Extreme Precipitation Appears a Key Driver of Mercury Transport from the Watershed to Cottage Grove Reservoir, Oregon.

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Abstract

An abandoned cinnabar mining and roasting site is in the major sub-basin of the watershed for Cottage Grove Reservoir, Oregon. Average surface sediment total mercury concentration in the river draining this sub-basin (0.61±0.52 µg/g) was about ten-fold higher than three smaller tributaries to the reservoir. Total mercury in reservoir surface sediments averaged 1.66 ± 0.70 µg/g. Stratigraphy for two sediment cores indicated generally decreased reservoir mercury loading from 1963-2002 but two pronounced peaks in mercury deposition. Years of extreme precipitation immediately prior to these peaks at least partially explained them. Epaxial muscle total mercury concentrations of largemouth bass increased with body weight up to 2.5 µg/g. A gradient of mercury concentrations in soils from a 3.3 km diameter grid indicated condensation of mercury vapors from the mine site polluted the sub-basin.

Capsule

Extreme precipitation increases transport of watershed mercury to aquatic ecosystems.

Keywords

Mercury transport; Pollution; Fish mercury contamination
1. Introduction

Mercury pollution is a problem on both global and local scales. Emissions from fossil fuel combustion, especially coal, are the primary source of global pollution. Production of gold is the second largest anthropogenic source of mercury to the atmosphere. Pacyne, et al. (2010) provide a quantitative inventory. Stratigraphy in peat indicates atmospheric mercury deposition rates are about 15-fold higher in the late 1990s than in prehistoric times (Roos-Barraclough et al., 2002). More than 95 percent of atmospheric mercury is elemental (Grigal, 2002). Sorption of this species of mercury to leaves of terrestrial plants; subsequent oxidation to highly water-soluble mercury (II); and transport to aquatic ecosystems is the predominant pathway for global scale pollution (Grigal, 2002). Mercury-cell chlor-alkali plant operations (Reis et al., 2009) and escape of elemental mercury during gold extraction and cinnabar roasting in mining are principle sources of local scale pollution.

Methylation of inorganic mercury by bacterial, especially sulfate reducing, activity occurs in wetlands and lakes (Rudd, 1995). Methylmercury undergoes trophic transfer in aquatic food webs and greatly biomagnifies in high trophic level fish. Neurodevelopmental toxicity in fetuses and infants, and potential to promote cardiovascular diseases drives regulatory action on methylmercury contamination of fish. Management of this problem is complex since fish is generally a healthy food: rich in protein, and in many species, beneficial fatty acids (Burger at al., 2005; Rheinberger and Hammitt, 2012). Federal fish consumption advisories pertain to
woman that may become pregnant, are pregnant or nursing, and young children.

Typically 90-95% of mercury in fish is methylmercury (Allen-Gil et al., 1995; Chang et al., 2007). Since it is much less expensive, analysis for regulatory purposes relies on total mercury in fish. For example, the current advisory limits consumption of fish containing 0.35 parts per million (ppm) mercury to one 170g meal per week (Rheinberger and Hammitt, 2012).

Cottage Grove Reservoir in the southern Willamette Valley of Oregon, USA (Fig. 1) contains fish with high mercury concentrations in edible flesh (Allen-Gil et al., 1995; Park and Curtis, 1997). The probable source of this contamination is the abandoned Black Butte Mine. This site is 15 km south of the reservoir, within its drainage basin, with a historical production of over 635,000 kg of mercury (Brooks, 1971). The work herein assesses: (1) the concentration of mercury in tributary and reservoir sediments, and chronology of mercury deposition in reservoir sediments; (2) food web mercury contamination in the reservoir; (3) the likelihood that atmospheric transport during cinnabar roasting was the primary route for mercury pollution in the surrounding watershed, (4) years of extreme precipitation markedly increased mercury transport to the reservoir and contamination in largemouth bass.

2. Methods

2.1 Sediment samples
Stream surface sediment grab samples were collected directly into I-Chem™ glass jars (Rockwood, TN) from each of the identified tributaries to Cottage Grove Reservoir. Particle size for each grab sample varied, and ranged from fine particulates to gravel material. Six surface sediment samples were collected from the reservoir by boat, representing a longitudinal transect through the center of the reservoir, using a ponar dredge (maximum volume 2.46L, 15.2 x 15.2 cm sample area) at approximately one km sampling intervals (Fig. 2).

Two sediment cores were collected from the deepest area of the reservoir; the depth of the water at the collection point was approximately 16 m. Both cores were collected by boat using a coring device (UWITEC, Mondsee, Austria) with a detachable, 83 mm diameter PVC barrel. The cores obtained were 38 cm in length, but do not represent the complete thickness of lake sediment as indicated by the absence of parent material from the bottom of each core (i.e. river gravel or sand). Following collection, each core was immediately cut into 2cm intervals (resulting in 19 samples per core), placed in ICHEM® glass jars, and stored at 4°C.

2.2 Samples for food-web analyses

Midge (Chironomid) larvae samples were collected from locations near the spillway of the dam, by boat, using a ponar dredge (Fig. 2). Sediment samples were sieved (1mm) until the number of midge larvae was sufficient for approximately three
All samples for food web analyses, except largemouth bass (*Micropterus salmoides*), were collected from the reservoir during August and September 2002. Fingerling brown bullhead catfish (*Ameiurus nebulosus*), snails (Physidae), bullfrog tadpoles (*Rana*), and dragonfly (Anisoptera) and damselfly (Zygoptera) nymphs were collected from the reservoir shoreline using a sweepnet. With the exception of the damselfly nymphs, enough invertebrate biomass was collected for three sample composites. For the damselfly nymphs, only two sample composites were collected. Largemouth bass were collected by electroshocking in 2002 and 2003 by the Oregon Department of Environmental Quality. Skinless epaxial muscle was analyzed for total mercury.

All surface sediment, sediment grab samples, and foodweb samples were placed in pretreated I-Chem™ glass jars, and placed in a cooler on ice until they reached the laboratory. With the exception of foodweb samples, all sediment samples were held at 4°C until analysis. Upon arrival to the laboratory foodweb samples were frozen at -20°C until the time of analysis.

### 2.3 Soil samples

Soil sampling was conducted within a 3.3 x 3.3 km grid centered around the Black Butte Mine site. Prior to sampling, target sampling sites were plotted using DeLorme 3-D TopoQuads software (2002) and coordinates loaded into a hand-held geographical positioning system (GPS). A total of 100 sample locations were selected. Sampling sites were arranged along 20 linear transects emanating radially
from the mine site. Samples were collected at intersection of the linear transects and
concentric rings representing increasing distance from the mine. Field crews
navigated to each predetermined sampling location, accuracy was within 15 m for
each location. For sites located closest to the mine site, a tape measure was used to
enhance spatial resolution between sampling locations. This applied to 14 sampling
locations located in close proximity to the north and south rotary kiln and furnace
locations. Each soil sample was a composite of five 1 cm diameter x 3-4 cm deep
cores. Cores were collected in a “W-shaped” pattern over a 1 m² area with a soil
probe. One core was collected at each point of the “W”. Soil composites were
thoroughly mixed at the field locations. Composite soil samples were transferred to
pre-cleaned I-Chem™ jars and sealed for transport to the laboratory. Duplicate
samples were collected at 10 locations. For additional quality assurance, rinsate
blanks from sampling equipment were collected daily and several transport blanks
of a reference soil verified no contamination was introduced during soil collection
or transport.

2.4 Precipitation Records
Precipitation records for Cottage Grove, Oregon were obtained from Climate Data
Online (National Climatic Data Center, National Oceanic and Atmospheric
Administration, USA). Monthly precipitation data from 1963-2002 were reviewed.
Cumulative annual rainfall for each of 40 years was determined.

2.5 Analytical Methods
Sediment, soil and foodweb samples were analyzed for total mercury concentrations as described by Park and Curtis (1997) with a mercury autoanalyzer using cold vapor atomic absorption (Leeman Labs PS200).

Surface sediment and soil samples were dried and sieved (1 mm) which yielded “fines.” Approximately 0.5 g of fines were then weighed into a clean bottle. Layers from the sediment cores and animal tissues were analyzed in 1.0 g wet weight subsamples. After addition of 5 ml of distilled water, 7 ml of aqua regia (10 volumes of concentrated hydrochloric acid with 3 volumes of concentrated nitric acid), and 5 ml of potassium permanganate (aqua regia) were added. Bottles were covered with aluminum foil and samples digested in an autoclave at 121°C for 15 min. After samples cooled, 6 ml of sodium chloride-hydroxylamine hydrochloride was dispensed into each bottle and the volume brought to 100 ml with ultra-pure water.

Mercury speciation in a subset of 10 soil samples was assessed as described by Bloom et al. (2003). Briefly, soils were dried at 50°C for 72 hr and sieved through a 1 mm mesh, and 8 g samples of fines were placed in acid-washed polypropylene bottles. Each sample was sequentially extracted with 80 ml distilled water (selective for mercurous chloride), 0.01M HCl/0.1 M acetic acid (selective for mercuric chloride, sulfate and oxide), 1M KOH, (selective for humic organic matter complexes) 12 M HNO₃ (elemental mercury selective), and aqua regia (selective for cinnabar). For each extractant, samples were shaken for 20 hr, and centrifuged at 2000 rpm for 30 min. The first three extractants were filtered through 0.2 mm nylon
membrane (47 mm Whaltman), washed in 40 ml of extractant, and centrifuged a second time. The fourth and fifth extractions were processed in the same manner as the first three, but without filtration. The liquid phases from the initial extraction and wash for each extractant were pooled for total mercury analysis as described above.

The mercury autoanalyzer was calibrated based on a linear six-point calibration curve (zero, 0.1 ppb, 0.5 ppb, 1 ppb, 2 ppb, and 5 ppb) with $R^2 = 0.995$ or greater. A continuing calibration verification standard and blank sample were analyzed at a 10 percent frequency and at the end of each analytical batch. A standard reference material sample (National Institute of Standards and Technology) and matrix spike/matrix spike duplicates were analyzed with each analytical batch of 20 samples or less. All sample analyses were performed in duplicate by the instrument, with the average of the analyses reported. The method detection limit was approximately 0.02 µg/g. Duplicates were within 10% or repeated until they meet this standard. Recovery of mercury from reference material ranged from 90-110%.

Percent total solid results converted all wet-weight analysis results for sediment core samples to a dry-weight basis. The percent total solids was determined for all sediment core samples in accordance with EPA Method 160.3 (EPA, 1983). Samples were weighed and measured in aluminum pans and placed in a drying oven at 46°C for 8 hr. Samples were then cooled in a desiccator and weighed.
2.6 Core dating

Select intervals within each lake-sediment core were analyzed for excess $^{210}$Pb, $^{226}$Ra, and $^{137}$Cs activity to determine age and sediment accumulation rates. The following sample intervals were selected for dating: 0-2 cm, 8-10 cm, 16-18 cm, 22-24 cm, 28-30 cm, and 34-36 cm. One gram subsamples of dried sediment from each interval was submitted to the University of Liverpool Environmental Radiometric Laboratory.

$^{210}$Pb, $^{226}$Ra, and $^{137}$Cs were measured by direct gamma assay, using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby et al, 1986; Appleby et al, 1992) and dates were determined according to the constant rate of supply (CRS) model (Appleby and Oldfield, 1978).

2.7 Statistical analysis

Means and standard errors were calculated for the mercury concentrations obtained from invertebrate composites, individual small vertebrates, the set of lake-sediment cores, and surface sediment samples. Mercury concentrations of tributary stream surface sediments were compared with one-way analysis of variance (ANOVA). Fish epaxial muscle mercury concentrations (dependent variable) were regressed against whole fish wet weights (independent variable) with simple linear, semi-log, and log-log models. Total mercury concentrations in invertebrates and small vertebrates were compared with the exact Kraskal-Wallis test. Statistical significance was set at $p<0.05$ for all analyses.
2.8 GIS analysis

Geographic information systems (GIS) software visualized the spatial distribution of soil mercury concentration around the Black Butte Mine site. Decimal latitude and longitude of each sampling location along with corresponding total mercury concentrations were imported into ArcGIS v. 10 (ESRI, Redlands, CA, USA). Ordinary kriging was applied using a spherical semivariogram model (default parameters). A variable search radius that interpolated log total mercury concentrations of the twelve nearest data points was used to interpolate the spatial variation over the landscape. The raster generated from kriging was divided into six classes based on log total mercury concentration using Jenks natural class breaks.

3. Results

3.1 Sediment Mercury Concentrations

Surface sediment mercury concentrations of three tributary streams were significantly lower than those from the largest tributary, the Coast Fork Willamette River (Fig. 2). Surface sediments from the Cottage Grove Reservoir averaged 1.66 ± 0.70 μg mercury/g. Surface sediment mercury concentrations downstream of the dam spillway were comparable to tributary streams, other than the Coast Fork Willamette River (Fig. 2).

The percent dry weight of the core layers increased with depth. The top 2 cm were 20% and 21% solids and the bottom 2 cm were 50% and 43% solids. The increase
in percent solids with depth was greater in the top 16 cm of the cores than the bottom 22 cm (data not shown). Sediment stratigraphy indicated temporal variation in mercury deposition in Cottage Grove Reservoir from 1963 to 2002 (Fig. 3). Abrupt peaks in mercury concentrations appeared in layers dated to 1965 and 1998. These times corresponded with two prior years of exceptionally high precipitation (detailed below).

In both cores, total $^{210}\text{Pb}$ activity exceeded supporting $^{226}\text{Ra}$ in the top 18 cm, and there was little or no unsupported $^{210}\text{Pb}$ in deeper layers (data not shown). $^{226}\text{Ra}$ was relatively uniform over both cores with a mean value of 21 Bq/kg. Unsupported $^{210}\text{Pb}$ concentrations were very low with maximum of 38±5 Bq/kg and 34±7 Bq/kg in the two cores. $^{137}\text{Cs}$ activities were similar in both cores, increased with depth and exhibited steep gradients between 23-24 and 35-36 cm. Minimum $^{137}\text{Cs}$ activities were 3.1±1.3 and 6.1±0.5 Bq/kg (0-2 cm) and maximum activities were 23.1±0.9 and 35.3±2.8 Bq/kg (34-36 cm) for the two cores. A date of 1963 was assumed for the 34-36 cm layer of the core based on peak atmospheric testing of nuclear weapons (Appleby and Oldfield, 1978) which allowed an estimated mean of 0.45 g/cm²/yr sedimentation rate over the 40-year histories of the cores. The $^{210}\text{Pb}$ records indicated sedimentation rates were not uniform over this time interval, however. The quality of the $^{210}\text{Pb}$ record supported by the CRS model (Appleby and Oldfield, 1978) allowed confidence in dating the top 18 cm of the cores (1972-
294 2002). $^{210}\text{Pb}$ flux to sediment was calculated as 60-90 Bq/m²/yr based on $^{210}\text{Pb}$ inventories in the two cores. Since this was comparable to estimated atmospheric flux, $^{210}\text{Pb}$ concentrations were likely diluted by rapid sedimentation between ca 1963-1972. Therefore, dating of the bottom 18 cm of the cores relied on the $^{137}\text{Cs}$ record. Ages of layers not analyzed by direct gamma assay were estimated by linear interpolation. The estimated post-1972 sedimentation rate was 0.21±0.02 g/cm²/yr, less than half the mean for 1963-1970. No date was estimated for the 37-38 layers of the cores (Fig. 3).

3.2 Precipitation Records

Review of precipitation records revealed mean precipitation at Cottage Grove, Oregon of 1.48 m/yr over the 40 years from 1963-2002. There were eleven years when precipitation exceeded this mean by more than 25%. For 1963 and 1964 precipitation totals were 1.90m and 1.69m, respectively. For 1995 and 1996 precipitation totals were 1.74 and 2.34m, respectively. Other years with precipitation more than 25% above the 40 year mean were 1968, 1971, 1973, 1981, 1983, 1986, and 1998.

3.3 Food Web Mercury Concentrations

Total mercury concentrations in epaxial muscle of largemouth bass collected in 2002 and 2003 increased significantly with body weight (Fig. 4). There was substantial variability between fish, particularly those about 1.5 kg or larger. The ANOVAs associated with linear, semi-log, and log-log models detected significant
correlations (p<0.022, 0.013, and 0.006, respectively). Correlation coefficients of 0.51, 0.54 and 0.60 for the respective models indicated no major advantage of a particular model over another.

(Place Figure 4 here)

Total mercury concentrations in two small vertebrates and several invertebrates provided some insight into food web concentration at trophic levels much lower than largemouth bass (Table 1). The predatory damselfly nymphs accumulated approximately twice the mercury burden (75±8ng mercury/g) of another predator, dragonfly nymphs (35 ng mercury/g). Despite collection from an area where surface sediments contained 1.8-3.6 µg mercury/g, concentrations in midge larvae were rather low (49±5 ng mercury/g). Aquatic snails were considered detritivious and contained quite low mercury concentrations (17±2 ng mercury/g). Both of the small vertebrates contained much lower mercury concentrations than largemouth bass (43±14 and 21±22 ng mercury/g whole catfish and bullfrog tadpoles, respectfully).

3.4 Mercury Contamination of Soil

Soil mercury concentrations in the immediate vicinity of the abandoned Black Butte Mine were variable, but often high (Fig. 5, inset). Soils from within 20 m of the abandoned rotary kiln contained up to 2090 mg mercury/kg. Interpolation of the log total mercury concentrations across the landscape surrounding the Black Butte
mine site revealed a contamination plume (Fig. 5). The gradient of contamination was quite steep, as indicated by the log scaling, and generally declined with distance from the abandoned mine site.

A subset of soil samples were sequentially extracted to assess biogeochemically relevant fractions of inorganic mercury (Bloom et al., 2003). Two samples collected in the immediate vicinity of the abandoned kiln contained 1669.1 and 997.1 μg mercury/ks soil, and 65-90% of this was in the fraction associated with cinnabar (Fig. 6). Two samples collected from the tailings pile were much lower in total mercury. About 5-40% of total mercury was in the cinnabar selective fraction, and the majority was in the fractions selective for humic organic matter complexed mercury and elemental mercury. Soils at a distance from the abandoned mine site contained detectable amounts of mercury in the cinnabar fraction, but 75-95% of the total mercury was in the fraction selective for humic organic matter or the fraction selective for elemental mercury (Fig. 6). Less than 0.01% of total mercury was extracted by distilled water (selective for mercurous chloride) in all of the sequentially extracted soil samples.

4. Discussion
The working hypothesis for this research was that the abandoned Black Butte Mine (Fig. 1) was the predominant source of mercury pollution in Cottage Grove Reservoir. Sampling of surface sediments in tributary streams supported this hypothesis (Fig. 2). Mercury concentrations in the tributary draining the sub-basin surrounding the mine site (Coast Fork Willamette River) were substantially higher that in three streams in smaller, adjacent drainage basins. This information was consistent with previous sediment sampling in these same streams (Park and Curtis, 1997) and provided rationale for more extensive soil sampling in the sub-basin surrounding the mine site.

Total mercury in surface sediments from the reservoir were generally higher than in any of the tributaries, including the Coast Fork Willamette River (Fig. 2). This indicated mercury was sequestered in reservoir sediments. The average concentration was 2.5-fold higher than for surface sediments collected from the same reservoir in 1994 (Parks and Curtis, 1997). Sediment stratigraphy indicated this difference was not due to random sampling variation (Fig. 3). The sediment cores from the reservoir offered a quantitative estimate of mercury loading of Cottage Grove Reservoir from 1963-2002. Sediment stratigraphy demonstrated generally decreased mercury loading of the reservoir over time with two notable exceptions (Fig. 3). There was a sharp peak in total mercury concentration in the layer with a date interpolated as 1965. Mercury concentrations decreased markedly over time to rather stable levels from 1970-1995. Total mercury markedly increased in the layer dated to 1998 and then declined. Heavy precipitation in 1963/64 and
1995/1996 appeared reflected in peaks in sediment layer mercury concentration in 1965 and 1998 (Fig. 3). While sediment movement rates from the watershed to the reservoir basin were not attempted, movement probably varied temporally based on timing and intensity of precipitation. Golden et al., (2012) applied watershed scale models that simulated total mercury concentrations and fluxes from soils to surface water. Modeling suggested the predominant transport pathway varied with precipitation. Flushing of organic-complexed mercury from surface soils was important during base flow, while shallow subsurface flow predominated during high flow events. Interpretation of mercury concentrations of the sediment core layers in the context of precipitation records strongly implicated the importance of extreme events in mobilization of mercury from the watershed into the reservoir. After almost 20 years of decreased loading, mercury sediment concentration again peaked in 1998, but was much lower than after the 1966 peak. While reduction of contamination over time was apparent, it was clear that active mercury loading of Cottage Grove Reservoir was still sensitive to watershed scale events decades after cessation of cinnabar mining and roasting. Recent increases in atmospheric mercury deposition were a potential contributor to time-dependent differences in Cottage Grove Reservoir sediment mercury concentrations. Prestbo and Gay (2009) reviewed wet deposition of mercury in North America from 1996-2005. There was no trend for altered mercury deposition over time for the site in the Northwest (Seattle) most intensively sampled. Further, mercury concentrations in Oregon and Northern California sites were consistently low (3-5.6 ng/L). These data indicated atmospheric deposition was a minor contributor to sediment mercury.
concentrations in Cottage Grove Reservoir. High sediment mercury concentrations in Coast Fork Willamette River relative to other reservoir tributaries supported this conclusion (Fig. 2).

Federal advisories indicated no consumption of highly mercury contaminated fish was safe for women that may become pregnant, are pregnant or nursing, and small children. Examples of commercially harvested fish in this category included shark (1.33 ppm mercury) and swordfish (0.95 ppm mercury) (Hightower and Moore, 2003). Across the size range of largemouth bass analyzed for mercury, all of these fish collected (Fig. 4) were unsafe for consumption as specified in advisories.

Mercury concentrations in largemouth bass collected were markedly higher than for those collected in 1993, 1994, and 1995 (Park and Curtis, 1997). In fact, across the range of sizes collected, fish muscle contained up to 2.5 times more mercury in 2002/2003 compared to those collected in the mid 1990's. The magnitude of this difference was similar to that in reservoir surface sediment mercury concentrations between 2002 (mean of 1.66 ppm) and 1994 (mean of 0.67 ppm). This was consistent with bioavailability of mercury newly introduced into reservoir sediments for methylation and subsequent trophic transfer.

Low total mercury concentration in bullfrog tadpoles and small catfish (Table 1), relative to largemouth bass, likely reflected lower trophic levels. Total mercury concentrations of several invertebrate species were generally low (Table 1) relative to reservoir sediments (Fig. 2). At sediment mercury concentrations comparable to
those in this study Suchanek et al (2008) found midge larvae contained about 3-fold higher total mercury than reported herein (Table 1). Age of larvae (hence time for bioaccumulation) or biochemical conditions in sediments (e.g., aerobic versus anoxic conditions that enhanced mercury methylation) at the time of sample collection may partially explain the differences observed. Snails were collected from shoreline areas where sediment mercury concentrations were lower than in the middle of the reservoir (Allen-Gil et. al., 1995; Park and Curtis, 1997) and there was little potential for anoxia and methylmercury production. Damselfly nymphs contained about twice the total mercury as dragonfly nymphs. Since both species were considered opportunistic predators, there was no obvious explanation for this.

Soil samples collected from the landscape surrounding the Black Butte Mine site clearly demonstrated a concentration gradient of mercury pollution that declined with distance from the abandoned kiln (Fig. 5). This suggested short-range atmospheric transport of mercury vapor and condensation on the landscape. Data reported herein (Figs. 2, 5) and previously (Park and Curtis, 1997) indicated sediment and waterborne mercury movement into the Coast Fork Willamette River and hence Cottage Grove Reservoir was the predominant pathway for pollution in the system. Mercury loading into the river from the watershed was a complex function of soil mercury concentration, water movement and downslope soil erosion. Intensity of cinnabar mining and roasting varied greatly from 1890 (initiation of operations) to 1969 (mine closing) but peaked in the mid-1940's (Brooks, 1971). From 1970 forward soil mercury concentration almost certainly...
decreased but at an unknown rate. Intensity of precipitation and other physical
disturbance (e.g., road building and logging) in the watershed were likely major
determinants of mercury movement into the river.

Fractionation of total mercury by selective extractions (Bloom et al; 2003) provided
some insight into mobility of the pollutant that remained on the landscape in 2002.
High concentrations of mercury occurred in the immediate vicinity of the
abandoned kiln (Fig. 6). Most of this was in the highly water insoluble cinnabar
selective fraction. Mercury was present in the cinnabar selective fraction at all sites
but was generally a minor constituent at locations distant from the abandoned mine
site. The elemental mercury selective fraction was generally a minor constituent of
total mercury in soil samples (Fig. 6). The hypothesis that framed this work was that
short-range atmospheric transport of elemental mercury from the kiln polluted the
watershed of the Coast Fork Willamette River and hence Cottage Grove Reservoir.
More than 30 years elapsed from closure of the Black Butte Mine (1969) and
collection of soil samples in 2002. Off-gassing of elemental mercury, conversion to
other chemical species and transport in solution, and downslope movement with
soil erosion probably all contributed to decreased concentration over time. Mercury
in the humic organic matter complex selective fraction was prominent in soils
collected at a distance from the abandoned mine site (Fig. 6). Sorption of elemental
mercury to leaves and other plant material and subsequent oxidation to divalent
inorganic mercury (Grigal, 2002) was probably an important process in deposition
of humic acid complexes in soil. Without selective fractionation data for soil
collected far prior to 2002, assessing the role of mercury conversions between biogeochemically relevant fractions to mobility in the watershed was not feasible.

5. Conclusions

The weight of evidence suggested short-range atmospheric transport of mercury vapors from cinnabar roasting at the Black Butte Mine polluted a major sub-basin in the watershed for Cottage Grove Reservoir. Sediment stratigraphy demonstrated mercury loading of the reservoir generally decreased over time after cinnabar mining and roasting stopped. However, episodes of markedly increased mercury loading occurred associated, at least in part, with extreme precipitation in 1963/1964 and 1995/1996. Edible flesh of largemouth bass contained about 2.5-fold more total mercury in the summers of 2002/2003 than in 1993-1995. These concentrations exceeded those allowed in fish consumption advisories.
Acknowledgements:

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Table 1.

Mercury concentrations and body weights of several invertebrate and two vertebrate taxa collected in Cottage Grove Reservoir in 2002.

<table>
<thead>
<tr>
<th>Taxa</th>
<th>Sample Weight (wet g)</th>
<th>Mercury conc. (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dragonflya</td>
<td>0.49 ± 0.03</td>
<td>35 ± 12</td>
</tr>
<tr>
<td>Midgea</td>
<td>0.54 ± 0.04</td>
<td>49 ± 5</td>
</tr>
<tr>
<td>Damselflya</td>
<td>0.25 ± 0.01</td>
<td>75 ± 8</td>
</tr>
<tr>
<td>Snaila</td>
<td>0.60 ± 0.04</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>Catfish</td>
<td>0.57 ± 0.06</td>
<td>43 ± 14</td>
</tr>
<tr>
<td>Tadpole</td>
<td>3.22 ± 0.96</td>
<td>21 ± 22</td>
</tr>
</tbody>
</table>

Results are means ± standard errors for n=3 samples, except for n=6 dragonfly and n=2 damselfly. Concentrations for all snail and tadpole samples are for detections at the reporting limit, and therefore of low precision. a composite samples.
Figure 1. Locations of Cottage Grove Reservoir, its watershed, tributary streams, and the abandoned Black Butte Mine Site.
Figure 2. Total mercury concentrations in stream and reservoir surface sediments collected in the summer of 2002. Each concentration is for a single sample collected and analyzed as described in the text.
Figure 3. Sediment stratigraphy for total mercury concentrations in 2 cm layers of cores collected in summer 2002. Results are means ±SD for two different cores. Dating of cores was radiometric.

Figure 4. Total mercury concentrations for epaxial muscle of individual largemouth bass collected in 2002 (open circles) and 2003 (closed circles). There was statistically a significant increase in mercury concentration with body weight.
Figure 5. Geographic information systems (GIS) representation of the interpolated distribution of soil mercury concentrations across the landscape surrounding the Black Butte mine site. Values on the plot and inset indicate total mercury concentration (mg/kg) measured at the corresponding sampling location. Spatial distribution across the landscape was interpolated using ordinary kriging based on log total mercury concentrations of the twelve nearest sampling locations and represented using six classes, each class break representing a range of approximately 0.4 log units.
Figure 6. Selective fractionation of inorganic mercury in a subset of soil samples collected in summer 2002. The black bar segment represents cinnabar selective; the dark gray segment represents elemental mercury selective; the medium gray segment represents humic organic matter complex selective; and light gray represents mercuric chloride, sulfate, and oxide selective. The white bands are for contrast.