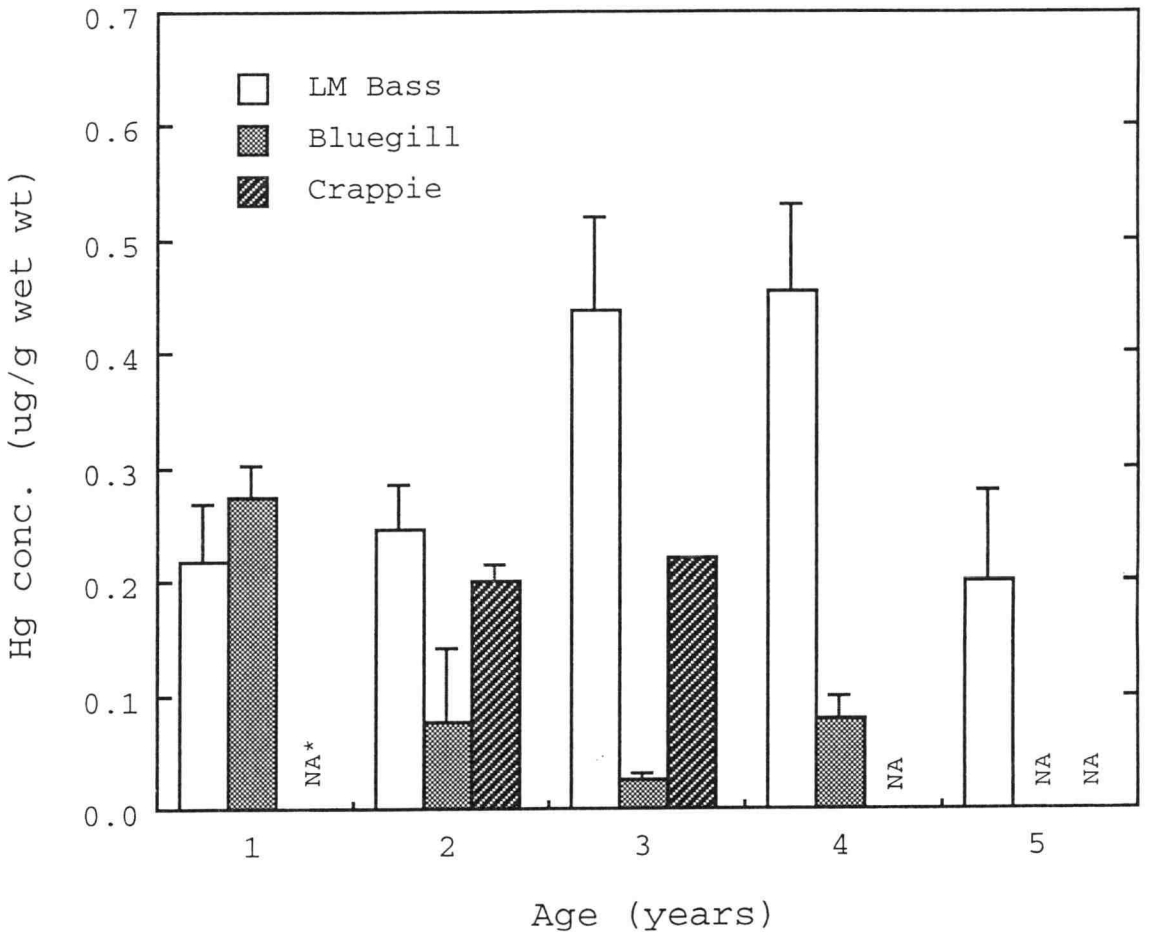

Fig. II-6 Mercury concentration in fish tissues by fish age for the three species from the Dorena Reservoir. Results are mean ± SEM for all fish collected from August 1993 until September 1994.

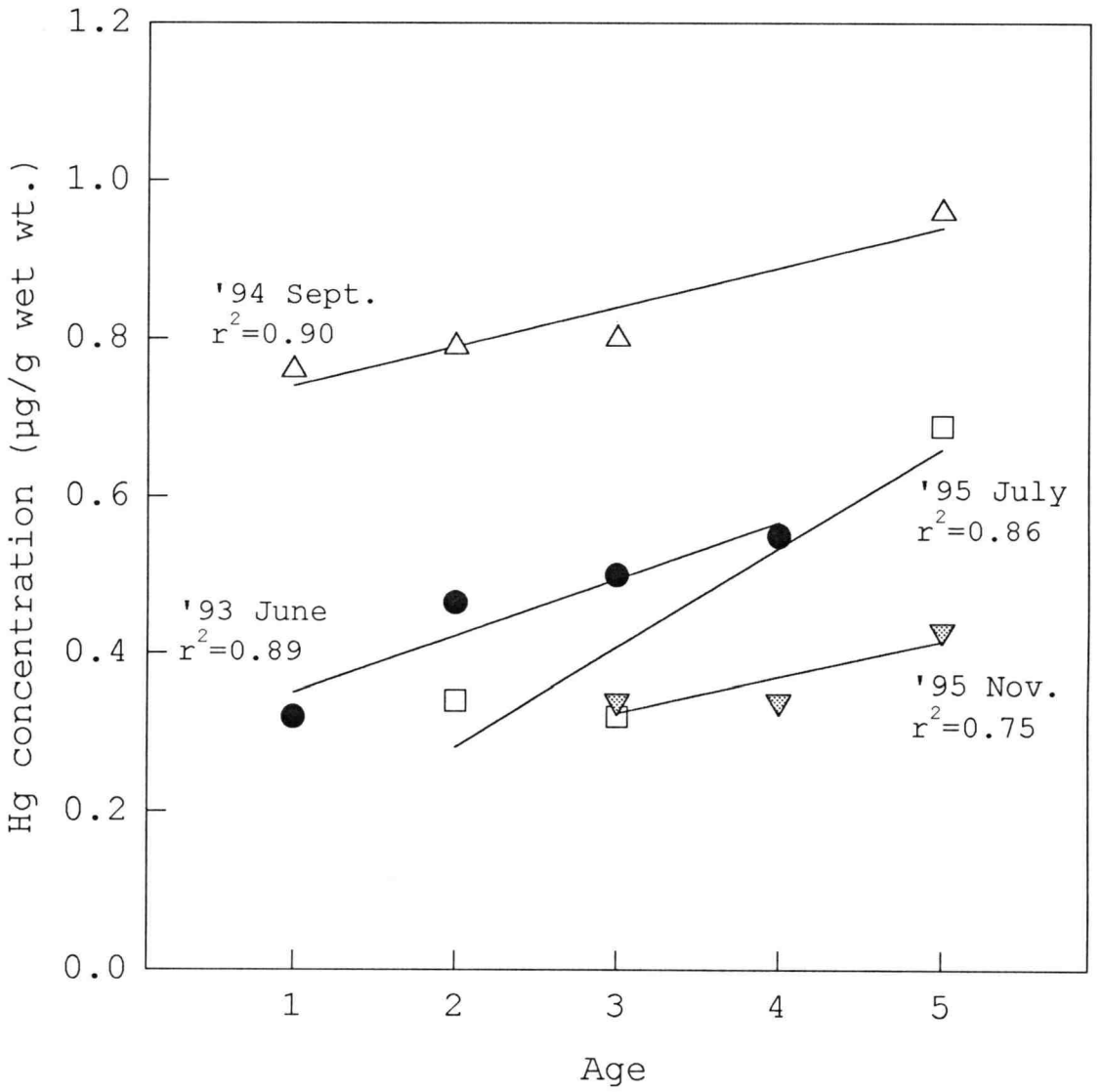

Fig. II-7. Seasonal variation of mercury concentration in largemouth bass from Cottage Grove Reservoir.

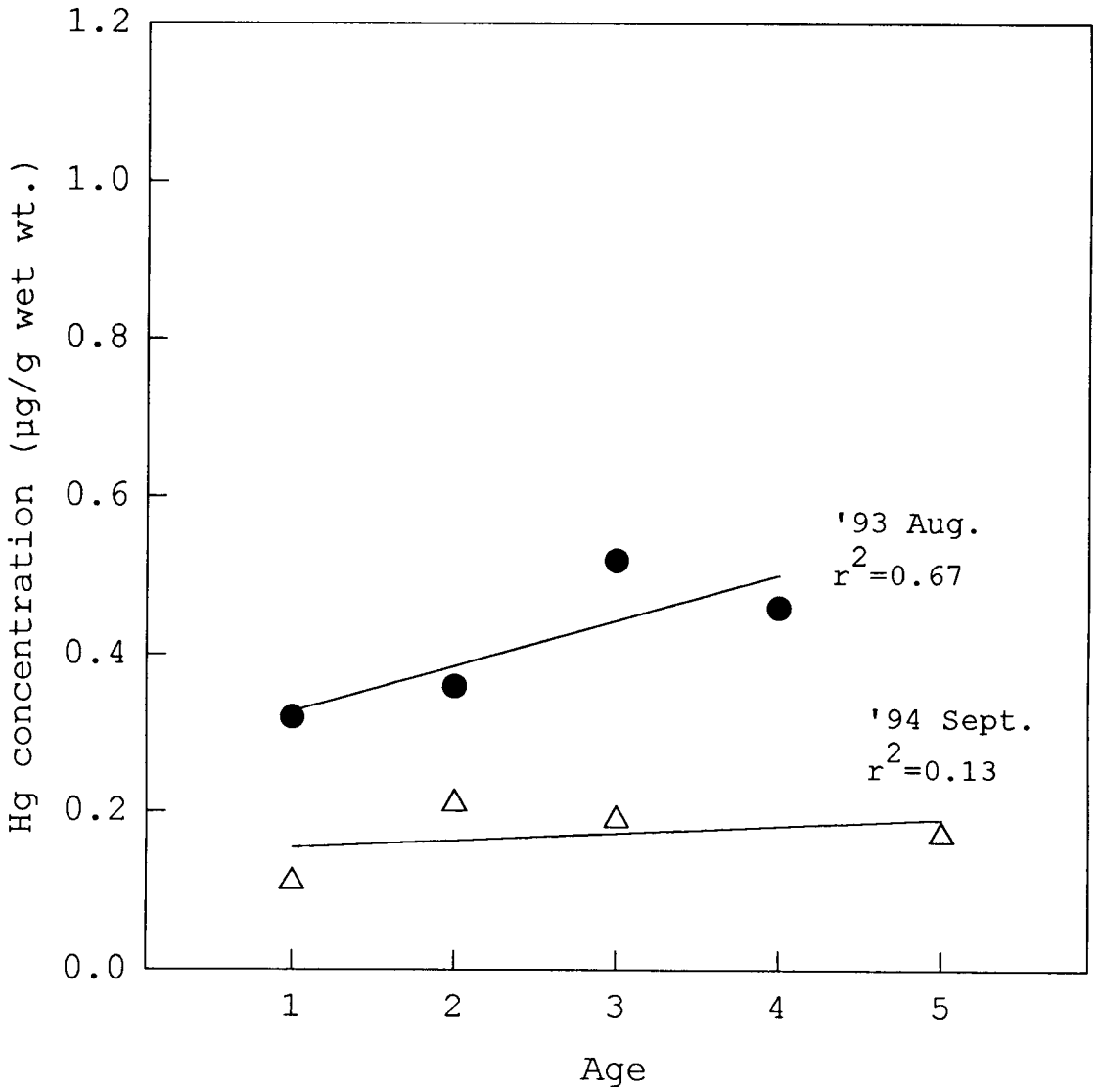

Fig. II-8. Seasonal variation of mercury concentration in largemouth bass from Dorena Reservoir.

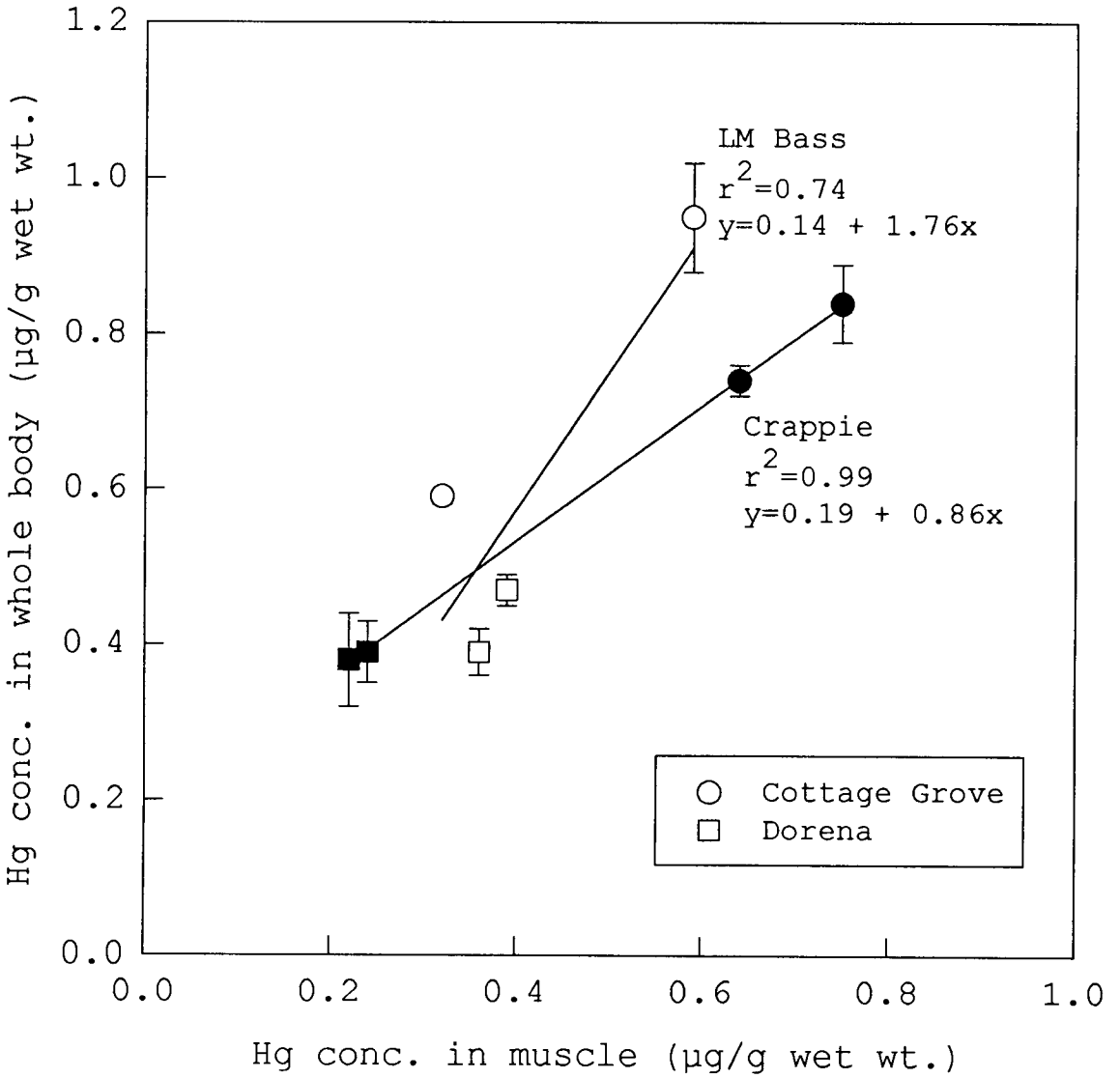

Fig. II-9. Relationship between mercury concentration in fish muscle and in whole body.

0.84 ± 0.2 µg/g, overlapping the range of mercury concentrations provided in Figure II-2 (0.18 to 1.11 µg/g). This study determined elevated mercury concentration in the deep areas of the Cottage Grove Reservoir (Fig. II-1, sites H, I, and J), which may have reflected the active deposition of particulate mercury and cinnabar. High mercury concentrations downstream from the dam may also be explained by the amount of sediment loading. Mercury loading rates are affected by the quantity of available mercury as either a natural source or as mining wastes, and from sediment transport rates.

A number of factors influence the re-mobilization of mercury from sediments. These factors include organic matter (humic and fulvic acids) and the sediment type (e.g., clay or silt) (Ottawa River Project Group, 1979). Sediment mercury concentrations were not significantly correlated with organic content (PVS) for either reservoir considered for this study. However, mercury generally has a high affinity for fine-grained particulate and is found as attached forms to various types of "carrier particles"; that is, suspended organic and inorganic particles (Håkanson & Jansson, 1983).

Contamination of sediments in the mine area are likely due to the transport and deposition of suspended particulate matter brought into the drainage by erosion from mining wastes (Siegel et al., 1987). Continuing research on mercury concentrations in particulate fractions of water samples is

expected to provide additional information on organic particles.

Sediments are effective sinks for mercury, once it has been released into the aquatic environment. The exchange of mercury back to the water column, particularly from oxidized sediments, is generally low because of the strength of the mercury binding to the sediments (Lindberg *et al.*, 1975).

However, mercury has a strong affinity for sulfhydryl groups and mercury mobility may be increased by the formation of sulfide complexes under reducing conditions (Benes & Havlik, 1979; Bothner et al., 1980; Bryan & Langston, 1992; Gravis & Ferguson, 1972; Lu et al., 1986). Craig and Morton (1983) found that the concentration of methylmercury increased in the sediment as the concentration of sedimentary sulfide increased. Sediment mercury levels, therefore, tend to be greater under anaerobic conditions (Meger, 1986).

Mercury in Fish

The mercury ranges in fish from Cottage grove Reservoir reported by Worcester (1979) and Allen-Gil et al. (1995) were similar to the range reported from the present study (largemouth bass, 0.31 to 0.96 µg/g), suggesting that mercury contamination in that reservoir has not changed over time. Of

the five species examined for mercury concentration in past research efforts, the highest values were observed in largemouth bass (Worcester, 1979).

Average mercury concentrations in fish from Dorena Reservoir was one-third that for fish taken from Cottage Grove Reservoir. According to the Oregon DEQ, mercury concentration in largemouth bass sampled in 1993-1994 ranged between 0.22 to 0.70 µg/g.

Mercury concentrations generally increased with length, weight, and age among fish (Driscoll *et al.*1994; Johnson 1987). Lange *et al.* (1993) observed a positive correlation for mercury concentration and age/size among largemouth bass from 53 Florida lakes.

Temperature was identified as an important factor in the seasonality of mercury methylation and availability, increasing from spring to late summer and decreasing in the fall (Jackson et al., 1982; Korthals & Winfrey, 1987; Winfrey & Rudd, 1990). Although some changes in mercury concentrations occurred between seasons and years in the data from the present study, there was little evidence of any overall seasonal pattern.

We considered two hypotheses regarding seasonal changes. One, the seasonal changes observed were due to the rate differences for mercury elimination. Bidwell and Heath (1993)

observed that the physiology of rock bass was significantly altered at certain times of the year. In particular, female rock fish had significantly higher levels of liver glutathione than did males. High hepatic glutathione increased the biliary excretion of methylmercury (Magos et al., 1978).

Second, dietary changes may have been involved with seasonal differences since mercury accumulation in fish was greatly affected by diet (Nicoletto & Hendricks, 1988; Phillips et al., 1980). Wydoski and Whitney (1979) reported diet of largemouth bass fry was composed principally of small crustaceans (copepods, cladocerans) and insects, including midge larvae, nymphs of mayflies, dragonflies, and damselflies. When fry reached a length of 7 - 10 cm, they consumed fishes, including smaller largemouth bass. Chabot and Maly (1986) examined the diet of yellow perch and found considerable variability in diet among individual fish.

From these studies, we made conclusion that nonpoint mercury pollution of Dorena Reservoir was not of significant magnitude to create a regulatory problem for fish consumption. By the way the point source appeared involved in a regulatory problem. Therefore additional work planned for more detailed examination of mercury contamination in Cottage Grove Reservoir.

III. Evidence for point source contamination of Cottage Grove Reservoir

Jeong-Gue Park[1] and Lawrence R. Curtis[2].

[1]Toxicology program, Oregon State University, Corvallis, OR 97331, USA.

[2]Department of Environmental Health, East Tennessee State University, Johnson City, TN 37614, USA.

ABSTRACT

Past mercury mining activities in the Black Butte Mine area, Oregon, have contaminated soils surrounding this site with mercury. Elevated sediment mercury concentrations in the Cottage Grove Reservoir appears to be derived from this point source. We collected six composite soil samples and three creek sediment samples at varying distances from the abandoned mercury mine. The highest concentration occurred close to the kiln. Average mercury concentration surrounding the kiln area was 254 µg/g (223 - 271 µg/g) and decreased markedly in a tailings dump. The mercury concentration in the sediment of a creek below the mine dump was up to ten times higher than that of the sediment from a creek in a watershed adjacent to that of mine area.

Sulfur content in soil (21,052 µg/g) was highest near a portal to Black Butte Mine and decreasing soil sulfur was observed from the mine portal to creek. The sulfur content was associated with distance from the suspected source, Black Butte Mine. There was no significant relationship between mercury and carbon content in sediments. However carbon contents in tailing soil appeared to relate to mercury concentration.

Two sediment cores were collected to construct pollution history profiles. Dating of the core was attempted by ^{137}Cs analysis. We detected no ^{137}Cs in the sediment samples. Subsample slices of the sediment core were chemically analyzed for total mercury and PVS (% volatile solid). The concentration of mercury increased from the surface to the bottom of the sediment core. The highest mercury level were observed at 24 - 26 cm (2.25 ± 0.12 µg/g) and 40 cm depth(2.37 ± 0.39 µg/g). Most of these mercury in the sediments of Cottage Grove Reservoir was believed to be of Black Butte Mine origin and likely related to mercury production of that mercury mine.

Mercury concentrations were measured in food chain specimens. Contents of total mercury in the food chain showed benthos had higher mercury levels than planktonic invertebrates. Brown bullhead had the highest mercury concentrations which ranged from 0.26 to 0.71 µg/g wet wt.

Sample distillation followed by gas chromatography-mass spectrometry allowed the detection of as about 1 pg methylmercury /ml for a 40 ml sample of water. Methylmercury in pore water increased in the sediment samples with collection depth. Methylmercury concentrations (23.27-35.32 pg/ml), were 0.002-0.003% of total mercury in these samples.

In the summary, our results indicated fish methylmercury contamination management problems in Cottage Grove Reservoir were associated with a point source of pollution.

MATERIALS AND METHODS

Field sampling

Sampling of Black Butte Mine

Soil samples were collected from six sites within the abandoned Black Butte Mine site: two at the opening of a mine portal, two around the Kiln, and two in mine dump. Sediment samples were collected from a stream in the watershed of Black Butte Mine, from a stream in an adjacent watershed, and from a river formed by the confluence of these streams in September 1993 (Fig. III-1).

Soil cores were taken using a deep sampling corer, comprised of a 18" length of stainless steel tubing. At each location, three rectangular sites of approximately 900 m^2 were selected and five 20 x 5 cm soil cores were taken in a W-shaped pattern across the sample site. All soil samples were placed in nitric acid-leached BOD bottles, sealed and stored away from direct sunlight (Golterman et al., 1983).

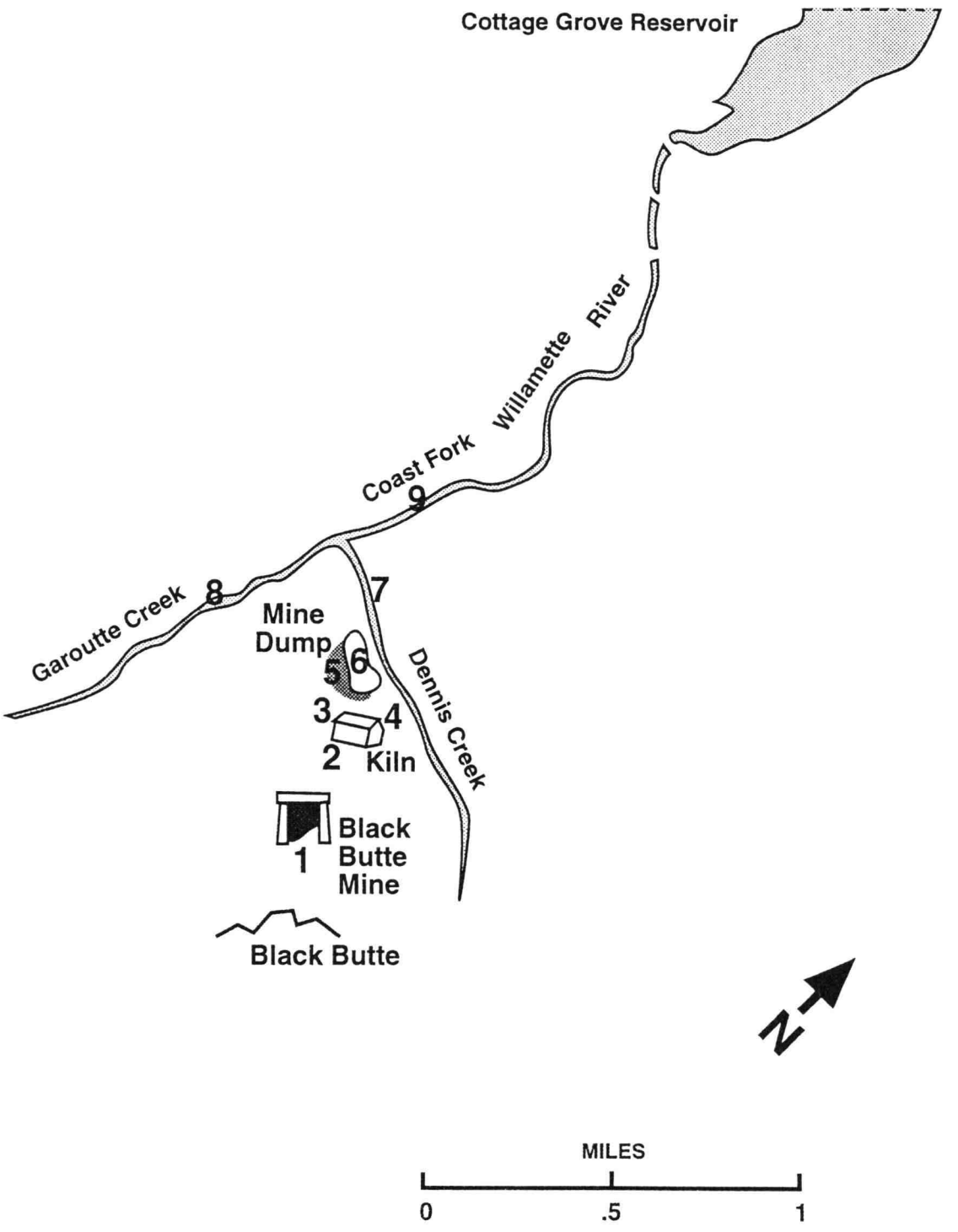

Fig. III-1. Sampling sites around Black Butte Mine.

Sediment samples were placed in the acid-pretreated I-Chem™ jars, frozen with 6 hr of collection and stored frozen until subsequent analysis.

Sampling for geochronology

Sediment cores were collected from two sites in Cottage Grove Reservoir (Fig. III-2) using a spihinter sampler with a PVC pipe of 12 cm diameter in January 1995. Two cores (26 and 40 cm) were collected at water depths of 7.3 and 8.2 m, respectively. Cores were subdivided by extrusion of 2 cm subsections and stored frozen in I-Chem® jars until analysis.

Sampling for trophic transfer

Brown bullhead (*Ictalurus nebulosus*) were collected at two times using electroshock methods (June 1993 and September 1994). Bullfrog (*Rana catesbeiana*) and tadpole were caught from the water column and vegetation with sweep nets in June 1995 (Fig. III-2). We also collected freshwater snail (Helisoma), damsel fly nymph (Zygoptera), and blood worm (Chironomus) with an Ekman dredge at several sites. Each grab sample was washed through a 0.5 mm sieve with lake water. All samples were retrieved from the screens with acid-washed forceps and transferred to acid-washed Nalgene® bottles. The bottles were kept on ice until returned to the laboratory.

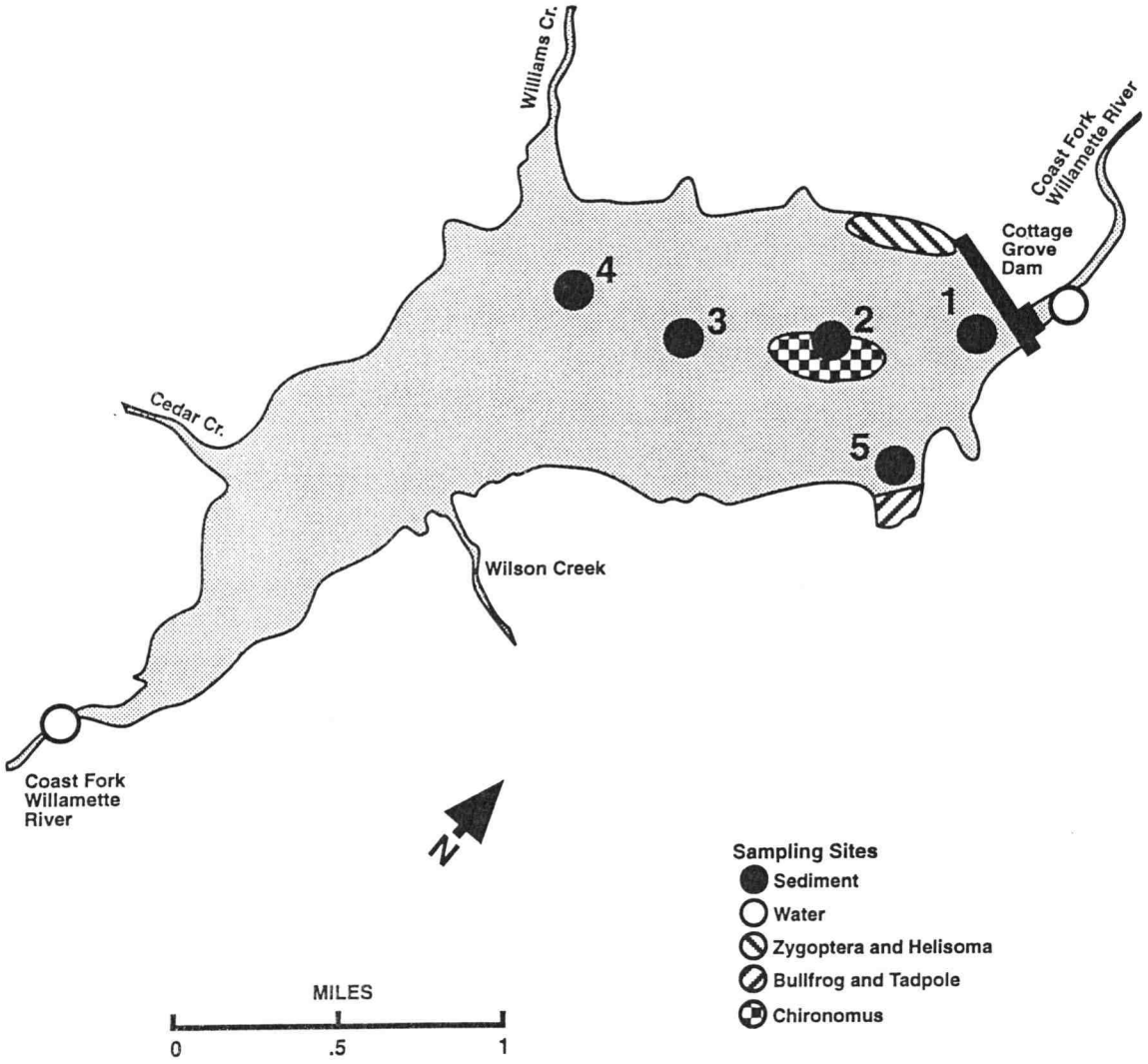

Fig III-2. Sampling sites in Cottage Grove Reservoir.

Before being frozen, all samples were bathed in water, with daily changes of water, for 2-3 d without food to void their gut contents. Snail shells were measured and the soft tissue was removed, and frozen in the laboratory. Zooplankton (Copepoda and Daphnidae) were taken by nonmetallic plankton nets. After each vertical tow, the net contents were back washed with surface lake water into pre-acid washed Nalgene^{R} bottles.

Sampling for methylmercury

Sediment samples for methylmercury analysis were obtained by PVC pipe of 40 cm in September and November of 1995.

Chemical analysis

Total mercury

Total mercury analysis were conducted using cold vapor atomic absorption (Perkin-Elmer Co.,Maywood, IL). The carbon and sulfur contents in the soil and sediment samples of Black Butte Mine were analyzed by Leico Analyzer (Model CS-144) with total combustion where the carbon was oxidized to CO_2 and the sulfur to SO_2. Both CO_2 and SO_2 were quantified by infrared spectrometry.

Cesium

The ^{137}Cs content in each sample was determined using a NaI (TI) detector coupled to a multichannel analyzer by Radiation Center at Oregon State University .

Methylmercury

* Cleaning procedure

Distillation vials and most of the other ware was made from PTFE. All glass and PTFE ware were throughly cleaned using the following procedure. PTFE vials and bottles were filled with conc. HNO_3 for 24 - 48 hr. After being throughly rinsed with Millipore deionized water, vials were bathed with dilute acid (0.25 M HNO_3) and final acid (concentrate HNO_3) for 24 hrs, respectively. Between each bath, all vials were rinsed with deionized water (Millipore).

* Centrifugation

We collected pore water samples from sediment as outlined in Batley and Giles (1979). A 300- to 350 g sediment sample was weighted into 500 ml polypropylene centrifuge bottle (Beckman) to which was added 70 ml fluorocarbon solvent (PF 5070), supplied by 3M Specialities Corp., USA.

Pore water samples were collected by centrifugation on a Beckman GPR tabletop centrifuge with rotor type horizontal-

swing arm buckets. Centrifugation speed was 2500 rpm at 2 - 3°C temperature for 2 - 2.5 hrs.

* Distillation

A distillation apparatus was conducted for methylmercury separation (Fig. III-3). After centrifugation of sediment samples (300 - 350 g), extracted pore water (~ 40 g) was placed into a 60 ml PTFE deep bodied vial (Salillex) followed by the addition of 1 ml of 8 M H_2SO_4 (Ultrex II, JT Baker, USA) and 0.025 ml 1.7169 M KCl (99.999%, Aldrich Chemical Co.) to bring the concentration of chloride ion to 0.08%. Then the vial was connected to the distillation apparatus at a nitrogen flow-rate of 25 ml min^{-1} and a core oven temperature of 115°C. The distillate was collected in a 60 ml PTFE vial kept in an ice cooled water bath. Prior to distillation 5 ml of Millipore deionized water was placed in the collection vial. Under the conditions described the distillation was finished in 7 hrs when 90% of the distillation was collected (6-7 ml hr^{-1}).

* Aqueous phase ethylation and collection

Methylmercury determination was by aqueous phase ethylation and GC/MS (Fig. III-4). Approximately 40 ml of sample was taken up with syringe from the distillate vial and injected through the stop-cock to the ethylation reaction-

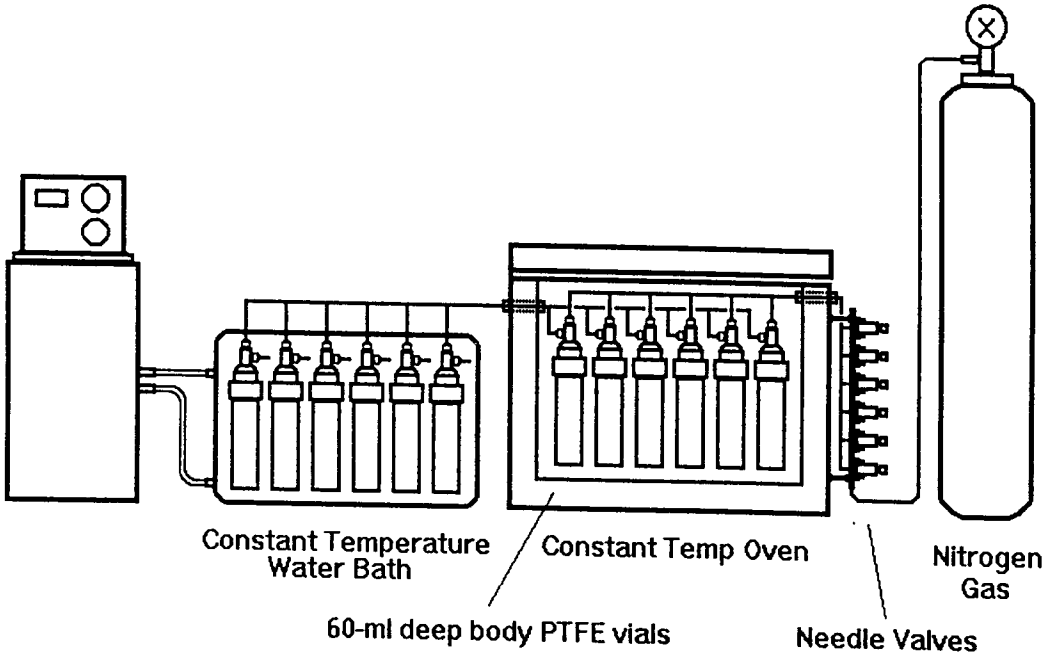

Fig. III-3. Overview of distillation isolation instrument.

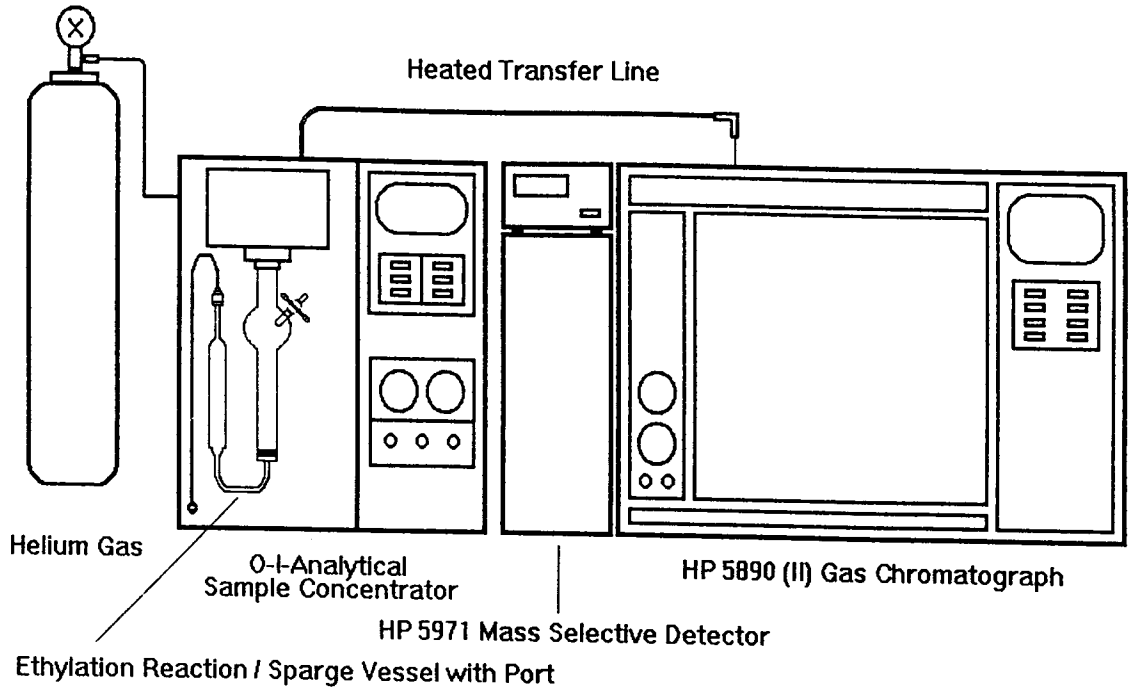

Fig. III-4. Overview of the aqueous phase ethylation, trapping, thermal desorption steps with GC/MS.

sparge vessel. The sample was buffered with 250 µl 2 M acetic acid (Ultrex^{R}, JT Baker, USA) - acetic acid, potassium salt (99.98%, Aldrich Chemical Co., USA), and then 15 µl of 1% sodium tetraethyl borate (98%, Strem Chemical Inc., USA) in 2% potassium hydroxide solution (99.99%, Aldrich Chemical Co.) was added through the stop cock.

The sample was allowed to equilibrate to reaction temperature of 25°C using a thermostated water bath core maintained by a refrigerated and circulating water bath apparatus (Haake DI G, Haakebuchler Inc., USA). The ethylation reaction resulted in the formation of ethylmethylmercury from reactive methylmercury and diethylmercury from inorganic mercury. The sparger vessel was immediately closed, and mixed using a micro spin stirrer. After the reaction period, the solution was purged for 15 min at a flow-rate of 40 ml min^{-1} with helium gas.

The purge gas outflow was passed through a Carbotrap. Columns for the pretrapping of purged organomercury species were constructed from 3.06 mm outside diameter x 2.57 mm inside diameter tubing. The columns were packed with ~200 mg of 20/40 mesh Carbotrap (Carbopack b, Supelco), held in place with silanized glass wool plugs.

Sample was desorbed from the column at 170°C for 1 min with the approximate 12-14 ml min^{-1} flow rate through transfer line of helium gas and injected port of GC (Hewlett Packard

5890) / MS (Hewlett Packard 5971) (Table III-1). The temperature of transfer line was 145°C and that of injection port of GC was 65°C. At the same time oven temperature was kept at 0°C for 1.20 min. Oven was cooled using "cryo-blast" option presented on the GC/MS. Operating conditions for the gas chromatograph and mass selective detector were reported in table III-2.

Methylmercury standard solution was made of methylmercury chloride (99%, Strem Chemical Co., USA) with HPLC grade isopropanol.

RESULTS

Black Butte Mine

The mercury concentration around the kiln area (Fig. III-5, sites 2, 3, and 4) was higher than near a portal to Black Butte Mine (Fig. III-5, site 1). Average mercury concentration around kiln area was 254 µg/g (223-271 µg/g) and decreased gradually to the tailing dump. Mercury was detected in the mine dump area soil (Fig. III-5, sites 5 and 6) at around 11 µg/g (3-19 µg/g).

The mercury concentration in sediments from the Dennis Creek (Fig. III-5, site 7), which is below the mine dump, was

Table III-1. Operation settings of purge and trap sample concentrator.

Purge time	15.00 min
Desorb time	1.00 min
Desorb temperature	170.00°C
Bake time	10.00 min
Bake temperature	200.00°C
X-line temperature	145.00°C
Purge flow rate	40 ml min^{-1}
X-line flow rate	12-14 ml min^{-1}

Table III-2. Operation settings of HP 5890 Gas Chromatograph and HP 5971 Mass Selective Detector.

*Gas chromatograph

Inlet temperature	Initially 50-75°C ramp to 200°C
Purge Valve	On
Septum purge flow	0 ml min^{-1}
Column flow	0.8-1.0 ml min^{-1}
Cryo blast	On
Oven temperature	Initially 0°C ramp to 100°C
	followed by a ramp to 200°C

* Mass Selective Detector

Mode	Scan or selective ion
	monitoring (SIM)
Mode of ionization	Electron impact (70eV)
settings	Mid-mass tune

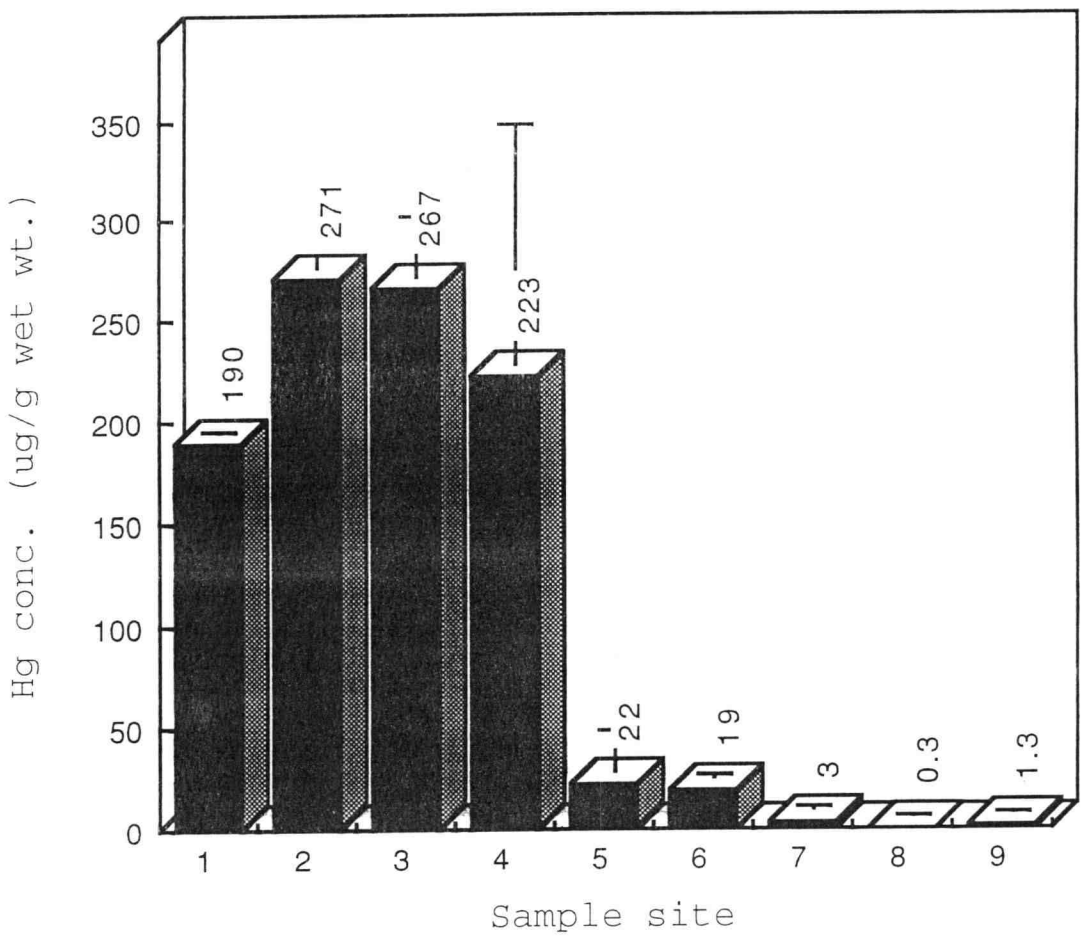

Fig. III-5. Mercury concentrations in soil and sediment samples from the Black Butte Mine area.

ten times higher that from the Garoutte Creek which is not in the same watershed as the mine (Fig. III-5, Site 8).

The confluence of the two creeks forms the Coast Fork of the Willamette river (Fig. III-5, site 9) and mercury contents in site 9 was only 43% of the mercury content in the Dennis Creek sediment.

Sulfur content was highest near a portal to Black Butte Mine (21,052 µg/g, Fig. III-6, site 1) and decreased sulfur concentration was observed from mine to creek. The sulfur concentration was associated with distance from the suspected source, Black Butte Mine. There was no significant relationship between mercury and carbon content in sediments (Fig. III-7).

Geochronology

All sediment cores consisted of fine-grained clay. The highest mercury concentrations occurred in the below 22 cm of both cores (2.25 ± 0.12 µg/g, Fig. III-8). The highest concentrations occurred at the greatest core depth (40 cm depth, 2.37 ± 0.39 µg/g). Mercury concentration was significantly increased from the surface to the bottom of both sediment samples (Fig III-9).

^{137}Cs, derived from nuclear weapons testing appeared in the environment since the 1950's and the greatest

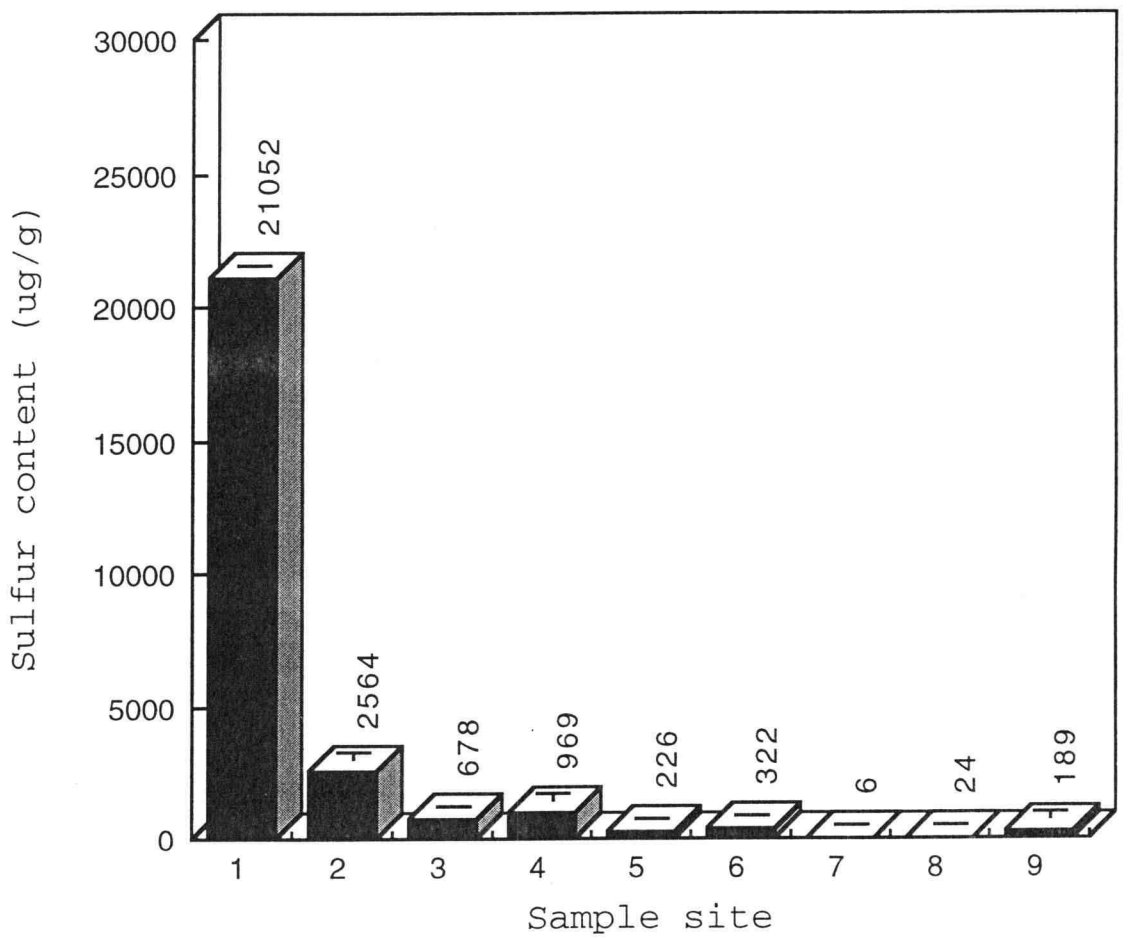

Fig. III-6. Sulfur contents in soil and sediment samples from the Black Butte Mine area.

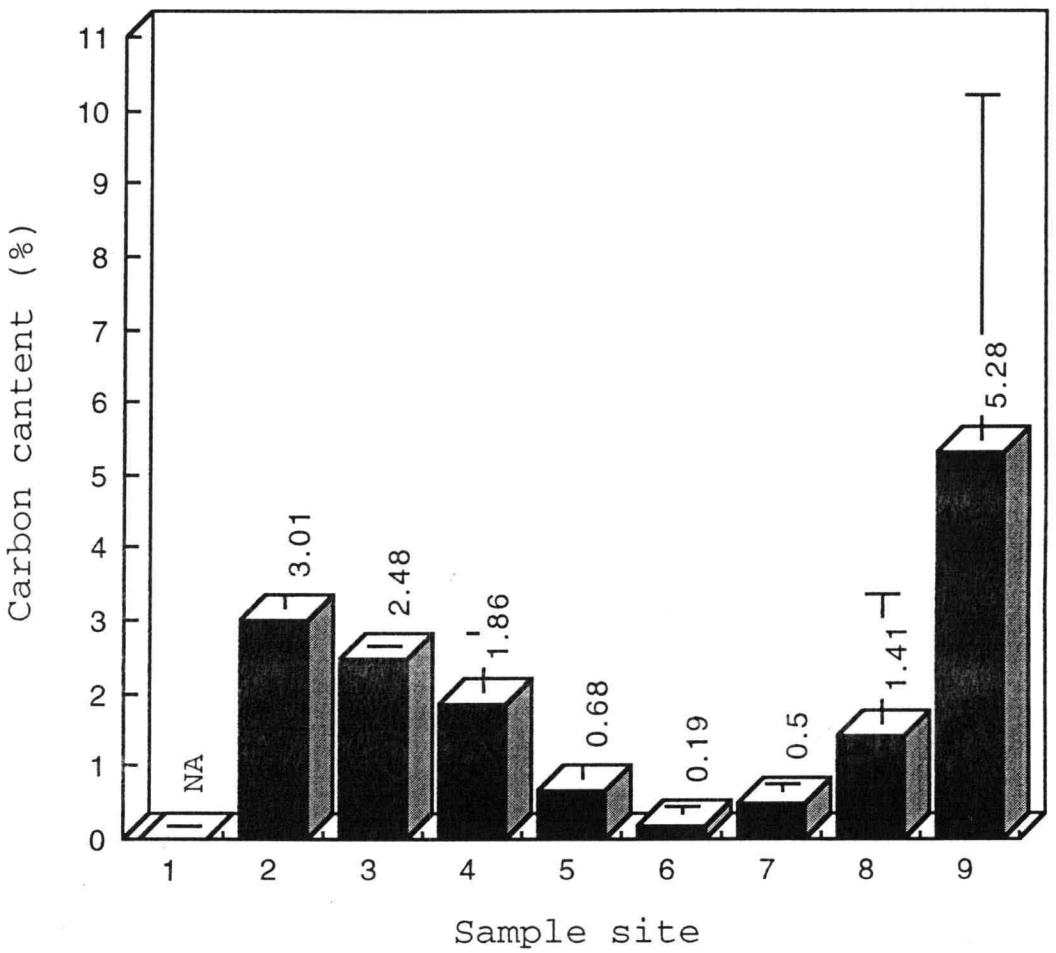

Fig. III-7. Carbon contents in soil and sediment samples from the Black Butte Mine area.

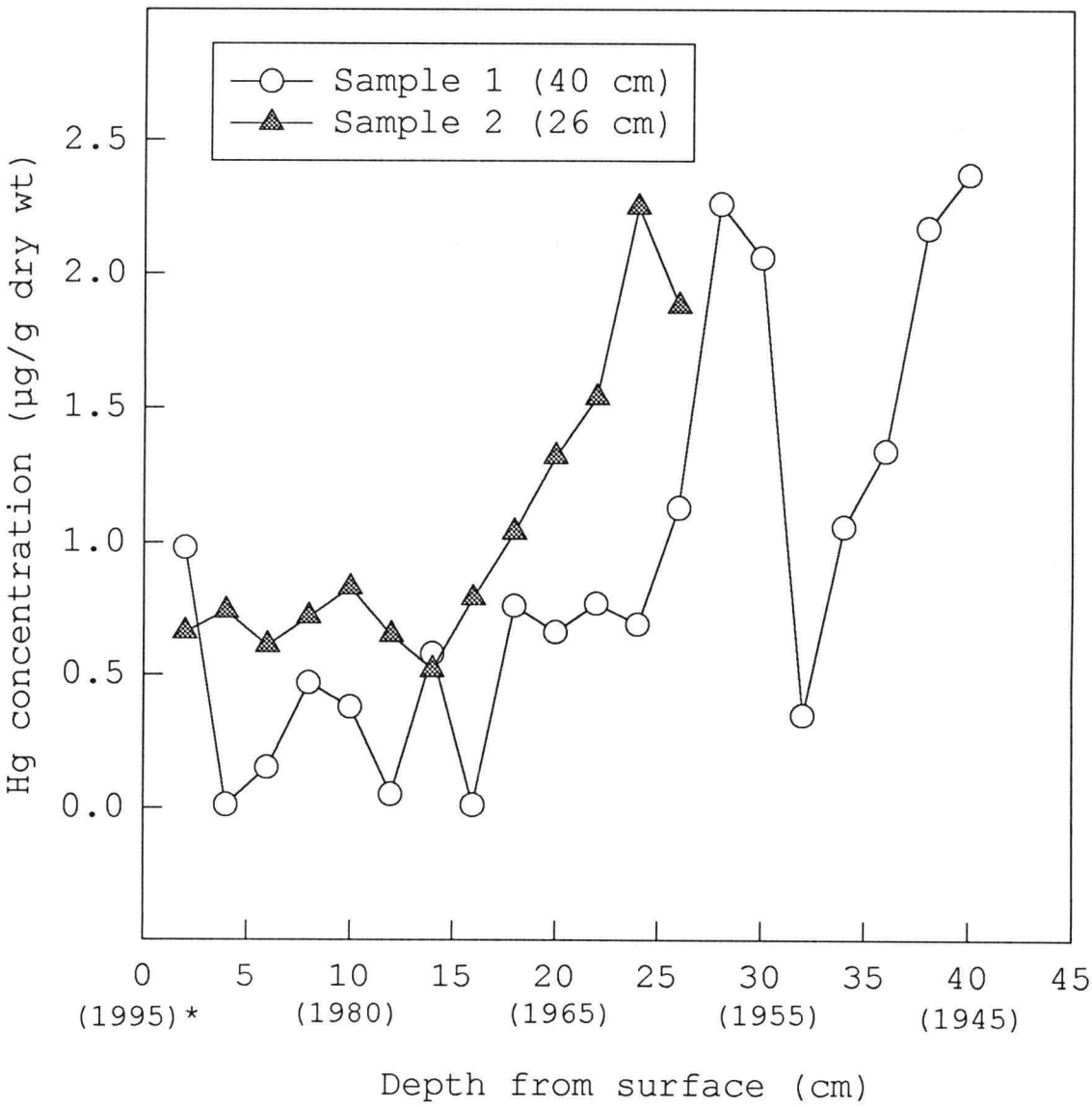

Fig. III-8. Mercury concentration in sediment from Cottage Grove Reservoir. *Parentheses show the probable year of the sediment.

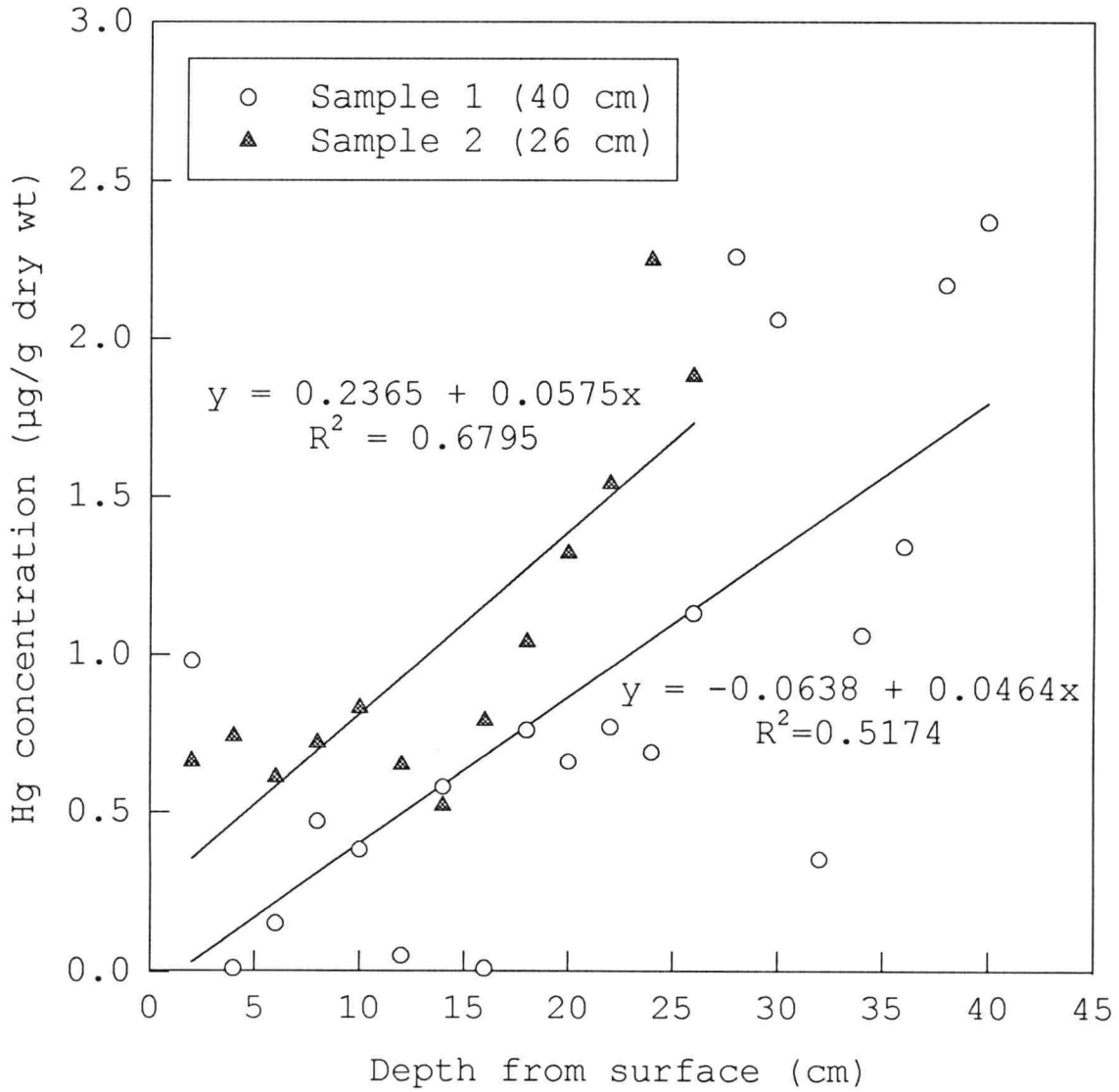

Fig. III-9. Relationship of total mercury concentration to depth from surface.

concentration in sediments corresponds to the year 1964 (Livingston & Bowen, 1979). All strata of both core samples were analyzed for ^{137}Cs and without detection of ^{137}Cs. Due to absence of adequate sediment core dating, we assumed the age of sediment was related to mercury production in Black Butte Mine (Fig. III-9).

Approximately 86% of mercury was produced by Black Butte Mine before 1942, when Cottage Grove dam was completed. From the early 1940's to the 1966, mercury production was rapidly reduced (Fig. III-10). If we assumed the bottom of the 40 cm sediment core was accumulated since the early 1940's, the sedimentation rate was estimated as 0.8 cm yr^{-1}. Percent volatile solid was significantly declined from the top to the bottom in both sediment cores (Fig. III-11).

Trophic transfer

Brown bullhead, a top predator, contained higher mercury concentration (0.49 ± 0.17 µg/g) than other species examined (Fig. III-12). Relatively high mercury concentrations were found in benthic invertebrates, Chironomus (blood worm) and Helisoma (snail), compared to two life stages of an amphibian. Mercury concentrations in blood worms and fresh water snails were 148 ± 11 ng/g and 198 ± 9 ng/g respectively.

There was no mercury detected in zooplankton.

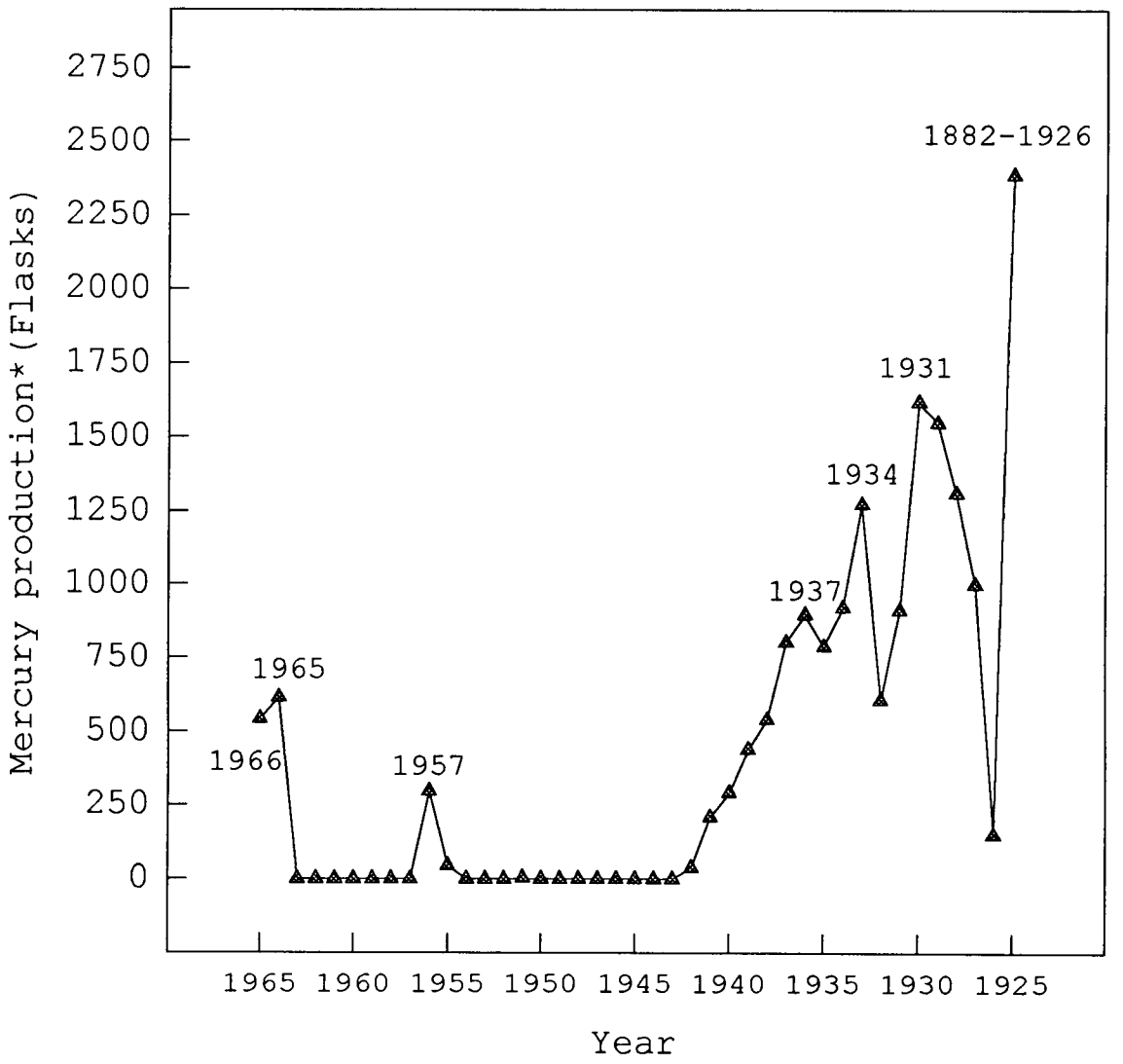

Fig. III-10. Past mercury production in Black Butte Mine. Total mercury production was 18,156 flasks. Flask is a unit of weight for mercury equal to 76 pounds. *: compiled from Brooks (1971).

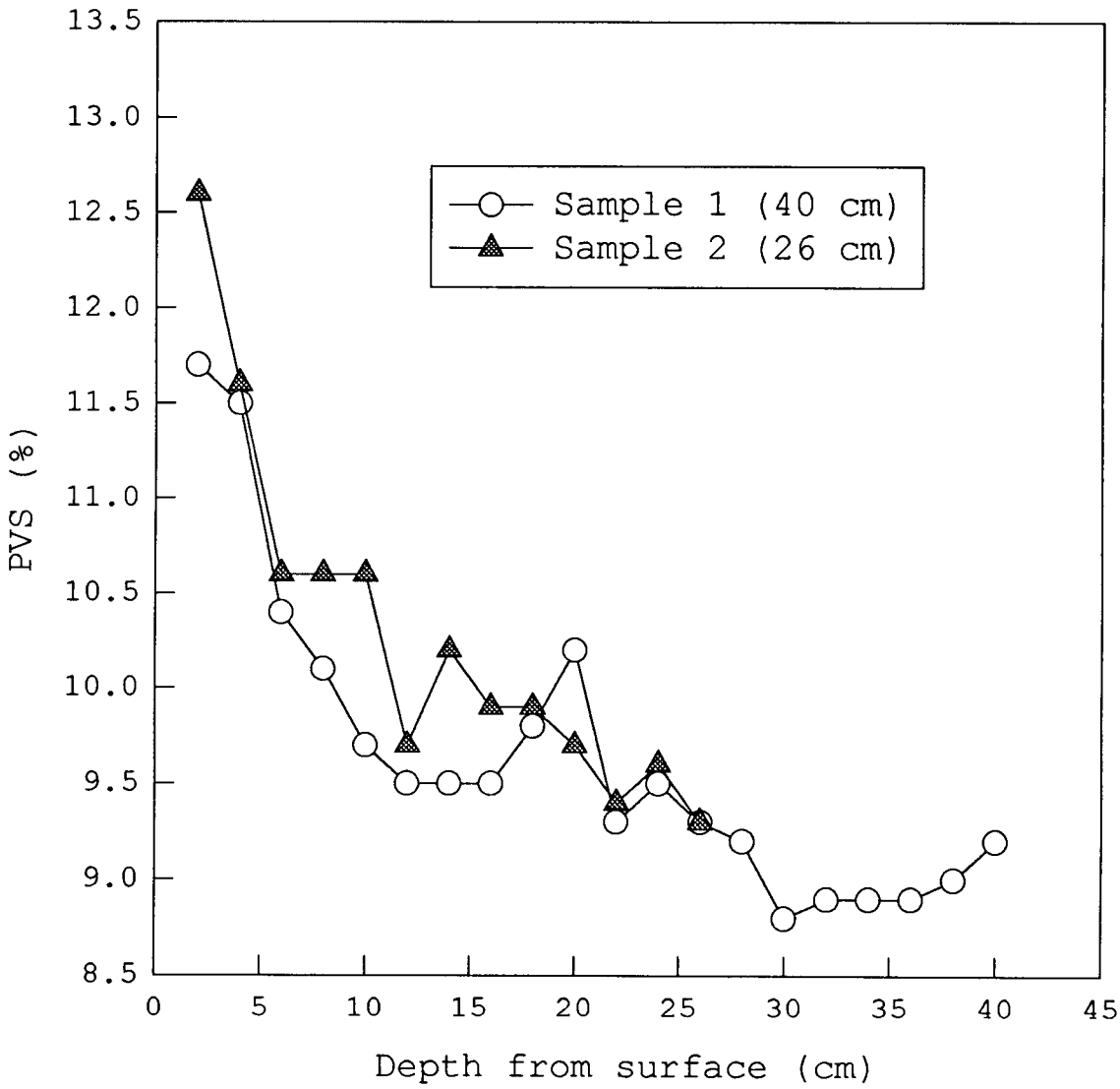

Fig. III-11. Percent volatile solids in sediment from Cottage Grove Reservoir.

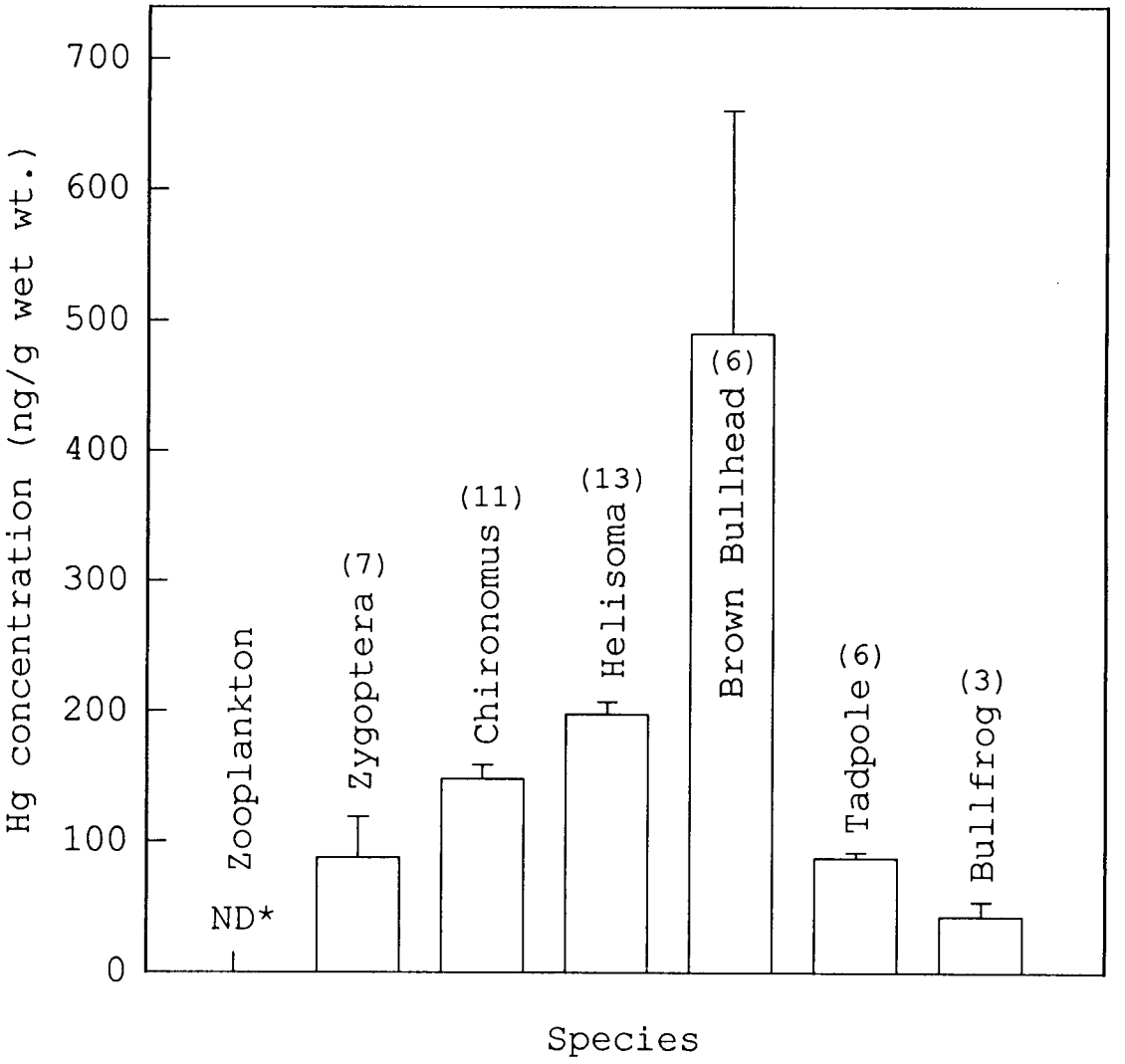

Fig. III-12. Total mercury concentration in different trophic level organisms from Cottage Grove Reservoir. *ND: No Detection at <10 ng/g wet weight. Parentheses show the number of each species.

Methylmercury in pore water.

Isolation of methylmercury from sediments by distillation, followed by aqueous phase ethylation, precollection on a carbotrap, and thermal desorption to GC/MS detection was investigated. Distillation gave consistent and high recoveries (~90%). Detection limits as low as 1 pg MeHg g^{-1} as mercury for 40 ml sample were obtained.

Methylmercury in pore water was higher in sediment samples collected from deep areas close to the dam (23.27-35.32 pg/ml, Fig. III-13, sites 1 and 2) than that in shallow areas (3.53-4.46 pg/ml, sites 3 and 4). Approximately 0.002 ± 0.0015% of total mercury in pore water was methylmercury forms in Cottage Grove sediments.

DISCUSSION

Black Butte Mine

Our results showed that mercury was elevated in a tailing dump, and in soils in the vicinity of kiln (mostly surrounding former sites of cinnabar roasting apparatus and mercury vapor condensers). This was similar to the findings of others (Bacci et al., 1994 ; Ferrara et al., 1991).

Several studies have examined the mercury concentration in the soil, which generally decreased rapidly with distance

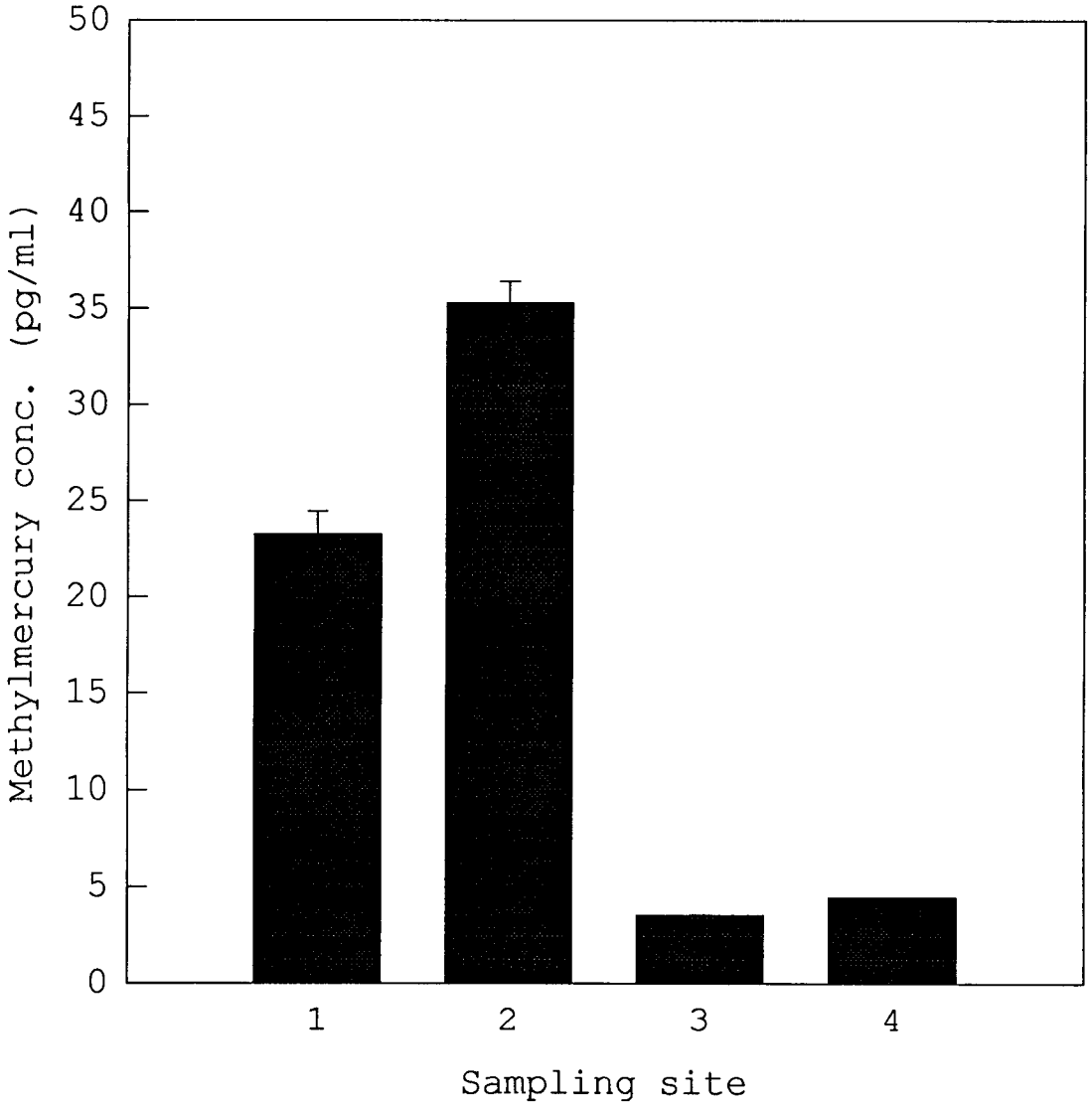

Fig. III-13. Mercury concentration in pore water of sediment.

from the mercury source. Malm et al. (1991) found mercury concentration of 30 - 340 µg/kg dry wt in forest soils from the Madeira River in Brazil and mercury concentration were higher (420-9900 µg/kg dry wt) in soils close to amalgam burning areas. Significant ($p=0.01$) elevations in soil mercury in British Columbia were observed at sites closely associated with the mine. Thus, soil mercury concentration (14000 ng/g) at mine area was decreased up to 3200 ng/g at the 2 km east from the mine (Siegel et al., 1984).

Recent monitoring of mercury in air also show that the highest values have been measured inside the mining area and roasting plant (Edner et al., 1993 ; Bacci et al., 1994). Today, tailings containing mercury deposited back to the 1800s are still an important source of pollution in some areas in Canada (Lane et al., 1988).

This study suggested that point source mercury originating from past mining activities were deposited in Cottage Grove Reservoir. Benoit et al. (1994) studied mercury concentration in the sediment from the mercury mine tailings and mercury levels were elevated as high as 570 µg/g dry wt. Pfeiffer et al. (1993) reported that sediment mercury content ranged 0.3 to 3 µg/g in contaminated sites of the Amazon River. Furthermore, 70% of mercury from mine areas was transported 1000 km downstream to the Amazon River i.e. the

mercury concentration of some stream sediments was 150 µg/g (Nriague et al., 1992).

Differences in sediment mercury concentrations between sites (Fig. III-5, sites 7-9) was expected. However, Garoutte Creek sediment (site 8) contained higher mercury concentrations than the other creeks in the Cottage Grove Reservoir drainage (Park & Curtis, 199x). This result may be explained by condensation of mercury vapor from mine tailings or during operation of the old kiln (Pfeiffer et al., 1993).

The mercury concentrations in soils were correlated with the contents of organic carbon and sulfur (Cameron & Jonasson, 1972). Our data also showed these correlations in the soil but not in the sediment.

Under the conditions chosen, Hg° is stable in the presence of H_2S or SH^- at the lower redox limit, but at increasing redox potential, HgS will precipitate or the soluble HgS_2^{2-} will be formed. Further increase will lead to oxidation of sulphur to sulfate, the last phase to be oxidized being the extremely stable HgS.

When initially deposited, mercury in mine wastes occurred primarily as HgS, the toxicity of which is limited by its extremely low solubility (Morel & Hering, 1993). However, under oxic conditions - as exist in surficial sediments, soils, and in most surface waters - HgS can be converted to dissolved divalent mercury (Hg^{2+}), elemental mercury (Hg°), and

methylmercury (CH_3Hg^+) (Klaassen et al., 1986). These other forms are more mobile, and can be transported either in solution or atmospherically (Kim & Fitzgerald, 1988). Benoit et al. (1994) reported 50% cinnabar can be altered to more bioavailable forms within a distance of only 10-40 m from the sediment in Honda Bay.

In soils, essentially three groups of components, namely clay minerals, sesquioxides and organic materials (humus) are responsible for the retention of mercury, the relative importance of each being dependent on soil type, particle sizes, and horizon of the soil profile.

Organic matter seems to play a double role in the turnover of Hg in soils in the sense that Hg complexed by organic components will be retained in the soil as long as the conditions are such as to keep the organic matter in a flocculated and precipitated state. If, however, the conditions are changed, for example due to leaching, the organic components including complexes of Hg, may pass into solution and reprecipitate in deeper horizons or leave the profile in the drainage water, as shown by Neibla et al. (1976). Dissolved organic molecules low in metals can increase the solubility and mobility of Hg in stable inorganic compounds, particularly in an acidic environment as shown by Trost and Bisque(1972).

Similarly, humic acids have been shown to reduce mercuric Hg to the metallic form, thus making it possible for gaseous Hg° to leave the soil and be transferred to the atmosphere (Alberts et al., 1974). On the other hand, organic matter has also been shown to be an effective adsorbent for gaseous Hg°; acid forms of organic matter from coniferous vegetation generally retain the Hg more effectively than more neutral ones from grassland and deciduous vegetation (Trost & Bisque, 1972; Maclean, 1974). Thus, removal of Hg by leaching is probably more likely in acid soils whereas removal by evaporation is more likely in neutral and alkaline ones.

Geochronology

Mercury profiles in sediments have been used to evaluate the historical mercury contamination in the aquatic environment (Aston et al., 1973; Breteler et al., 1984; Klein & Goldberg, 1970; Thomas, 1970; Younget al., 1973).

Though our study was at a disadvantage of lacking ^{137}Cs detection, the determination of sedimentation rates in sediment was important to understanding of source of mercury contamination (Krom et al., 1994).

^{210}Pb and ^{137}Cs have been widely used to estimate sediment accumulation rates and to determine chronologies of chemical deposition in sediment (Breteler et al., 1984; Lavelle et al.,

1986; Orson et al., 1990). The supply of ^{210}Pb, a naturally occurring radio nuclide in the U-^{238} decay chain, to the marine environment is usually assumed to be constant over several decades (Sugai, 1990). In contrast, ^{137}Cs is a highly time-dependent, man-made radio nuclide distributed globally as a result of atmospheric testing of nuclear weapons (McLean, 1991).

We considered two hypotheses, one was that the sediment cores we collected were deposited after 1965. If that was true, the sedimentation rate would be very fast. The other hypothesis was ^{137}Cs was not detectable for another reason, possibly ^{137}Cs within the core was removed by either leaching or mass wasting due to the drawdown practices of the U. S. Army Corps of Engineer. Therefore, we assumed the sediment in Cottage Grove Reservoir was deposited since the 1940's and interpreted the history of sediment accumulation cores based on the mercury production of Black Butte Mine.

World War I-related industrial expansion likely resulted in the peak concentrations of mercury in the 1920s and mercury production gradually declined during the Great Depression in the 1930s. Since mercury production in Black Butte Mine was very active until the end of World War II, high mercury concentrations in bottom sediment perhaps originated from highly mercury contaminated soil mobilized around that mine. The most likely explanation for high mercury concentration in

cm 25-30 of core 1 was the relatively high mercury production in 1957 and by the mercury runoff from the source. After the peak at 25 cm depth, mercury concentration was gradually decreased, probably reflecting reduced mercury loading of the reservoir.

In conclusion, geochronologies of mercury concentration in sediment cores of Cottage Grove Reservoir were consistent with the mercury production of Black Butte Mine.

Trophic transfer

Uptake from food and water have been shown to be two major routes through which contaminants accumulate in aquatic organisms (Bigginger & Gloss, 1984). Mercury is an element which exhibits clear biomagnification within the aquatic and terrestrial food chains, reaching high concentrations in top consumers such as large predators, including man (Cabana et al., 1994; Wren et al., 1983). Mercury enters aquatic systems as inorganic mercury, but is converted to the more toxic methylmercury by sediment microorganisms. Most of the mercury in the food chain is methylmercury, which is bioaccumulated as it moves up through successive trophic levels (Bloom, 1992).

Biddinger and Gloss (1984) reported bioaccumulation was determined by the differences in size, age, and metabolic rate between predator and prey. The tissue concentration of mercury

appeared to be greatly influenced by association with bottom sediments. Friant (1979) reported that benthic molluscs and rooted plants accumulated metals in greater concentrations than either sediments or fish. Prosi (1979) found that benthic organisms had greater metal concentrations than other biota, including fish.

Our data also showed benthic organism such as Chironomid and Helisoma had higher mercury concentrations than other invertebrates and amphibians. Chironomid larvae were chiefly herbivorous and sediment feeding was most common in deep water. Helisoma was herbivorous, primarily filter feeders and benthic detrital feeders. Many organisms considered low on the food chain, such as herbivorous and detrital feeders, were largely benthic dweller and so directly subjected to sediment influence (Pennak, 1978).

Brown bullhead feed on the bottom, primarily at night. The young feed on zooplankton and midge larvae. Larger fish feed on midges, may flies, worms and crustaceans. Adults feed on many food items, such as insect larvae, molluscs, worms, terrestrial insects, other aquatic plants, and fish. Midges form a substantial part of the brown bullhead diet (Wydoski, 1979). Zygoptera nymphs (damsel fly) feed other aquatic insects, annelids, and small Crustacea and mollusks (Pennak, 1978).

We considered three trophic levels in Cottage Grove Reservoir: omnivores such as brown bullhead; invertebrate planktivores such as Zygoptera nymph, and benthic organisms such as Chironomus and Helisoma; zooplankton and small crustacean. Our findings indicated mercury accumulated in higher trophic levels within these food web and aquatic organisms in contact with sediment accumulated high level of mercury relative to other species.

Methylmercury

A large number of methods for the determination of methylmercury compounds in biological and sediment samples have been published. Most of them are based on solvent extraction and gas chromatographic determination (Horvat et al., 1993). Recently two isolation techniques were developed. One was based on extraction of methylmercury into methylene chloride and back extraction into water by solvent extraction. The other was based on the distillation of methylmercury compounds. Horvat et al(1993) reported distillation was more consistent and had lower detection limits with high recoveries than solvent extraction method. Our results with distillation method also achieved better detection limits than other classical isolation methods.

As previously mentioned, virtually all (>95%) of the mercury present in fish is methylmercury (Bloom, 1992). Because fish tissues and organs do not methylate mercury, inorganic mercury entering aquatic ecosystems must be converted to methylmercury prior to accumulation through the food web (Pennacchioni et al., 1976; Huckabee et al., 1978). Inorganic mercury can be methylated abiotically (Nagase et al., 1984; Lee et al., 1985) or biotically (Jensen & Jernelov, 1969). Abiotic methylation is more important in lake water and in the streams of the lake watershed (Lee et al, 1985). However, in sediment biological methylation may play a more important role (Berman & Bartha, 1986; Korthals & Winfrey, 1987). The efficiency of methylation is dependent on the metabolic activity of the methylating organisms and the total concentration and biochemical availability of inorganic mercury (Beijer & Jernelov, 1979).

Lindberg and Harris (1974) found high mercury concentrations in pore water of sediment and suggested that mercury may exist as organic and polysulfide complexes in pore water. Usually, methylmercury in sediments does not exceed 1.5% of the total mercury present. Our results were lower than the values reported by Lindberg and Harris (1974) for the pore waters of Mobile bay (Alabama) and the Florida Everglades and those obtained by Bothner et al. (1980) in their study of the highly contaminated Bellingham Bay (Washington). The

interpretation of methylmercury concentration in pore water will be more precise compared to the mercury concentration of water.

The results of this study demonstrated Black Butte Mine is to be believed as the main mercury source of Cottage Grove Reservoir. A significant portion of mercury deposited in the mine area is likely transported to the reservoir and biotransformed in the pore water to become more available form for mercury bioaccumulation through the food web. In conclusion, continuing mercury transportation from the point source has created a management problem in Cottage Grove Reservoir.

IV. Conclusions

In this study, we characterized a regulatory problem in Cottage Grove Reservoir. By the way, nonpoint mercury pollution of Dorena Reservoir, which is of similar age and volume in the same ecoregion with Cottage Grove Reservoir, was not of significant magnitude to create a regulatory problem for fish consumption. Sediment mercury concentration in tributary streams indicated point source mercury pollution in Cottage Grove Reservoir but not in Dorena Reservoir. Mercury concentration gradient from the suspected point source, Black Butte Mine, to the Cottage Grove Reservoir supported a point source pollution hypothesis. Geochronological mercury distribution in sediment cores also indicated termination of mining activities of Black Butte Mine reduced mercury loading of Cottage Grove Reservoir. Methylmercury contents which was determined by a highly sensitive GC/MS method showed mercury methylation was much greater in deep than in shallow areas of Cottage Grove Reservoir. Mercury analysis of organisms at different positions of the Cottage Grove Reservoir food web confirmed trophic transfer of mercury in this system.

Though Cottage Grove Reservoir is impacted by a point source from which mercury transfer is slowly declining over time, mercury concentration in deep reservoir sediments

contain significant mercury burdens. Therefore, any management options and decisions must consider the potential effects of continued mercury contamination to Cottage Grove Reservoir and its organisms for protection of humans and wildlife which depend on fish as a food resource.

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