FINAL REPORT

Reconnaissance Soil Sampling at the

Black Butte Mine

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By

Lawrence R. Curtis

Environmental & Molecular Toxicology

Oregon State University

Corvallis, Oregon

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Abstract

The abandoned Black Butte Mine intermittently mined, crushed, and roasted cinnabar in kilns for elemental mercury production from 1882 until 1969. Mercury mobilized by these activities yielded a diffuse point-source of contamination for down-gradient surface waters including the Coast Fork of the Willamette River and Cottage Grove Reservoir. Largemouth bass from Cottage Grove Reservoir contained up to 2 µg mercury / g fillet in recent surveys.   Total mercury concentrations were determined in 99 soil samples from seven, roughly concentric circles up to 1.5 miles from the abandoned kilns. Total mercury concentrations ranged from 2090 to 0.1 µg / g soil. Soil in the immediate vicinity of the abandoned kilns contained the highest total mercury concentrations. There was a general trend for decreased total mercury in soil with increased distance from the abandoned mine site. Total mercury in soils from slopes of ridges facing the Black Butte Mine site and slopes opposite the site were determined. Two slopes facing Black Butte Mine contained 3 to 6-fold higher total mercury concentrations than slopes of the same ridges opposite Black Butte Mine.   This suggested potential atmospheric mercury transport in the past.   Ten soil samples from the study area were sequentially extracted with distilled water, pH 2 HCl/HOAc, 1N KOH, 12N HNO_3, and aqua regia. The first two, highly mobile fractions were rarely detected as significant percentages of total mercury. This was probably explained by leaching over the years since the Black Butte Mine was abandoned. Samples near kilns contained up to 2 mg total mercury / g

soil that was 67-89% cinnabar. Soil ranged from pH 4.3 to 7.0 Samples collected

near the tops of surrounding ridges facing the Black Butte Mine contained up to 8

µg total mercury / g soil that was less than 20% cinnabar and 44-87% soluble in

1 N KOH, suggesting substantial concentrations of complexes with organic

matter. These data were consistent with historical, short-range atmospheric

transport of mercury in the watershed that contains Black Butte Mine. Areas with

highest mercury contamination were in the immediate vicinity of the abandoned

kilns on the Black Butte Mine site, and contained a substantial percentage of

cinnabar.

Introduction

The U.S. Army Corps of Engineers operates Cottage Grove Reservoir for

flood-control and recreation. While fishing is a popular recreational activity in this

reservoir, the Oregon Health Division advises the public not to consume fish from

it. Fillets from older heavier largemouth bass and bluegill sunfish from Cottage

Grove Reservoir often contain over 1.0 part per million mercury (ppm) (Park and

Curtis, 1997; 2003). The U.S. Food and Drug Administration action level for

mercury in fish is 0.5 ppm. The Oregon Division of Health Services and United

States Environmental Protection Agency advise restrictions on consumption of

fish containing 0.3 ppm or higher mercury concentrations. For women who are

or may become pregnant, nursing mothers, and young children special caution is

necessary. Recommendations are available on the web site:

http://www.cfsan.fda.gov/~dms/admehg3.html

Analyses of sediment mercury concentrations in the reservoir and tributary streams indicate the Coast Fork of the Willamette River as the only significant source of particulate mercury (Park and Curtis, 1997). A gradient of increasing sediment mercury concentration occurs from the confluence of the Coast Fork of the Willamette River upstream to a tributary, Dennis Creek (Curtis, 2003). Dennis Creek passes down-slope of the boundary of the abandoned Black Butte Mine (BBM). A 1995 survey indicates a tailings pile that extends to the south bank of Dennis Creek that contains about 20 µg mercury /g (Curtis, 2003). Other data from the same survey indicate soils around abandoned BBM ore processing areas contain at least 10-fold higher mercury concentrations. Taken together, available data suggest the abandoned BBM is a diffuse point-source for mercury contamination of Cottage Grove Reservoir.

Objective of This Work

The general objective of this work is to increase understanding of spacial distribution and mobility of mercury in soils in and around the abandoned BBM. This information is important in development of a strategy to reduce mercury inputs into tributaries of the Coast Fork of the Willamette River and Cottage Grove Reservoir. One specific aim is expanding the spacial characterization of mercury concentration in shallow soil in and around the BBM site. This can identify mercury "hotspots" on the site. It can also contribute to assessment of the likelihood of past atmospheric mercury transport within the watershed due to escape of elemental mercury vapors during cinnabar roasting. The second specific aim is mercury speciation analyses of a select subset of soil samples.

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Speciation analysis provides a quantitative estimate of mercury mobility via assessment of potential leaching in soil water at neutral and slightly acidic pH. It also estimates the percentage of total soil mercury that exists as tightly bound complexes with organic matter or the mineral lattice of soil. Processing of cinnabar ore yields elemental mercury that is reactive in aerobic soils. Finally, speciation analysis can detect presence of cinnabar and chemical forms of mercury that are likely products of reactions of elemental mercury in soil.

Methods

A total of 99 soil samples were collected for analysis. Sample locations were determined from a radial, grid pattern on a map with the BBM site at its center. The reconnaissance grid was plotted on a U.S. Geological Survey 7.5 minute series topographic map of the Harness Mountain Quadrangle. The map scale was 1:24,000 (2000 feet/inch = 609.6 m/inch). Samples were collected at locations corresponding to intersecting lines on the grid. Each location was identified by its X-Y location on the grid, and a corresponding longitude and latitude determined from the 7.5 minute series topographic map using commercially-available mapping software. During sample collection, a hand-held global positioning system (GPS) unit located the sampling locations on the ground. Accuracy was within 50 feet or less (≈15 m) for each X-Y direction (N-S, E-W). When obstacles precluded sample collection from the designated location, the nearest viable location was sampled, and the GPS location of the adjusted sample location noted. In some cases, restricted access to private property

limited the ability to sample locations plotted on the initial grid. In these circumstances, additional relevant sample locations were identified, such that the total number of samples collected totaled 99. Relevant topographic features were considered in selecting alternative sampling sites beyond the original sample grid, and again, longitude and latitude of each potential sample site were determined from the 7.5 minute series topographic map. The utilization of GPS throughout the site reconnaissance sampling facilitated accurate spatial representation and analysis of the contamination profile using geographic information systems (GIS).

The reconnaissance site was a 1.5 mile radius circle centered on the BBM. This equated to approximately 1600 acres or 2.5 square miles. This area encompassed the BBM site, the BBM tailings and waste rock dump (located approximately 2500 ft from the mine adits), and all of Black Butte itself. It extended east to the peak of Stennett Butte and west to that of Alton Hill. To the south, it extended to the peak of Little Baldy and Scorpion Butte. It extended north to the region roughly half-way between Dennis Creek and Big River. This area at least partially encompassed Brauti Creek, Garoutte Creek, Little River, Trail Creek, Dennis Creek, and Blood Creek. The area included Bureau of Land Management lands as well as Weyerhaeuser-owned forest land and private residential lands, thus access to some areas was restricted.

Soil composites consisted of five sample locations within a square meter area. Surface samples were taken in a "W-shaped" pattern. One sample was taken at each point of the "W" at a depth of 3-10 cm using clean stainless steel

spoons.   Soil samples were placed in "zip-lock" type plastic bags and admixed

thoroughly through the walls of the bags by hand. Particles larger than 1.5 cm

were removed before transfer of soil composites to "ICHEM" jars. After transfer

to "ICHEM" jars they were sealed for transfer to the laboratory. Composite soil

samples were analyzed for total mercury without additional preparation. Soil

composites were thoroughly admixed and sieved to 1 mm prior to speciation

analysis.

Total mercury concentrations were measured in 99 composite soil

samples collected by cold vapor atomic absorption spectrometry (USEPA, 1996).

Total mercury was probably the most useful measurement of contamination to

inform decisions on soil clean-up. Questions were likely to remain regarding the

extent to which past activities in the mine/kiln explained spatial patterns of soil

contamination. We assessed the source of mercury in soils through

determination of the chemical forms of mercury (i.e., speciation). Mercury

speciation also largely determines mobility in groundwater and bioavailability.

Digestion of soil in aqua regia (USEPA, 1996) solubilized all mercury for

detection including the most recalcitrant species, cinnabar. Digestion of soil with

12 N HNO_3 solubilized mineral lattice, Hg_2Cl_2, and elemental mercury for

detection. This group of species was classified as strong-complexed. Digestion

with 1N KOH solubilized Hg_2Cl_2 and mercury bound to humic substances in soil.

Digestions with distilled water or HC1/HOAC at pH 2 dissolved species with

potential mobility in groundwater (HgO, $Hg\ Cl_2$, and $Hg\ SO_4$). We conducted the

speciation analyses described above on 10 composite soil samples: two from the

tailings pile, four from sites in the lower end of total mercury concentration range of soils collected, and four from sites at the higher end of the total mercury concentration range of soils collected.

High percentage of total mercury content as cinnabar likely indicated natural weathering of rock or localized impacts of hard rock mining. High percentage of strong-complexed and organo-complexed species suggested impact by atmospheric transport from past activity of the kiln. Given high water solubility of mercury species extracted by distilled water or pH 2 HC1/HOAC low or undetectable concentrations of these species were anticipated.

Results

A total of 99 shallow soil samples were collected in roughly seven concentric circles in and around the abandoned BBM site in early Fall of 2003. The most intensive sampling was focused on the mill-site itself (Figure 1). Soils in the immediate vicinity of furnace areas were heavily contaminated with mercury. Total soil mercury concentrations around the "old furnace area" ranged from 1120-2090 µg/g. Soils near the "new furnace area" ranged from 41-727 µg/g. This probably reflected improved ore handling and processing practices in the more recent (1960s) compared to the distant past (late 1800s and early 1900s). Overall, the data for the immediate BBM site indicates targeted remedial actions are feasible rather than a site-wide effort.

There were a few sample locations outside the immediate mill-site that contained rather high total mercury concentrations (Figure 2). Two locations

(S35 and S46) were probably influenced by ore transport for road construction since the Black Butte was extensively tunneled for cinnabar mining. There was no definative explanation for a single high soil total mercury concentration across Dennis Creek from the BBM site (S14). The main ore body exploited by BBM exhibited very limited exposure at ground surface. Mining revealed a linear feature extending from Black Butte northward across Dennis Creek. This was one potential factor that produced high soil mercury at S14.

The BBM site was developed between a number of ridges and buttes. If there was significant loss of elemental mercury vapor associated with cinnabar roasting, these were potential barriers to atmospheric transport. Total soil mercury concentrations were collected on slopes facing and opposite the BBM site (Figure 2). One such comparison was for an unnamed ridge immediately across Dennis Creek from the BBM site. The Bohemia Trail crosses this ridge. The southwest slope soils (facing the BBM) collected from 1600-1700 feet elevation averaged 1.43 ± 0.52 mg total mercury /g soil (mean ± standard deviation, n=4). The northeast slope (opposite the BBM) soils collected from 1600-1700 feet elevation averaged 0.55 ± 0.20 mg total mercury /g soil (mean ± standard deviation for n=4). Two slopes of Black Butte were also compared. The north slope (facing BBM) soils collected at 2200-2400 feet elevation contained 4.67 ± 0.51 μg total mercury /g (mean ± standard deviation, n=3). South slope soils (opposite BBM) from this elevation contained 0.80 ± .033 μg total mercury /g (mean ± standard deviation, n=3). These data suggested past atmospheric transport of elemental mercury subsequent to cinnabar roasting and

escape of vapors was possible. Indeed, Hardin and Conger (1909) reported visible deposits of elemental mercury on trees surrounding the BBM in the early days of mine activity.

Speciation analyses indicated most of the mercury in soil near abandoned kilns was in cinnabar (Figure 3). Some strong-complexed organo-complexed mercury was present in these soils. The South Furnance soil contained about 10% of the mercury as pH 2 soluble material. This highly mobile mercury perhaps persisted since this soil was sheltered by remains of the kiln structure. Tailings pile samples contained mostly strong-complexed and organo-complexed mercury, and lower percentages of cinnabar (Figure 3). More mobile forms probably leached away long ago. Soil samples from the watershed around the BBM site consistently contained high concentrations of organo-complexed mercury (Figure 3). Elemental mercury is subject to volatilization and this increases with increase in soil pH and temperature but decreases with soil carbon content due to formation of organo-complexes (Grigal, 2002). High percentages of 1 N KOH soluble mercury in soils outside the immediate mill-site (Figure 3) suggests previous loadings with elemental mercury from kiln activity is probable. Some samples, especially one composite from Black Butte, contained significant percentages of strong-complexed mercury. Both organo-complexed and strong-complexed mercury were potentially derived from oxidation of elemental mercury deposited by atmospheric transport. Black Butte, but not other watershed soils, contained 10-20% cinnabar. Perhaps this was due to ground surface exposure of the ore body in this area.

Conclusions

There are distinct "hotspots" of mercury contamination on the BBM site. This may simplify remediation by focusing effort on the most contaminated areas.

The report provides two lines of circumstantial evidence for past atmospheric transport of elemental mercury from the BBM site to the surrounding watershed.

- Soils from slopes of a ridge and a butte facing the BBM site contain 3 to 6-fold higher total mercury than those opposite the site. This may reflect their barrier function in atmospheric mercury transport.

- Soils in the watershed surrounding BBM contain substantial concentrations of organo-complexed mercury. This may reflect reaction products of elemental mercury deposited on the landscape by atmospheric transport during BBM operation.

References

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