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Mercury Distribution in Sediments and Bioaccumulation by Fish in Two Oregon Reservoirs: Point-Source and Nonpoint-Source Impacted Systems

J.-G. Park,¹ L. R. Curtis²

¹Toxicology Program, Oregon State University, Corvallis, Oregon 97331, USA

²Department of Environmental Health, East Tennessee State University, P.O. Box 70682, Johnson City, Tennessee 37614, USA

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Abstract. Mercury pollution was compared in two Oregon reservoirs of similar size and age, located within the same ecoregion. Cottage Grove Reservoir was distinguished by a history of mercury mining and processing within its watershed, while Dorena Reservoir was not. Mercury concentrations in sediments of the reservoirs, tributary streams, and three species of fish were measured. Sediment mercury concentrations in the main tributary of Cottage Grove Reservoir, which drains the subbasin where past mercury mining occurred, was tenfold higher than mercury in sediments from other reservoir tributaries. There were no significant differences between sediment mercury concentrations in the tributaries of Dorena Reservoir. The average mercury concentration in the basin sediment of Cottage Grove Reservoir ($0.67 \pm 0.05 \mu\text{g/g}$ dry wt) was higher than for Dorena Reservoir ($0.12 \pm 0.01 \mu\text{g/g}$ dry wt). At Cottage Grove Reservoir, maximum mercury concentrations were near or exceeded $1 \mu\text{g/g}$ wet wt for largemouth bass (*Micropterus salmonides*) and bluegill (*Lepomis macrochirus*) epaxial muscle. Muscle mercury concentrations in largemouth bass and crappie (*Pomoxis nigromaculatus*) from Cottage Grove Reservoir were significantly higher than from the same species from Dorena Reservoir. Numbers of bluegill of the same age available from both reservoirs were too small for statistical comparisons. Mercury concentrations in largemouth bass muscle fluctuated annually in both reservoirs. Fish ages were consistently positively correlated with muscle mercury concentrations in only the point-source-impacted reservoir. These results indicated that a point source, Black Butte Mine, contributed amounts of mercury greatly in excess of mobilization from natural deposits, atmospheric deposition, and small-scale uses of the metal as an amalgamating agent in gold mining.

enter the environment from ore wastes and via atmospheric deposition of mercury vapor that escapes condensers during roasting of cinnabar (Bargagli, 1990). In areas rich in geological mercury deposits, questions may arise as to whether fish mercury contamination is "natural" or due to human activities. A 20-mile belt of scattered mercury ore deposits extends from Lane, Douglas, and Jackson counties in the Southern Coast Range to the California border in western Oregon. Two abandoned mines, Black Butte and Bonanza, account for about half of Oregon's historical mercury production (Orr *et al.* 1992). The abandoned site of Black Butte Mine is located 15 miles south of Cottage Grove Reservoir, within its drainage basin (Brooks 1971). Total cumulative production of this mine exceeds 635,000 kg of mercury (Brooks 1971).

In addition to influences of point-source pollution, mercury-contaminated fish occur in lakes with no point source of mercury. This study compares mercury distribution in sediments and bioaccumulation by fish in two Oregon reservoirs: one with and one without a mercury point source. Mercury pollution from the abandoned Black Butte mine likely affects Cottage Grove Reservoir. There are no mercury mines in the Dorena Reservoir basin. Mercury contamination in this system is attributable to natural weathering of rock, atmospheric deposition, and small-scale local uses of mercury as an amalgamating agent in gold extraction from glacial deposits. Both reservoirs are located in same ecoregion (Figure 1). Drainage basin and limnological characteristics of these reservoirs are similar (Johnson *et al.* 1985) and representative of reservoirs of similar size within the ecoregion. For example, some respective water chemistry parameters for Cottage Grove and Dorena Reservoirs are: pH 7.7 and 7.9; alkalinity 21 and 11 mg/L; conductivity 63 and 49 μmhos ; and phosphorus 0.002 and 0.003 mg/L (Johnson *et al.* 1985). Establishment of both reservoirs dates to the 1940s as part of a U.S. Army Corps of Engineers multipurpose water project.

Bioaccumulation of methylmercury by fish presents a significant environmental health risk in many areas of the world. Mobilization of mercury by human activities frequently underlies contamination problems. Mercury releases from mining

Materials and Methods

Field Sampling

Duplicate sediment samples were collected from 10 sites at each reservoir in March 1994 (Figures 2 and 3) with an Ekman® dredge.

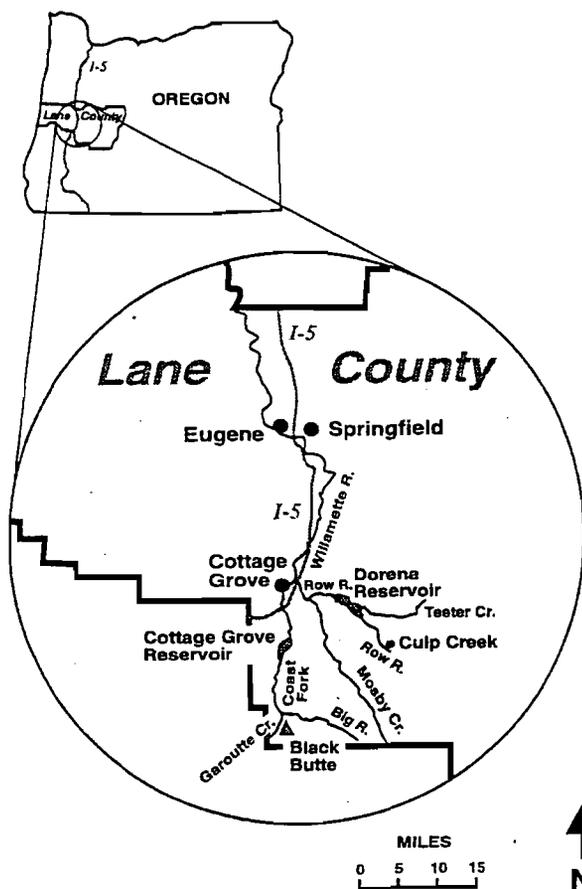


Fig. 1. Locations of Cottage Grove and Dorena Reservoirs

Sediment samples were placed in acid-pretreated I-Chem[®] jars, placed on ice, and stored frozen in the laboratory until subsequent analysis.

Three species of fish, largemouth bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*), and crappie (*Pomoxis nigromaculatus*), were collected at four times using electroshock at Cottage Grove Reservoir (June 1993, 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 filleted and frozen in the laboratory.

Total Sediment Mercury

Sediment texture was determined with the hydrometer method (Bouyoucos 1962). Sediment samples were analyzed for mercury as outlined in Allen-Gil *et al.* (1995). 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, and 5 ml deionized H₂O and 5 ml aqua regia (3 vol. conc. HCl to 1 vol. conc. HNO₃) was added. Samples were placed in a 95°C water bath. After 2 min, 50 ml of deionized H₂O and 50 ml of 5% KMnO₄ were added to each sample. Samples were digested in the water bath for 30 min, and then cooled to room temperature.

Fifteen minutes prior to analysis, the samples were treated with 50 ml of deionized H₂O and 8 ml of 24% NaCl-hydroxylamine 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 0.5 N SnCl₂ in 0.5 N H₂SO₄ 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 (Recorder Company, San Marcos, TX).

Sediment mercury concentrations were determined for samples from each site in duplicate. Standard curves were prepared from HgCl₂ in HNO₃ (0.01–1.0 ppm). Method accuracy was confirmed by comparison with standard materials purchased from the National Institute of Standards and Technology. All the recoveries were 90% or greater. Sediment dry weight was determined by drying at 55°C to stable weight. Organic matter, as percent volatile solids (PVS) was determined by combustion at 550°C for 5 h.

Total Mercury in Fish

Mercury concentrations in fish epaxial muscle was determined using hot-base digestion followed by cold vapor atomic absorption (Magos *et al.* 1972). Muscle samples (1–2 g each) were placed in screw-top test tubes, to which 2 ml 10 N NaOH was added. Samples were placed in a heat block (95°C) for 30 min and then cooled to room temperature. Total mercury was determined by placing 1-ml subsamples in reaction flasks, along with 3 ml 1% cysteine, 4 drops octanol, 1 ml 50% SnCl₂ (w/v), and 10% CdCl₂ (w/v) in 4 N HCl. The flask opening was then covered with a septum, through which 4 ml 10 N NaOH was injected by syringe. After 30 s, nitrogen gas was supplied at 1.5 l/min. The recorder was set at 5 mV.

Standards were prepared as mercury in HNO₃ (0.01–1.0 ppm), prepared from a commercially available standard (Johnson and Mathey, Seabrook, NH). The blank values for the reagents from one analysis ranged between 5 ng and 7.5 ng. Duplicated analyses of fish muscle were within 10% of one another, or repeated until this standard was reached. Fish ages were estimated by scale analysis (Jearld 1983).

Statistical Analysis

Means and standard errors of the mean (SEM) were calculated from duplicated mercury analyses for two sediment samples from each site. The mean mercury concentrations for duplicated muscle analyses from each individual fish were grouped by species and age. Student's "t" test was used for comparison of two means. One-way analysis of variance (ANOVA) assessed whether there were significant differences between groups in data sets with three or more means. Two-way ANOVA assessed differences between muscle mercury concentrations influenced by fish age and reservoir for largemouth bass. The relationship between age and epaxial muscle mercury concentration in largemouth bass was examined by simple linear regression.

Results

Sediment Mercury

Sediment mercury concentrations averaged 0.83 ± 0.14 µg/g at the confluence of Cottage Grove Reservoir and the Coast Fork of the Willamette River, 10 times higher than sediments from other reservoir tributaries (Figure 2). This tributary drains the subbasin of the abandoned mercury mine. The average mercury concentration within the Cottage Grove Reservoir basin was

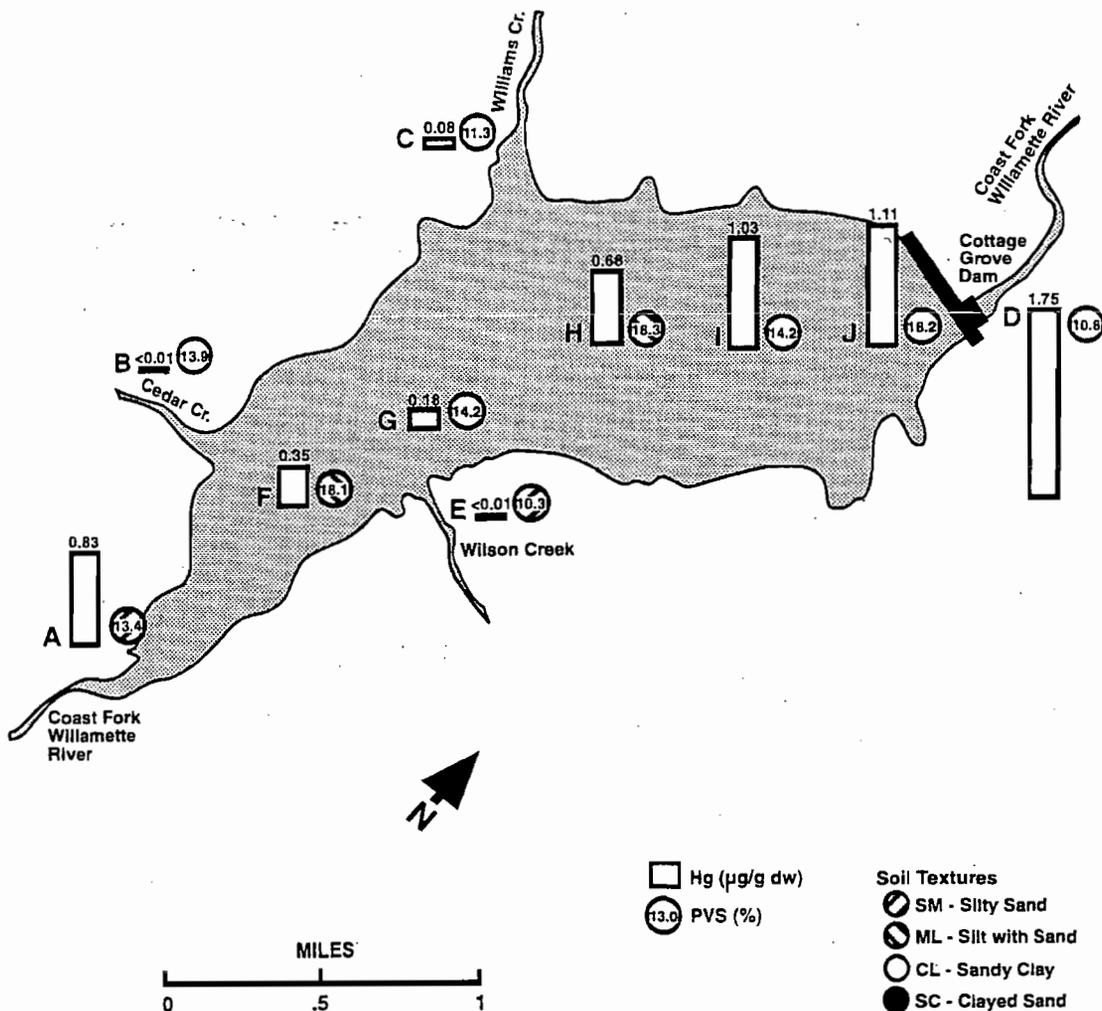


Fig. 2. Mercury and percent volatile solids in sediment of Cottage Grove Reservoir and its tributaries. Two samples were collected at each sample site and each sample was analyzed in duplicate

$0.67 \pm 0.41 \mu\text{g/g}$. Mercury contamination appeared elevated in the deepest areas of the reservoir (Figure 2, sites H, I, and J). This probably reflected the active deposition of particulate mercury. The highest mercury concentration ($1.75 \pm 0.1 \mu\text{g/g}$) was downstream of the dam, more than twice the 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 $0.08 \pm 0.04 \mu\text{g/g}$ (Figure 3). The average sediment mercury concentration within the Dorena Reservoir basin was $0.18 \pm 0.05 \mu\text{g/g}$. The mercury concentration of sediment downstream of the dam was within the range measured in the reservoir basin (Figure 3).

Sediments from three of five sampling sites in the Cottage Grove Reservoir basin were classified as sandy clay while the other two were silt with sand (Figure 2). Sediments from two of four Dorena reservoir sampling sites were silt with sand, one was silty sand, and the other was sandy clay (Figure 3). The mean PVS in Cottage Grove Reservoir basin sediments

($16.6 \pm 2.2\%$) was higher than that for Dorena ($11.1 \pm 1.7\%$). The PVS values for individual sediment sampling sites were not correlated with mercury concentration.

Mercury in Fish

Epaxial muscle of three fish species (largemouth bass, bluegill, and crappie) from each reservoir were analyzed for total mercury content. Maximum mercury concentrations were near or exceeded the U.S. Food and Drug Administration (FDA) human consumption limit of $1 \mu\text{g/g}$ wet wt for larger and older largemouth bass and bluegill from the Cottage Grove Reservoir (Figure 4). Mercury concentrations in fish from the Dorena Reservoir were about one-third those of fish from the Cottage Grove Reservoir. No fish species from Dorena Reservoir exceeded the FDA human consumption limit for mercury (Figure 5).

There was a trend for increased mercury concentrations in fish muscle with age when data for all Cottage Grove Reservoir

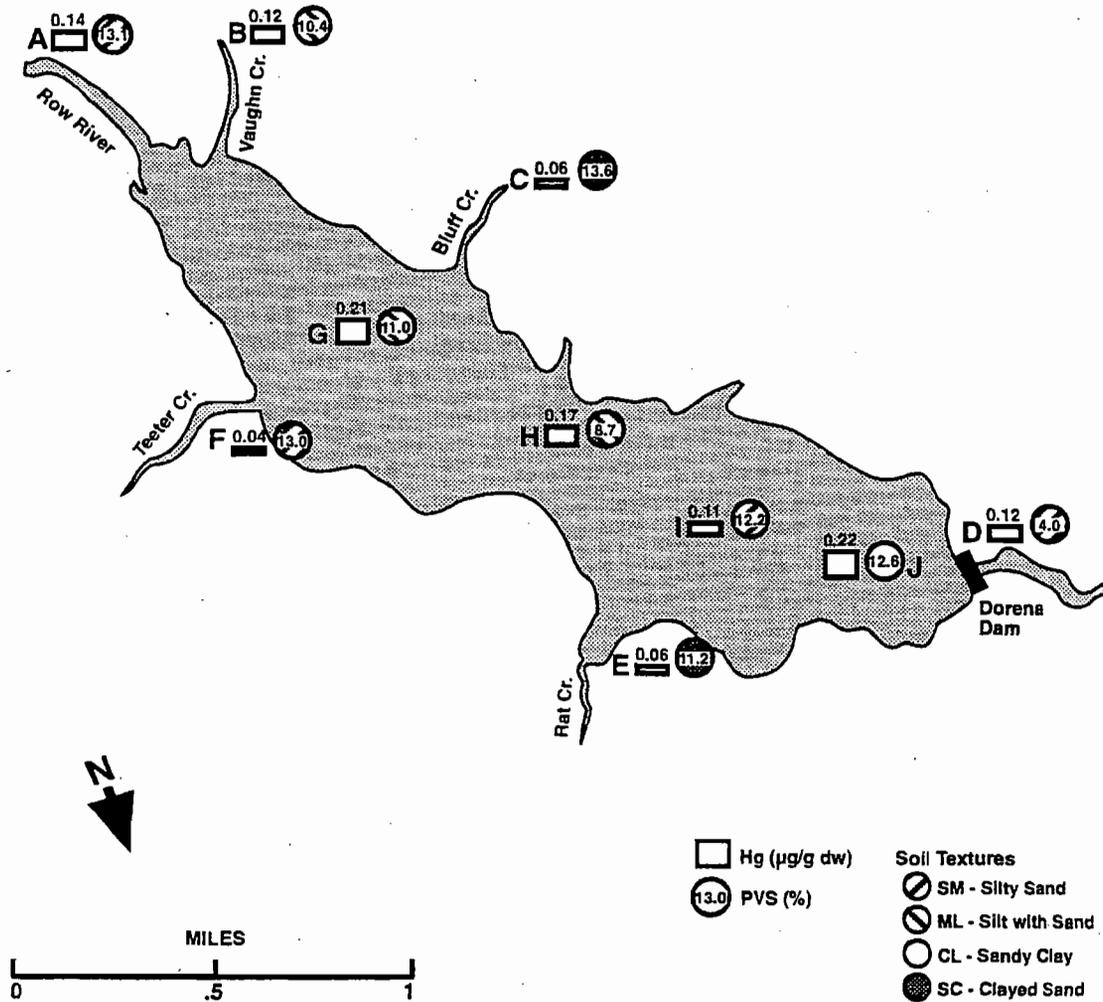


Fig. 3. Mercury and percent volatile solids in sediment of Dorena Reservoir and its tributaries. Two samples were collected at each sample site and each sample was analyzed in duplicate

sampling dates were pooled (Figure 4). The trend was not evident for species from Dorena Reservoir. There were clear differences in largemouth bass muscle mercury concentrations in each reservoir between sampling times (Figures 6 and 7). Two-way ANOVA compared epaxial muscle mercury concentrations of all largemouth bass from Cottage Grove and Dorena Reservoirs grouped by age. The muscle mercury concentrations of largemouth bass from Cottage Grove were significantly higher than for those from Dorena Reservoir. There were a sufficient number of 2-year-old crappie from the two reservoirs for a statistical comparison. Muscle mercury concentration for Cottage Grove crappie was higher than for Dorena Reservoir. There were strong, positive, linear correlations between age and muscle mercury concentrations for Cottage Grove largemouth bass when sampling dates were analyzed independently (Figure 6). This correlation was not consistently observed for largemouth bass from Dorena Reservoir (Figure 7). Sample sizes for other fish species were too small for regression analyses of fish age and muscle mercury concentration or other statistical comparisons.

Discussion

Sediment Mercury

Cottage Grove and Dorena Reservoirs were selected for comparison of mercury point- and nonpoint-source-influenced aquatic systems in the same ecoregion (Figure 1). With the exception of the Coast Fork of the Willamette River (Figure 2), sediment mercury concentrations were similar in tributaries for the two reservoirs. This indicated that the main mercury input for Cottage Grove Reservoir was Black Butte Mine (Figure 2). There was no evidence of point-source mercury contamination of Dorena Reservoir (Figure 3). Allen-Gil *et al.* (1995) reported that the total average mercury concentration in the sediments of Cottage Grove Reservoir was $0.84 \pm 0.2 \mu\text{g/g}$, within the range of mercury concentrations reported here (Figure 3, 0.18 to $1.11 \mu\text{g/g}$). This study detected elevated mercury concentrations in the deep areas of the Cottage Grove Reservoir (Figure 2), which probably reflected the active deposition of particulate mercury

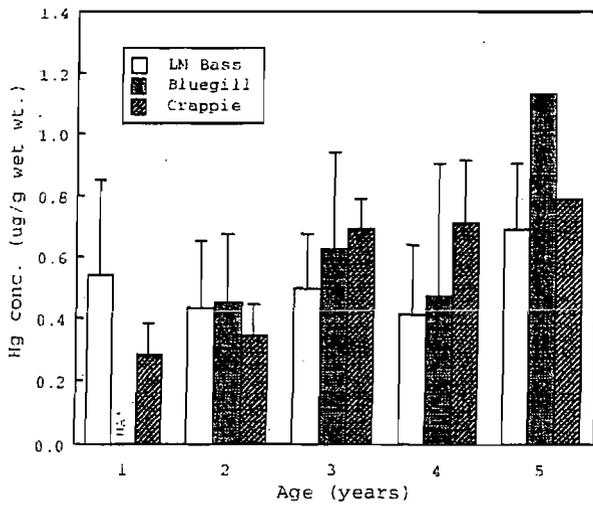


Fig. 4. Mercury concentration in fish tissues by fish age for the three species from the Cottage Grove Reservoir. Results are mean \pm SEM for all fish collected from June 1993 until November 1995. Total numbers of fish of respective ages (1, 2, 3, 4, and 5 years) were: largemouth bass (2, 5, 6, 3, 4), bluegill sunfish (0, 5, 3, 2, 1), and black crappie (4, 3, 2, 2, 2)

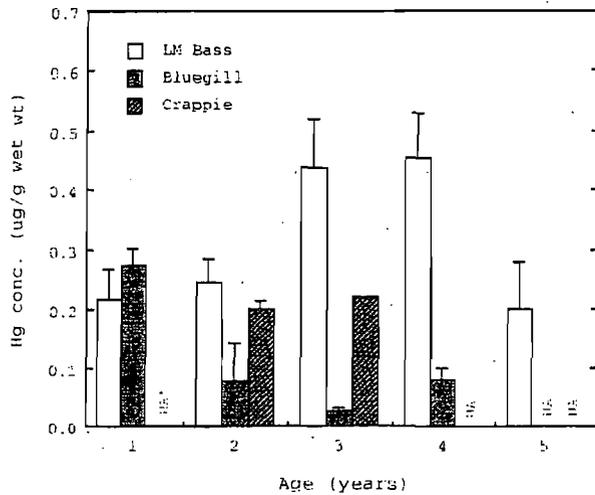


Fig. 5. Mercury concentration in fish tissues by fish age for the three species from the Dorena Reservoir. Results are mean \pm SEM for all fish collected from August 1993 until September 1994. Total numbers of fish of respective ages (1, 2, 3, 4, and 5 years) were: largemouth bass (4, 2, 4, 2, 2), bluegill sunfish (3, 1, 0, 0, 0), and black crappie (0, 7, 1, 0, 0)

and cinnabar. Reservoir management practices, especially reduction of water level during drawdown, perhaps influenced sediment mercury concentrations. Shallow areas were potentially exposed to air during low water-level periods. Physical and chemical loss of mercury from dried sediments perhaps contributed to differences between deep and shallow areas. High mercury concentrations in sediments downstream from the dam was likely explained by reservoir sediment mobilization during drawdown and major storm events.

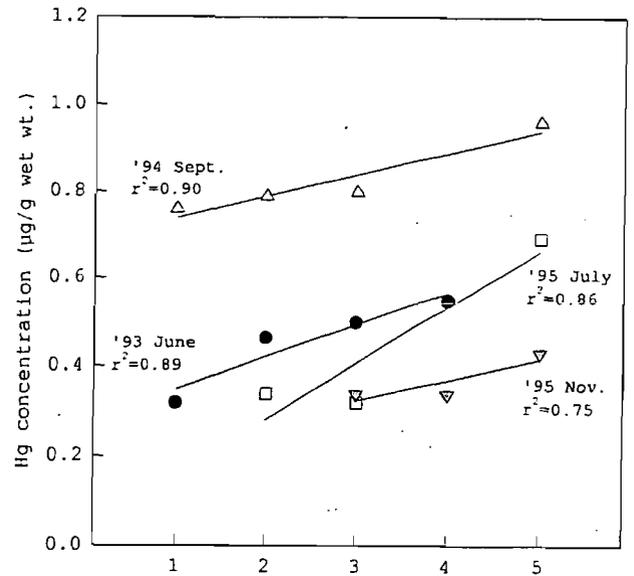


Fig. 6. Annual and seasonal variation of mercury concentration in largemouth bass from Cottage Grove Reservoir. Each symbol is the concentration for one fish (n = 1) with the following exceptions: age 2 years for June 1993 and July 1995 (n = 2), age 3 years for June 1993 (n = 3), age 4 years for June 1993 (n = 4), age 4 years for November 1995 (n = 2), and age 5 years for July 1995 (n = 2).

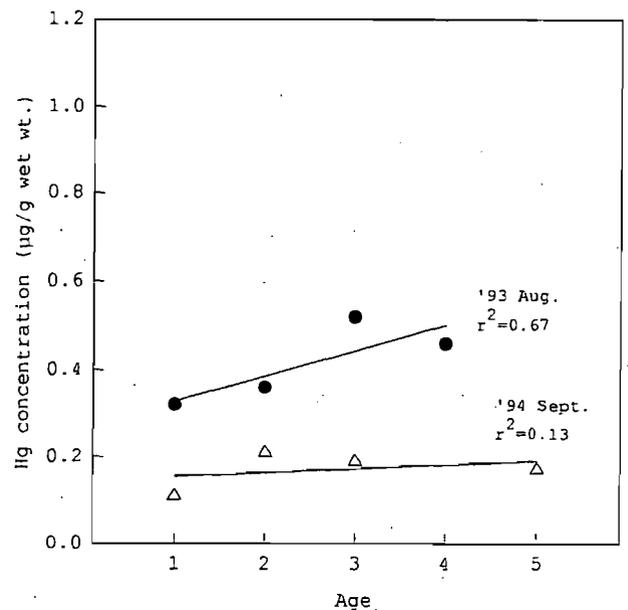


Fig. 7. Annual variation of mercury concentration in largemouth bass from Dorena Reservoir. Concentrations are the means for 4, 2, 3, and 2 fish of ages 1, 2, 3, and 4 years, respectively for August 1993. Concentrations are for 1 fish except age 5 years (n = 2) for September 1995

An number of factors influence mobilization of mercury from sediments. These factors include organic matter content (humic and fulvic acids) and the sediment type (e.g., clay or silt). Sediment mercury concentration and PVS were not significantly correlated for either reservoir studied here. However, mercury generally has a high affinity for fine-grained particulates and is attached to various types of suspended organic and inorganic "carrier particles" (Håkanson and Jansson 1983).

Contamination of Cottage Grove Reservoir sediments are likely due to the transport and deposition of suspended particulate matter brought into the drainage by erosion from mining wastes (Seigel *et al.* 1984). 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.* 1987). However, mercury has a strong affinity for sulfhydryl groups and mercury mobility may be increased by the formation of sulfide complexes under reducing conditions (Bothner *et al.* 1980; Bryan and Langston 1992; Lu *et al.* 1986). The concentration of methylmercury increased in the sediment as the concentration of sedimentary sulfide increased (Craig and Morton, 1983).

Mercury in Fish

Mercury concentrations ranges in fish from Cottage Grove Reservoir reported by Worcester (1979) and Allen-Gil *et al.* (1995) were similar to those reported here (largemouth bass, 0.31 to 0.96 $\mu\text{g/g}$, Figure 4). This suggested that mercury contamination in that reservoir has not changed significantly 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 were one-third those for fish taken from Cottage Grove Reservoir (Figure 5). According to the Oregon Department of Environmental Quality (personal communication) mercury concentration in largemouth bass sampled in 1993–1994 ranged between 0.22 to 0.70 $\mu\text{g/g}$. Mercury concentrations generally increased with fish length, weight, and age (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. Increased muscle mercury with age was generally consistent with our results when sampling times were analyzed independently (Figures 6 and 7). This was not evident for our data when different sampling times were pooled (Figures 4 and 5). This relationship was stronger in point-source-impacted Cottage Grove Reservoir than slightly contaminated Dorena Reservoir.

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 and Winfrey 1987; Winfrey and Rudd 1990). Mercury methylation rate was also sensitive to pH (Lindberg *et al.* 1987). 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.

While this study was not designed as an assessment of annual variation in fish mercury accumulation, the data indicated it was

substantial (Figures 6 and 7). More than 90% of total mercury in largemouth bass epaxial muscle was methylmercury (Allen-Gil *et al.* 1995). Laboratory work indicated that the rate of methylmercury elimination from fish was very slow. Biological half-lives of 1–3 years were estimated in studies with brook trout (McKim *et al.* 1976) and bluegill (Burrows and Krenkel 1973). McKim *et al.* (1976) measured no loss of whole body mercury 16 weeks after termination of methylmercury exposure. Appreciably decreased tissue mercury concentrations over this time were explained by "dilution" due to growth. This information suggested that differences in muscle mercury between sampling times were more likely explained by variation in methylmercury availability than elimination rates. Environmental conditions within a reservoir may influence methylmercury production and/or bioavailability. As reviewed above, temperature, dissolved oxygen, pH, and dissolved solids concentration all influenced mercury methylation rates in lakes and reservoirs. Variation in temperature and rainfall can directly influence lake stratification and/or factors which determine oxygen concentrations; hence mercury methylation rates at the sediment-water interface. Also, climate variation indirectly influences lake conditions via variation in management practices (*i.e.*, time and volume of drawdown events).

Conclusions

Sediment mercury concentrations in tributary streams indicated that point-source mercury pollution impacts Cottage Grove Reservoir but not Dorena Reservoir. Mercury concentrations in the basin sediments of Cottage Grove Reservoir averaged 5.6-fold higher than those of Dorena Reservoir. Muscle of fish from the point-source-impacted reservoir contain about three-fold more mercury than fish from a reservoir in the same ecoregion without a point source. This indicates that the dominant role of mercury mobilization by mining and processing of cinnabar in contamination of a fisheries resource.

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